

ADVANCED TEXTILE ENGINEERING MATERIALS



Edited by
Shahid-ul-Islam and
B. S. Butola

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Preface

Advanced materials are undoubtedly becoming very popular as substitutes for traditional materials in textile engineering field. Advanced textile engineering materials are giving way to innovative textile materials with novel functions and are widely perceived as offering huge potential in a wide range of applications such as healthcare, defense, personal protective equipment, personal communication, textile antennas, garments for motion capture, and sensors. This book contains 13 chapters that cover fundamental and advanced approaches associated with the design and development of textile implants, conductive textiles, 3D textiles, smart-stimuli textiles, antiballistic textiles and fabric structures designed for a medical application intrabody/extra-body, implantable/non-implantable) and various modification and processing techniques. Global research & development and also some funding agencies, such as the Indian Defence Research and Development Organisation (DRDO), are also providing substantial funding for research in this area. The book is intended to be of interest and useful to a wide group of people: researchers, post and undergraduates in the field of textile engineering, functional finishing, chemical processing and material sciences.

We thank Mr. Martin Scrivener who did a great deal of work to bring this book to completion. Finally, we wish to acknowledge our sincere appreciation to the authors who have written in-depth and informative chapters that collectively has made this book a reality.

Shahid-ul-Islam and B.S. Butola
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Part 1

CHEMICAL ASPECTS

Application of Stimuli-Sensitive Materials in Smart Textiles

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Abstract

Stimuli-sensitive materials have the ability to sense and respond to various kinds of physical and chemical or biochemical stimuli in their environment. These materials are a convergence of different sciences such as material sciences, physics, chemistry, electrical engineering, wireless and mobile telecommunications, and nanotechnologies. They have many potential applications in smart textiles in the fields of medicine, protection, security communication, and textile electronics. Smart textiles are an interesting class of materials that can be prepared by a variety of methods. The functionality of smart textiles consists of many fields such as informing, protecting, and relaxing the wearer. The objective of this chapter is to present the latest research results together with basic concepts related to the preparation methods, characterizations, and applications of stimuli-sensitive materials in smart textiles and their importance in clothing. Future trends in this area of research are presented and issues regarding technology development and its uptake are highlighted.

Keywords: Smart textile, chromic materials, conductive materials, electronic textiles, phase change materials, shape memory materials

1.1 Introduction

Processability and flexibility are usually the two most important parameters of fine and elastic fibers used in order to make comfortable fabric and

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clothing. The wearable and comfortable fibrous materials such as yarn, fabric, and garments should be able to withstand handling in processing and end use without damaging functionality. The smart wearable textiles are fibrous materials made of smart materials such as shape memory materials (SMMs), phase change materials (PCMs), chromic materials, optic fibers, conductive materials, mechanical responsive materials, hydrogels, intelligent coating/membranes, micro and nanomaterials, and piezoelectric materials able to sense both the human body and external environment thanks to the presence of various kinds of sensors in their structure [1–4]. In other words, a smart textile allows the user to wear functionalized common clothes in which the user can access information about his personal biophysical data and/or environmental data. The potential of smart textile is enormous. One could think of smart clothing that makes us feel comfortable at all times, during any activity and in any environmental condition. A suit that protects and monitors, that warns in case of danger and even helps to treat diseases and injuries, is an example of smart clothing. Such clothing could be used from the moment we are born till the end of our life. These clothes should be like ordinary clothes providing special functions in various situations according to their design and application [5].

All smart materials involve an energy transfer from the stimuli to response given out by the material. They have the ability to do some sort of processing, analyzing, and responding. The amount of energy transferred to the response is determined by the properties of the material. For example, a material's specific heat (property) will determine how much heat (energy) is needed in order to change its temperature by a specified amount. The smart materials can be incorporated into the textile substrates at any of the levels, namely, fiber spinning level, yarn/fabric formation level, and finishing level [6]. Numerous scientists are researching to develop products with the emerging demand of smart textiles in various phases of life.

This chapter highlights all the main fields of applications of stimuli-responsive smart materials in textiles in various fields of applications such as healthcare, health monitoring, medicine, personal protective equipment, personal communication, textile antennas, garments for motion capture, and sensors (Table 1.1).

1.2 Phase Change Materials

Phase change materials (PCMs) are theoretically able to change state at nearly a constant temperature and therefore to store a large quantity of

Table 1.1 Examples of application of stimuli-responsive materials in textile.

Stimuli-sensitive materials	Benefits of treating textile	Examples of potential applications
Phase change materials (PCMs)	Cooling, insulation, thermoregulating	Blankets, bed sheets, dress shirts, T-shirts, jackets, vests, undergarments, socks, gloves, helmets, shoes and boots, earmuffs, hats and rainwear, seat covers in cars and chairs in offices, firefighters protective clothing, bulletproof fabrics, space suits, sailor suits, and other textile products
Shape memory materials (SMMs)	Insulation, shape forming, protection, compression, moisture management	Shoes, breathable fabrics, thermal insulating clothes, crease- and shrink-resistant fabrics, fishing yarn, shirt neck bands, cap edges, casual clothing and sportswear, shape-formed dresses, protective clothing, flame-retardant fabrics, compression stocking, aesthetic effects, etc.
Chromic materials	Color change	Fancy clothes, sports garments, workwear, soldier and weapons camouflage fabrics, technical and medical textiles
Conjugated polymers	Sensing	Sensors for various biologically and chemically important target molecules, scaffolds for nerve tissue engineering

(Continued)

Table 1.1 Examples of application of stimuli-responsive materials in textile. (*Continued*)

Stimuli-sensitive materials	Benefits of treating textile	Examples of potential applications
Conductive materials	Electrically conducting	Electrically conductive textiles (fibers, yarns, fabrics), wearable electronics and fashion for healthcare, safety, homeland security, computation, thermal purposes, protective clothing, child monitoring, health monitoring, space programs, interior design
Piezoelectric materials	Energy harvesting, energy conversion, sensing, electricity generating	E-textiles and wearable computing, electricity generation for various device applications, motion sensor
Optic fibers	Sensing, illumination, radiation, signal transmission	Flexible flat panel displays, optic fiber fabric display
Hydrogels	Swelling/shrinkage change	Water vapor-permeable fabrics, thermal-responsive hygroscopic fabrics

energy to regulate temperature fluctuations [4, 7]. PCMs can exist in at least two different phases (an amorphous and one or more crystalline phases), and they can be switched repeatedly between these phases. The thermal energy storage in PCMs occurs when they change from solid to liquid and the energy dissipates when they change back from liquid to solid. The different phases of PCMs have distinctly different physical properties such as electrical conductivity, optical reflectivity, mass density, or thermal conductivity. PCMs keep people comfortable through the absorbing, storage, and releasing of the heat. Without PCMs, the thermal insulation capacity of clothing depends on the thickness and density of the fabric. Incorporating microcapsules of PCMs into textile structures improves the thermal performance of the textiles [4]. There are many thermal benefits of treating textile structures with PCM microcapsules such as cooling, insulation, and the thermoregulating effect. PCMs are applicable in blankets and comforters, bed sheets, dress shirts, T-shirts, undergarments, swaddling blankets, and other textile products. There are several factors that need to be considered when selecting a PCM. An ideal PCM will have high heat of fusion, high thermal conductivity, high specific heat and density, long-term reliability during repeated cycling, and dependable freezing behavior.

Paraffin waxes are the most common PCMs, which can be microencapsulated and then either integrated into fiber or used as a coating in textiles that have a high heat of fusion per unit weight, large melting point selection, and a low thermal conductivity; provide dependable cycling; are noncorrosive; and are chemically inert. When designing with paraffin PCM, void management is important due to the volume change from solid to liquid. Hydrated salts are another category of PCMs. These PCMs have a high heat of fusion per unit weight and volume, have a relatively high thermal conductivity for non-metals, and show small volume changes between solid and liquid phases. There are many other classes of PCMs. PCMs that have a melting point from 15 to 35°C are the most effective useful PCMs in textile fields. Other required properties for a PCM for a high-efficiency cooling system in textile fields are the slight temperature difference between the melting point and the solidification point, having low toxicity and being harmless to the environment, being non-flammable, ease of availability, and low price. The specified roles of PCMs in outdoor and protective smart textiles are the absorption of body heat surplus, insulation effect caused by heat emission of the PCM into the fibrous structure, and thermoregulating effect, which maintains the microclimate temperature to nearly constant [8].

The incorporation of PCMs within a fiber in the spinning process, coating, and laminating on the fabric are various methods of using PCMs in

textiles [4]. In manufacturing the fiber, the selected PCM microcapsules are added to the liquid polymer or polymer solution, and the fiber is then expanded according to the conventional methods such as dry or wet spinning of polymer solutions and extrusion of polymer melts. Fabrics can be formed from the fibers containing PCMs by conventional weaving, knitting, or nonwoven methods, and these fabrics can be applied to numerous applications including apparel and clothing, home textiles, and technical textiles [9–11]. In this method, the PCMs are permanently locked within the fibers, the fiber is processed with no need for variations in yarn spinning, fabric weaving/knitting, or dyeing, and properties of fabrics (drape, softness, tenacity, etc.) are not altered in comparison with fabrics made from conventional fibers. The small content of PCM microcapsules incorporated into the fibers in this method (upper loading limit of 5–10%) and the improvement of thermal capacity of the textile are limited.

A larger amount of PCM microcapsules (from 20% to 60% by weight) can be incorporated by coating on the smart textile surface. In this method, PCM microcapsules are embedded in a coating compound such as acrylic, polyurethane, and rubber latex, and applied to the surface of a fabric. In the lamination of foam containing PCMs onto a fabric, the selected PCM microcapsules can be mixed into a polyurethane foam matrix, from which moisture is removed, and then the foam is laminated on a fabric [12]. PCM microcapsules should be added to the liquid polymer or elastomer prior to hardening. After foaming, microcapsules will be embedded within the base material matrix. The application of the foam pad is particularly recommended because a greater amount of PCM microcapsules (from 20% to 60% by weight) can be introduced into the smart textile. In the foam coating method, different PCMs can be used, giving a broader range of regulation temperatures. Additionally, microcapsules may be anisotropically distributed in the layer of foam. The foam pad with PCMs may be used as a lining in a variety of clothing such as gloves, shoes, hats, and outerwear. Before incorporation into clothing or footwear, the foam pad is usually attached to the knitted/woven fabric by any conventional means such as glue, fusion, or lamination.

The addition of PCM foam to the back of a fabric significantly increases the weight, thickness, stiffness, flammability, insulation value, and evaporative resistance value. It is more effective to have one layer of PCM foam on the outside of a tight-fitting, two-layer ensemble than to have it as the inside layer. This may be because the PCMs closest to the body do not change phase. PCM protective garments should improve the comfort of workers as they go through these environmental step changes (e.g., warm to cold to warm, etc.). For these applications, the PCM transition temperature

should be set so that the PCMs are in the liquid phase when worn in the warm environment and in the solid phase in the cold environment [13]. The effect of PCMs in clothing on the physiological and subjective thermal responses of people would probably be maximized if the wearer was repeatedly going through temperature transients or intermittently touching hot or cold objects with PCM gloves.

The PCM microcapsules are also applied to a fibrous substrate using a binder (e.g., acrylic resin). All common coating processes such as knife over roll, knife over air, screen-printing, gravure printing, and dip coating may be adapted to apply the PCM microcapsules dispersed throughout a polymer binder to fabric. The conventional pad-mangle systems are also suitable for applying PCM microcapsules to fabrics. The formulation containing PCMs can also be applied to the fabric by the direct nozzle spray technique.

The application of PCMs to a garment provides an active thermal insulation effect acting in addition to the passive thermal insulation effect of the garment system [6, 14]. The active thermal insulation of the PCM controls the heat flux through the garment layers and adjusts the heat flux to the thermal circumstances. The active thermal insulation effect of the PCM results in a substantial improvement of the garment's thermophysiological wearing comfort [15]. The intensity and duration of the PCMs' active thermal insulation effect depend mainly on the heat-storage capacity of the PCM microcapsules and their applied quantity. In order to ensure a suitable and durable effect of the PCMs, it is necessary to apply proper PCMs in sufficient quantity into the appropriate fibrous substrates of proper design [16]. The PCM quantity applied to the active wear garment should be matched with the level of activity and the duration of garment use [8]. Furthermore, the garment construction needs to be designed such that it assists the desired thermoregulating effect. Thinner textiles with higher densities readily support the cooling process. In contrast, the use of thicker and less dense textile structures leads to a delayed and therefore more efficient heat release of PCMs. Further requirements on the textile substrate in a garment application include sufficient breathability, high flexibility, and mechanical stability.

In order to determine a sufficient PCM quantity, the heat generated by the human body has to be taken into account, carrying out strenuous activities under which the active wear garments are worn. The heat generated by the body needs to be entirely released through the garment layers into the environment. The necessary PCM quantity is determined according to the amount of heat, which should be absorbed by the PCMs to keep the heat balance equalized. It is mostly not necessary to put PCMs

in all parts of the garment. Applying PCM microcapsules to the areas that provide problems from a thermal standpoint and thermoregulating the heat flux through these areas are often enough. It is also advisable to use different PCM microcapsules in different quantities in distinct garment locations.

PCMs are used in winter and summer clothing not only in high-quality outerwear and footwear but also in the underwear, socks, gloves, helmets, and bedding of worldwide brand leaders [17]. Seat covers in cars and chairs in offices can consist of PCMs. In outdoor apparels, PCMs are being used in a variety of items such as smart jackets, vests, men's and women's hats and rainwear, outdoor active-wear jackets and jacket lining, golf shoes, trekking shoes, ski and snowboard gloves, ski boots, and earmuffs. In protective garments, PCMs are being used in a variety of items such as firefighter protective clothing, bulletproof fabrics, space suits, sailor suits, and so on.

A new generation of military fabrics features PCMs that are able to absorb, store, and release excess body heat when the body needs it, resulting in less sweating and freezing, while the microclimate of the skin is influenced in a positive way and efficiency and performance are enhanced [4]. In the medical textile field, a blanket with PCMs can be useful for gently and controllably reheating hypothermia patients. Also, using PCMs in bed covers regulates the micro climate of the patient. In domestic textiles, blinds and curtains with PCMs can be used for reduction of the heat flux through windows.

One example of the practical application of PCM smart textile is the cooling vest (TST Sweden Ab) [18]. This is a comfort garment developed to prevent elevated body temperatures in people who work in hot environments or use extreme physical exertion. The cooling effect is obtained from the vest's 21 PCM elements containing Glauber's salt, which starts absorbing heat at a particular temperature (28°C). Heat absorption from the body or from an external source continues until the elements have melted. After use, the cooling vest has to be charged at room temperature (24°C) or lower. When all the PCMs are solidified, the cooling vest is ready for further use.

Although the current focus of smart textile designers is mostly on fashion and appearance of the clothing, from the perspective of the human physiology–clothing–environment system and thermal physiology, the safety and protection engineers and physiologists emphasize functions in terms of developing functional and protective clothing by using phase change materials (PCMs) [8].

1.3 Shape Memory Materials

Shape memory materials (SMMs) are smart materials that can remember and recover substantial programmed deformation upon activation and exposure to an external stimulus such as temperature, magnetic field, electric field, pH value, and UV light [19]. They can be used comfortably with human skin because of their low weight and softness. The application of both alloys and polymers of SMMs in textile has gained momentum to shape memory smart textiles and they have been used in many areas of textiles [20, 21]. The shape memory polymers have a wider application in textile applications and polymers are more advantageous than alloys in terms of their ease of use, aesthetics, and price [20]. Commercialized shape memory products have been based mainly on metallic shape memory alloys (SMAs), taking advantage of the shape change due to either shape memory effect or the super-elasticity of the material, the two main phenomena of SMAs. Shape memory polymers (SMPs) offer a number of potential technical advantages that surpass other SMMs such as shape memory metallic alloys and shape memory ceramics. The advantages include high recoverable strain (up to 400%), low density, ease of processing and the ability to tailor the recovery temperature, programmable and controllable recovery behavior, and, more importantly, low cost.

An example of a natural shape memory textile material is cotton, which expands when exposed to humidity and shrinks back when dried. Such behavior has not been used for aesthetic effects because the changes, though physical, are generally not noticeable to the naked eye.

Shape memory polyurethane (SMPU) is an example of SMPs, which is based on the formation of a physical cross-linked network as a result of entanglements of the high molecular weight linear chains and on the transition from the glassy state to the rubber-elastic state. It is a class of polyurethane that is different from conventional polyurethane in that these have a segmented structure and a wide range of glass transition temperature (T_g). The long polymer chains entangle each other and a three-dimensional network is formed. The polymer network keeps the original shape even above T_g in the absence of stress. Under stress, the shape is deformed and the deformed shape is fixed when cooled below T_g . Above the glass transition temperature, polymers show rubber-like behavior. The material softens abruptly above the glass transition temperature T_g . If the chains are stretched quickly in this state and the material is rapidly cooled down again below the glass transition temperature, the polynorbornene chains can neither slip over each other rapidly enough nor become disentangled.

It is possible to freeze the induced elastic stress within the material by rapid cooling. The shape can be changed at will. In the glassy state, the strain is frozen and the deformed shape is fixed. The decrease in the mobility of polymer chains in the glassy state maintains the transient shape in polynorbornene. The recovery of the material's original shape can be observed by heating again to a temperature above T_g . This occurs because of the thermally induced shape memory effect [22]. The disadvantage of this polymer is the difficulty of processing because of its high molecular weight [23]. Some of the other SMPs such as polyethylene/nylon-6 graft copolymer, styrene-1,4-butadiene block copolymer, ethylene oxide-ethylene terephthalate block copolymer, polymethylene-1, and 3-cyclopentane polyethylene block copolymer are suitable for textile applications. For instance, in smart compression stocking using shape memory polyurethane and nylon filaments, it allows externally controlling the pressure level in the wrapped position on the leg using the external heat stimuli [24, 25]. Compression stockings or bandages are the preferred choice for the management of venous ulcers and also for the prevention of recurrence ulcers. Nevertheless, current textile-based compression products have many shortcomings such as size fitting, and the shape control ability of the shape memory textile will promote the development of one size stocking that could be programmed to fit different leg sizes [24].

SMA or SMP can be used in textile in accordance with needs for clothing and textile as fibers, yarns, and fabrics. They can be laminated, coated, foamed, and even straight converted to fibers. There are many possible end uses of the SMP smart textiles. Although SMAs have some applications such as in brassieres and flame-retardant laminates, SMPs have better potential for textile and clothing and related products. Shape memory fibers based on SMPs can be implemented to develop smart textiles that respond to thermal stimulus. The smart fiber made from the SMPs can be applied as stents and screws for holding bones together. SMP fiber can be produced with the spinning methods, allowing us to produce SMP yarns and consequently related textile products. These products are shoes, various breathable fabrics, thermal insulating fabrics and crease, shrink-resistant finishes for apparel fabrics, etc. SMMs can be used in textile with different production methods, and their products can be made with finishing, coating, laminating, blending, and other innovative structures. SMM fabrics including woven, knitted, braided, and nonwoven fabric easily returns to its original shape when heated above the switch temperature, even if it has been wrinkled or severely deformed. Therefore, the SMM fabric can be applied in collars and cuffs, which need to keep their shape, and for elbows and knees, which need to recover their shape if wrinkled. SMMs are useful

in many technical textiles, so it is obvious that interest on SMMs will continue to improve in the future [26]. One of the most well-known examples of SMPs is a clothing application, a membrane called Diaplex. The membrane is based on polyurethane-based SMPs developed by Mitsubishi Heavy Industries.

SMP-coated or -laminated materials can improve the thermophysiological comfort of surgical protective garments, bedding, and incontinence products because of their temperature-adaptive moisture management features. Films of SMPs can be incorporated in multilayer garments, such as those that are often used in the protective clothing or leisurewear industry. The SMPs revert within a wide range of temperature. This offers great promise for making clothing with adaptable features. Using a composite film of SMPs as an interlining in multilayer garments, outdoor clothing could have adaptable thermal insulation and be used as protective clothing. SMP membrane and insulation materials keep the wearer warm. Molecular pores open and close in response to air or water temperature to increase or minimize heat loss. In apparel made with shape memory fibers, forming the shape at a high temperature provides creases and pleats in such apparel as slacks and skirts.

The incorporation of the shape memory material into textile structure makes it possible to increase heat insulation because of the increase in the air layer thickness in the transverse direction of a flat textile fabric [27]. With the increasing temperature in the layer, the air pocket expands, and then the garments of shape memory materials make the firefighter less susceptible to burn injuries [28]. Other applications include fishing yarn, shirt neck bands, cap edges, casual clothing, and sportswear. Also, using a composite film of SMPs as an interlining provides apparel systems with variable tog values to protect against a variety of weather conditions. With the further development of currently available SMPs and the emergence of new types of SMPs, the range of applications is expected to expand more widely in the near future.

1.4 Chromic Materials

Chromic materials (CM) are the general terms used to refer to the materials that change their color according to the outside environmental conditions and stimuli [29–33]. Chromic materials are the materials that radiate, erasing their color because they induct color caused by the external stimuli. According to the stimuli type, chromic materials can be categorized as photochromic, thermochromic, electrochromic, piezochromic,

solvatechromic, and carsolchromic, which change their color by the external stimulus of light, heat, electricity, pressure, liquid, and an electron beam, respectively.

Photochromic materials are colorless in a dark environment and emit reversible color change when activated by ultraviolet radiation. The ultraviolet radiation changes the molecular structure of the photochromic materials, and it exhibits color. When the light source is taken away, the color disappears. In thermochromic materials, the liquid crystal type and the molecular rearrangement type are thermochromic systems in textiles. The thermochromic materials can be made as semiconductor compounds, from liquid crystals or metal compounds. The change in color occurs at a predetermined temperature, which can be varied. In electrochromic materials, the variation of the optical properties is caused by applied electric potentials. Solvatechromism is the phenomenon where color changes when it comes to contact with a solvent or liquid. Materials that respond to water by changing color are also called hydrochromic, and smart textiles containing these kinds of materials can be used, e.g., for swimsuits.

Chromic materials are one of the challenging material groups when thinking about future textiles. Textiles with chromic materials may find applications in design area and fancy clothes, sports garments, workwear, soldier and weapons camouflage fabrics, and technical and medical textiles [34]. Chromic materials can be applied into the textiles by inserting them into the fiber matrix using a traditional dyeing technique, blending them with a polymer and then extruding or wet spinning them into photochromic fibers, mixing them with a resin and surface coating them onto a fabric surface, and printing [35,36]. The combination of SMMs and thermochromic coating is an interesting area, which produces shape and color changes of the textile material at the same time.

1.5 Conjugated Polymers

Conjugated polymers are semiconductors or conductors that appear very attractive for use in sensors either as sensitive components or as a matrix for easy immobilization of specific substrates. They have been broadly explored as colorimetric sensing materials due to the intriguing optical and electrical properties associated with their extensively delocalized π -electrons and intrinsic conformational restrictions [37, 38]. When the backbones of these conjugated polymer chains are perturbed, the delocalized π -system induces changes in electronic absorption and emission properties. Thus, a variety of conjugated polymers such as polythiophene, polyaniline,

polypyrrole, polyphenylene, poly(phenylene ethynylene), polyacetylene, and polydiacetylenes (PDAs) have been employed as sensing matrices [39]. Among the conjugated polymers reported to date, PDAs have gained special attention owing to their meritorious features [40, 41]. These polymers can be produced by UV or γ -irradiation or plasma treatment of the self-assembled diacetylene monomer. PDAs undergo a blue-to-red color change in response to the various external stimulations, including heat (thermochromism), solvents (solvatochromism), mechanical stress (mechanochromism), ligand–receptor interactions (affnchromism), etc. (Figure 1.1).

These advantages make PDAs particularly attractive for sensing various biologically and chemically important target molecules [43–48]. The diverse types of PDA sensors have been prepared including microarrays, aqueous suspensions, thin films, electrospun nanofibers, and microbeads [49, 50]. Fibrous materials with different dielectric properties can be made from conjugated polymer composites and used in the electronic industries, in sensors and batteries, for electrical stimulation to enhance the nerve-regeneration process, and for constructing scaffolds for nerve tissue engineering. In the field of smart textiles, the conjugated polymers can be electrospun into nanofibrous mats in which they have higher surface-to-volume ratio in comparison with films and microfibrinous materials. In a study by Moazeni *et al.*, the electrospun polyvinylidene fluoride (PVDF) nanofibrous mats have been used as a matrix polymer for PDA immobilization [42]. The results of this research demonstrated that PDA

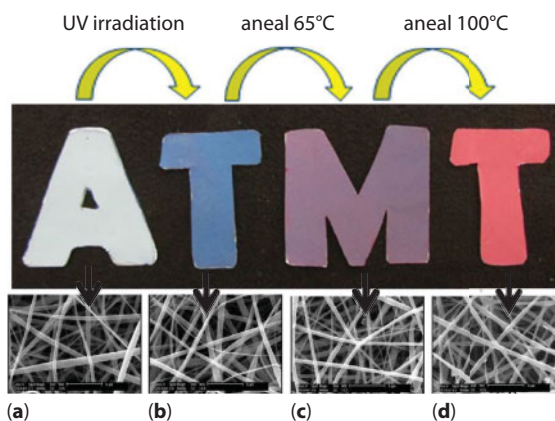


Figure 1.1 Optical and SEM images of a PDA-embedded PVDF nanofiber mat (a) before UV irradiation, (b) after UV irradiation, (c) after annealing at 65°C, and (d) after annealing at 100°C for 1 min (PVDF concentration of 23 w/v%; mass ratio of PVDF to PDA of 1:5 w/w%) [42].

has the effect of inhibiting the growth of nonpolar α -phase crystals, while promoting the growth of the polar β -phase.

1.6 Conductive Polymers

In addition to conductive metals, chemical plating and dispersing metallic particles at a high concentration in a resin are two general methods of coating polymeric fibers to create conductive fibers. The main advantages of conductive polymers are that they possess not only the electronic and optical properties of metals and inorganic semiconductors but also the flexible mechanics and processability of polymers [51]. Conductive polymers usually have an amorphous structure, in some cases with ordered domains. The conductivity of conductive polymers is closely related to the doping degree and the degree of ordering of the polymer main chain in the solid structure. Conductive polymers are usually insoluble and infusible because of their rigid conjugated main chain, which limits their application. Conductive polymers, such as polyacetylene (PA), polypyrrole (PPy), polythiophene (PTh), and polyaniline (PAn), offer an interesting alternative of conductive metals. Among them, PPy has been widely investigated owing to its easy preparation, good electrical conductivity, and good environmental stability in ambient conditions, and because it poses few toxicological problems [52, 53]. Conductive polymers can be prepared by chemical or electrochemical oxidation polymerization or by chemical catalytic synthesis. Conductive polymers can be used in electrically conductive smart textiles including fibers, yarns, fabrics, and textile goods [54].

The conductive fibers obtained through special treatments such as mixing, blending, or coating are known as conductive polymer composites (CPCs), and can have a combination of the electrical and mechanical properties of the treated materials. Conventional polymer fibers may be coated with a conductive layer such as PPy, copper, or gold [55]. PPy-based composites may overcome the deficiency in the mechanical properties of PPy, without adversely affecting the excellent physical properties of the substrate material, such as its mechanical strength and flexibility. The resulting products combine the usefulness of a textile substrate with electrical properties that are similar to metals or semiconductors. Nanoparticles such as carbon nanotubes can be added to the matrix to achieve conductivity. Polymeric fibers containing conductive carbon are produced with several methods such as loading the whole fibers with a high concentration of carbon, incorporating the carbon into the core of a sheath-core bicomponent fiber, incorporating the carbon into one component of a side-side

or modified side-side bicomponent fiber, and suffusing the carbon into the surface of a fiber.

Conductive fibers/yarns can be produced in filament or staple lengths and can be spun with traditional nonconductive fibers to create yarns that possess varying wearable electronics and photonics degrees of conductivity. Conductive yarns can be sewn to develop smart electronic textiles. Through processes such as electrodeless plating, evaporative deposition, sputtering, coating with a conductive polymer, filling or loading fibers, and carbonizing, a conductive coating can be applied to the surface of fibers, yarns, or fabrics. Printing of circuit patterns is carried out on polymeric substrates such as films and fabrics using conductive inks. Textiles coated with a conductive polymer, such as PAn and PPy, are more conductive than metal and have good adhesion, but are difficult to process using conventional methods.

Electrically conductive textiles make it possible to produce interactive electronic textiles. There are many applications for conductive textiles. They can be used for communication and antennas, entertainment, health-care, safety, homeland security, computation, thermal purposes, protective clothing, wearable electronics, and fashion. The application of conductive smart textile in combination with electronic devices is very widespread. In location and positioning, they can be used for child monitoring, geriatric monitoring, integrated GPS (global positioning system) monitoring, live-stock monitoring, asset tracking, etc. In infotainment, they can be used for integrated compact disc players, MP3 players, cell phones and pagers, electronic game panels, digital cameras, video devices, etc. In health and biophysical monitoring, they can be used for cardiovascular monitoring, monitoring the vital signs of infants, monitoring clinical trials, health and fitness, home healthcare, hospitals, medical centers, assisted-living units, etc. They can be used for soldiers and their personal support in the battle-field, space programs, protective textiles and public safety (firefighting, law enforcement), automotive, exposure-indicating textiles, etc. They can also be used to show the environmental response such as color change, density change, heating change, etc. Fashion, gaming, residential interior design, commercial interior design, and retail sites are other applications of conductive smart textiles.

1.7 Piezoelectricity

Piezoelectric materials respond to applied stress and convert energy between mechanical and electrical domains. The piezoelectric effect occurs when a piezoelectric material accumulates electrical charges with applied

mechanical stress, while the reverse piezoelectric effect occurs when the electric field is converted to the mechanical strain by a piezoelectric material. Piezoelectric ceramics and crystals commonly used as piezoelectric materials show good piezoelectric property, but they cannot be used in flexible applications due to their rigidity. Lightweight and flexible piezoelectric polymers like PVDF are good candidate materials for sensors because of their sustainable piezoelectricity and high piezoelectric constant [56]. PVDF is a semi-crystalline and chemically stable piezoelectric polymer that exhibits the highest piezo, pyro, and ferro electric properties with great potentials for various device applications. PVDF is most widely used in transducers and sensors for its extraordinary properties including easy moldability, good toughness, flexibility, and particularly excellent electrical properties [57, 58]. This polymer has also shown wonderful growth in energy conversion applications between electrical and mechanical forms because of its high flexibility, low cost, and biocompatibility [59]. The crystallinity of the PVDF polymer will be a major factor on the piezoelectric constant of polymers. Depending on the processing conditions of PVDF, four different crystal structures of α , β , γ , and σ can be obtained [60, 61]. In α -phase, the dipole moments have a random orientation and the net dipole moment is zero in this condition. The dipole moments pointing have the same direction in β -phase. Thus, the piezoelectricity of PVDF originates from the polar β -crystalline phase formation and is highly dependent on the orientation of dipoles in the β -phase [62]. The β -crystalline phase can be formed from modification of the α -phase by different processing conditions such as mechanical stretching, the application of high electric field, and crystallization under high pressure [63–66]. It has been shown that the higher β -phase portion of the PVDF film shows a higher piezoelectric constant as sensor material.

In addition to mechanical stretching and electrical poling, the electrospinning process is another interesting method to achieve a high percentage of β -phase PVDF nanofibers. The electrospinning process is useful for the piezoelectric polymer PVDF because it can provide both effects of mechanical stretching and electrical poling simultaneously. Copolymers of PVDF such as PVDF-tetrafluoroethylene (PVDF-TrFE) show higher crystallinity due to its chemical structure, resulting in better piezoelectric response.

1.8 Optical Fibers

Optical fibers have been developed using glass and polymers. The polymer-made optical fibers are flexible and have lightweight properties that are

demanding by textile products. Today, the processing of optical fibers in different textile technologies brought up a wide range of applications such as in displays and communication devices, or as sensing in a broad field of applications, such as medicals, healthcare, architecture, public premises, stage, fashion design, security and military devices, data communication, or automotive engineering [67].

Connected to an external light source, polymer optical fibers (POFs) incorporated in textile allow light transmission not only to selected locations but also holohedral on the textile surface. Textiles seem to be ideal substrates for 2D arrangements to fulfill specific photometric or radiometric requirements. With the integration of light in textiles, many companies followed the trend to combine modern design and functionality, and patented, for example, a light distribution system, flexible flat panel displays, and automotive solutions with fabric-like behavior and optic fiber fabric display. A textile-based display is created using the optical fibers in a fabric made of classic yarns [68]. The display matrix is created during weaving or knitting, using the texture of the fabric. These flexible textile-based displays have a very thin size and are ultra-lightweight. Integrating optical fibers into a woven fabric requires bending because of the crimping that occurs as a result of weave interlacing. However, standard POF materials like polymethylmethacrylate, polycarbonate, and polystyrene are rather stiff compared to standard textile fibers and therefore their integration into textiles usually leads to stiffening of the woven/knitted fabric and the textile touch is getting lost. Alternative fibers with appropriate flexibility and transparency are not commercially available yet.

POF sensors and devices integrated in textiles comply with an increasing request for flexible and flat structures, which are required for many different sensing applications. In most cases, woven structures that incorporate POFs are used, but embroidery or weft-knitted devices have also been developed. Dimensions of textiles rank from small embroidered structures to large woven fabrics or knitted webs. Some of the main advantages of textile products are their thin and lightweight structure, their drapability and bendability, and their manifold 2D design possibilities. Textile combined with POFs offers large possibilities for illumination, radiation, and signal transmission. Flexible and flat fabrics of POFs were used as a safe way to provide illumination because at the point of illumination, they are free of heat. Longitudinal transmitted light inside the POF can be used to sense the environmental conditions or stimuli. Compared with single-fiber solutions, the integration of more than one fiber into large area arrays allows further advantages for the detection of localization of single points in a fiber grid. Other than in traditional fiber optics, where light emission

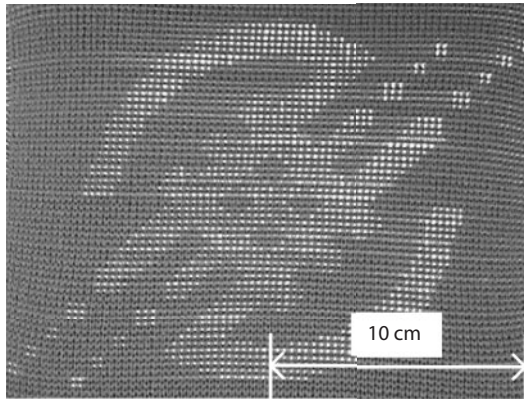


Figure 1.2 An example of an optic fiber-knitted fabric display [69].

occurs on the distal fiber end, in textiles, radiation emission happens laterally on defined places on the side of the POFs with useful effectiveness (Figure 1.2). This optic leakage occurs in different ways; for example, when bending the POF with a small curvature radius, it increases with a smaller bending diameter. The mechanical and chemical process can be used to create optic leakage for a defined pattern on a textile.

The POF textiles having external light source allow varied and easy-to-handle illumination. Their specific benefit is that the light source and emitting surface can be separated [70]. The luminosity of POFs depends on POF specifications such as diameter, the light source, optic leakage method, and processing of the fibers. In addition to the flexibility and lightweight feature of POFs, other properties such as durability, transmission capacity, easy handling, simple connections, robustness, and biocompatibility make them compatible with textile structures.

1.9 Hydrogels

Smart hydrogels are an interesting class of materials that can be used in diverse applications. They have the ability to respond to various kinds of physical, chemical, or biochemical stimuli. A group of stimuli-responsive polymers (SRPs) can be applied in textiles to produce stimulus-responsive textile surfaces in thermal/pH-responsive polymeric hydrogels. Thermal-responsive polymeric hydrogels (TRPGs) increase or decrease their degree of swelling at below or above a critical temperature [71]. Poly(*N*-isopropylacrylamide) (PNIPAAm) hydrogel coated on fabrics can

exhibit reversible swelling/shrinkage (hydration/dehydration) change and can cause changes in the water vapor transmission rates, permeance, and permeability of the fabrics. These properties enable the achievement of temperature-sensitive hygroscopic fabrics, temperature-sensitive deodorant fibers, and temperature-sensitive nutrient delivery fabrics. The application of PNIPAAm hydrogels into textiles is to fabricate thermal-responsive hygroscopic fabrics, environment-sensitive deodorant fibers, and stimuli-sensitive nutrient delivery fabrics [71]. Researchers have developed the copolymer P(MEO2MA-co-OEGMA) composed of 2-(2-methoxyethoxy) ethyl methacrylate (MEO2MA) and oligo(ethylene glycol) methacrylate (OEGMA) as an ideal substitute for PNIPAAm [72].

pH-responsive hydrogels (PRPGs) are the pH-dependent swelling materials with changes in hydrophilicity and morphology, when placed in different pH environments. They usually have weak acid or alkaline groups and they accept or release protons, changing the swelling of the hydrogels as a response to the pH value. The pH-responsive, drug-loaded electrospun nanofibers release at the characteristic pH of the disease, and when the condition is improved and the pH shifts to the normal value, such nanofibers could reduce the release rate or completely cease the release. Chitosan [poly(*N*-acetyl-D-glucosamine-co-D-glucosamine)] is a typical pH-responsive hydrogel with good biological activity, antibacterial activity, biocompatibility, and biodegradability that has been integrated into textiles [73].

SRPs can be grafted onto the surface of cotton, polypropylene, wool, and polyester yarns and fabrics using different techniques. The temperature-sensitive random linear and cross-linked copolymers of *N*-*tert*-butyl acrylamide (NTBA) and acrylamide (Am) were chemically integrated into the cotton yarns by Jassal *et al.* [74]. They concluded that the cotton yarns coated with this copolymer show a broad transition in the temperature range of 15–30°C, and an equilibrium volumetric swelling of ~4500% in about 5 min and deswelling within 10 s. Studies on the properties of cotton fabric modified with nanoparticles of poly(*N*-isopropylacrylamide)/chitosan (PNIPAAm/Cs) hydrogel indicate that these fabrics have acquired new smart responsiveness against pH and temperature [75]. Other researchers used the PNIPAAm/Cs hydrogel to modify cotton fabric using glutaric dialdehyde (GA) as a cross-linking agent following a double-dip-double-nip process [76]. They showed that the modified cotton fabric showed obvious thermosensitive behavior and high antibacterial activity.

The durability of stimuli-responsive hydrogel coating on the textiles, the physical and chemical compatibility between the hydrogel and textile substrate, and the thickness of the hydrogel coating are critical issues that significantly affect the designing of stimuli-responsive hydrogel-treated

textiles. However, much research should be carried out in order to have proper integration of SRPs into textile products promising more potential applications.

1.10 Smart Textiles and Nanotechnology

Coating a fabric with nanoparticles is being widely applied within the textile industry to improve the performance and functionality of textiles. Nanotechnology can add permanent effects and provide high durability fabrics [77]. Coating with nanoparticles can enhance the textiles with antibacterial, water-repellant, UV protection, and self-cleaning properties while still maintaining the breathability and tactile properties of the textile. Nano-tex has a range of products using such coatings to resist spills, repel and release stains, and resist static.

Electrospun polymer nanofibers represent an ideal class of sensing materials due to their inherently high surface-area-to-volume ratio, small interfibrous pore size, good interconnectivity [78], surface functionality, superior mechanical performance, low cost, and ease of construction [79]. Electrospun nanofibers have been incorporated into a diversity of detection schemes, including colorimetric, fluorescent, and electrochemical approaches. Among them, colorimetric readout is a desirable sensing technique, owing to the portability and low cost of the devices [80–85].

Among the various preparation methods of polydiacetylene (PDA) sensors, electrospun nanofibers have gained much attention. Electrospinning of PDAs without another polymer is challenging because the viscosity of PDA solutions is relatively low. Then, it should be mixed with another polymer named the matrix polymer. The matrix polymer serves as a supportive component in the fiber. Previously, PDA electrospun fibers have been developed with matrix polymers such as polymethylmethacrylate (PMMA), polystyrene (PS), tetraethyl orthosilicate (TEOS), and poly(ethylene oxide) (PEO) and polyvinylidene fluoride (PVDF) as a matrix polymer for PDA [42, 86–89].

The electrospinning technique offers a simple method of producing the PVDF nanofiber mat containing the β -crystalline phase without any requirements for posttreatment processes including electric poling and mechanical stretching. In fact, the dipole moments can be oriented in the electric field of electrospinning [90, 91]. Stretching of the material during the electrospinning process promotes polar β -phase formation [92]. The use of electrospun PVDF as a matrix polymer provides the opportunity to combine the advantages of two smart materials of PVDF as piezoelectric

and PDA as chromic materials. PDA-embedded electrospun PVDF nanofiber mats could have various applications in sensing due to the versatility to empower either colorimetric or electrical signaling.

1.11 Future Trends

Smart textiles are certainly becoming increasingly popular and not the exception in everyday life, as they offer significant enhancements to human comfort, health, and well-being. The development of high value-added textile products such as smart fabrics, technical textiles, and protective textiles has increased rapidly in the last decade. The application of stimuli-responsive materials in the textiles is a key path to produce flexible electronics, sensors, and actuators to develop a new generation of smart and adaptive electronic fibers, yarns, and fabrics for application in smart textiles.

To commercially improve the application of stimuli-responsive materials in high-strength, flexible, and electrically conductive smart textiles with energy storage and harvesting capabilities, biological functions, anti-microbial properties, and many other new functionalities, the application of nanotechnology and nanomaterials should be rapidly developed and the biocompatibility and safety of the developed devices must be seriously considered. In the next generation of smart textiles, the devices should be fully integrated into the garment through the use of stimuli-sensitive materials in the flexible fibrous structures such as fibers, yarns, fabrics, and garments. The market for smart textile is predicted to grow rapidly in the next decades. Smart textiles in the military, protection, and health sectors accounted for the largest share in comparison with other segments such as sports and fitness, home and lifestyle, industry, and fashion. It is obvious that the stimuli-sensitive smart textile will occupy a wider place in technical textiles and break new grounds for casual clothes, sports clothes, and medical textiles in the near future.

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Functional Finishing of Textile Materials and Its Psychological Aspects

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Abstract

Fabric is one of the basic human needs since the beginning of human history. Typically, various fibers and its blend lack certain essential performance due to the natural deficiencies in the fibers. However, due to the advancement in technology and consumer demand, textile finishes for various functional properties are gaining importance. Consequently, nowadays, functional finishes are the most imperative fabric treatment and play a vital role in the value addition of textile. This chapter will discuss the market share of various finishes and its application method for textile. It will also describe the top four most commonly used functional finishes (softeners, oil and water repellents, fire retardants, and easy care finishes) in detail. Each finish chemistry and mechanism of working for the desired effect for textile is thoroughly described in this chapter. Human psychology and consumer behavior have also been discussed with respect to functional finished fabrics.

Keywords: Easy care finishing, softeners, oil and water repellents, fire retardants, human psychology

2.1 Introduction

Textile wet processing is divided into three main stages: pretreatment, dyeing, and finishing. The finishing process is the last opportunity to incorporate certain properties required by the customer. Finishing can be divided

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into two further subcategories: mechanical finishes and chemical finishes. Details on mechanical finishes can be found in other published work [1].

Chemical finishes are more widely used; therefore, in this chapter, chemical finishes will be discussed in detail. Formulation or recipe plays a key role in the final result of the finish. Recipe is typically optimized by considering certain important factors like type of textile, especially its fiber content and construction, and performance requirement, especially its level and durability, cost-to-benefit ratio, availability of skilled labor and machinery, as well as the legally allowed limits and environmental impact of the finish ingredients. Normally, more than one finish is required to achieve the final performance; therefore, it is desirable to select and apply those functional finishes that are compatible and can be applied in one bath as a combination, which can lead to significant savings in water, energy, and machine availability. However, extra care is required when using a combination of functional finishes in a single recipe due to compatibility issues of the various finishes [2–4].

The importance of chemical finishes is increasing day by day due to the high demand of functional finished fabrics. The highest usage of chemicals (around 40%) in textile is related to finishing, as shown in Figure 2.1. The world market of textile finishing agents has been estimated to be 111.2 million tons in 2015. In addition, it is predicted to expand at 5.3% from 2017 to 2021. Softeners, repellents and resisting agents, flame retardants, and

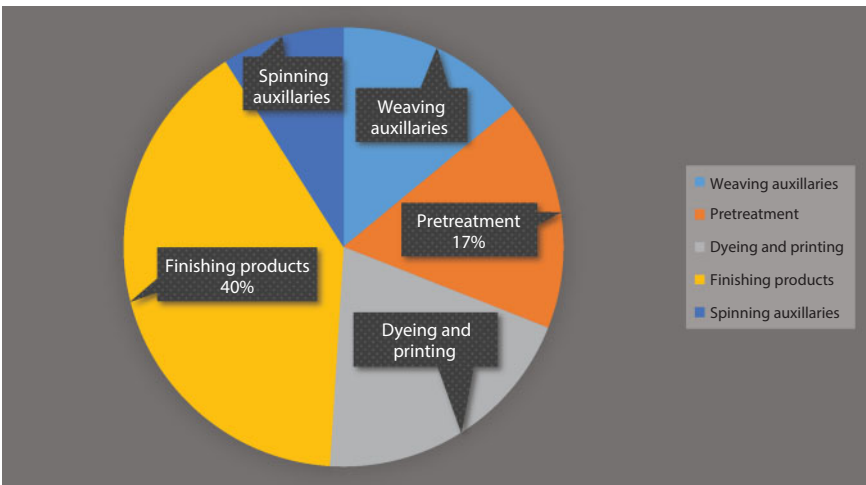


Figure 2.1 Textile auxiliaries distribution by market share [2].

wrinkle-resistant agents are among the top consumed finishes for textiles (Figure 2.2) [2].

Typically, there are two main methods that are most frequently used to apply the finishes onto the textile: continuous and exhaust/batch. In continuous application, mostly the pad-dry-cure method is used. The padding step involves the uniform application of the chemical finish recipe onto the fabric, the drying step is responsible for uniform water removal, and the curing/fixation step involves the bonding or fixation of the finish onto the textile fabric. In continuous application of the textile, pickup is very important, which actually reflects how much of the chemical is applied onto the fabric. Equation 2.1 exhibits the formula for the fabric pickup %. It is very important that the fabric is absorbent and very well prepared for continuous application method as typically less than 1 min is given to the fabric for picking up the desired finish recipe from the recipe bath [4].

$$\% \text{ Pickup (PU)} = \frac{\text{Wet fabric weight} - \text{Dry fabric weight}}{\text{Dry fabric weight}} \times 100 \quad (2.1)$$

In case of exhaust application of finish, the chemical is used with respect to the weight of the fabric. It is generally described as % OWF (on weight of fabric) or % OWG (on weight of good). Equation 2.2 exhibits the calculation as % OWF:

$$\% \text{ OWF} = \frac{\text{Weight of chemical}}{\text{weight of fabric}} \times 100 \quad (2.2)$$

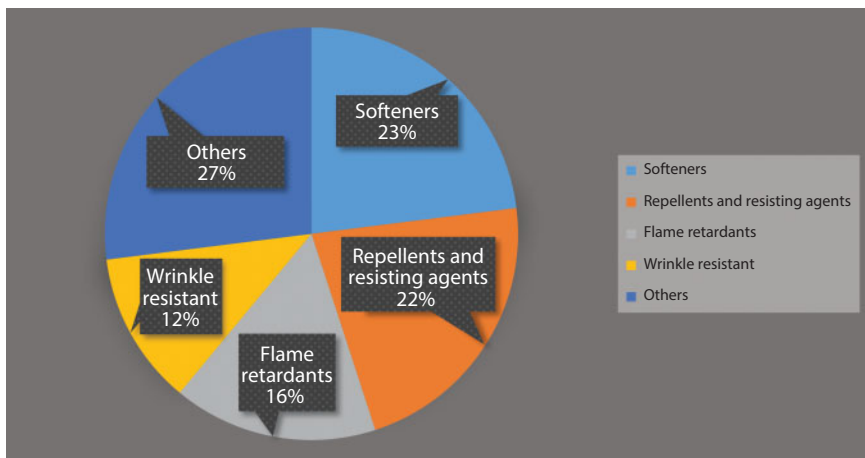


Figure 2.2 Functional finishing agent market share [3].

It is also important to note that the commercial chemical finish formulations are provided as a solution and can contain various amounts of the solid content of the actual finish. Therefore, the solid content will be crucial for the desired performance effect [4].

This chapter will discuss the functional finishes in the following order: softeners, oil and water repellents, fire retardants, and easy care finishes, which is also the sequence of its market share as exhibited in Figure 2.2.

2.2 Softeners

Softeners are the most widely used finishes for textile, as exhibited in Figure 2.2. Typically, fabric loses its natural softness to some extent due to the removal of natural waxes and oils, especially in the case of natural fibers. In addition, machine friction and other finishes that cross-link with the fabric, especially resins, will also impart a negative impact on the softness of the fabric. Garment manufacturing also requires a certain level of softness and lubrication due to the high machine speed. Softeners can also impart additional performance properties in the fabric like fullness, anti-static properties, sewability, improved tear strength, and easy care properties, to name a few [4].

There are a range of softeners that are being used, depending on the end use performance. Softeners can be classified into various aspects like ionic nature. In the category of ionic nature, softeners can be divided into four subcategories: anionic, cationic, nonionic, and amphoteric. Similarly, softeners can be differentiated based on the size of the particle or dispersion like macro, micro, and now even nano [5].

Waxes and polyurethanes have been reported as softeners and fillers. Polyethylene-based softeners can be divided into low-density, medium-density, and high-density categories. Polyethylene-based softeners are quite helpful in improving the tear strength of the treated fabric as well.



Fatty acid amide-based softeners are widely used in multifunctional finishes as they impart good softness, facilitate cutting and sewing, and are cost-effective. Typically, fatty acid amide-based softeners contain the 16- to 18-alkyl chain mixtures (Figure 2.3). Although the longer alkyl chain (such as the 22-alkyl chain) imparts superior softness, (but) it is difficult

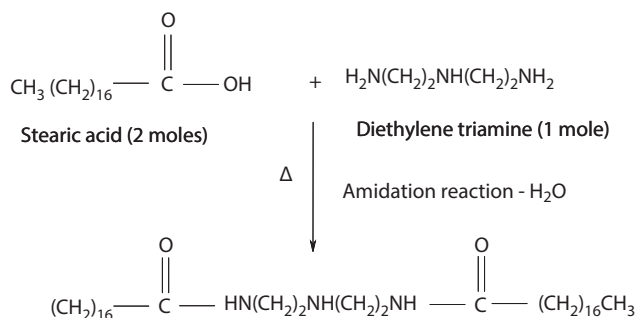


Figure 2.3 Fatty acid amide formation [5].

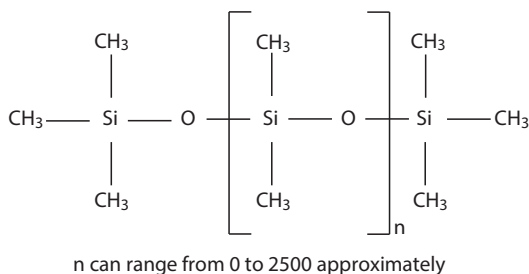


Figure 2.4 Structure of poly(dimethyl siloxane) [5].

to formulate and comparatively expensive as well. Fatty acid amide-based softeners can be made more cationic by leaving one amine group unreacted. Although amine value can be helpful in imparting cationization, it can also lead to yellowing of the fabric [5].

Silicone-based softeners hold almost one-third share of the softener market for textile. It imparts the best and unique softness in the fabric; however, it is comparatively expensive than other softener finishes. Typically, softeners used in textile are poly(dimethyl siloxane) based. It is highly flexible back bone with the ability of the Si-O bonds to rotate freely (Figure 2.4). The extended molecular flexibility of the siloxane chain is mainly responsible for the relatively low glass transition temperature of poly(dimethyl siloxanes) and their associated silky softness [4].

Alone, softeners have also been reported to impart the easy care performance of the treated fabric to some extent [6]. Softeners are also quite commonly used with resins, cross-linkers, and other finishes. Therefore, compatibility is the key in such combined application of the finishes.

2.3 Oil- and Water-Repellent Finishes

Oil- and water-repellent finishing is among the important functional finishes for textile. It is used for a variety of end usages like paper, leather, carpet, and textile. In the case of textile, it can be used for rain and outer wear, upholstery, workwear, tents, medical, technical textile, and nonwoven. Apart from chemical treatment, the type of fiber in a fabric, fabric weave, cover factor, and yarn twist also play an important role in determining the repellent property of the fabric [1].

The contact angle of the liquid and surface (textile) is very important in defining the repellency or spread of the liquid. If the contact angle is higher than 90° , then the liquid will not wet the textile, while the liquid will wet the textile when the angle is lower than 90° ; however, the fabric will be completely wet when the angle is 0° .

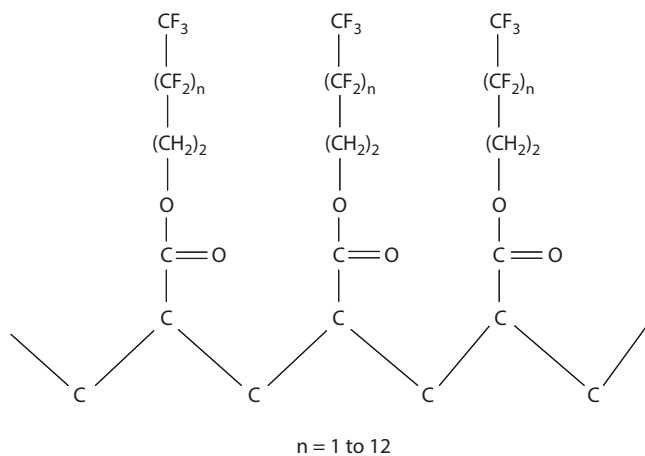
Surface tension plays a critical role in deciding the efficiency of the oil- and water-repellent finishes. Oil- and water-repellent finishes can be divided into two categories: water repellent and oil repellent. Typically, water-repellent finishes can only lower the surface tension of the fabric up to 30 dynes/cm while oil- and water-repellent finishes can reduce the surface tension of the fabric to as low as 6 dynes/cm (Table 2.1). It is also quite obvious that every oil repellent will be automatically water repellent as well due to the lower surface tension [7].

Compounds of aluminum and zirconium are among the oldest water repellents. There are a number of compounds that have been reported as water repellents, such as paraffin wax or its combination like bees wax, carnauba wax, and vaseline wax; glue; gelatin; aluminum salts; chrome complex; quaternary ammonium pyridinium compounds; stearamidomethyl pyridinium chloride; stearic acid; stearic acid with formaldehyde derivatives; and silicone-based chemicals like dimethyl polysiloxane and methyl hydrogen polysiloxane. However, all of the above mentioned compounds can only impart water repellency, while fluorocarbon-based finishes are the only practically applicable finishes that can impart oil and water repellency [8].

The discovery of fluorocarbon as being oil and water repellent was accidental; in 1953, a few drops of fluorocarbon liquid fell on tennis shoes and exhibited good repellency. Now, it is one of the most effective and widely used oil- and water-repellent finish. It is quite obvious from Table 2.1 that the higher the number of atoms of fluorine in the finish, the better will be the repellency. The uniform distribution of the finish; the orientation, structure, and length of the fluorocarbon; and % of the finish applied will

Table 2.1 Critical surface tension of various substrates [7].

Surface constitution	γ_c (dynes/cm)
Oriented perfluoro alkanes ($-\text{CF}_3$)	6
$-\text{CF}_2\text{H}$	15
PTFE ($-\text{CF}_2-$)	18
Oriented alkanes ($-\text{CH}_3$)	23
Silicone	24
PE ($-\text{CH}_2-$)	31
$-\text{CH}-$ (benzene ring edge)	35
$-\text{CCl}_2$	43
PVC	39
Polyester	43
Cotton	44
Wool	45
Polyamide	46

**Figure 2.5** Structure of perfluorinated acrylate [9].

affect the end product performance. Generally, an acrylic backbone is attached to a fluorocarbon chain (Figure 2.5), which will enable the covalent bonding of the fluorocarbon with cellulose (Figure 2.6) [9, 10].

Fluorocarbon finishes are expensive and researchers have recently incorporated zero formaldehyde cross-linkers to enhance the repellency performance and washing durability of the treated fabric. Dihydroxy ethylene urea has been reported with some good effect to enhance the performance of the fluorocarbon finishes [10]. Citric acid has also been reported with fluorocarbon finishes with much enhanced performance (Figure 2.7) [9].

The position of the fluorocarbon applied onto the fabric is changed during its washing and needs ironing to reorient itself. However, finishes that can carry out the reorientation by just tumble drying or air drying

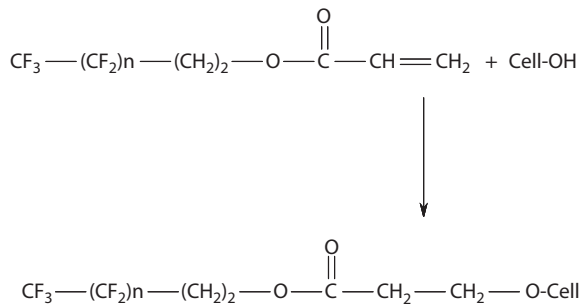


Figure 2.6 The direct bonding of the fluorocarbon finish to cotton [9].

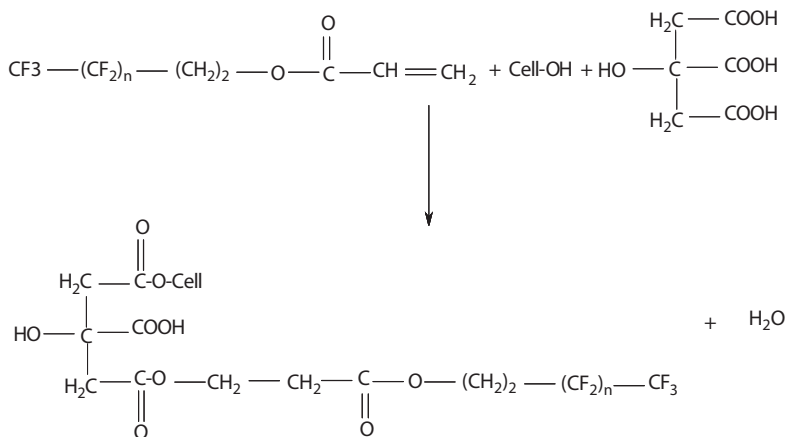


Figure 2.7 The cross-linking reaction between fluorocarbon finish and cotton via citric acid [9].

have been developed. It is true that fluorocarbon finishes are the most effective oil and water repellents but serious concerns have been raised on the toxicity of fluorocarbon. Historically renowned C8-based fluorocarbon finishes have been withdrawn due to their toxicity for human and aquatic life in 2015. ZDHC has already placed the C6-based fluorocarbon in their 11 priority substance list. Therefore, more research efforts are required in developing effective C2 oil and water repellents for textile [10].

2.4 Fire Retardants

There is no doubt that fire is one of the important tool for humans; however, it can be very dangerous if out of control. Cellulosic-based textile, especially cotton, is among the most flammable materials. A number of flame retardants have been reported since ancient times, and asbestos has been reported as one of the first fire retardants. Aluminum, ferrous sulfate, and borax have been reported as one of the first patented fire retardants for cellulosic textile. Typically, flame retardants can be divided into three subcategories: non-durable, semi-durable, and durable. Non-durable flame retardants are mostly related to water-soluble inorganic salts. Boran, boric acid, borax, ammonium sulfate, diammonium hydrogen phosphate, carbonates, and certain metallic salts like zinc chloride have been reported as non-durable fire retardants for cellulose [11]. Under the category of semi-durable flame retardants, ammonium polyphosphate, aluminates, zinc phosphate, antimony phosphate, aluminum phosphate, as well as certain metal oxides like iron, titanium, and zirconium have been used for textile [12].

There are certain durable fire retardants that have been used and still under use by the textile industry. Phosphonium derivatives like tetrakis(hydroxymethyl)phosphonium chloride (THPC) are very effective fire retardants. However, they require a special ammonia chamber and ammonia treatment for best results; therefore, their use is comparatively less. *N*-methylol dimethylphosphonopropionamide (MDPA) (Figure 2.8), under the trade names Pyrovatex CP and Pyrovatex CP New, has been one of the most successful durable flame retardant agents for cotton [13].

To obtain the best results, trimethylolmelamine (TMM) is incorporated with MDPA to enhance fire retardancy and washing durability as TMM provides the nitrogen to impart the synergistic effect with phosphorus and also bind the MDPA more effectively to cotton [14–16].

The MDPA formed a covalent bond under suitable conditions with cotton as shown in Figure 2.9. Unfortunately, both MDPA and TMM release

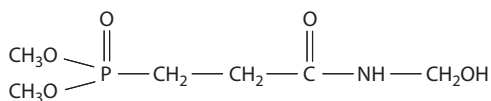


Figure 2.8 MDPA structure [14].

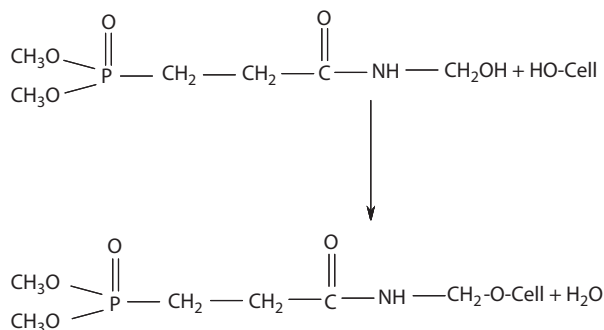


Figure 2.9 Formation of covalent bond between MDPA and cotton [14].

formaldehyde, especially TMM, which releases a high amount of formaldehyde, which is one of the reactant precursors. Therefore, researchers have reported the use of MDPA with citric acid as a replacement for formaldehyde enhancer [14].

Different fibers behave differently when exposed to fire. Pyrolysis temperature and limiting oxygen index (LOI) are the key parameters that affect the fire retardancy of the fiber. Table 2.2 describes the melting point, pyrolysis temperature, ignition temperature, and LOI of some of the most commonly used fibers for textile [17].

Fabric weight and fiber type play a key role in the fire resistance of the textile (Table 2.3). In addition, ignition time and flame spread rate are also crucial for the fire resistance of the textile [18].

The demand for fire-retardant fabrics increases day by day. However, the challenge is to find and optimize sustainable as well as halogen- and formaldehyde-free fire retardants. It is also important to note that typically 200–400 g/L of the fire retardant is required for cotton to impart the acceptable fire retardancy. The requirement of a high dosage of the fire retardant that also contains toxic ingredients will cause greater concern for sustainability; in addition, this high dosage will typically lead to high strength loss and color change of the treated fabric. Zero discharge of hazardous chemicals (ZDHC) and vision 20:20 have placed the halogenated fire retardants in their 11 priority substance list. Therefore, more research

Table 2.2 Flammability properties of the commonly used fibers [17].

Fiber	Melting temperature (°C)	Pyrolysis temperature (°C)	Ignition temperature (°C)	LOI (%)
Natural fibers				
Cotton	–	350	350	18.4
Wool	–	245	600	25
Silk	–	320	600	23
Synthetic—thermoplastic				
Nylon 6	215	431	450	20–21.5
Nylon 6,6	265	403	530	20–21
Polyester	255	420–477	480	20–21.5
Polypropylene	165	469	550	18/6
Poly vinyl chloride	>180	>180	450	37–39
Synthetic—char formers				
Viscose	–	350	420	18.9
Acrylic	>320	290	>250	18.2
Modacrylic	>240	273	690	29–30
High-performance fibers				
Meta-aramid (e.g., Nomex)	375	310	500	28.5–30
Para-aramid (e.g., Kevlar)	560	590	>550	29
Oxidized acrylic	–	>640	–	55
Polybenzylimidazole (PBI)	–	>500	>500	40–42
Polytetrafluorethylene (PTFE)	>327	400	560	95

Table 2.3 Ignition, flame spread, and heat release properties of widely used fibers [18].

Fiber	Ignition time using BS 5438 Test 1 (s)		Auto ignition		Flame spread rate using modified BS 5438 Test 3 (m/s)			Cone results at 35 kW/m ² heat flux		
	Face ign.	Edge ign.	Ign. temp (°C)	Ign. time (s)	Vertical	45° angle	Horizontal	TTI (s)	PHRR (kW/m ²)	THR (MJ/m ²)
Lightweight cotton (87 g/m ²)	2	1	480	16	57	37	6	9	94	1.0
Heavyweight cotton (180 g/m ²)	4	1	480	35	27	18	3	14	128	3.2
Polyester cotton (65:35,105 g/m ²)	2	1	574	20	37	24	9	10	154	1.9
Acrylic (118 g/m ²)	*		–	–	23	13	6	17	292	4.5
Lightweight silk (71 g/m ²)	2	2	909	3	***	***	***	***	***	***
Heavyweight silk (174 g/m ²)	**	3	655	4	***	***	***	28	45	1.0
Wool (173 g/m ²)	3	3	746	3	23	12	14	16	171	2.9

*Flame extinguished when the flame was moved away.

**Fabric melted away from the flame.

***Test not performed.

efforts are needed to develop a sustainable and efficient fire retardant for the textile industry [15].

2.5 Easy Care Finishing

Wrinkling or the presence of creases is one of the serious issues for most natural fibers, especially cellulosic ones. Therefore, easy care finishes are one of the most commonly used finishes for textile. The first resin finish was developed by Foulds and fellow scientists during the end of the 1920s. However, since then, it is the quite frequently used finish in textile [19]. In all types of cross-linker finishes, dimethylol dihydroxyethylene urea (DMDHEU) is the most widely used easy care finish till today, although its modified version is only allowed to use nowadays due to formaldehyde limit restriction. The synthesis of the DMDHEU is exhibited in Figure 2.10 [4].

DMDHEU reacts with cellulose as ether linkages under acidic conditions through the formation of carbonium ion, as shown in Figure 2.11.

A catalyst is essential to carry out the reaction in a faster and effective way. Although zinc nitrate is reported to be the most effective catalysts for DMDHEU, zinc nitrate leads to the yellowing of white fabric and exhibits a change in the shade of certain dyed fabrics. Consequently, magnesium chloride is typically preferred over zinc nitrate [20].

In order to obtain the easy care effect, DMDHEU under suitable conditions (pH around 5 and curing temperature of 150–160°C for 3–5 min) will cross-link the adjacent cellulose polymer chains as exhibited in

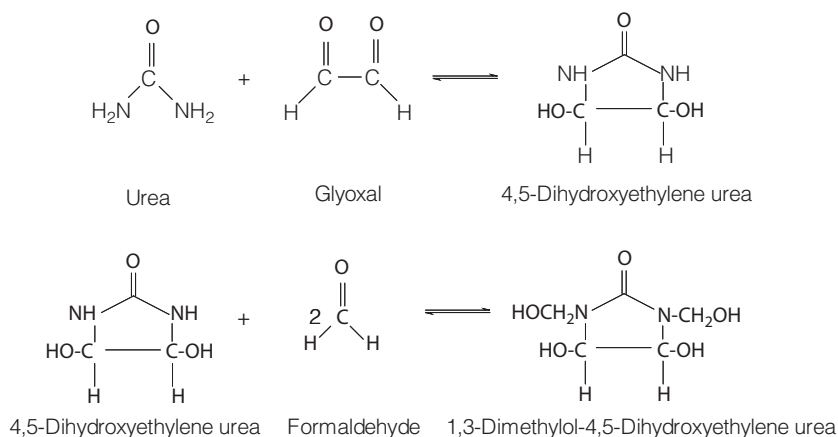


Figure 2.10 Synthesis of DMDHEU [4].

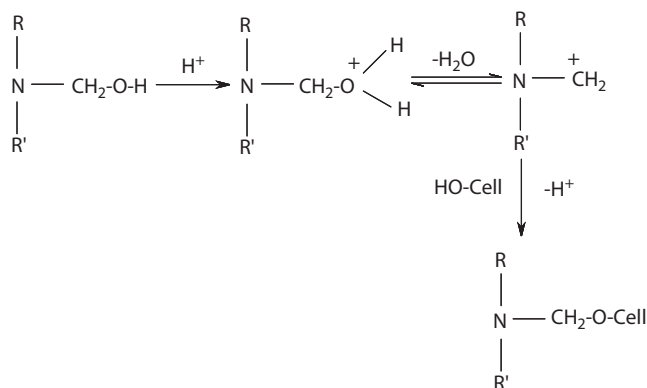


Figure 2.11 Acid catalyzed reaction of *N*-methylol compounds [4].

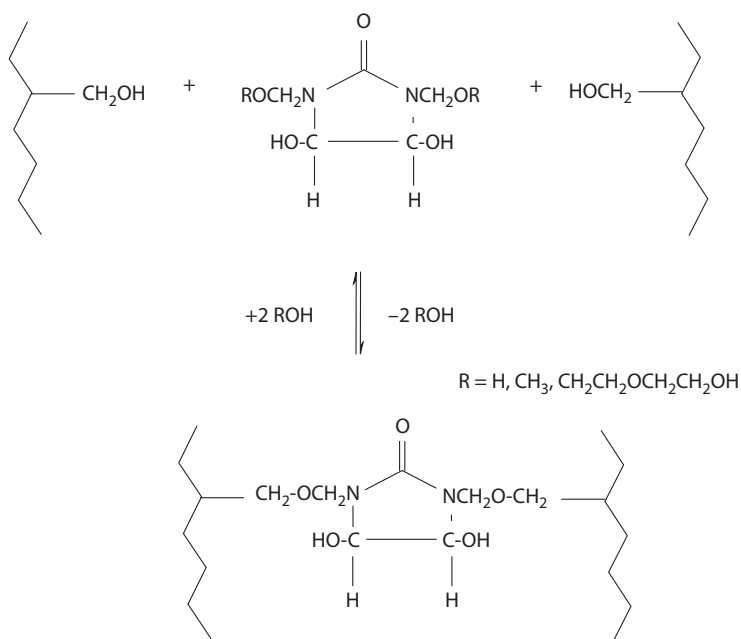


Figure 2.12 Cross-linking of cellulose with DMDHEU [1].

Figure 2.12. These newly introduced cross-links will restrict or prevent the free movement of cellulosic chains; consequently, it will control wrinkle formation [1].

Although DMDHEU is one of the most cost- and performance-effective cross-linker, it releases higher than the currently allowed formaldehyde

amount. Therefore, nowadays, DMDHEU in its pure form is not allowed to be used for textile, and its alkylated products are used nowadays as shown in Figure 2.13. The greater the alkylation of DMDHEU, the lesser the release of the formaldehyde and the lower the efficiency of the finish [4].

There are other ways to reduce formaldehyde release like polyol addition. Diethylene glycol is one of the most efficient polyols in controlling formaldehyde content. Figure 2.14 describes the modification of DMDHEU by using polyols [4].

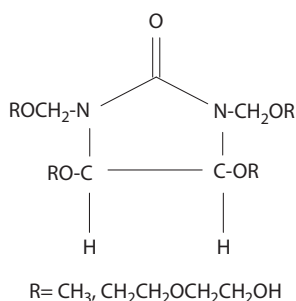


Figure 2.13 Alkylated DMDHEU [4].

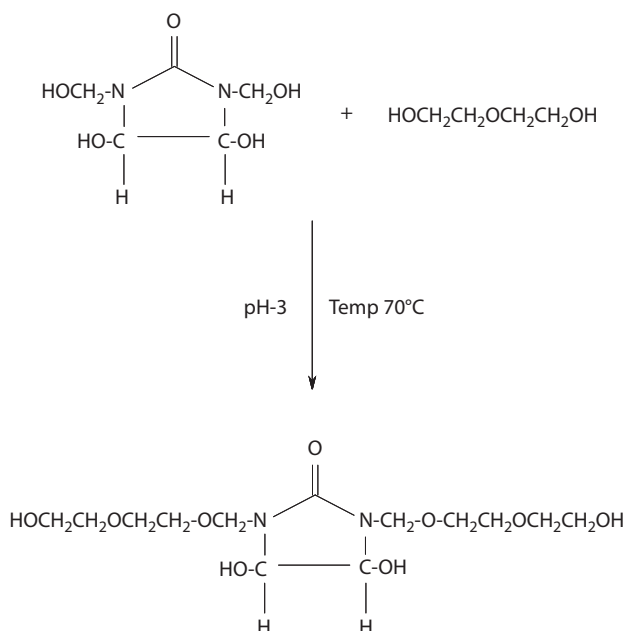


Figure 2.14 Modification of DMDHEU by using polyols [4].

The addition of the extra rinsing step or application of formaldehyde scavengers and mildly acidic after treatments also lowers the amount of formaldehyde release, although these agents are not as effective as the derivatization of DMDHEU [21]. It is also evident that derivation of DMDHEU to control the release of formaldehyde makes it less effective as a cross-linker and more expensive as compared to the precursor DMDHEU [22].

Formaldehyde-based cross-linkers are the cheapest and DMDHEU is one of the best; however, formaldehyde is toxic, is an irritant, and, most dangerously, has been confirmed as a human carcinogenic by the WHO International Agency for Research on Cancer. Therefore, formaldehyde has already been completely banned in certain countries and others have put strict limits on its usage and release. Significant modification of DMDHEU is needed to pass the currently allowed formaldehyde limits, which make the product more expensive, and formaldehyde release can be increased during storage and transportation of fabric in humid conditions as well as after washing. Therefore, formaldehyde-free cross-linkers are gaining significant importance. Table 2.4 presents various finishes that have been used commercially as a cross-linker and their formaldehyde release [22].

Dihydroxy ethylene urea (DHEU) is one of the most widely used urea-based zero formaldehyde cross-linkers, but it is significantly less effective than DMDHEU and needs modification to exhibit an acceptable performance, especially regarding yellowing control. Dimethyl dihydroxyethylene

Table 2.4 Classification of commercial cross-linkers [1].

Formaldehyde release of cross-linking agent (ppm)	Type
High (>1000)	Phenol formaldehyde Methylol melamine Dimethylol urea
Reduced (700–1000)	Dimethylol ethylene urea Dimethylol dihydroxyethylene urea
Low (<100)	Etherified, dimethylol dihydroxyethylene urea
Free	Dimethyl dihydroxyethylene urea Dihydroxy ethylene urea Polycarboxylic acids

urea Dimethyl dihydroxyethylene urea (DMeDHEU) is another urea zero formaldehyde-based cross-linker, but it is twice as expensive as DMDHEU and also requires double the amount to obtain a comparative performance to that of DMDHEU, leading to its less usage in the textile industry [27].

Polycarboxylic acids are a good alternative to DMDHEU and other formaldehyde-based cross-linkers. The most commonly reported carboxylic acids are maleic acid [23], itaconic acid, citric acid [24–26], and butane tetracarboxylic acid (BTCA). However, dicarboxylic acids like maleic acid and itaconic acid are less effective, while BTCA has four carboxylic acids, but it is too expensive. Although citric acid is a good cross-linker, it exhibits yellowing. Significant research is currently being carried out to enhance the performance of the carboxylic acid, and a couple of products are sold as a modification of carboxylic acid, but their technology is kept secret. A detailed chapter related to zero formaldehyde cross-linkers, especially carboxylic acid structure, mechanism, and application conditions, has already been published by the author [27] and can be consulted for further details. It is quite clear that the future for formaldehyde-free cross-linkers looks promising, but more research is needed to enhance their performance [27].

2.6 Psychological Aspect of Functional Textiles

Fabrics and, consequently, clothing are among the most important needs of humans after air, water, and food. Clothing provides essential covering of the human body, aesthetics, protection, as well as comfort. Initially, clothing was only used to cover the human body, but later, with the advancement of human knowledge, other features also became vital. Nowadays, human psychology and comfort play a critical role in the selection of certain types of clothing by consumers. Functional finished fabrics are getting more and more important due to their ever-increasing demand, human psychology, and comfort preferences. Functional finished fabrics or garments that are preferred by the consumer will be more popular, produced, and sold. Nowadays, one of the most obvious purposes of clothing is to provide and improve wearer comfort by providing physical protection from weather, environmental dangers, occupational hazards, and enemies [28].

In this era of competitive market, every industry's success depends largely on how accurately the industry understands its target customers. Understanding the views and thoughts of wearers is vital to textile production and marketing. The wearer's decision about buying textile reflects the customer's rational behavior. It is important to understand the consumer

behavior, and it can be defined as “the study of human response to products or services and the marketing of products and services.” According to different researchers, it is important to understand the expectations and reactions of customers as they are purchasing textiles in various finished forms [28].

It is quite obvious that consumers did not think about the processes of textile rather its main focus is on the end product, how it will look like and behave under different circumstances. The selection of clothing depends on many human psychological factors, of which two of the most important are the desire of a person and the specific end use application. In addition, both of these are consumer dependent. However, the preferences of people are not restricted to these two factors, as there are other psychological and environmental factors that can influence preferences like comfort, functional performance, season, color, age, fashion, tradition, and types of activity being performed by the potential wearer [29].

Functional finished fabrics like softener-treated fabrics can increase the comfort of the wearer. According to the latest research, comfort is considered one of the most important criteria in assessing wearers' clothing preferences [30, 31]. Hatch [30] defines comfort as a “neutral state”; in this state, the person feels no discomfort or any kind of pain. Rather it is considered as a balance of aspects (physical, physiological, and psychological) between an individual and his/her environment [32]. Comfort of clothing is mostly related to the stimuli and the sensations that wearers feel in accordance with the change of human activity or change of microclimate [33].

Liu (2012) in his research stated that although customers may focus on different aspects of clothing, such as the latest design or fashion, fitting of the clothing, workmanship, style of clothing, and color of clothing, during the purchase of the garment, the most common and most sought factor is comfort [34].

The main focus of psychological comfort is on the wearer's comfort in accordance with his role, value, and social being. The focus of psychological comfort is the person's inner satisfaction with the choices that are available, so the main concern here is inner self-consciousness [35, 36]. Personal features, such as a person's body image, personality, culture, belief, religion, political values, personal interests, and level of awareness, are all part of the psychosocial spectrum. However, like these, there are also different features of clothing based on fabric details and finishing. Some of these features are style of clothing, texture, design and color of the fabric, aesthetics, functional performance, fashion, and suitability [37].

On a psychological perspective, perception is very important and is an integral part of everything that we know, feel, learn, or think. Whatever

humans perceive is based on stimuli from the sensory receptors of vision, touch, smell, sound, and taste. A functional finished fabric that is treated with easy care finish will obviously control the wrinkles on it, consequently leading to a better appearance and a higher desirability from customers. Numerous researchers study “sensorial comfort” in detail, which is defined as the different sensations that a person feels toward discomfort when the fabric touches the person’s skin [38, 39]. Therefore, when our clothing touches our skin, this physical stimulus (clothing) stimulates several sensory receptors such as thermoreceptors related to temperature and photoreceptors related to image, which results in psychophysical perception [39].

In textile, as well as in psychology, “fabric hand” is a term that is used to examine the sensory property of the textiles [40]. When a person touches the cloth, he gets tactile sensations or feelings of smoothness or roughness, prickliness or scratchiness, stickiness, softness, or stiffness. For example, a person feels discomfort or pain when he wears an article of clothing made of fibers that produce sensations of prickliness or itchiness. Therefore, it can be said that when a person touches the clothing, the “fabric hand,” which, in a way, involves subjective analysis, is associated with the psychological result. Consequently, a person gets a series of information by moving his fingers across the surface of a fabric, which leads to the development of emotions and related cognitions within his mind. Therefore, those perceived impressions or feelings are considered parameters for a particular type of hand tests, and such decision can also be influenced by other factors such as personality, environment, past experience, moods, and the criteria of rating or scaling [41–43]. Particularly, tactile sensations are linked with somatic sensory receptors and are responsible for the sensory analysis of the body. These somatic receptors depend on the information that is obtained from the stimuli like texture and pressure of fabric, thermal reaction of stimuli, softness, easy care performance, and elongation or tightness of the fabric based on the type of technique or style used for touch [44].

In order to measure the comfort, subjectively different psychological scales were also developed. For example, Berry *et al.* [45] developed a four-point rating scale in order to measure different levels of clothing comfort: 1, comfortable; 2, slightly uncomfortable; 3, uncomfortable; and 4, very uncomfortable. Similarly, a 13-point rating scale known as the “McGinnis Thermal Scale” was developed for the wearer to rate according to his/her subjective perception based on questions related to behavioral description, sensory details, and affective descriptors [46]. As discussed earlier, apart from clothing attributes, the attitude, norms, and beliefs of the wearer also contribute in the perception of comfort. The results of the study by He *et al.*

are also consistent with those of previous studies in which consumers have a clear and distinctive attitude toward specific fabrics that are generally popular across several wearer categories [47].

2.7 Challenges and Future Directions

There is no doubt that the demand for functional finishes will increase further in the near future. However, functional finishes also face the tough challenge of being toxic free, water and energy efficient, sustainable and yet performance efficient. Padding and exhaust are the most common methods of application for functional finishes. Recently, new technologies are being developed to make the application process more energy and water efficient. Foam technology is one of them, where an overall savings of 38% (in energy and water) is expected. Similarly, plasma finishing technology and nano bubble technology can also impart their positive impact in the near future. In addition, another tough challenge is to develop such functional finishes that are environment friendly and sustainable. There is a need to develop efficient and durable fluorine-free water repellents as well as C2 (or lower)-based oil and water repellents. In addition, more efforts are required in developing effective halogen- and formaldehyde-free fire retardants as well as formaldehyde-free resins. The zero discharge of hazardous chemicals (ZDHC) program has already established the priority list in which the above mentioned toxic ingredients are banned. In addition, ZDHC has also developed the research list and is planning to ban those chemicals in the next phase; therefore, finding alternatives to such toxic chemicals is very crucial for the growth of the functional finished fabric industry. It can easily be said that the future for sustainable functional finishes looks promising. In addition, it is also desirable that such functional finishes are also applicable to new emerging water- and energy-efficient technologies (foam, plasma, and nano bubble). Psychological aspect and consumer behavior also play a crucial role in the future of functional finishes. More efforts need to be carried out in order to understand consumer behavior and the psychological aspects of various regions, as well as the correlation of gender and age group to these functional finishes.

2.8 Conclusion

It can be concluded that softeners, easy care finishes, oil- and water-repellent finishes, and fire-retardant finishes are among the most important

functional finishes for textile, and the demand for these finishes will further increase. New chemistries in these functional finishes improve the performances of the treated fabrics. In addition, psychological aspect and consumer behavior are also important in the selection of certain types of functional finished fabrics or garments; therefore, they should also be kept in mind. It is also clear that only sustainable functional finishes as per the desire of the consumer can survive in the future.

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Recent Advances in Protective Textile Materials

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Abstract

Protective textiles are saving human beings from various adverse environmental conditions like fire, heat, bullets, microorganisms, mosquito bites, etc. In connection with flame-resistant textiles, fish DNA, casein, whey protein, and wastage plant-based bio-macromolecules, such as spinach juice, banana pseudostem sap, coconut shell extract, and so on, are well reported as flame-resistant materials on cellulosic, lignocellulosic, and protein-based textile products. Apart from it, different nano-based metal oxides are also very popular because of their fire-retardant efficacy at low add-on percentage. Recently, bulletproof and the stab-resistant textile materials are also capturing the defense market very quickly. Concerning this area, designing lightweight bulletproof materials is the major target for the researchers for its wide application. As regards mosquito-repellent protective textiles, different synthetic-based products and eco-friendly plant-based oils (like citronella, clove, eucalyptus) are explored by researchers for their efficient mosquito-repellent properties. Besides, to evaluate the efficacy of mosquito repellency, cone tests, cage tests, etc., are also developed by research societies. Wastage plant extracts like coconut shell extract, neem, aloe vera, etc., are reported to have excellent micro-organism protective efficacy when it is applied on the fabric surface.

Keywords: Fire retardant, bulletproof, mosquito repellent, microorganism protective, textile

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3.1 Introduction

Protective textile clothing is now a major part of the advanced engineered technical textile materials and it is one of the fastest-growing areas in textile consumption in the world. Protective textile materials protect humans from injury or death and save their lives from various natural/industrial hazards as well as when people are in the vicinity of an extreme surrounding situation. For example, some of the common environmental hazards are heat, fire, cold, rain, smoke, ultraviolet radiation, dust, microorganisms, etc. Among the natural and the industrial hazards, fire, car gas fumes, smoke, toxic chemicals, sharp edged and impact of high-velocity objects, molten metal, and electricity protection are predominant. Fire protective textiles is one of the major concerning field among all the protective textile materials used by the normal human beings, and may be attributed with the mass life-threatening effect of the fire temperature and toxic smoke in very less period of time duration. Recently, different chemicals (proban, Pyrovatex, natural plant, protein-based waste, other phosphorous- and nitrogen-containing compounds, etc.) have been used for making fire-retardant and fire-resistant textile. However, in most of the aforementioned cases, the add-on percentage is maintained more than 30%. Connected to this area, nanoparticles are also showing promising effect as they are showing fire-retardant efficacy at lower add-on percentage (less than 10%). Another area where protective textiles are of utmost importance is the defense sector. Concerning this area, people need efficient lightweight bullet- and stab-resistant textile materials. To this end, different high-performance fibers, namely, *p*-aramid-based fibers (Kevlar, Twaron) and gel spun ultra high molecular weight polyethylene (UHMWPE), have been used most popularly by researchers. Very recently, non-Newtonian shear thickening fluid has also been explored with nanofiller for reducing the weight of body armor. Camouflage textile is very much useful in the defense sector and is mostly used by soldiers in western countries due to its high cost and more developed technology. Among the insect-protective textiles, mosquito-repellent materials are mostly important because these insects cause many life-threatening diseases like dengue, malaria etc. In the last two decades, different synthetic chemicals like pyrethrin, permethrin, DEET, etc., have been used popularly in textile materials. However, due to their toxic effect, recently, different natural oils like citronella oil, clove oil, lemongrass oil, eucalyptus oil, etc., have been used most popularly by research communities. Moreover, durability is a major challenging concern in this area. Different testing methods like the cage test and the cone test are popularly used by the researchers

for measuring the efficacy of mosquito repellency. Apart from the mosquito-repellent textile, bug-, bee-, and ant-repellent textile materials are also used by certain people who are associated to it by profession or by any other means. As regards antimicrobial textiles, different synthetic chemicals (quaternary-based compounds, cationic large molecular weight compounds, etc.) are popularly used by industries. However, different wastage plant extracts (e.g., pomegranate rind extract, green coconut shell extract, neem bark extract, tulasi leaves extract, etc.) have also been explored by researchers. Concerning wash durability, the microencapsulation method of the application of the natural antimicrobial is more effective than the pad dry process. As far as the challenge of the protective textile field is concerned, in most of the cases, synthetic costly chemicals have been used by industries for making different protective textiles. According to reports, Europe is a major consumer of protective textiles. However, major research work and government initiative are required in this area to commercialize the protective textile materials (especially fire-protective, bullet-resistant, insect-repellent, etc.) in developing countries.

3.1.1 Advancement in Flame-Resistant Textiles

Since 2000, many research communities have been involved in developing more eco-friendly and cost-effective alternatives for producing flame-retardant textile materials. To this end, in the last 5 years, people have developed more eco-friendly alternatives like bio-macromolecules where all natural protein and plant-based products have been used for making fire-retardant textile [1]. Researchers have used protein-based ingredients like DNA, wastage whey proteins, casein, hydrophobins, etc. As per the report, these bio-molecules contain nitrogen, phosphorous, sulfur, etc., and help to catalyze the dehydration of the treated cellulosic material. As a result, char formation has been enhanced with increasing the LOI value of the sample. However, in all cases, more than 25% add-on is required on the treated fabric surface to get the self-extinguishing effect [2–5]. On the contrary, in the last 3 to 4 years, different plant-based bio-macromolecules like spinach juice (SJ) [6], banana pseudostem sap (BPS) [7, 8], coconut shell extract (CSE) [9], and pomegranate rind extract (PRE) [10] have also been explored by researchers for making fire-resistant textiles. It was found from the research that most of the plant-based bio-molecules showed more effective fire retardancy results when they have been applied from an alkaline condition. Some of the bio wastage products like BPS have worked efficiently on the tannic acid mordanted cotton fabric [11]. Another

interesting observation is that all of the explored bio-molecules showed more effective results on the lignocellulosic jute material in terms of flame retardancy. Moreover, due to the more amorphous region and the presence of lignin, no extra mordanting process is required. Those aforementioned bio-based products are environmental friendly; however, they still have some shortcomings like higher add-on %, treatment uniformity, extent of flame retardancy, durability of finish, etc. [12–15]. Because of these aforementioned limitations, bio-based processes are currently available at the lab scale only. Very recently, some research works have also been carried out to improve phosphorus-based products apart from the popular and the widely acceptable Pyrovatex and PROBAN finishes. One of the alternatives was phosphorus-based compounds containing diol groups toward a more eco-friendly solution, which also resulted in lesser heat release rate and more char generation [16]. Researchers have developed a novel oligomeric secondary phosphoramidate, poly(phenyl *N*-(2-aminoethyl)phosphonamidoate) (PPAP), which is halogen free and eco-friendly and also has both nitrogen and phosphorus compounds to give a synergistic effect of flame retardancy. When cotton fabric is treated with the compound, it gave an increased LOI value and an increased char length [17]. Today, the most established products in the market are Pyrovatex (*N*-methylol dimethyl phosphopropionamide)- and PROBAN (tetrakis hydroxymethyl phosphonium chloride)-based formulation products, which are commercially available, but the required concentration of such products is high (around 450 gpl) to get the adequate flame retardancy. Moreover, the treatment also adversely affects the physical and the chemical properties of the fabric. To avoid these problems, different nano-based materials emerged in the market that have at least one nano dimension and gives advantages like higher surface area and lower add-on % required on the substrate compared to its bulk counterpart. In relation to these nano-based formulation processes, the treated fabric can retain its mechanical properties up to a certain extent due to the application of nano material in very small amounts. There are several nano-based products that are available in the market today that can fulfill the requirements of fire retardancy such as nano titanium dioxide (TiO_2), nano zinc oxide (ZnO), carbon nanotubes (CNTs), POSS, nanoclay, silanosol, etc.

3.1.2 Flame Protection by Plant-Based Bioproducts

In the last 5 years, different plant-based wastage bio-molecules have been explored to make fire-retardant textile materials. Basak *et al.* have used banana pseudostem to make fire-retardant jute and cotton fabric [7, 8]. As

per their report, banana pseudostem sap (BPS) has been extracted from the outer sheath of the pseudostem of a banana tree (*Musa Cavendish*). It looks like colorless clean water immediately after extraction. However, with the passage of time, it slowly turns into natural light khaki due to the oxidation of phenolic rings present in it. Apart from the other end uses, very recently, BPS has also been used to impart flame retardancy to cellulosic, lignocellulosic, protein textiles and paper substrates [11–13]. On the other hand, green coconut shell extract (GCSE), a wastage product of the coconut tree, has also been explored to make fire-retardant cellulosic paper material [14]. In connection to the fire-retardant effectivity testing methods, the LOI, a measure of the flammability of a sample, is defined as the minimum quantity of oxygen in the oxygen/nitrogen mixture that is required to support combustion. Textiles having an LOI value of more than 26 are generally considered as fire retardant. The LOI values of the control, the mordanted, and the BPS- and GCSE-treated jute and paper samples are given in Table 3.1.

The results from Table 3.1 indicate that both BPS and GCSE act as a fire-retardant material for cellulosic products. The LOI of the jute fabric has improved after treatment with BPS. Further, the burning rate of the treated jute fabric has been reduced. Like the jute fabric, BPS treatment has also been found to be very much beneficial to the cotton and the proteinous wool fabric [13]. However, most of the cellulosic fabric treated with BPS showed afterglow and smoke. This dangerous afterglow can be arrested by the addition of small amounts of boric acid into the BPS formulation. The vertical burning behavior of the control and the BPS-treated cotton fabric samples are represented in Figure 3.1. On the contrary, GCSE also acts as a fire retardant on the cellulosic paper material. Further research on the application of GCSE on cotton and jute fabric is ongoing. Very recently, wastage spinach leaf extracts (SJ) have also been used for making fire-retardant cellulosic and lignocellulosic material. It has been reported that the SJ contains different nitrogen-containing alkaloids and polyphenolic tannin, which gives the combined effect of aromatizing the cellulosic structure and restricting the formation of flammable gases during burning [10].

Chromatography analysis of the GCSE extract shows the presence of butanol nitroso acetate (nitrogen-containing alkaloid) [$C_6H_{11}NO_3$], guanidine succinimide (nitrogen-containing alkaloid) [$C_5H_7N_3O_2$], aminononadecane [$C_{19}H_{41}N$], erucic acid [$C_{22}H_{42}O_2$], ethylene brassylate [$C_{15}H_{26}O_4$], butanol nitroso acetate [$C_6H_{11}NO_3$], phosphate [PO_4], phosphite [PO_4^{3-}], furfural [$C_5H_4O_2$], and polyphenolic 3,5 dihydroxy-6 methyl-2,3 dihydro-pyran 4, a tannin-based thermally stable phenolic compound [18]. Analysis shows that the PRE (pH 4.5) contains nitrogen-based carbamic

Table 3.1 Flammability parameters of the control and the plant bioproduct-treated textile material [11–16].

Flammability parameters	Control	Mordanted	BPS- and GCSE-treated material	
			BPS—jute/SJ—cotton/ GCSE—jute	GCSE-treated paper
Add on (%)	Jute/paper/cotton	Jute/paper/cotton	15/17/21	25.8
LOI	21/18/18	22/18/18	33/28/39	27
Vertical flammability (sample length: 250 × 40 mm)				
Flashing occurring over the surface	Yes/Yes/Yes	Yes/Yes/Yes	No/No/No	No
Burning with flame time (s)	60/60/60	60/60/60	5/nil/nil	1–2
Burning with afterglow time (s) extinguished	25/30/60 (after being completely burnt with flame)	25/30/25 (after being completely burnt with flame)	600/500/400	140
Char length (mm)	Nil/nil/nil	Nil/nil/nil	Nil/40/nil	Nil
State of the fabric in contact with flame	Completely burnt with flame	Completely burnt with flame	Burnt initially with flame followed by afterglow and in some cases specific char length has been observed	Burnt initially with flame followed by afterglow

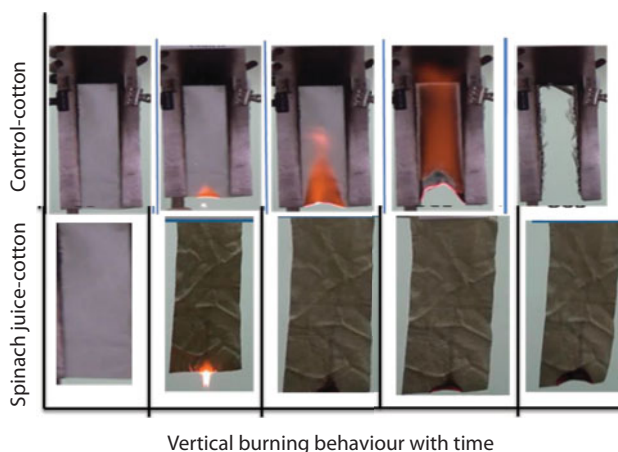


Figure 3.1 Flame-retardant behavior of the control and the spinach juice-treated cotton fabric [6].

acid [CH_3NO_2], ammonium salt, hexacontanoic acid [$\text{C}_{69}\text{H}_{138}\text{O}_2$], aminoguanidine (arginine-based protein) [CH_7N_5], 1,3 di aminoguanidine [CH_6N_4], asparagines (amino acid of protein), hydrazine, ethanamine, piperidine [$(\text{CH}_2)_5\text{NH}$], etc. These nitrogen-containing alkaloid biomolecules combined may assist in the flame retardancy of the PRE-treated lignocellulosic fabric [10]. As far as the BPS is concerned, it contains different positive metal ions, tannins (polyphenolic-based branched compound), phosphorous-based phosphate and phosphate, chlorine, potassium, and other alkaloids. These materials combined enhanced the flame retardancy effect of the BPS-treated cotton fabric [7, 8]. From the discussion, it has been clear that all the plant-based extracts responsible for the fire retardancy of the treated fabric are working on the condensed phase mechanism.

3.1.3 Flame Retardancy by Protein-Based Bioproducts

Very recently, one research group has employed DNA extracted from herring sperm and herring testis to impart flame retardancy to cotton fabric. DNA powder was dissolved in distilled water at pH 5.5 at 30°C for 30 min. Cotton fabric was impregnated into the DNA solution at different concentrations (5%, 10%, and 19%). Concerning the horizontal flammability test, 10% and 19% DNA-treated cotton fabric showed a char length of 35 and 6 mm, respectively [2]. Researchers have concluded that 10% DNA concentration is optimum to get adequate flame retardancy effect while

maintaining the quality of the treated fabric. TG curves of the DNA-treated fabric signify that the DNA treatment shifted the peak mass loss temperature and catalyzed the dehydration process. As a result of the extensive dehydration process, at higher temperatures, the amount of char mass left is 64.4% instead of 45.8% of the control fabric. Thermogravimetry and the char morphology of the control and the DNA-treated cotton fabric are shown in Figure 3.2. The mechanism behind the fire retardancy proposed by researchers is that both the phosphate and polysaccharide present in the DNA coating form an endothermic intumescent layer on the fabric surface that helps to absorb external heat [2, 3]. Nitrogen-containing amino acids like guanine, adenine, thymine, and cytosine that are present in the DNA also help to release ammonia during pyrolysis and block the oxygen present in the surrounding of the burning sample as well as enhance thermal stability [2–4].

Researchers also applied casein, a wastage milk protein for making fire-retardant fabric. Phosphorous and nitrogen are present in the casein bio-molecule responsible for the fire retardancy action of the treated textile material by condensed phase mechanism [5]. Further char morphology of the casein-treated fabric showed small bubble formation. Indeed, it proved the intumescent fire retardancy action of the casein bio-macromolecule [3–5]. Very recently, wastage whey protein material and hydrophobin

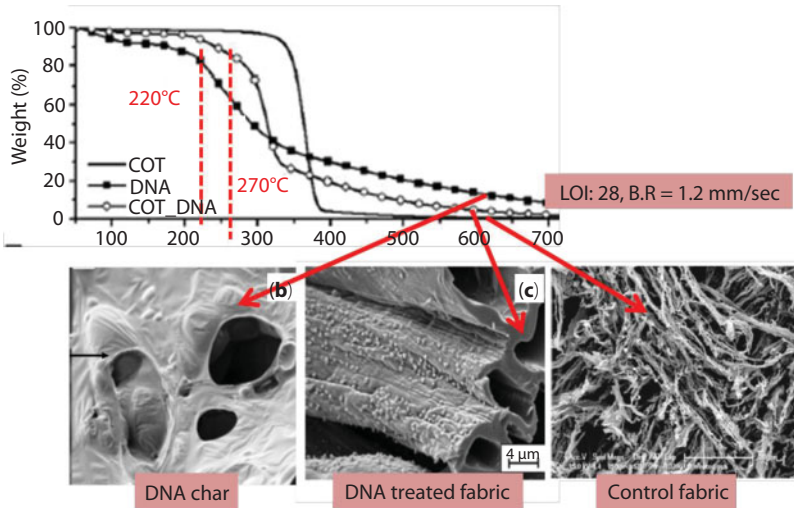


Figure 3.2 Thermogravimetry and the char morphology of the control and the DNA-treated cotton fabric [2, 5].

(a fungal protein based on sulfur and nitrogen) have also been used to make fire-retardant cellulosic textiles [3].

3.1.4 Flame Retardancy Imparted by Nanoparticles

In all the aforementioned processes, the add-on % required for the flame retardancy effect is more than 30%–40%, which is detrimental to the physical properties of the treated fabric. Moreover, hand value and the feel of the fabric have also been hampered due to the use of large amounts of the flame-retardant chemical. Therefore, to reduce the add-on % of the chemicals on the fabric surface, recently, different nanoparticles and nano metal oxides have been used to make fire-retardant textile materials. These nano materials help to get a fire retardancy effect at low add-on %. Being a metal oxide, these nanoparticles reported to have flame-retardant properties, which act as an insulator between the fabric and the flame due to its char-promoting characteristics. Sheshama *et al.* have reported on the treatment of the lignocellulosic sisal fiber yarn with bulk ZnO and nano ZnO. They have reported the comparative fire retardancy and other testing results of the nano and the bulk ZnO-treated sisal yarn. To this end, the add-on % was 12% for bulk and 1% for the nano ZnO, which is 70% lower for the nano form than bulk ZnO. They have also reported the 20% increase in strength of the nano formulation-treated sisal yarn compared to the bulk ZnO-treated yarn. However, the values of the limiting oxygen index (LOI) are almost the same for the bulk and the nano ZnO-treated yarn [19]. The same research group has also tried to cross-link the nano ZnO with the sisal fiber by using butane tetra carboxylic acid (BTCA) formulation-based cross-linking agents to get better durability in terms of flame retardancy. Nejad *et al.* have reported the cross-linking of the cotton fabric with BTCA, a sodium hypophosphite catalyst, and citric acid and then treated with the nano ZnO. In an another research work, Sun *et al.* have reported on the treatment of the cellulosic fabric with nano ZnO and different polycarboxylic acids like succinic acid (SA) and 1,2,3,4-butane tetra carboxylic acids (BTCA). They used sodium hydrophosphite (SHP) as a catalyst for the treatment. The application on the fabric was carried out via the pad-dry-cure process. This process showed an increase in the char length value of the treated fabric. It is a combined reaction effect of the char-enhancing capability of ZnO and the flame reduction capability of the phosphorus component of SHP [20]. Samanta *et al.* have treated jute fabric with nano ZnO and potassium methyl siliconate (PMS) as dispersant and observed the fire retardancy effect. They have reported that by increasing the amount of ZnO by 0.01%, there is a reasonable increase in

the flame retardancy effect. The treated fabric showed the maximum LOI value of 35 and also helped in more char formation up to 25% [21]. Nano titanium dioxide (TiO_2) can also act as a fire-resistant material. Carosio *et al.* have reported that the treatment of the silk fabric with nano titanium dioxide along with phytic acid and butane tetra carboxylic acid, which has a high amount of phosphorus, resulted in the increased LOI value compared with the only phytic acid-treated silk fabric [22]. Horrocks *et al.* have reported in their research that the inclusion of the TiO_2 in the Pyrovatex-based flame-retardant formulation of the cotton fabric improves the cross-linking efficacy of the Pyrovatex CP with the cotton fabric. Here, they used Pyrovatex CP with melamine resin and phosphoric acid as cross-linking agents along with TiO_2 , which was used as a cocatalyst [23]. Wang *et al.* have reported that the application of 0.5% nano titanium dioxide with SHP and citric acid could provide multifunctional finish of flame retardancy, anti-pilling, hydrophilicity, self-cleaning, and antimicrobial and UV protection [24]. Nano alumina is another example of nano-based flame-retardant materials. Alongi and Malucelli have treated cotton linen blend fabrics with silica and alumina nanoparticles via the sol-gel process. They have reported that the use of silica decreases the ignitability and the total burning rate and increases the final residual char mass. As per their research report, the presence of alumina with silica works in synergistic medium and increases the char generation in conjunction with controlling the burning rate of the treated fabric [25, 26] flame retardancy and mechanical properties (namely, abrasion resistance. Nano caolinite and nano clay can also act as a flame-retardant material for the cotton fabric. POSS is polyhedral oligomeric silsesquioxane. It is a cage structure and is made of silicon and oxygen (Si-O) along with eight organic groups. The silsesquioxane cage structure contains molecules of silicon and oxygen. When they are mixed with the polymers, they are bonded to an organic molecule present in the polymer, which creates a long nanoscale structure.

3.1.5 Future Thrust and Challenges in the Field of Flame-Resistant Clothing

The concept of using bioproducts to achieve the fire retardancy of textile materials is a novel and relatively new thought. However, most of the finishes are not durable to home laundering. Further, some finishes produced a lot of smoke due to afterglow after extinguishing the flame. It is also not favorable due to the presence of large amounts of carbon monoxide in it. Some of the bioproducts like DNA are too costly and very difficult to get in large quantities for commercial use. In addition, the proper mechanism

behind the fire retardancy imparted by plant bioproducts is still a major challenge for researchers. Most of the flame-retardant fabrics produced by the treatment of protein based bio-molecules (casein, hydrophobin, whey protein, etc.) are very much prone to attack from different toxic microbes. As far as the nanoparticle-treated textile materials are concerned, a major advantage is the less add-on % of the fire-retardant treatment. However, deposition of the treatment is not uniform and the treatment is not durable to washing and rubbing. These limitations are the major challenges for the commercialization of the nanoparticle-treated flame-retardant textile material.

3.2 Application of the Protective Textile in the Defense Arena

3.2.1 Bullet-Resistant Textile Material

A bullet-resistant vest is a kind of personal protective gear used as protection from the use of firearms. Throughout history, people have used various personal protective gears based on threat levels that they had to face. Animal skin was the first protective gear used by humans during the Stone Age to protect themselves from nature. During the emperor era, wooden shields, metallic shields, and chains were various protective gears used to get protection from sword or arrow attacks.

The first polymeric or textile-based personal protective system was made by medieval Japanese, and protein-based silk fiber was used to make it successful. Silk-based armors were extremely efficient to give protection from arrow attacks due to their high toughness (work of rupture). These armors were able to give protection from very low speed projectile attacks. These silk-based armors were used during World War I [27, 28]. But these armors were unable to give any protection from a projectile if the impact speed is more than 150 m/s. After the invention of nylon fiber by Carothers, the next polymeric armor was made from nylon flakes. These armors were used during World War II. They performed very well against low-speed projectile attacks. However, these armors also failed to protect the human body from most pistol and rifle attacks. Another major disadvantage associated with these armors was that they were very bulky and heavy [29]. The true revolution in the textile-based bullet-resistant material development started with the invention of the *p*-aramid-based Kevlar fiber by DuPont in 1965. In the early 1970s, armor scientists developed new and more efficient bullet-resistant jackets. Generally, there are mainly

two types of body armors available, namely, hard and soft body armors. As regards the hard body armor, metal or ceramic plates are inserted in between the fabric layers. This type of armor is heavy, hard, and inflexible. Hard body armors are used at very high risk regions to get protection from very high speed projectile attacks like from an AK47. On the other hand, a soft body armor is made of multiple layers of fabric. Thus, they are lighter in weight, soft, and flexible. This type of armor is used at low-risk regions to face low-speed projectile attacks, namely, hand guns, pistols, etc. A complete body armor assembly consists of two parts: main component and additional components. Soft armor panel, hard armor panel, carrier fabric, and outer cover are the elements of the main component. Trauma mitigation, neck protector, groin protector, etc. are the different elements of the additional components. Research communities in the field of body armor material development are continuously trying to reduce the armor weight and improve the efficacy of the armor material. Invention of new high-performance fibers, proper fabric design, and treatment with smart materials are the different approaches taken by material scientists to reduce the weight of the armor.

Over the years, fiber scientists have invented various high-performance fibers, such as *p*-aramid-based Kevlar, Twaron, Technora, ultra high molecular weight polyethylene (UHMWPE), high-performance polyethylene (HPPE)-based Spectra, Dyneema, Tensylon, Endumax, Sunfine, Carbon, PPID (M5), Zylon (PBO), E-Glass, S-Glass, etc. The basic properties of any high-performance fiber are high tenacity, high modulus, low density, and low elongation at break (possibly less than 3%). These properties make high-performance fibers suitable for armor applications. Zylon shows much better tensile properties than any other fiber available in the world. However, it is sensitive to hydrolytic and photolytic degradation during use and storage. Therefore, the usage of the Zylon fiber as a textile-based body armor material is no longer recommended by the U.S. army [30]. M5 fiber also has a similar problem, although the extent is lower as compared to the Zylon fiber. Moreover, this fiber may exhibit brittleness at continuous loading [31]. So in the present context, HPPE fibers are found to be the most suitable for ballistic applications owing to their special attributes such as high strength, low elongation, high modulus, very low density (0.97 g/cc), high fatigue durability, excellent chemical resistance, high UV resistance, low dielectric constant, hydrophobic, good abrasion resistance, and good cut resistance.

After the invention of a suitable high-performance fiber, proper yarn making is the next important step toward armor development. Normally,

the gel spinning technique is used to spin the above fibers into multi-filament forms. Sometimes, researchers apply a very small amount of twist to make a single strand. However, the optimum twist angle should be less than 5° [32]. Beyond this, a reduction in tensile strength and an increase in breaking elongation are observed due to the obliquity effect. Researchers have further concluded that moderate yarn-to-yarn friction ($\mu = 0.2$) is best to obtain maximum energy absorption during projectile impact [33].

Development of a proper fabric structure and an appropriate fabric cover is the next important step. Using different weave structures, researchers have tried to make bullet-resistant panels. They have used structures like unidirectional (UD) fabrics; 2D fabric weave structures, namely, plain (DuPont's Kevlar plain woven fabric Kevlar 802F and 363), twill, matt, satin, etc.; warp knitted fabric structures; and 3D woven fabric structures like orthogonal, angle interlock, and warp interlock [34–41]. Among the 2D woven fabric structures, plain woven fabric is the best structure for ballistic applications and the optimum fabric cover should be in between 0.6 and 0.95 [42]. If the thread density is too low, i.e., the fabric cover is less than 0.6, a very frail structure is obtained. Therefore, projectiles can easily penetrate through the fabric just by displacing the yarns sideways. On the other hand, if the thread density is too high, a very firm structure is obtained. Yarns are almost always jammed, and huge wear and tear of the yarn occurs during weaving [43]. Thus, selection of the proper fabric structure and the optimum thread density is the most important parameter to be taken into account. Fiber manufactures have introduced different patented products, like Spectra Shield, Gold Shield, Gold Flex, Dyneema SB51, Endumax Shield made of UD sheets, and Kevlar XPs fabric structure made of Kevlar, which are most widely used nowadays as ballistic materials. Recently, researchers have been using nonwoven and spacer fabrics as trauma packs to reduce blunt trauma [44]. Multiple layers of fabrics are required to obtain sufficient protection. Stacking of multiple layers is another area of interest for researchers. Fabrics can be kept in the same manner (i.e., 0° , $0/90^\circ$, $0/45^\circ$) and some specified angle ($[0/30/60]$, $[0/22.5/45/67.5]$, and $[(0/22.5/45/67.5)_2]$) for different numbers of layers [45]. Researchers have found that an overall 11.4% to 18.5% increase in the impact energy absorption was obtained just by using this specified angle of stacking technique. After stacking these fabric layers, they are assembled together by means of stitching. Different stitching patterns are used: only perimeter, perimeter and diagonal lines, 1-inch field diamond stitch, and 2-inch field diamond stitch [46].

Researchers are continuously trying to reduce the number of layers to reduce the armor weight, and at the same time, they want to increase the efficacy of the bullet-resistant material. Recently, Ahmad *et al.* [46] and Roy *et al.* [47] coated the Kevlar fabric with natural rubber latex. They used single dipping, double dipping, and triple dipping methods for rubber latex coating. They found a substantial increase in both impact and puncture resistance after latex coating.

Over the last two decades, body armor researchers have been applying various smart materials to improve the efficacy of the ballistic materials. Shear thickening fluid (STF), nano filler compounded STF, magnetorheological fluid (MRF), and a combination of STF and MRF are a few of the most successful ones [48–52]. STF is typically a kind of non-Newtonian fluid. It consists of a solid phase like silica, calcium carbonate, or polymethylmethacrylate (PMMA) and a dispersion medium like water, silicon oil, polyethylene glycol (PEG), and 1-butyl-3-methylimidazolium tetrafluoroborate [54, 55]. At a low shear rate region, STF behaves like a shear thinning material; that is, viscosity decreases with an increase in shear rate. However, after achieving a particular shear rate, called critical shear rate, viscosity increases abruptly, and STF behaves like a solid material. This shear thickening is an instantaneous incident; that is, the response time is very low and it is also reversible. Thus, it again has the ability to flow after shear removal [56, 57]. Material scientists thought of taking STF in ballistic-resistant material development. They treated Kevlar fabric with diluted STF and then removed the diluents. Average add-on % may vary from 5% to 20% depending on the fabric type (scoured or water repellent treated) and fabric structure (2D or 3D woven structure). Laha *et al.* [40] and Majumdar *et al.* [41] reported that the flexibility of the STF-treated fabric was almost unaltered. The impact resistance increased after STF treatment. Concerning the 2D plain woven fabric, an increase in the impact energy absorption of as high as 147.6% was obtained after the STF treatment, whereas for the 3D woven orthogonal fabric, an increase of 80% was obtained using the STF treatment.

Recently, researchers have been adding very small amounts of nano fillers like graphene oxide, carbon nanotubes, halloysite nanotubes (HNTs), etc. into STF to improve the efficacy of STF. Huang *et al.* [49] added very small amounts of graphene oxide into STF. They found that the critical shear rate has been decreased and the peak viscosity increased with the addition of the graphene oxide. In a similar study, Wang *et al.* [50] used halloysite nanotube (Hal nanotube or HNT) as nano filler. Laha *et al.* [52] added very small amounts of HNT as nano filler (0.05% to 0.5%) and

found that around 15% to 20% increase in the impact energy absorption was obtained after HNT compounded STF treatment.

The above discussion is confined within recent developments in soft armor materials. Another type of armor is the hard body armor. It consists of two parts, namely, the hard plate or break layer and the catch layer. Maximum bullet deformation or bullet breaking takes place at the break layer. The break layer is mainly made of alumina, silicon carbide, and boron carbide. Recently, researchers have been using boron carbide (B_4C) due to its low density (2.5 g/cm^3) coupled with high toughness [54]. With the aim of further reducing armor weight, most recently, researchers have been using fiber-reinforced composites as a break layer for particular types of projectile attacks. On the other hand, the catch layer takes care of the fragments and also helps to reduce the blank trauma. The catch layer is generally made of woven fabric from high-performance fibers.

3.2.2 Stab-Resistant Textile Materials

Stab-resistant vests are another type of personal protective gear that provide protection from stabs or impact from sharp and pointed objects. Stab-resistant vests are also made of high-performance fibers like *p*-aramid, ultra high molecular weight polyethylene (UHMWPE), etc., similar to bullet-resistant materials. The UHMWPE fiber is found to be the most suitable due to its inherent cut-resistant nature. One should keep in mind that a very efficient, flexible bullet-resistant vest made of high-performance fibers may not be a good stab-resistant vest. Because the fabric used to make a bullet-resistant material armor is not very tightly woven, it can be easily penetrated by sharp objects, whereas a stab-resistant vest made of high-performance fibers is woven very tightly, which acts as a barrier against stabs. Like bullet-resistant jackets, in stab-resistant vests, the type of protection depends on the impact energy, toughness, etc.

Researchers are relentlessly working to improve the protection level of stab-resistant vests. Chiou [58] has developed a protective jacket that will give protection for both bullet and stab attacks. Tien *et al.* [59] suggested the use of the core spun yarn in stab-resistant vests. Apart from the conventional woven structure that is normally used for stab resistance, Bao *et al.* [60] developed a very good stab-resistant material from high-density nonwoven structures. The density ranges from 0.14 to 0.46 g/cm^3 . Most recently, researchers impregnate the tightly woven fabric into STF to increase the efficacy. They observed a significant increase in stab protection after the STF treatment [61].

3.3 Recent Advancements in Engineering to Create UV-Protective Textiles

Optimum exposure in the sun has been found to be beneficial in many folds. It helps in the synthesis of vitamin D, important in human body and bones, especially for the kids. Further, it also improves blood circulation, metabolism, and resistance to different microorganism growth. However, some recent studies have revealed that overexposure to sun is detrimental to the human body. As the ozone layer in the atmosphere is depleting in a very fast rate, the amount of ultraviolet radiation (UVR) reaching the Earth has increased significantly. Thus, it is becoming carcinogenic to the human body. MacKie [62] and Gallagher and Lee [63] reported that overexposure to any source of UVR, whether from a solar or artificial origin, is found to have a detrimental effect on our health, especially to the keratosis (the precursor of skin cancer), immune system, and eyes. Premature aging and roughening of the skin, wrinkles, sagging, blotches, erythema, cancer of the lip, squamous cells, and basal cell cancer are some of the most common skin diseases seen nowadays due to overexposure to UVR [64]. Halliday *et al.* [65] reported that overexposure to UVR may result in photokeratitis, photoconjunctivitis, and cataracts. Because of the geographical location, people from Australia, New Zealand, the United States, Switzerland, Norway, Scotland, and Britain as well as those from Scandinavian countries have high melanoma rates due to the high levels of solar UV radiation reached in the said countries. Recently, a steep increase in the number of skin cancer patients is found in the abovementioned countries. The Australian Institute of Health and Welfare [66] reported that, in 2008, Australia had the world's highest age-standardized incidence rate of skin melanoma. Thus, proper protection from UVR is mandatory to avoid any skin disease. Avoiding exposure to the sun from 10 am to 2 pm and the use of sunscreen, sunglass, umbrella, hats, etc. are some of the precautionary measures that can be taken. Major disadvantages associated with sunscreen and sunglass are discomfort and continuous use. Proper clothing can provide adequate UVR protection, and it does not have any drawback. Thus, it is the most useful and most convenient UVR protector. Ultraviolet protection factor (UPF) is the single parameter used to judge a fabric's UVR protection capability. UV protection of a fabric is subdivided into four categories (based on the UPF number): poor protection ($UPF < 15$), good protection ($UPF = 15-24$), very good protection ($UPF = 25-39$), and excellent protection ($UPF > 40$). Type of fiber and yarn used, fabric structure and porosity, areal density, fabric thickness, thread density,

color, any finish application, presence of UVR absorbers, moisture content, and degradation due to subsequent laundering are major factors to determine the UPF of a fabric [67–69].

Researchers have done an in-depth study on the factors affecting UPF and how to improve it. For the same fabric construction, fabrics made of polyester, bamboo, modal sun, and silk fiber have a high UPF due to their chemical structure and have an inherent UV protection capability, whereas fabrics made of cotton and rayon are the most vulnerable to UVR [68, 69]. Yarn-related parameters like yarn twist, yarn hairiness, yarn structure (hollow or compact), and linear density are few important parameters that affect UPF. Appropriate twist level and yarn hairiness are found to be beneficial (i.e., they provide UV protection) [70–72]. Researchers have concluded that the higher the linear density of the yarn, the higher the UPF [68, 73]. Another important parameter is fabric construction. A higher UPF is obtained when the fabric cover and thickness are greater. When the fabric cover is greater, that is, the fabric is very compact, UV light cannot pass through it, and as a result, the UPF value of the fabric is increased. For the same cover fabric, the UPF of a thicker fabric is greater than that of a thinner one [74, 75]. If the relative fabric tightness is kept the same, then the highest UPF can be obtained from a satin weave and the lowest can be obtained from a plain weave. There would not be any difference in UPF on the fabric structure if the fabric is made of the same yarn and the same thread density [74]. After bleaching, the UPF reduced drastically for a fabric made of cotton fibers. As we all know, bleaching is carried out to remove the natural pigments present in the cotton fabric. Hence, a cotton fabric shows very poor UPF property after bleaching, even though the structure is very compact. The fabric UPF properties can be increased by adding different additives, namely, dye, pigment, delusterant, optical brighteners, and UV absorbers. The UPF is generally increased after dyeing or pigment application. However, the percentage increase in the UPF will depend on the type of dye or pigment and concentration. In general, deep dyed materials especially black and blue dyes show more UPF than lighter ones [68, 69, 76]. The application of a UV absorber will increase the UPF further. A UV absorber is a colorless compound. The chromophore of a UV absorber is mainly responsible for absorbing UV rays [77, 78]. The addition of a UV absorber can be done during the fiber manufacturing stage by means of dope application of manmade fibers or surface treatment like any finish application. If the UV absorber is applied during the fiber stage, it becomes permanent. On the other hand, if it is done during surface treatment, it is not permanent. UV absorbers will leach out during subsequent laundering. Very recently, researchers have been using different

nanoparticles like titanium dioxide (TiO_2), zinc oxide (ZnO), and silicon dioxide (SiO_2) as inorganic UV absorbers using different deposition techniques [79–81]. The UPF is found to be increased drastically after the nano UV absorber application.

3.3.1 Sustainable Materials Used for Making UV-Protective Textiles

Use of bio-colorants is a very old practice to make the apparel attractive. They were used prevalently before the invention of synthetic dyes and pigments. Most bio-colorants are obtained from different parts of a plant, namely, flowers, fruits, seeds, leaves, barks, trunks, and roots, or through extraction of the dried bodies of insects. Thus, bio-colorants are cheap and eco-friendly. Recently, researchers have been using natural dyes to improve UPF. Researchers have found that a number of natural dyes could improve the UPF of linen and hemp fabrics [82]. Extraction of the eucalyptus leaf and Flos Sophorae can be used to improve the UPF property of silk fibers [83, 84]. Paragai *et al.* [85] used madder (*Rubia cordifolia*) and cutch (*Acacia catechu*) to improve the UPF of nettle fabric. Very recently, Teli *et al.* [86] have reported that dye extraction from the fruit shell waste of *Sterculia foetida* has very good potential to improve the UPF of linen fabric. Thus, it can be concluded that sustainable wastage materials are useful to improve the UPF of textile fabrics.

3.4 Insect-Repellent Textiles

Insect-repellent textiles are another type of protective textiles; they help protect the body from insects that can cause damage. These textiles act as a barrier and protect humans from the bites of mosquitoes and other insects, thereby preventing diseases like malaria, chikungunya, dengue, Nile fever, and filariasis [87]. In addition to health concerns, insect repellents may also prevent valuable loss of textile products, including carpets, garments, upholstered furniture, blankets, and priceless heirlooms, by preventing insect attacks on these textiles. Because of this, the use of insect repellents that are safe, pleasant to use, and environment friendly is recently gaining popularity among consumers. Insect repellents are of two types, namely, synthetic repellents and natural or plant-based repellents. In general, synthetic repellents are more effective than the plant-based ones but they are more toxic as well. Hence, current discussions focus on developing

non-toxic or less toxic plant-based insect-repellent textiles [88]. This section discusses the different organic and synthetic materials used to produce insect-repellent textiles, their application procedures, and assessment methodologies. The future of insect-repellent textiles is discussed at the end of this section.

There are several insect-repellent synthetic chemicals available in the market, which are successfully applied on textile substrates. *N,N*-diethyl-*m*-toluamide (DEET) is one of the most effective insect/mosquito repellents used over the last 50 years. However, DEET is toxic in nature and causes problems like dermatitis, allergic reactions, and cardiovascular toxicity, to name a few [89]. Dimethyl phthalates (DMP) and di-*n*-butyl phthalates (DBP) are also popular mosquito repellents and exhibit excellent insect repellency [90]. Cypermethrin, *p*-menthane-3,8-diol, permethrin, cyclodextrins, and their derivatives are other well-known insect-repellent chemicals used for insect-repellent textiles. However, these chemicals are also toxic in nature and are extremely harmful for children [91]. The current research trend on insect-repellent textiles focuses on the exploration of plant-based products. Certain plants contain compounds that protect themselves from plant-eating insects [92]. Essential oils like *p*-menthane-3,8-diol (PMD) from lemon, eucalyptus, citronella, azadirachtin from neem, and soya oil are some effective plant-based insect repellents. The main disadvantage of plant-based repellents is that some of their active ingredients tend to be volatile, so although they are effective repellents for a short period after application, they rapidly evaporate, leaving the user unprotected [93]. Hence, plant-based insect repellents are generally applied on the textile in encapsulated form. Ferreira and Moore, 2011 [94] have investigated the complex formation between *b*-cyclodextrin and limonene, a naturally occurring insecticide present in citrus and other fruits for the development of durable insect-repellent cotton fabrics. Moreover, naturally occurring quinone-, flavonoid-, and indigoid-rich compounds from different plant extracts such as madder, walnut, chestnut, logwood, and indigoid have shown promising results in obstructing the growth of many insects (especially moth) that cause serious destruction of wool-made textiles [95]. Tulasi leaves also have good mosquito-repellent properties as they contain the natural oil "euganol." Apart from it, long citronella oil-, pudina oil-, and clove oil-treated fabrics also have the ability to protect mosquitoes from their surroundings. In the last 5 years, different kinds of nano metal oxides have also been used by researchers to make moth-proof wool textiles. Recently, Josh *et al.* have developed a moth-proof woolen textile by using nano kaolinite (a clay-based material).

3.4.1 Methods for Imparting Insect- and Microbe-Protective Agents on Textiles

Available literature suggests that there are several techniques available for imparting insect repellency to textile substrates. Banks *et al.* [97] have classified these techniques into four main groups: absorption, incorporation, polymer coating, and microencapsulation. The absorption technique includes spraying, dipping, or pad-dry-cure of fabrics along with the use of a repellent agent. The incorporation technique is mainly used in the carpet industry and involves the pretreatment of carpet during manufacturing or dyeing. Existing developments on insect-repellent textiles using synthetic repellents mainly fall in these two categories. In these cases, textile materials are directly impregnated in synthetic insect-repellent formulations that have high doses of toxic chemicals; hence, prolonged skin contact to such textile materials causes problems such as itching, dermatitis, etc. Coating of textile substrates with polymers containing insect-repellent chemicals is another way of manufacturing insect-repellent textiles. As per this technique, textile yarns or fabrics are coated during the finishing process using permethrin or other insect-repellent chemicals at the dipping process stage. Insect-repellent textiles developed through these techniques exhibit rapid washing, but the same major problems (harmful and toxic to humans especially to children) regarding the use of synthetic repellents arise.

Present inventions on insect-repellent textiles focus on using natural oils as insect repellents. These oils are volatile in nature; hence, these oils evaporate before their incorporation into the textile fabric via the pad-dry-cure method or by addition during the rinse cycle. In general, natural or plant-based products are perceived to be safe in comparison to the long-established synthetic materials. However, this assertion cannot be made with 100% certainty as toxicological studies on these agents have been very limited [83]. Hence, to overcome the abovementioned problems and to enhance the durability of the finishes on textile substrates, plant essential oils are microencapsulated. Microencapsulation could be defined as the process of covering a substance with materials of different nature in order to obtain particles of micrometer size. Functional agents used in the formulation are protected from environmental factors, and their (repellent oil) release can be controlled by diffusion through the capsule wall, pressure, and/or rupture of the microcapsules. In relation to this, recently, Specos *et al.* have reported that textiles treated with microencapsulated citronella oil provide higher and longer-lasting protection against mosquitoes as compared to fabrics sprayed with an ethanol solution of essential oils [97–99].

3.4.2 Insect Protection Efficiency

There are several methods available to evaluate the insect repellency of textile materials. However, most of the studies have reported the insect repellency of a textile substrate based on its mosquito repellency assessment. The most used techniques are the cage test, the cone test, and the excito chamber test.

The cage test assesses the insect/mosquito repellency of a textile substrate by visually observing the mosquito landing on the untreated and treated fabric in the cage. This testing method provides a real situation where mosquitoes probe and bite humans along with the behavior of mosquitoes toward the treated substrates. The cone test is a well-known test for evaluating the insect/mosquito repellency of insecticide-treated textile substrates. This test does not involve human participants, which is one of the advantages of this method. The excito chamber method is another method for evaluating the insect/mosquito repellency of insecticide-treated textile substrates. Like the cone test method, the excito chamber test also does not involve human participation and both test methods determine the behavior of mosquitoes toward the treated materials only. However, in the excito chamber test, mosquitoes are starved overnight before the test, and the behavior of mosquitoes are observed in terms of the number of mosquitoes that escaped and the number of mosquitoes that remained inside the chamber filled with the treated product.

3.5 Microorganism Protective Textile Materials

3.5.1 Microbes, Antimicrobial Agents, and Their Modes of Action

Microorganisms are very small organisms that are visible only under a microscope. There is a wide range of microorganisms such as fungi, viruses, and bacteria. Microorganisms are both useful and harmful to humans, plants, and animals. These microorganisms are also responsible for food contamination and may cause food- and water-borne diseases like cholera, jaundice, and typhoid. Therefore, the importance of antimicrobial agents that are capable of killing or inhibiting the growth of microorganisms is increasing day by day. Western Europe is the leading manufacturer of antimicrobial textiles. In 2000, the total production of antimicrobial textiles was around 30,000 tonnes, whereas the worldwide production was around 100,000 tonnes. In between 2001 and 2005, the production of antimicrobial

textiles increased around 15% in Western Europe, and this textile type was the fastest-growing sector of the textile industry [90]. Different types of antimicrobial compounds like the chlorine-based triclosan, quaternary ammonium compounds, metal salts, metal oxides like sodium metasilicate, and different natural polymers are popularly used for making antimicrobial textile materials [92].

When the microorganism touches the textile surface, the applied antimicrobial agent comes into action. The antimicrobial agent may be attached on the fiber surface or mixed with the polymeric matrix, which migrates from the textile surface to an external medium to engage with the microorganisms [95]. Basically, the microbes have an integral cellular structure with a well-composed polysaccharide cell wall at the outermost layers. These layers act as a protection. Under the outer cell wall, there is a semipermeable membrane, enclosing the intracellular organelles and enzymes. These enzymes and organelles are mainly responsible for chemical reactions within the cell. The cell integrity is responsible for the growth, survival, and proper functioning of a microorganism. An antimicrobial agent or material can be classified according to its action toward the cells' function or integrity. If the antimicrobial agent inhibits cell growth, it is called a biostatic effect, but if the agent is capable of destroying the microorganisms, then the effect is called biocidal or bacteriocidal [95–97]. The most used antimicrobial agents in commercial textiles are biocides, which act in different paths as per the nature of their structure and level of affinity to the target. The different modes of action are as follows [97]: provides damage to the cell wall, stops the function of the cell membrane, resists protein synthesis, suppresses the synthesis of nucleic acid (DNA and RNA), and discontinues other metabolic processes.

3.5.2 Plant-Based Products Used for Making Microorganism Protective Textiles

Apparels and other home textile products (specially made by cellulosic and lignocellulosic structures) are very good carriers of the different types of microorganisms as they are in permanent contact with human skin and the environment and they create health hazards for the users. Microorganisms have a detrimental effect on textile materials, such as discoloration, fiber damage, and bad odor, to name a few [97]. Hence, to avoid these problems, different antimicrobial agents are applied to the textile fabric. Antimicrobial textiles with improved functionality have a variety of applications: as medical garments (such as for infection control and as a barrier material), as health and hygiene products, and as garments worn close to

the skin, home textiles, etc. [95]. In the last three decades, different synthetic antimicrobial compounds like quaternary ammonium-based products, cationic polyhexamethylene biguanide, chlorine-based triclosan, etc. have been popularly used by different textile industries to make antimicrobial textiles. However, the plant-based natural herbal antimicrobial finish is becoming popular day by day not only because of its toxicity but also because of its sensitivity to the skin and its eco-friendliness [96]. There are many plant spices (like clove, cardamom, and turmeric) and some medicinal plants (like neem, tulsi, amla, and aloe vera) that contain bioactive molecules and antioxidants that show both antibacterial and antifungal activity [92, 97]. The most used plant-based natural antimicrobial agents are clove, cardamom, tulsi stem, curry leaves, neem, and aloe vera [98]. The curry plant is basically a tropical tree with aromatic leaves of 2–4 cm. The leaves are popular for imparting taste in dishes. The following chemical components are present in curry leaves: linalool (32.83%), elemol (7.44%), geranylacetate (6.18%), myrcene (6.12%), alloocimene (5.02%), α -terpiene (4.9%), β -ocimene (3.68%), and neryl acetate (3.45%) [99]. Tulasi has been reported to be a good antimicrobial agent due to the presence of the euganol-based compound in its structure [96]. Researchers have also reported that Tulsi (*Osimum tenuiflorum*) is a shrub class plant that contains different acids like oleanolic, ursolic, and rosamarinic acid, and other components like eugenol, carvacrol, linalool, β -elemene, and germacrene as antimicrobial chemical constituents [94]. Recently, different researchers have reported that the pomegranate rind extract is also an efficient antimicrobial agent against both gram-positive and gram-negative bacteria. It may be due to the presence of polyphenolic tannin and other positive metal ions in its extract [17]. Waste material-based coconut shell extract also showed efficient microbe protection activity due to the presence of tannin and other polyphenol-based compounds in it [18]. Clove oil is an effective antimicrobial agent for textiles and contains eugenylacetate, caryophyllene oxide, eugenol, caryophyllene, gerillin A, and triazolopyrimidine phthalazine derivative as its antimicrobial chemical components [98]. Cardamom is a widely used antimicrobial spice and contains 1,8-cineole (43.7%), α -terpineol (9.5%), terpinen-4-ol (3.2%), spathulenol (2.7%) and α -pinene (1.6%) [99]. Neem is another applied natural antimicrobial evergreen tree having 20- to 40-cm-long leaves. Neem contains acetic acid, hydroxy pivalic, phytol, 1,3-diphenyl-2-azafluorene, acetate, and germnicol 4,4-cyclooctenol. Several studies have also been carried out by different researchers like the effect of aloe vera treatment on the antimicrobial activity of cotton fabric. All the above natural agents are found to be very effective against microbes, but in all cases, after

washing the agents were sharply diminished, which is still a big challenge for the researchers in the antimicrobial sector [10, 99]. Few other researchers studied the application of *Murraya koenigii* (curry leaf) and *Zingiber officinale* (ginger) oil on the cotton fabric. They are generally applied to the textile substrate via the pad-dry-cure method. Curry leaves are naturally occurring antifungal agents that are noncarcinogenic in nature. On the other hand, ginger is popular as a natural antioxidant and is an anticarcinogenic compound that is also antimicrobial in nature. Compounds such as α -pinene, borneol, camphene, and linalool present in ginger are mainly responsible for its antimicrobial properties [10]. Recently, researchers have also tried cross-linking agents such as BTCA, citric acid, and glyoxal as antimicrobial agents applied on the textile surface. Microencapsulation is another effective technique to achieve a strong antimicrobial effect on the textile surface. Nano-based antimicrobial finishing of textiles is another eco-friendly approach. Different textile industries use nano-silver, nano-gold, etc. as antimicrobial agents and usually apply the nano-based formulation via the pad-dry-cure process. Silver has a bacteria-killing property as the positive charge of the silver ions reacts efficiently with the negatively charged cell wall of the bacteria and destroys it.

3.6 Camouflage Application as Protective Textile

In earlier times, visual camouflage is obtained by using different types of colors, shade, and printing techniques. The choice of using color depends on the place or ground in which the camouflage is aimed to be used. Generally, different thermochromic (color changed by thermal energy), electrochromic (chromophore structure changed with electric field), and photochromic colors, pigments, and polymers are used by researchers to make camouflage textile materials for use by the defense sector. The structure of these colors or pigments has been changed and has been turned into another color as per the surrounding temperature, environmental condition, etc. However, in the last two decades, because of the advancement in electronic devices, detection devices became very efficient [91]. Nowadays, the detection techniques used are ultraviolet (spun), infrared (near and far), radar and seismic sectors with integrated multi-sensor system through visual black and white color, false color. On the other hand, foliage-penetrating and sideways-looking radars are also available recently. Other popular detecting devices are remote ground sensors. Therefore, it is almost impossible to stay protected from such a wide range of hi-tech

detection devices with only visual camouflage on woven fabric [92]. With the development of different electronic detectors, the camouflage structure technique has also changed. The spun bonded nonwoven fabric is used as a material on the outer surface of a camouflage structure in which a large number of fine metal wires are attached. Thereafter, a single PVC (polyvinyl chloride) coating is done on both sides of the fabric. To obtain a desired camouflage pattern, the PVC is infused with specific pigments [92, 93]. It is clear that the camouflage does not remain the same after battle, resulting in the camouflage becoming more visible and an easy target. This remains a challenge for researchers. Very recently, few research groups have engaged in developing an automatic camouflage. The basic concept of automatic camouflage is the use of hollow fibers, filled with a mixture of liquid dye and a solid pigment. A computerized camera is used to change the generated electric field to get a response from the solid pigments, resulting in changing the overall color mixture of the camouflage system according to the surrounding environment of the soldiers. Recently, the Mission Research Corporation (Santa Barbara, California) designed an automatic camouflage system by using hollow fibers, filled with a mixture of liquid dye and a solid pigment.

3.7 Challenges and Future Directions

To date, protective textiles are facing major challenges in commercializing textile industries in subcontinent countries because of their high cost, the lack of applied technical knowledge, and lower availability. Various global studies are ongoing to address these problems. Concerning the fire-protective textile, eco-friendly, cheap, low add-on percentage, uniformity of the finish and the adequate washing with rubbing (especially wet rubbing) fastness, is required for commercial popularity. Decreasing the weight of bulletproof and stab-proof textiles is also a major concern for researchers. Apart from this, access to camouflage-based protective textiles proves to be very difficult due to their high cost and lower availability in developing countries. Concerning antimicrobial textiles, synthetic chemicals are more popular in the market because of their high wash durability and uniformity. However, initially, in some rural areas, plant-based antimicrobial textiles can be distributed at low cost. Access to eco-friendly (plant extract-based) mosquito-repellent finished fabrics is also an important concern because of their lifesaving effect. However, the said fabric cannot be commercialized easily because its repellent property decreases with time due to the evaporation of the aromatic oil of the extract. Additionally, more standardized test methods

need to be adopted by the researchers in this field. Three things are needed for the rapid commercialization of eco-friendly protective textiles in developing countries: 1) greater awareness, 2) government initiative (in terms of financial investment and commercialization), and 3) more research projects.

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Antibacterial Aspects of Nanomaterials in Textiles: From Origin to Release

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Abstract

Various types of nanomaterials have been recently applied for textile engineering, from manufacturing to the treatment of industrial effluents. Antibacterial activities of nanomaterials for textile manufacturing are a main category in this regard with high interest. However, having a high antibacterial activity for a specific type of nanomaterials may raise the concerns of its fate if released to the receiving environments. It is assumed that the inherent properties of the nanomaterials can critically control their efficiency. The release of the nanomaterials into the environment is considered another subject with a high degree of importance. Hence, the aim of this chapter is to critically discuss those characteristics of nanomaterials with the ability to make them appropriate for antibacterial activities for textile engineering and the possible routes for their release after being used.

Keywords: Nanomaterials, antibacterial activity, release

4.1 Introduction

Since ancient times, natural fibers and textiles as well as vegetable fibers (e.g., flax and cotton) have been used for human dressing applications and

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to protect them from the harsh environmental conditions [1]. After the Industrial Revolution in the 18th century, the machines accelerated the fabrication of the textiles and made them easily available for the community [2]. However, the synthesis of the advanced artificial textile fibers such as nylon, polyester, and rayon only happened after the Second Revolution in the 20th century. Thanks to the technological developments, high-quality and low-cost textiles were fabricated successfully during this period.

Nowadays, advanced manufacturing of the textiles by the development of the associated technologies, such as coloring and high-performance textile fabrication processes, has pushed the industry toward the Third Revolution. One of the main aspects of this third generation of textiles is their antibacterial performance, which is of high importance especially in terms of human health considerations. The antibacterial properties are mainly given to the textile through the addition of specific materials through the spinning process, or during the finishing stage. Various materials such as triclosan [2,4,4-hydroxyphenyl trichloro (II) ether] [3] added during the spinning process have demonstrated their good antimicrobial performances. Also, finishing antibacterial agents such as quaternary ammonium [4] have been used to reinforce the textiles against antibacterial pollution.

Synthesis and application of various types of nanomaterials with advanced properties have considerably increased in recent years for a number of applications [5]. One of the main properties of the nanomaterials that make them attractive for textile engineering is their activities against bacteria, viruses, and microorganisms [6–8]. In this regard, metals and metal oxide nanomaterials, mainly silver (Ag), zinc oxide (ZnO), titanium dioxide (TiO₂), and copper oxide (CuO), have promoted the development of new biocides. However, various studies have indicated the effects of various characteristics of nanomaterials on their antibacterial activities. Optimization of the antibacterial activity of nanomaterials, taking economic issues into consideration, is directly related to the precise consideration of these properties and also their simultaneous effects. The modifications in the surface of the textile using advanced types of nanomaterials have attracted huge attention in recent years. However, it seems that there is a need for the optimization of the nanomaterial performance to transfer these technologies from lab-scale to real-scale applications. In this chapter, the main properties of the nanomaterials with important effects on the induced antibacterial activity have been discussed. In order to prevent subsequent environmental drawbacks, it would be also essential to minimize the releases of the applied nanomaterials into the environment. It is of high importance because there is some evidence of the toxic effects

of the nanomaterials on living organisms [9–11]. Hence, the main release routes and the involved parameters in the release of the nanomaterials from the fabrics have also been reviewed and discussed.

4.2 Nanomaterial Properties

The properties of the nanomaterials prepared may have a drastic effect on their activity toward microbial activities. In this regard, the main characteristics of nanomaterials attributed to the composition and morphology can potentially determine their appropriateness for textile engineering applications. In this chapter, an overview on the main properties of nanomaterials, which can determine their antibacterial activities, has been provided based on the more recent scientific published reports in the literature (see the summary in Table 4.1).

4.2.1 Composition

So far, various types of nanomaterials have been tested for their antibacterial activities for textile engineering applications. However, it seems that the development of the applications of advanced nanomaterials is directly related to their relative disinfection abilities. One of the most important factors in this regard is the chemical composition and nature of the nanomaterials used. For instance, Beddow *et al.* [12] studied the antibacterial efficiency of ZnO and CuO sonochemically coated on a cotton fabric. They observed higher levels of bacterial reduction with CuO coating against all the studied bacteria [*Staphylococcus aureus* (ATCC 6538), *Pseudomonas aeruginosa* (ATCC 15442), *Acinetobacter baumannii* (NCTC 10303), *Escherichia coli* (ATCC 8739), and methicillin-resistant *Staphylococcus aureus* (MRSA, NCTC 10442)]. Although they did not discuss the reasoning for the high antibacterial activity of CuO nanomaterials, it can be attributed to the higher OH radicals produced by CuO nanomaterials [13]. The high performance of CuO nanomaterials has also been indicated by Abramova *et al.* [14]. They indicated that the nanomaterials (200–400 nm) sonochemically dispersed on textiles can show good antibacterial activity against *E. coli*, *Klebsiella pneumoniae*, *S. aureus*, and MRSA.

It has also been reported in the literature that composites of the widely used nanomaterials for antibacterial activity, such as silver nanoparticles, can show enhanced antibacterial activities. For instance, Attia and Morsy [15] indicated that the diphosphate malonate compound (DPHM)-Ag

Table 4.1 The effects of nanomaterials' properties in their antibacterial activity.

Nanomaterials			Attachment method	Fabric type	Antibacterial activity		Reference
Type	Size (nm)	Shape			Targeted bacteria	Main mechanisms involved	
CuO	N.G.	N.G.	Sonochemical coating of textile by NMs	Cotton	ATCC 6538, ATCC 15442, NCTC 10303, ATCC 8739, MRSA, and NCTC 10442	Generation of high amount of OH radicals	[12]
CuO	200–400	Ellipsoidal	Sonochemical dispersing of NMs on the textile surface	N.G.	<i>Escherichia coli</i> , <i>Klebsiella pneumoniae</i> , <i>Staphylococcus aureus</i> , and MRSA	Generation of high amount of OH radicals	[14]
Diphosphate malonate -Ag	17–102	Irregular shape	Spraying the NMs on the surface of the textiles	Polyester and cotton- polyester blend	<i>Staphylococcus aureus</i>	Direct release of NMs and their interaction with the bacteria	[15]

B (Boron)	50	Flaky shape	Dip-coating of textile by the NMs	N.G.	MRSA and <i>V. cholerae</i>	Electrostatic or hydrophobic interactions of bacteria cell wall	[19]
ZnO	21–25	N.G.	Evaporation of the solution containing fabric and ZnO particles	Cotton	<i>Escherichia coli</i> and <i>Staphylococcus aureus</i>	a) Formation of hydrogen peroxide b) ZnO may affect the bacteria membrane inhabiting their growth	[23]
Ag	10–30	Spherical and few rod-like	Dip-coating of textile by the NMs	N.G.	<i>Escherichia coli</i> , <i>Staphylococcus aureus</i> , and <i>Streptococcus pneumoniae</i>	Size-dependent antibacterial activity	[27]

(Continued)

Table 4.1 The effects of nanomaterials' properties in their antibacterial activity. (Continued)

Nanomaterials			Attachment method	Fabric type	Antibacterial activity		Reference
Type	Size (nm)	Shape			Targeted bacteria	Main mechanisms involved	
Ag	2-4	N.G.	The radiochemical reduction of Ag ions onto the textile fabrics	Rayon Cotton Acryl polyamide polyester polypropylene	<i>Staphylococcus aureus</i> , <i>Klebsiella pneumonia</i> MRSA, <i>Escherichia coli</i> , <i>Pseudomonas aeruginosa</i> , <i>Salmonella enterica</i> , <i>Vibrio parahaemolyticus</i> , <i>Bacillus cereus</i>	N.G.	[28]
ZnO	12, 25, 30, 88, 142, 212, 307	Spherical	N.G.	N.G.	<i>S. aureus</i> strains RN6390, SH1000, Newman, and UAMS-1; methicillin resistant <i>S. aureus</i> hospital associated,	a) Production of reactive oxygen species b) Accumulation of nanoparticles in the	[29]

Ag	>50	- Spherical - Rod shape	N.G.	N.G.	HA-MRSA, strain COL and community associated, CA-MRSA, strain MW2; <i>Staphylococcus epidermidis</i> ; <i>Streptococcus pyogenes</i> N315; <i>Enterococcus faecalis</i> ; <i>Bacillus subtilis</i> ; <i>B. cereus</i> , <i>Escherichia coli</i> , <i>Proteus vulgaris</i> , <i>Salmonella typhimurium</i> , <i>Shigella flexinari</i> , <i>Pseudomonas alcali genes</i> , and <i>Enterobacter aerogenes</i>	cytoplasm or on the outer membranes of bacteria	[35]

(Continued)

Table 4.1 The effects of nanomaterials' properties in their antibacterial activity. (Continued)

Nanomaterials			Attachment method	Fabric type	Antibacterial activity		Reference
Type	Size (nm)	Shape			Targeted bacteria	Main mechanisms involved	
Ag	~190	- Spherical - Truncated octahedral	N.G.	N.G.	<i>Escherichia coli</i> and <i>Enterococcus faecium</i>	AgNMs attachment to bacteria and penetrate the bacteria cell	[36]
Ag	- 15 to 90 - 150	- Spherical - Triangular particles	N.G.	N.G.	<i>Pseudomonas aeruginosa</i> and <i>Escherichia coli</i>	a) AgNMs interact with and destroy the DNA of bacteria b) Disruption of the cell membrane	[37]
Ag	20	Spherical	Coating	Cotton	<i>E. coli</i> and <i>S. aureus</i>	Release of silver ions	[42]

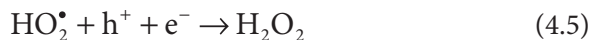
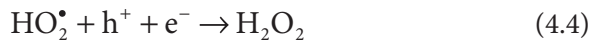
Ag	38.3, 19.3, 16.0 ^a	Spherical	N.G.	N.G.	<i>Escherichia coli</i> and <i>Staphylococcus aureus</i>	Reaction of large surface area of nano-Ag with the active functional groups of antibiotics toward bacteria	[43]
Ag-TiO ₂	35–200	Nano-fiber	N.G.	N.G.	<i>Staphylococcus aureus</i>	Reaction of hydroxyl radicals with cell membranes and DNA of bacteria	[47]
ZnO	25–45	Spherical	N.G.	N.G.	<i>B. subtilis</i> and <i>E. coli</i>	Physical damages to the bacteria induced by bacteria	[56]
Ag	5–50	Spherical	N.G.	N.G.	Various types of bacterial species	N.G.	[57]

^aFor citrate, SDS, and PVP capped nanoparticles, respectively.
N.G., not given.

nanoparticles loaded on textile fabrics can exhibit enhanced antibacterial activities that facilitate the release of the Ag to react with the bacteria.

The composition of the nanomaterials can also determine their activities against various types of bacteria. Although silver nanoparticles are the most widely used type of nanomaterials for the antibacterial activities in textile fabrics, studies have shown that these types of materials are more appropriate to be used for Gram-positive bacteria [16–18]. In order to overcome this issue, some other types of nanomaterials have been developed and used for textile engineering in recent years. Boron is among the nanomaterials effective in restriction of both Gram-negative and Gram-positive bacteria. Akbar *et al.* [19] observed that the boron nanoparticles (50 nm) effectively limited the bacterial growth of both Gram-negative and Gram-positive species. Such properties have also been reported for some other types of nanomaterials. ZnO is among the nanomaterials with a number of environmental applications [20]. They have demonstrated their high performance to be used in self-cleaning applications, for instance, in medical textiles, to decrease the risk of hospital-acquired infections [21, 22]. Budama *et al.* [23] showed that ZnO nanoparticles, synthesized via a reverse micelle process (21–25 nm), were very effective to enhance UV-blocking, self-cleaning, and antibacterial properties of the coated textiles with the synthesized nanomaterials. The particles showed very high antibacterial activity against facultative Gram-negative *E. coli* and aerobic Gram-positive *S. aureus*.

The composition of the nanomaterials can also determine the mechanisms involved in the antibacterial activities of nanomaterials. Various mechanisms have been proposed so far to be involved in these processes. Generation of reactive oxygen barriers has been considered as the main involved mechanism [24, 25]. Reactive oxygen species (ROS) generation pathways can lead to producing superoxides [O_2^-], hydrogen peroxide (H_2O_2), and hydroxide (OH^-)], for instance, according to the following mechanisms:



Among these compounds, hydrogen peroxide can penetrate the membrane, leading to cell death [26].

The release of the metallic ions from the surface of the nanomaterials is considered another mechanism for the toxic effects of the nanomaterials toward microbial communities.

4.2.2 Particle Size

In materials science, as well as in many other branches of science, the size of the materials is considered as one of the most important parameters for the development of engineered materials. Although for the spherical shape nanomaterials, the average diameter (in SI units) of the particles is considered as the particle size, for the other types of nanomaterials, it depends directly on the shape of the nanomaterials.

It is assumed that the size of the nanomaterial particles can have a direct impact on their antibacterial activities. This is mainly due to the fact that the lower sizes of the particles can provide a higher surface area-to-volume ratio. Hence, the reactions resulting in the antibacterial activity of nanomaterials are facilitated. There are some evidences in the literature to support this idea when the nanomaterials are used for textile engineering. Mahltig *et al.* [27] indicated that the silver nanoparticles with particle sizes of 10–30 nm can exhibit considerably higher antibacterial performance against *E. coli*.

Maintaining an effective surface for nanomaterials is another issue for the application of nanomaterials for the antibacterial activities in textile fabrics. The fact is that the nanomaterials tend to aggregate and form large-size particles that considerably affect the available surface area for the nanomaterials. To overcome this problem, some solutions such as the use of surfactants have been proposed so far, which needs additional materials and effort. In order to find an applicable method to disperse the nanomaterials on the surface of the textile, Seino *et al.* [28] applied a new technique for immobilizing silver nanoparticles on the surface of fabrics utilizing a radiochemical process. A high-energy electron beam was irradiated on a silver-containing solution forming the well-separated small-size Ag nanoparticles (2–4 nm together with some particles larger than 10 nm). They achieved excellent antibacterial activity even after washing the fabrics 100 times.

The effects of particle size on the antibacterial activities of nanomaterials have also been observed in ZnO nanoparticles. For instance, Raghupathi *et al.* [29] reported the size-dependent antibacterial activities of zinc oxide nanoparticles. They indicated that the lower-sized nanoparticles can exert

higher antibacterial behavior. Such observations have also been reported in other relevant studies [30]. In order to explain the effects of the size on the antimicrobial activity of nanomaterials, it can be stated that the smaller-sized nanoparticles can easily penetrate the media and also the membranes of the bacteria [31]. Some studies also indicated that the release of metallic ions is higher in the lower-sized nanomaterials, which is responsible for the higher activity of the lower-sized nanomaterials [32].

4.2.3 Particle Shape

Shape and surface are two significant properties of the nanomaterials with considerable effects on their reactivity. It is mainly due to some factors such as the relationship between the shape and movement behavior of nanomaterials and also its effects on other inherent properties such as band gap energy [33]. Various studies have indicated the effects of the shape and antibacterial activities of nanomaterials [34].

By the beginning of the 21st century, there was a lack of knowledge on the effects of various shapes of the materials on their antibacterial activity. Since then, experimental results achieved showed a highlighted difference between the antibacterial activities induced by various geometries. Probably the systematic work to fill the gaps was started by Pal *et al.* [35]. They concluded that the presence of the {111} lattice plane as the basal plane resulted in stronger antibacterial activities of truncated triangular silver nanoplates compared with spherical and rod-shaped ones against the Gram-negative bacterium *E. coli* (Figure 4.1). Such results were

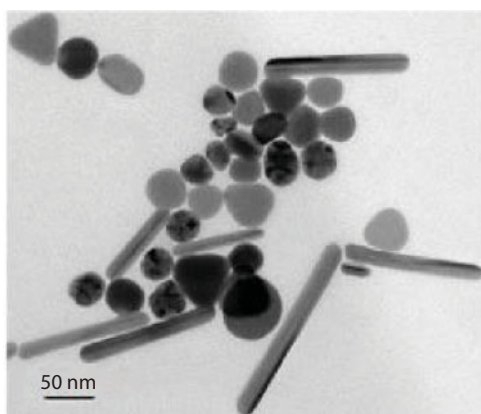


Figure 4.1 TEM images of different silver nanoparticle shapes, adapted from Pal *et al.* [35].

also achieved by other recent studies. For instance, Alshareef *et al.* [36] observed that spherical silver nanoparticles represent weaker antibacterial activity against both Gram-positive bacteria and Gram-negative bacteria, *E. coli* and *Enterococcus faecium*, compared with truncated octahedral Ag nanoparticles. However, the effect of size on the antibacterial activity of Ag nanomaterials can be of more importance compared to the shape. For instance, Raza *et al.* [37] indicated that the spherical Ag nanoparticles in the range of 15 to 90 nm can demonstrate a better antibacterial activity against two types of Gram-negative bacteria, *P. aeruginosa* and *E. coli*, compared with triangular particles with an edge length of about 150 nm.

Regardless of the simultaneous effects of various characteristics of nanomaterials on their antibacterial activities, the antibacterial mechanisms induced by nanomaterials can be explained by the presence of active facets in the synthesized nanomaterials, which can considerably determine the shape-dependent antibacterial activity of nanomaterials. It has been demonstrated that the synthesis techniques and the growth conditions are the main determinants for the shape of the synthesized materials [38]. In this regard, the facets with high atom density can exhibit enhanced activities [35]. Rod-like structures have normally (111) and (100) facets, whereas spherical particles have (100) facets. Hence, the materials with active (111) facets can potentially represent higher antibacterial activities. Such results have already been observed in nanomaterials such as ZnO nano rods with enhanced antibacterial activities [39]. Such shape-dependent antibacterial activities have also been observed in other nanomaterials. As an example, Penders *et al.* [40] showed that gold nanoflowers represented the greatest shape-dependent antibacterial activity among the studied nanomaterials (including spheres, stars, and flowers). The shape-dependent antibacterial activity of nanomaterials can also be related to the physical penetration of the particles in the media. For instance, wires and rods have the ability to pass through the cell membrane and to penetrate the cell of the bacteria more easily than spherical-shaped particles [41].

4.2.4 Surface Modifications

Surface modifications can also have a significant effect on the antimicrobial activity of the nanomaterials. Budama *et al.* [42] indicated the synthesized silver nanoparticles within the reverse micelle cores of a polystyrene-block-polyacrylic acid copolymer (Figure 4.2) and used the prepared nanomaterials for the antibacterial activities against Gram-negative *E. coli* and Gram-positive *S. aureus*. They determined esterification reactions as between the corona and the hydroxyl groups on the surface of the

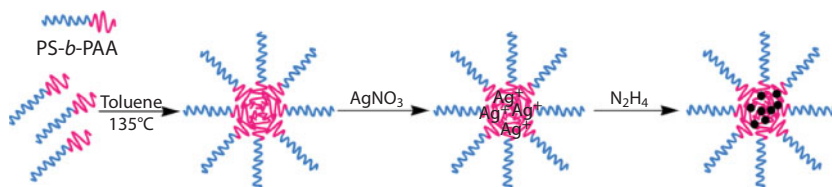


Figure 4.2 A silver-coated nanomaterial with enhanced antibacterial activity, adapted from Budama *et al.* [42].

textile creating an inhibition zone surrounding the coated nanomaterials in the textile fabrics.

The effects of various capping agents on the antimicrobial activity of nanomaterials have also been investigated in some recent studies. Kora and Rastogi [43] tested three different capping agents (trisodium citrate dihydrate, sodium dodecyl sulfate, and polyvinylpyrrolidone) for the synthesis of silver nanoparticles. Antibacterial activity experiments against both Gram-positive and Gram-negative bacteria indicated the enhanced activity of all three capped particles. However, polyvinylpyrrolidone-capped particles represented higher potential against bacteria.

4.2.5 Crystallinity

Crystalline structure is one of the main factors that determine the performance and stability of nanomaterials especially when they are expected to work under real environmental conditions [33]. When a nanomaterial has an amorphous crystalline structure or when there are defects in the structure of nanomaterials, the nanomaterials can resist hardly under harsh environmental conditions, for instance in the low acidic pHs. Under these conditions, the reactivity of nanomaterials can be highly influenced. In addition, the release of the nanomaterials with low crystalline structure from the surface of the fabrics to the environment can be accelerated, causing subsequent environmental drawbacks. Hence, some attention has been paid in order to enhance the crystalline structure of the nanomaterials [44, 45]. The low-ordered crystalline structure can also affect the photocatalytic activity of the nanomaterials against microbial communities. Hence, there may be a need for some techniques such as UV light irradiation to improve the performance of the nanomaterials [46]. In order to overcome such problems and to enhance the antibacterial activity of the nanomaterials used in fabrics, Lee *et al.* [47] developed anatase titanium dioxide nanofibers having hierarchical structures and improved crystalline

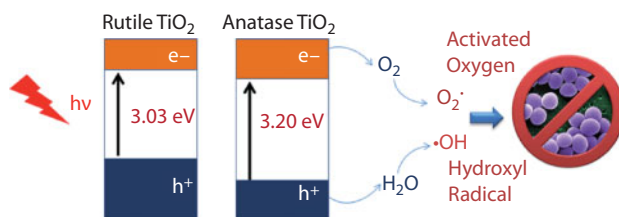


Figure 4.3 A schematic of the enhanced antibacterial activity of TiO₂ nanofibers by controlling the crystalline structure, adapted from Lee *et al.* [47].

structure against *S. aureus* (Figure 4.3). They achieved 90% of the antibacterial performance even in a very short period of time (1.5 min).

The enhanced antibacterial activities of the anatase phase have also been reported by other recent studies [48]. Also, some studies have reported the improvements in the activity of titanium-based nanomaterials through developments of oxygen vacancies in the crystal structure of nanomaterials [49–52]. The reports have also emphasized the effects of oxygen vacancies on the promotion of the visible light activity of the nanomaterials. Hence, using the nanomaterials with enhanced oxygen vacancies for antibacterial purposes in fabrics can enhance the visible light adsorption. Oxygen vacancies have been known to promote the ROS generation [53].

4.2.6 Surface Charge

Moving colloid particles represents an electrical charge at their slipping plane under an electric field. This potential is known as zeta potential [33, 54]. This parameter can play an important role in the interactions between the nanomaterials in the reaction medium and bacteria. Under neutral and acidic pH conditions, most of the inorganic nanomaterials hold a positive surface charge, facilitating their attachment to the bacteria with a negative surface charge [55]. This phenomenon can considerably enhance the potential of the nanomaterial to destroy the bacterial cell wall, to enter the bacterial cell, and to damage various organs. Various studies have been carried out in order to show such an interaction and its effects on the antimicrobial activity of the nanomaterials when used in the fabrics. Arakha *et al.* [56] prepared ZnO nanoparticles without and with surface citrate coating with sizes of 25–35 and 35–45 nm, respectively. While the nanomaterials without coating represented a zeta potential of +12.9 mV, the coated nanomaterials had a zeta potential of –12.9 mV. The antibacterial tests on both Gram-positive and Gram-negative bacteria

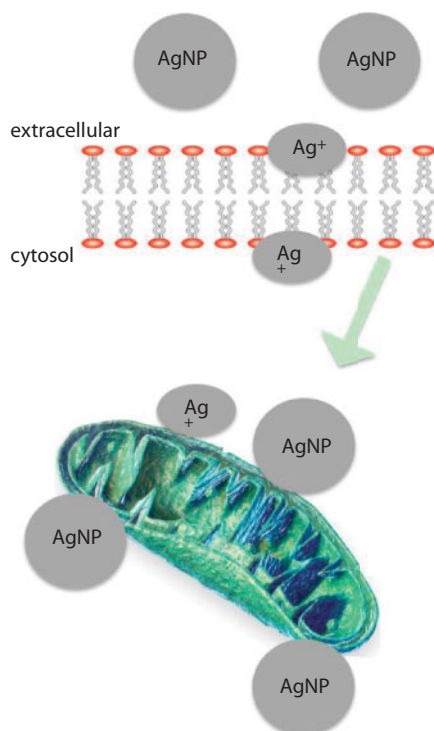


Figure 4.4 Damage to the mitochondria induced by Ag nanoparticles and Ag ions. ROS may be released from damaging the mitochondria damaging the DNA, adapted from Franci *et al.* [58].

indicated a higher efficiency of the uncoated materials with a positive surface charge.

However, there are some reports showing the efficient antibacterial activity of some nanoparticles even with a negative surface charge. As an example, Haider and Mehdi [57] indicated the high antibacterial activity of silver nanoparticles with a surface charge of -25.5 to -38.3 against various types of bacterial species. Such observations can reinforce this idea that beside the adsorption of nanomaterials to the surface of the bacteria having the opposite surface charge, other mechanisms including the release of the ions from the nanomaterials can also play a significant role in their antimicrobial activities (Figure 4.4).

4.3 Release

Due to the increasing use of nanomaterials in antibacterial applications in fabrics, it is necessary to have more scientific-based knowledge on the release of the nanomaterials in the environment [59]. In this regard, some parameters can determine the release and transformation of the nanomaterials in the environment such as the properties of nanomaterials and environmental conditions [59, 60]. The released nanomaterials may have the potential for different environmental impacts according to their type and (accumulated) concentration in freshwater, soil, and sediments [61]. Hence, the amount and the form of a nanomaterial emitted into the environment have a significant impact on the extent of the associated environmental risks [62, 63].

Nowadays, a number of materials are used in large quantities for antibacterial purposes in fabrics. For instance, about 9 to 45 tons of silver are used in the textile sector; 13% to 79% of this amount is estimated to be nano-scale. A part of these materials is normally released into the environment from the fabrics. As an example, about 20% of nano-Ag used in the textile industry is released through sewage to the environment [64, 65]. Because of the relatively low environmental allowed concentration of nano-Ag in the aquatic environment (about 0.03 $\mu\text{g/L}$), the release of the nanomaterials from the fabrics may cause adverse effects on marine organisms [59, 60] or on human health [66]. It seems that several factors such as the amounts of nanomaterials embedded in the textiles, the textile production process, the fabric type, the method used for the attachment of nanomaterials to the fabrics, the properties of the nanomaterials, and the environmental conditions can influence the amount and also the form of materials released (see the summary of the literature in Table 4.2). In case of silver, the release may occur in the form of single particles or agglomerated particles, or as free cations. For example, the major released form in sweat is dissolved silver rather than individual or aggregated particulate [60]. Also, the washing process and the type and the amount of the washing agents are other factors for the extent of the nanomaterials released to the environment [59–62, 67, 68].

4.3.1 Textile Properties

The morphology of the textile can have an important effect on the nanoparticles released into the environment. For instance, the amount of silver in the fabric, the fiber composition, fabric density, and the desired application for the textile can play a significant role in the amount of silver released [62]. Limpiteprakan and Babel [68] showed that commercial

Table 4.2 Factors that influence the released nanomaterials from textile.

Release measures	Explanation	Examples	Reference
Textile properties	The effects of the morphology of a textile on the nanoparticles released into the environment	In comparison to polyester fiber and textiles made of a cotton and nylon mixture, commercial products made of cotton can release less Ag	[68]
		Natural fabrics such as cotton release less silver than synthesized fabrics such as polyester and cotton and polyester blend fabric (35%:65%)	[68]
The amount of NMs on the textiles	The effects of the NMs amount added to the textiles on the nanoparticles released into the environment	Body suit and car sheet containing more silver compared with other fibers can release more Ag	[68]
Attachment method	The effects of the attachment method of NMs on the textile on the release of NMs into the environment	The products in which nanomaterials are attached to the polymers release less particles than the NMs sprayed on their surface (car sheet)	[68]
		The amount of released Ag into artificial sweat from the master batch process is about 0.21%, less than that in the finishing process, which measured about 0.51%	[70]
		The stability of nano-Ag on the nylon knitted fabric would increase due to the padding process and using 1,2,3,4-butanetetracarboxylic acid and sodium hypophosphite	[71]

	The stabilization of nanomaterials on the surface of some materials can lead to stability of the nanomaterials on the surface of the fabrics	The stability and durability of nanomaterials for antibacterial activities would be increased by decorating vermiculite with copper nanoparticles	[75]
Nanomaterials position	The effects of attachment pattern of the nanomaterials on the textile on the nanoparticles released into the environment	The textile with a low amount of silver at its edges release more Ag than the textile with uniform distribution of silver and the textile with higher amounts of silver at its center	[86]
Binder properties	The effects of the binder properties on the nanoparticles released into the environment	The amount of released silver can be reduced when calcium phosphate is used as a binder in textiles	[64]
		Hydrogen binding of nanomaterials with the fabric would be increased by the sonochemical coating process for deposition of ZnO nanoparticles on cotton fabrics by pretreating the cotton fabrics with cellulose	[72]
	Some additives can also be added in order to stabilize the nanomaterials on the surface of the fabric	Very low amounts of the released nanomaterials from cotton fabric resulted from cotton with dyes [Reactive Orange (RO16) and Reactive Black (RB5)] and CuO and ZnO	[73]
		Using lecithin on the wool fabric can maximize the loading efficiency of nano-Ag and inhibition zone	[74]

(Continued)

Table 4.2 Factors that influence the released nanomaterials from textile. (*Continued*)

Release measures	Explanation	Examples	Reference
Washing conditions	Using efficient methods in order to improve the nanomaterials bonding on the textiles	The efficiency of nano-TiO ₂ bonding in polyester fiber would improve by using a constitutional alkalinity hydrolysis method	[77]
	The effects of the detergent used for washing on the release and transformation of nanomaterials into the environment	Using oxidizing agents for washing led to a sharp decrease in the particle size of released Ag nanoparticles and physical fracturing of particles	[78]
		Bleaching agents in the washing solutions can facilitate the dissolution of silver and convert Ag ⁺ to AgCl	[60]
		Using powders as detergents can provide sufficient surfaces for conducting the reactions	[78]
	The effects of detergent nature and washing conditions (pH and temperature) on the form and the amount of released materials into the environment	The release of the nanomaterials would accelerate in higher temperatures.	[60]
		The rate of the ion release increases at elevated temperatures in the range of 0–37°C, and drops in line with either pH increase or humic or fulvic acid addition	[80]
		Higher amounts of Ag nanoparticles released in the basic pHs (10) in comparison to lower pHs, i.e., pH 7	[59]

		The dissolution amounts of nano-Ag dispersed in ultrapure deionized water with a pH of 7 were less than that in acetic acid with a pH of 3	[81]
	The amount of dissolved oxygen in the washing solution can affect the extent of the released materials into the environment	H ⁺ and oxygen will be consumed during the silver dissolution. Thus, silver dissolution will reduce under the low dissolved oxygen condition	[82]
Sweating properties	The effects of pH and formulations of artificial sweat on the form and the amount of released materials into the environment	The released amounts of Ag for laboratory-made and commercially obtained fabrics were least in the ISO artificial formulation at pH 5.5 (which did not contained urea). In contrast, the highest amount of Ag was released into the EN artificial sweat formulation that contained urea.	[85]
		The pH had no tangible effect on the release of Ag into the artificial sweat with a pH of 5.5 and 8	[87]
		Different pHs led to different forms of released silver. In the artificial sweat, which is more acetic, the released silver was in the form of ion, while in the laundry wash solution, it was in the form of particles in the size range smaller than 450 nm	[86]
		The release of Ag is not affected by the presence of either urea or lactic acid, whereas the total amount of released silver decreased when none of these materials are present in the medium	[82]

(Continued)

Table 4.2 Factors that influence the released nanomaterials from textile. (*Continued*)

Release measures	Explanation	Examples	Reference
		The amount of chlorides in the sweat content affects the amount of the released Ag	[86, 88]
Mechanical stresses	Adhesion of particles to the textile is a main factor in the release of nanoparticles into the environment	In the release of ZnO and CuO through the abrasion test, the released nanoparticles from the water-reacting solvent were more than those from the ethanol-reacting solvent	[89]
Nanomaterial properties	The effects of size of the nanomaterials on the nanoparticles released into the environment	More Ag would release into the textiles that contain smaller sizes of nano-silver without the binders	[68]
		The amount of dissolved Ag nanoparticles in both water (pH 7) and acetic acid (pH 3) increases with lowering the sizes of nanoparticles (AgNP, 6 nm > AgNP, 9 nm > AgNP, 13 nm > AgNP, 70 nm)	[81]

products made of cotton can release less Ag compared to polyester fiber and textiles made of a cotton and nylon mixture. They also indicated that the fabrics having more nano-Ag can release more silver into the environment. For instance, a body suit and a car sheet containing more silver (2.82 and 2.69 $\mu\text{g Ag/g}$ product, respectively) compared with other fibers can release more Ag (64.9 and 52.4 $\mu\text{g/L}$, respectively) [68]. Nanomaterials can be added to the fabrics through different methods such as surface coating or they can be added to the polymer that is used for the production of the fiber. The products that nanomaterials are sprayed on their surface would release more particles than the products that nanomaterials are attached to the polymers [68]. These results can indicate that the binding process may affect the amount of released silver [64, 69]. This is the reason why the car sheet with spray attaching method releases more Ag compared with other products. So far, various binders including zeolite, silica, calcium phosphate, and zirconium phosphate have been used in order to attach the nanomaterials such as silver to the fibers. For instance, calcium phosphate as a nontoxic material that is non-allergenic, non-irritant, non-mutagenic, and non-carcinogenic can dramatically reduce the amount of released silver when used as a binder in textiles [64]. Üreyen and Aslan [64] studied the release of silver from antibacterial cotton and polyester woven fabrics into the water in 20 rounds of washing. They used two different commercial types of silver. In order to reduce the impact of the attachment methods applied, all of the agents were attached on the surface of fibers using the pad dry cure method. All three antibacterial finishing agents were applied to 100% cotton (200 g/m^2) and 100% polyester (200 g/m^2) woven fabric samples. The cotton samples treated by the A_1 agent (silver chloride and titanium dioxide suspended in an aqueous solution) and the A_2 agent (nanosized silver chloride and reactive organic-inorganic binder) and the polyester fiber treated by the A_2 agent released almost 90% of silver after 20 rounds of washing. This release was due to mechanical forces and also to the presence of larger amounts of particles in these samples and the lack of the binder. The least amount of released silver was observed for the fibers (cotton and polyester, 73% and 77%, respectively) treated by the A_3 agent (calcium phosphate-based silver ion-doped powder). They stated that the main reason for these results is the higher amounts of the binder used in the A_3 agent. They also indicated that cotton fiber can be destructed more than polyester fiber in the washing process due to the highly crystalline structure and hydrophobic structure of polyester fibers.

The way the nanomaterials are added to the textile can also be counter-effective in the amount of the nanomaterials released. Nanoparticles can coat the surface of the textiles or they can be integrated into the fibers. Final

processing with nanomaterials has so far been applied in 90% of all the cases [61]. Stefaniak *et al.* [70] observed that the amount of released Ag into artificial sweat from the finishing process (silver nanoparticles are coated on the textile surfaces) is about 0.51%, more than that in the master batch process (silver is incorporated into the fiber threads), which measured about 0.21%. In order to reduce the release of nanomaterials, some new methods have been developed with the aim of stabilizing nanomaterials on the fibers' surface. For instance, Montazer *et al.* [71] stabilized nano-Ag on the nylon knitted fabric via the padding process and using 1,2,3,4-butanetetracarboxylic acid and sodium hypophosphite. Their findings indicated that the antibacterial activities of these fibers toward both Gram-positive and Gram-negative bacteria were maintained at about 96% after 20 runs of washing. This method had a negligible effect on the properties of the fibers such as the color and dimensional stability of the fabrics. In another study with the same purpose, Perelshtein *et al.* [72] used a sonochemical coating process for the deposition of ZnO nanoparticles on cotton fabrics by pretreating the cotton fabrics with cellulose, which increases the hydrogen binding of nanomaterials with the fabric.

Some additives can also be added in order to stabilize the nanomaterials on the surface of the fabric and to prevent their release. For instance, Perelshtein *et al.* [73] coated the cotton with dyes [Reactive Orange (RO16) and Reactive Black (RB5)] and CuO and ZnO, as antibacterial agents. They observed a very low amount of the released coating (2.5%–12.5%) while the antibacterial activity was not adversely affected. Barani *et al.* [74] used lecithin, a biological lipid, to maximize the loading efficiency of silver nanomaterials and inhibition zone on the wool. They observed that the presence of lecithin can considerably limit the amount of nano-silver released. However, it must be noted that the presence of additives may bring other issues. For instance, dyes may have some toxic effects on the human body. Thus, when such additives are desired to be used in such applications, toxicology studies are recommended to be carried out. The stability of the nanomaterials on the surface of the fabrics can also be achieved through the stabilization of nanomaterials on the surface of some materials such as clay. For instance, Drelich *et al.* [75] developed a strong antibacterial material by decorating vermiculite (a low-cost mineral material with high stability, layered structure, and high capacity for cation exchange) with copper nanoparticles (1 to 400 nm). Strong adhesion of nano-Cu to the vermiculite carrier led to increasing the stability and durability of nanomaterials for antibacterial activities. This hybrid material exhibited a strong antibacterial activity at 37°C against *S. aureus*.

Some materials such as titanium dioxide may reduce the washing because of their self-cleaning properties. However, efficient bonding methods for

fibers and nano-TiO₂ may be required to prevent the defects in the stability and durability of nanocomposites during use [76]. In order to improve the efficiency of nano-TiO₂ bonding in polyester fiber, Hashemizad *et al.* [77] indicated that the amount of TiO₂ released from a polyester fiber can be reduced using efficient methods such as the constitutional alkalinity hydrolysis method. Also, they used the alkaline hydrolysis method in order to introduce hydrophilic groups onto the surface of the polyester fabric to achieve better binding of TiO₂.

In order to have an estimation of the quantity of nanomaterials released from fabrics into the environment, it would be vital to study the main factors for the release of nanomaterials during use. Washing, mechanical stresses, leaching in landfills, and sweat are among the most important parameters in this sense.

4.3.2 Washing

Washing is one of the most important methods for the release of nanomaterials into the sewage. Generally, large volumes of effluents containing nanomaterials are produced through washing the textiles. It is believed that the amount and the properties of nanomaterials released in the washing effluents depend on various washing conditions such as the type of water, the detergent used, washing conditions (e.g., pH and temperature), textile properties, and nanomaterial properties [59, 62].

The detergent used for the washing is among the most important factors in the release and transformation of nanomaterials. The dissolution of the nanomaterials and the formation of new types of materials are directly determined by the washing solution chemistry. For instance, utilization of powders as detergents can provide sufficient surfaces for conducting the reactions [78]. Using a set of commercially available liquid and powdered detergents, Mitrano *et al.* [78] showed a sharp decrease in the particle size of Ag nanoparticles and physical fracturing of particles when oxidizing agents are used for the washing. Mitrano *et al.* [67] illustrated that a higher concentration of the oxidizing agent can result in the promotion of oxidative dissolution of the Ag nanoparticles. However, they did not observe such a trend when Au nanoparticles were used as antibacterial agents in the textile.

In addition to the nature of the detergent, washing conditions including pH and temperature may affect the form and the amount of released materials from the washing process. It is believed that the higher temperatures can accelerate the release of the nanomaterials [60]. Such a result was observed by Kittler *et al.* [79]. Through the synthesis of citrate or PVP

surface-modified Ag nanoparticles, they indicated that the dissolution is directly attributed to the temperature. Any increase in temperature resulted in a higher dissolution degree [79]. Similar results were also achieved by Liu and Hurt [80]. They found that the rate of the ion release increases under elevated temperature in the range of 0–37°C and drops in line with either pH increase or humic or fulvic acid addition. pH can also influence the complicated reactions involving the release of nanomaterials during the washing process. For instance, Geranio *et al.* [59] emphasized the effects of pH, as the basic pHs (10) resulted in the release of higher amounts of Ag nanoparticles, compared to lower pHs, that is, pH 7. Washing solutions usually have a pH of greater than 10 with the compounds such as chloride ions that are highly reactive with Ag [62]. The presence of bleaching agents in the washing solutions can facilitate the dissolution of silver and convert Ag^+ to AgCl [60]. In addition, the solubility of nanoparticles will generally increase under low pHs. For instance, Peretyazhko *et al.* [81] investigated the dissolution of nano-Ag dispersed in ultrapure deionized water with a pH of 7 and in acetic acid with a pH of 3. More nano-Ag particles were dissolved in acetic acid compared to water.

The amount of dissolved oxygen in the washing solution can also affect the extent of the released materials. Oxidation of the metallic particles by dissolved oxygen can be considered a main reason for this phenomenon [81–83]. For instance, silver dissolution will be reduced under low dissolved oxygen conditions because H^+ and oxygen will be consumed during silver dissolution [82].

4.3.3 Sweating

The contact of the nanomaterials already embedded in the textile structure with the dermal sweat is another possibility for the release of nanomaterials. Von Göetz *et al.* [84] indicated that the release of nanoparticles from commercial textiles exposed to artificial sweat can be altered by the properties of both textile and nanoparticles, properties of sweat such as pH and the formulation [85, 86], and the time of exposure [84]. In addition, the initial amount of nanomaterial, the existence of coating, and fabric quality can also determine the form and the amount of released materials from textiles [85]. For instance, Kim *et al.* [86] estimated the highest released amount of Ag in both forms (dissolved and particle) during 1 h of sweat exposure, about 0.81/2.03 μg Ag/kg body weight, considering a standard male body weight of 77 kg. They also evaluated the release of silver in two different environments: artificial sweat and laundry wash solution. Although each textile released a similar amount of silver in both

environments, in the artificial sweat, the released silver was in the form of ion, while in the laundry wash solution, it was in the form of particles in the size range smaller than 450 nm. This difference may be due to the difference in pH between the two environments, as the artificial sweat is more acidic than the laundry wash solution. In fact, fewer particles are dissolved in the alkaline sweat compared with acidic conditions [84]. Kulthong *et al.* [85] studied the impact of pH and formulations of artificial sweat on the release of Ag in different pHs (4.3, 5.5, 6.5, and 8.0) from laboratory-made and commercially obtained fabrics. They found that the lowest amount of released Ag occurs in the ISO artificial formulation at pH 5.5 for both fabrics. In contrast, the highest amount of Ag was released into the EN artificial sweat formulation at pH 6.5. EN artificial sweat formulation contained urea, while in the other artificial sweat formulation, urea was not detected. As a result, pH and formulations of artificial sweat probably have a significant impact on the release of Ag from the fabrics [85]. However, there are some reports stating that pH has no important effect on the released materials. For instance, Wagener *et al.* [87] observed that the pH has a negligible effect on the Ag release of the artificial sweat with pH values of 5.5 and 8.

The presence of other materials in the medium can also affect the extent of the released materials. Quadros *et al.* [82] studied the release of Ag from the textile containing nano-silvers in an artificial sweat. Their results showed that the release of Ag is not affected by the presence of either urea or lactic acid, whereas the total amount of released silver decreased when none of these materials are present in the medium. The particles of nanomaterials are normally dissolved in the sweat [60, 70, 87]. For instance, for Ag, the amount of the released Ag is determined by the amount of chlorides in the sweat content. Then, salts such as sodium chloride may also affect the dissolution reactions involved in the release of particles into the media [86, 88].

4.3.4 Mechanical Stresses

The release of the nanomaterials from the surface of the textiles may also happen due to mechanical tensions and stresses. Mechanical stresses can be induced by abrasion, heat, pressure, and so on. It may lead to the release of the nanoparticles in different phases of the textile's life cycle. Abrasion is the most important mechanical route for the release of nanoparticles from the textiles. As a result of abrasion, a fabric loses about 10% of its weight during the usage period [59, 60]. Adhesion of particles to the textile is a main factor in the release of nanoparticles. Some studies have been carried out to emphasize the role of this parameter on the extent of the released

particles [59, 87]. Mantecca *et al.* [89] studied the release of ZnO and CuO through abrasion test. They coated cotton and polyester–cotton (65%:35%) fabrics by the sonochemical technique using two different reacting solvents including water and ethanol. The released nanoparticles from the water-reacting solvent were more than those from the ethanol-reacting solvent. Since the surface tension of ethanol is lower than that of water, particle adhesion is stronger in alcohol-based textile synthesis processes [89].

However, the release of nanoparticles from textiles into the air by abrasion is negligible (about 5%). Also, this amount is very low compared to other routes such as waste incineration [65].

4.3.5 Leaching in Landfills

Disposal in landfills is one of the final destinations of the textiles after being used. In the USA, about 85% of total textiles used are disposed in landfills every year [90]. Boldrin *et al.* [91] estimated that the average amount of Ag in a textile that ends up in landfills is about 0.78–5.6 mg [68, 91]. The amount of Ag released into European landfills was estimated to be about 5.24 tonnes in 2012 [68]. It can be stated that almost all nanoparticles that remain in the textile after use will be leached in the landfills. Several factors can influence the amount of the particles released from a textile. The methods used for the attachment of nanoparticles to the textile, the properties of nanomaterials (such as size), the type of fabrics, and the presence or absence of a binder in the coating solution are among the most important factors. Limpiteprakan and Babel [68] studied the potential of Ag released from the variety of textiles with different concentrations of Ag via the toxicity characteristic leaching procedure test. Their results showed that the textiles that contain smaller sizes of nano-silver without the binders released more Ag. Also, synthesized fabrics such as polyester and cotton and polyester blend fabric (35%:65%) release more silver than natural fabrics such as cotton.

It seems that the main portion of the released nanomaterials from textiles occurs at landfills. Also, the release from abrasion is the minimum, and the amount of released nanoparticles from washing is supposed to be more than that released from sweating [65].

4.3.6 Nanomaterial Properties

The properties of nanomaterials can also be considered as a main determinant for the amount of nanomaterials released from the textile. As can be realized from the literature, the solubility of nanoparticles may increase

as a result of decreasing the size of nanoparticles embedded in the textile structure. For instance, Peretyazhko *et al.* [81] investigated the size-dependent dissolution of Ag nanoparticles exposed to ultrapure deionized water (pH 7) and acetic acid (pH 3) at different sizes (6, 9, 13, and 70 nm). Their results showed that the amount of dissolved Ag nanoparticles in both water and acetic acid increases with lowering the sizes of nanoparticles (AgNP, 6 nm > AgNP, 9 nm > AgNP, 13 nm > AgNP, 70 nm). The higher solubility rates for smaller particles can be attributed to their larger surface area [88], although the size is not the only parameter for determining the surface areas of the nanomaterials. Other properties of the nanomaterials can also be effective in the release of nanomaterials from the textiles. Zhang *et al.* [92] studied the ion release kinetics of nano-Ag at two initial concentrations (300 and 600 $\mu\text{g/L}$) with three different sizes of the nanomaterials (20, 40, and 80 nm). Their results showed that an increase in the initial concentrations of nanomaterials from 300 to 600 $\mu\text{g/L}$ can cause an increase in the rate of ion release for all sizes of nano-Ag, as can be seen in Figure 4.5.

The attachment pattern of the nanomaterials on the textile is also an important factor in the release of nanomaterials. Kim *et al.* [86] showed that the distribution pattern of Ag on the surface of textiles has more impact on the release of Ag compared with the total Ag content in the textile. They compared a textile with a low amount of silver at its edges (a) with two other textiles that contain considerably higher amounts of

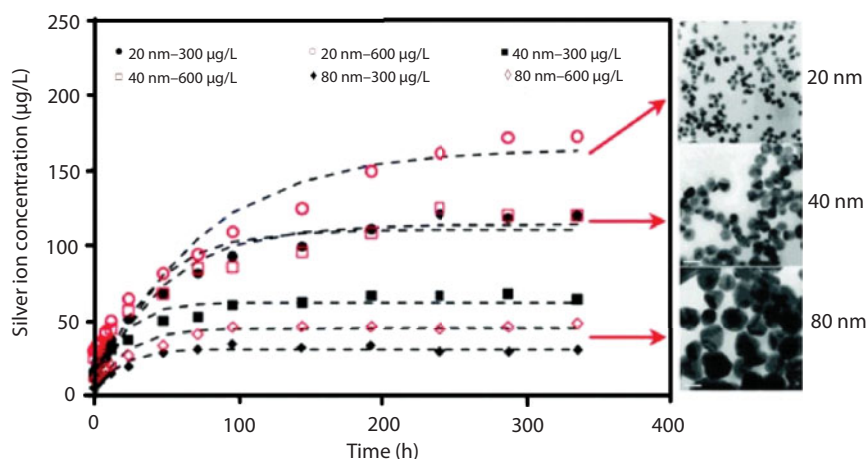


Figure 4.5 Release kinetics of Ag^+ in two different concentrations (300 and 600 mg/L) and three different sizes (20, 40, and 80 nm), adapted from Zhang *et al.* [92].

silver with a uniform distribution throughout the textile (b) and the other in the center of the textile (c). First, textile (a) released 25.7% and 19.67% of Ag in artificial sweat and laundry wash, respectively, while uniform distribution textile (b) released 10% and 11% of Ag in artificial sweat and laundry wash, respectively. The third studied textile (c) released only 1% of Ag. Ag can be released both physically and chemically. It seems that the silver nanomaterials located at the edge of the fabric can be easily separated from the textile by physical force compared to those particles located in the center of the textile. Chemical release occurs due to the weakness of silver and textile bonding and changes the silver due to the reaction of surrounding materials. Chemical release of Ag distributed at the edge of the textile seems to be greater compared to those located in the center of the textile due to the easy access of the surrounding materials to the silver that lie at the edge of the textile and can affect them. Also, the presence of titanium composite in the textile will make the release of the silver more difficult [86].

4.4 Conclusion

Antibacterial activity is one of the interesting fields of nanomaterial applications. Among the various types of nanomaterials, Ag is the most widely used in this respect, especially in its metallic form. However, some other types of nanomaterials such as titanium dioxide and zinc oxide nanomaterials have proved their potential to be used in fabrics. The properties of nanomaterials have a determinant role on the activities of the nanomaterials against various types of bacterial communities. Adopting efficient synthesis procedures can lead to enhancing the antibacterial activities of nanomaterials and to developing the novel engineered types of nanomaterials with enhanced properties to produce textiles with high antibacterial performances. Due to the rising environmental concerns on the fate of nanomaterials when released into the environment, it is very important to design and produce nanomaterials with minimum release. There are several methods involved in the release of nanomaterials that must be taken into consideration when producing a textile decorated with nanomaterials. Washing and releasing in the sweat medium are two main routes that should be controlled in the consumption phase. Hence, providing information of the nanomaterials embedded in the textiles, for instance, by labeling with adequate information, can be useful to minimize the release of the nanomaterials. Overall, it must be concluded that there is an urgent need to conduct

cooperative studies to identify the most appropriate types of nanomaterials to enhance the antimicrobial performance in textiles and to prevent the probable subsequent environmental drawbacks resulting from the release of the nanomaterials into the environment after being used.

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Modification of Wool and Cotton by UV Irradiation for Dyeing and Finishing Processes

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Abstract

UV radiations can act in different ways on the functionalization of textiles, through pre- or posttreatments, in order to modify their behavior in dyeing and finishing processes. Specific photomodification can occur in a particular textile substrate due to UV irradiation, so the effect of UV exposure was investigated, focusing principally on wool and cotton as textile substrates.

The UV treatments applied in the textile field, in addition to required specific effects, should also meet the following requirements:

- easy application, not needing technical or sophisticated equipments;
- durability and fastness of the degree of treatment for future uses;
- limited treatment costs, not precluding any market segment;
- environmentally friendly characteristics, for a sustainable textile process.

In this chapter, the existing UV procedures and/or recent proposals, with its consequent conferred functionalities, are described.

Keywords: UV radiation, wool, cotton, dyeing, finishing

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5.1 Introduction

Chemical processes on textiles are known from ancient times; they have been more and more refined over the centuries, from knowledge of alchemical type to physical–chemical concepts, enabling the achievement of high-quality standards. The introduction of synthetic dyes and the progress of the chemical industry in general (auxiliaries and inorganic products) greatly enhanced this development. Today, the challenge of textile dyers and finishers is looking for dyeing and/or finishing processes aimed at conferring new functionalities on textile products, both yarns and fabrics [1]. Meanwhile, an even more demanding market requires environmentally sustainable and energetically advantageous solutions bringing together, where possible, the greatest number of benefits toward the final textile object.

To this aim, radiation processes appear to offer good perspectives. They have several commercial applications for the coating of metals, plastics, and glass, in printing, wood finishing, film and plastic cross-linking, in adhesives and electrical insulations. The advantages of this technology are well known: energy saving (low temperature process), low environmental impact (no solvent emissions), simple, cheap, small equipment, and high treatment speed. Despite these advantages, there have been few applications of radiation curing in the textile industry, such as nonwoven fabric bonding, fabric coating, pigment printing, silk grafting, and surface modification of cotton and synthetic fibers [2–8]. In fact, in textile finishing processes, the conventional thermal curing technique is still used, regardless of energy consumption and cost. Among the textile treatments by radiation curing, pigment printing of fabrics has received much attention [9], whereas coatings for shrink-resistant wool, flame-retardant fabrics, and durable press finishes have also been investigated. Recently, studies on the effects of radiations on textile coloration and finishing have been reviewed by Shahid-ul-Islam and Mohammad [10], while the application of UV irradiation to dyeing and finishing processes has been further experimented [11–13].

The present chapter is aimed at illustrating research works about dyeing and finishing improvement on textiles through the application of UV radiations. A preliminary review of literature about the interaction of UV radiation with textile fibers is reported. Wool and cotton, in the form of both fibers and fabrics, are considered as substrates, since these natural fibers have a cellular structure, more complex than that of manmade fibers obtained by chemical spinning.

The influence of wavelength, moisture, and temperature on the degradation of the substrates is investigated in the second section. In the third section, results about the interaction between UV radiation with naturally present chromophores of the target fibers are discussed.

After the first chemical approach, aimed at describing the theory of the involved reactions, the description focuses on the application of UV radiation processes in pre- or posttreatments of textiles in order to modify their behavior in dyeing and finishing processes.

In the fourth section, wool is considered as a substrate. The dyeability improvement is one of the most required objectives for practical applications; hence, the effect of surface modification of the fiber due to UV exposure is investigated for a possible increase of absorption rate and affinity of acid dyes. This can allow dyeing at a temperature lower than that is required in the conventional process, reducing the fiber damage due to longtime maintenance at high temperature with some economic and ecologic benefits. In the meantime, UV irradiation can give better color yields on wool fabrics than untreated ones. Experimental results on wool dyeing after UV irradiation, both under static and dynamic conditions, are widely presented.

Another topic of interest about wool treatment by UV light is the possibility of achieving differential dyeing effects. Two effects were investigated: one shade, double face with different depth, higher on the UV-treated side, or two shades, double face with a different color and depth. Dyes of different classes were involved in the study.

Finally, UV treatments providing grafting or coating on wool fibers are reported. Improvement of shrinkage resistance, hydrophobicity, oil repellency, or stain resistance can be obtained through UV surface modification by photoreactive monomers, while chitosan UV grafting is reported as multifunctional finishing conferring antibacterial and anti-felting properties.

In the fifth section, the attention is focused on cotton. UV irradiation coupled with mild oxidation can improve some properties such as pilling resistance, water swelling, and dyeability. Differential dyeing effects by fading of dyed cotton yarn can be obtained by applying UV irradiation on dyed samples. As for wool, grafting or coating the cotton fibers by suitable UV-curable monomers can confer the corresponding functional properties, such as water and oil repellency with polysiloxanes or fluorocarbon monomers, or antibacterial finishing by chitosan UV grafting.

The most promising results are summarized in the conclusion, while future perspectives are suggested.

5.2 Interaction of UV Radiation with Textile Fibers

5.2.1 Introduction

UV light is composed of electromagnetic radiations with wavelengths shorter than visible light, but longer than X-rays, that is, in the range 10–400 nm, corresponding to photon energies from 3 to 124 eV. These frequencies are invisible to humans, but visible to a number of insects and birds.

The totality of electromagnetic radiations, different in their wavelength and energy, travels in the vacuum at ca. 2.997×10^8 [m s⁻¹].

The energy of the *photon* (*quantum of light* ϵ) referred to a given radiation is in inverse relation to the wavelength of the luminous beam and is expressed in Joule [J] in Equation 5.1, while the energy of one mole of photons (E) in some studies of photochemistry is defined [Einstein] (Equation 5.2)

$$\epsilon \text{ [J]} = h\nu = hc/\lambda \quad (5.1)$$

$$E \text{ [Einstein]} = N_A h\nu = N_A hc/\lambda \quad (5.2)$$

where

N_A = Avogadro constant = 6.023×10^{23} [mol⁻¹]

h = Planck constant = 6.63×10^{-34} [J·s]

ν = frequency [s⁻¹]

c = light speed = 2.997×10^8 [m s⁻¹]

λ = wavelength [m]

UV radiations are ideally divided into four ranges:

E-UV from 10 to 121 nm from 1.20×10^7 to 1.00×10^6 [Einstein]

UV-C from 100 to 280 nm from 1.20×10^6 to 4.27×10^5 [Einstein]

UV-B from 280 to 315 nm from 4.27×10^5 to 3.80×10^5 [Einstein]

UV-A from 315 to 400 nm from 3.80×10^5 to 3.00×10^5 [Einstein]

5.2.2 Influence of Wavelength

The photochemistry of polymer materials is based on two principles:

- electromagnetic radiation must be absorbed, in order to initiate a photochemical process;
- absorption takes place in discrete quanta (photons) whose energy is determined by the frequency of the radiation.

These groundwork led research laboratories to devote extensive attention to the wavelengths that are responsible for the degradation of specific materials. As potentially fruitful as this approach is in principle, the quest has not always yielded results as significant as initially expected.

Berger [14, 15] clearly states: "Absorption curves need not always be identical with the pertaining curves of damage, since not every type of absorption causes changes in the material."

One reason for misdirection is that determination of the activation spectrum may show an apparent wavelength of peak activity, not because of the maximum absorption of a particular component, but simply because the available energy of the light source falls off rapidly at the lower wavelengths.

When the range of wavelengths considered is extensive (from 254 nm or lower to 450 nm or greater), it is expected that differences in photodegradation behavior will be observed.

The gases specifically emitted by wool, studied over a wide range of wavelengths by Launer and Black [16], provide an example: distinctly different combinations of gases were generated by 254-, 365-, or 436-nm radiation (Table 5.1).

Bousquet and Foussier [17] referred to differences induced by wavelengths as far apart as 254 and 313 nm as a "macroscopic" wavelength effect. Another work carried out by Johnson *et al.* [18] reported the loss of tensile strength versus wavelength, finding major activity between about 330 to 390 nm. As noted earlier, as the wavelengths of radiation decrease through blue, violet, and into the ultraviolet, the energy of the photons increases. Thus, a basic point of view regarding the damaging effect of exposure to visible and ultraviolet radiation would be to state simply that the shorter the wavelength, the more energetic the photons, and therefore the more potentially damaging the radiation.

Table 5.1 Percent gaseous product evolved from wool in vacuo by irradiation of light of various wavelengths and by heat.

Wavelength (nm)	CO ₂	CO	H ₂	H ₂ O	COS	H ₂ S	CH ₄
254	34	28	23	11	4	Trace	—
365	75	—	—	—	—	—	—
436	100	—	—	—	—	—	—
546	—	—	—	—	—	—	—
Dark (160°C)	22	2	—	63	1	2	8

However, an important generality is implied in the principle of reciprocity. This concept states that the net exposure, which influences the total amount of photochemical damage, is represented by the product of the intensity of the irradiance (or the illumination, the luminous flux) and the radiation time, other factors being negligible. In other words, 100 lux of intensity for 1 h is considered to produce as much damage as 1 lux of the same radiation for 100 h; the product in each case is the same: 100 lux hours and the total number of photons striking the sample would be the same.

In a series of tables, Harrison [19] gave detailed examples showing how the factors of damage for a given wavelength could be used in conjunction with numbers related to the spectral distribution of emission from various light sources and the spectral transmission of various filters, in order to estimate the relative damage that might occur under various combinations of sources and filters.

He proposed a logarithmic relationship between the damage factors ($D\lambda$) versus wavelength on semilog paper, achieving a straight-line relationship.

On the other hand, attention was drawn to the following facts:

- a. degradation of rubber Bateman [20],
- b. erosion of paint Miller [21],
- c. tendency of certain methacrylate polymers to cross-link Feller [22],

all of which respond in a similar way to decreasing wavelength.

Later, it was found that the development of carbonyl groups in poly(vinylchloride) Martin and Tilley [23] exhibited much the same behavior Feller *et al.* [24].

In an extensive consideration of the problem of minimum tolerable exposure, Aydinli *et al.* [25] took particular note of a logarithmic relationship.

This was based on Equations 5.3 and 5.4:

$$S(\lambda)\text{dm rel.} = ae - b\lambda \quad (5.3)$$

$$\ln S(\lambda)\text{dm rel.} = \ln a - b\lambda \quad (5.4)$$

where λ is the wavelength in nanometers and $S(\lambda)\text{dm rel.}$ is the relative spectral damage or responsivity of the material, comparable to the $D\lambda$ introduced by Harrison [19].

In the case of specific materials and photochemical changes, the intercept and slope become important specifications. Using these principles,

Aydinli and his coworkers determined the slope b , for a series of water-colors, oil paints, paper, newsprint papers, and textiles. They used this approach to estimate the minimum exposure under various lamps, causing a "just perceptible" color change, considered to be a ΔE of 1 according to the CIE $L^*a^*b^*$ color-difference formula.

Yano and Murayama [26] found that the dynamic modulus of nylon was only affected by wavelengths below 300 nm. The tendency of poly(methyl-methacrylate) to undergo chain scission also becomes particularly important at wavelengths below 300 nm Torikai *et al.* [27].

When evaluating the photochemical activity of TiO_2 , Blakey [28] reported that a radiation source rich in the short wavelengths of ultraviolet (ca. 290 nm) exaggerated the photochemical degradation of the binder and minimized the effect of the pigment photoactivity. It became particularly important when the behavior of different TiO_2 pigments was first tested in an air-drying alkyd and later compared to the behavior of the same pigments in a more durable binder based on a thermosetting acrylic.

In summary, there is ample evidence that UV-B wavelengths can occasionally induce differences in degradation chemistry as opposed to the same source filtered by borosilicate or soda-lime glass.

Concerning the long-held interest in a threshold below which photochemical damage will not occur, there are indeed many examples of the fact that various reactions will not be induced above a certain wavelength. In contrast, there is theoretically no limit of *intensity* (more properly, *exposure*, intensity times) of an activating irradiance, below which a photochemical process will cease. Evidence has been provided about the fact that UV-B radiation, not significantly transmitted by ordinary window glass, is capable of inducing degradation reactions.

Close attention must be paid to the wavelengths involved, particularly if 254 nm radiation is involved, or if low- and medium-pressure mercury vapor lamps are used without an effort to filter out the lower wavelengths, responsible for photolytic degradation. Solarization affects the shortest, usually most damaging wavelengths, seriously altering their intensity during the normal lifetime of lamps. The change in intensity of wavelengths between 290 and 340 nm may require more careful monitoring than is often done.

Sources of intense illumination commonly cause the rising temperature of test samples, nearly always introducing unwanted heat effects. Besides the obvious effects of heat, there is usually also a decrease in moisture content of the specimens. A simple method to demonstrate the gross effects of heat as opposed to light during exposure outdoors, as well as under an intense artificial light source, is simply to place a covered control sample

either alongside (preferable) or behind an exposed sample. This is particularly useful in estimating the degree of protection of textiles provided by ultraviolet filters. Results related to silk and linen showed a certain loss of strength during the exposure, simply due to thermal effects.

If the effect of UV radiations with short wavelengths is evaluated, the possible ozone generation must be considered. This chemically active gas in fact can seriously attack many organic materials, masking the purely photochemical effects Cass *et al.* [29]. Wavelengths below about 242 to 248 nm should be absent if one intends to avoid the generation of ozone.

5.2.3 Influence of Moisture

It is generally agreed that oxidative degradation will be speeded up by the presence of moisture. Nonetheless, Lemaire *et al.* [30] take the position that “the chemical role of water in weathering is far from being understood.”

Kamal and Saxon [31] point out that water can have at least three kinds of important effects in the degradation of polymers:

- chemical: hydrolysis of the ester or amide bonds;
- physical: loss of the bond between the vehicle and a substrate or pigment;
- photochemical: generation of hydroxyl radicals or other chemical species.

Another influence of moisture could be the help in ionization and mobility of ionic entities, an important aspect of corrosion chemistry.

Polymer formation by condensation reactions with loss of water can be reversed. Ester groups in cellulose acetate–butyrate polymers hydrolyze, yielding destructive acidity Allen *et al.* [32].

The effect of moisture should always be checked. Moreover, the elevated temperatures achieved in samples exposed to high-intensity light sources tend to reduce the moisture content of samples.

Graminski *et al.* [33] note that, when the atmosphere was desiccated, little if any change in physical properties of paper occurred at temperatures between 60°C and 90°C. There are nonetheless notable examples in which increased levels of moisture have a negligible effect on the rate of degradation.

Some workers, therefore, consider their results to be more fundamentally significant if expressed in terms of the moisture content of the material under test, inappropriately named “object humidity,” rather than of relative humidity.

The response of cellulose to decreasing moisture content does not decrease monotonically, but goes through a minimum at about 0.8% moisture content DuPlooy [34]. At this point, the absorbed moisture is zero and the only water remaining is the so-called *bound water*. Further reduction of water content begins to eliminate the bound water, generally leading to an increased rate of degradation. Graminski *et al.* [33] also state that the minimum occurs because a portion of the water in cellulose, namely, the bound water fraction, is chemically inactive.

Hon [35] has pointed out that below a water content of 5%–7%, the opportunity to form free radicals is reduced. Instead, as stated by Holt and Waters [36], “In the photodegradation of wool, humidity is a relatively unimportant parameter.”

At 100% RH, Calvini [37] emphasized the fact that there can be differences in behavior between situations that principally involve absorbed water vapor, and situations that involve water in the condensed liquid phase. If the latter occurs, contact with water may cause leaching and cracking effects that lead to distinctly different results than that would occur when only the absorption of water vapor is the affecting behavior Abeysinghe *et al.* [38].

Instances are also known in which the hydrolysis of bonds, thought to be the principal process of degradation in a polymer, did not take place in the absence of oxygen. The diversity of these possible modes of action led to assert that the role of water in weathering remains far from being understood. The action of moisture in degradation, difficult to predict, must be verified in each specific situation.

Because reactions initiated by ultraviolet and short wavelength visible radiation are likely to be more rapid than thermally initiated reactions, it is usually the case that samples need to be much thinner for photochemical aging tests than for thermal Cunliffe and Davis [39]. This general circumstance is further supported by the fact that the diffusion of oxygen is likely to be greater at the higher temperatures customarily employed in the thermal degradation studies; hence, thicker samples can be tolerated at higher temperatures.

5.2.4 Influence of Temperature

The direct breaking of chemical bonds upon exposure to ultraviolet and visible light in the absence of oxygen is termed *photolysis*. There are also *pyrolytic* chemical changes that can be induced by high temperatures in the absence of oxygen.

Vachon *et al.* [40] claimed that the degradation of nylon was not a purely hydrolytic process as might be expected. They found instead that

the scission of the amide linkages did not occur in the absence of oxygen. Measurement of the rate of degradation of nylon and Kevlar versus relative humidity allowed Auerbach [41] to conclude that at 150–170°C, there was a purely thermal reaction that took place in the absence of moisture.

There are some limitations:

- if the mechanism of the reaction at higher or lower temperatures should differ, this, too, would alter the slope of the curve;
- it is necessary that the energy of activation is independent on temperature, that is, constant over the range of temperatures of interest;
- the Arrhenius equation applies to homogeneous reaction conditions, while it has little significance in solid-state reactions.

Agrawal [42] cites two reasons for nonlinearity between $\log k$ and $1/T$ in the Arrhenius plot: a change in reaction mechanism, as just mentioned, but also the existence of a temperature gradient within the sample, due to heat and mass transfer effects.

Day *et al.* [43] describe an example where the rate of oxidation became diffusion-controlled at lower temperatures.

Kelly *et al.* [44] report nonlinear Arrhenius plots for the fading of certain dyes on acrylic and poly(vinylalcohol) substrates.

It is necessary to consider also if the reactions take place above or below the second-order transition temperature, T_g ; in general, if irradiation tests are carried out solely at temperatures above the second-order transition temperature, the rate of certain key reactions may be sufficiently altered that Arrhenius-based extrapolations of possible behavior down to room temperature (specifically to temperatures below T_g) can be in error.

The effect of stress may become important in the case of materials on exhibition, perhaps a textile hung or draped over a frame; the greatest rate of degradation should occur where the textile, or leather work, experiences the greatest stress of bending or tension.

The reason the applied stress leads to a more rapid rate of reaction is that mechanical tension contributes to chemical bond scission. The thermal energy of activation (E) is lowered by the potential energy of the stress, $\delta\sigma$.

Thus, the familiar Arrhenius equation becomes:

$$K = K_0 \exp [-(E - \delta\sigma)/RT] \quad (5.5)$$

5.3 Interaction of UV Radiation with Naturally Present Chromophores of Different Fibers

5.3.1 Introduction

When a dyed or pigmented material fades, it may not be the absorption of light by the colored substance, the most obvious absorber, that represents the wavelengths principally responsible for its degradation. Instead, it may be that absorption by chromophoric groups, in a trace of impurity, activates the vehicle, leading to the degradation of the dyestuff.

Occasionally, the discoloration of specimens apparently will be reversed by removal from exposure. It can pose a problem if the fading on samples is not measured either immediately or after precisely the same period of time following their exposure to heat or light Morris *et al.* [45].

In the darkening or intentional bleaching of oils and paper, both changes can go on at the same time: the result after a period of accelerated aging will be the net effect of the equilibrium state between the two processes. It is particularly true if certain components react in one fashion and other components in another or if the light source emitted both visible and ultra-violet radiations inducing opposite reactions.

5.3.2 Interaction between Wool Chromophores and Radiation

In wool fibers, there are several UV-absorbing chromophores, present in the form of the aromatic amino acid residues (Trp, Tyr, Phe, and also Cys), absorbing in the UV region between 250 and 320 nm. There are also visible chromophores absorbing from the near-UV into the visible region of the spectrum (350–500 nm), which confer the cream color of natural undyed wool. Surprisingly, little is known about the identity of the natural yellow chromophores in wool; it is likely that they are a complex mixture of compounds, including wool protein oxidation products. Because wool has a very high absorption coefficient for high-energy UV, a wool fabric exposed only to UV-B (or UV-C) wavelengths is oxidized and discolored specifically at the surface, to a depth of 1–2 μm . Exposure of dry wool to high-energy UV-C wavelengths results in a green color because of the formation of two species: one absorbing blue light and one absorbing in the red region at 600 nm. The presence of oxygen is not necessary for the green coloration to occur, thanks to free radicals derived from cystine residues, quite stable in the absence of oxygen and water. UV radiation in the presence of atmospheric oxygen results in rapid wool photoyellowing, accelerated in

the presence of water, whereas the exposure of natural cream wool to blue light causes photobleaching.

About wool, various mechanisms for the explanation of photobleaching and photoyellowing were proposed; the most relevant are cited in the following list.

5.3.2.1 *Free-Radical Oxidation of the Peptide Chain at α -Carbon to Form α -Ketoacids*

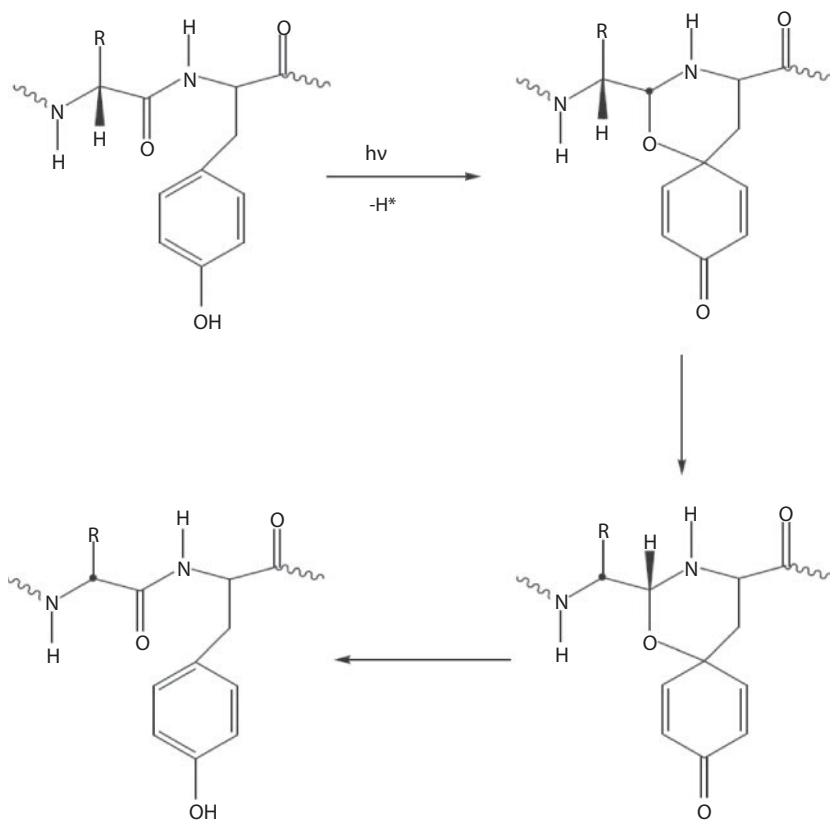
Meybeck and Meybeck [46] hypothesized the following steps:

1. energy absorption by aromatic amino acid residue of Tyr;
2. energy transfer to the α -carbon position via the formation of a six-membered ring;
3. formation of α -carbon radicals (Scheme 5.1);
4. α -carbon radicals can either react with oxygen to form α -hydroperoxides or lose hydrogen to form dehydropeptide;
5. both routes would yield α -ketoacids (RCOCOOH) through hydrolysis (Scheme 5.2);
6. yellowing of wool would be due to the formation of pyruvyl peptides (λ_{max} at 310–317 nm) close to the peak of absorption (320–330 nm) of yellowed wool;
7. decomposition of Trp residues, due to their reaction with α -ketoacids;
8. Trp can react with α -ketoacids, via the Pictet–Spengler reaction, to form yellow chromophore beta-carboline carboxylic acids (Scheme 5.3).

However, α -ketoacids could not be detected after irradiation of wet wool, which becomes yellow at a much faster rate. Maybe there are a number of different photoyellowing pathways available, so α -ketoacid formation via this mechanism is more favorable under dry conditions. Under wet conditions, a different and more rapid yellowing pathway may dominate.

5.3.2.2 *Chromophore Formation via Increased Conjugation: Semiconductor Theory*

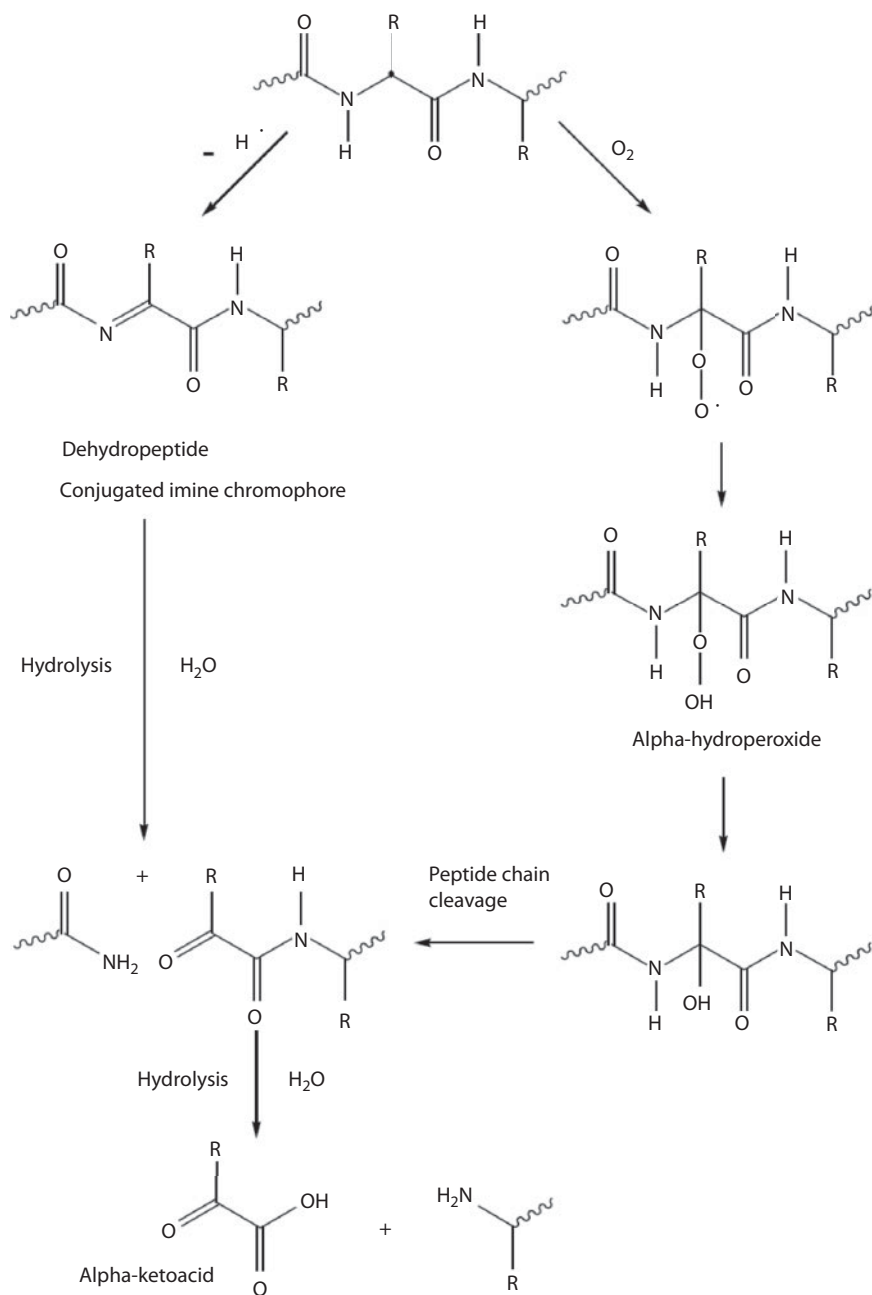
According to Hoare [47], during irradiation, wool keratin produces mobile-free electrons that are promoted into a conduction band, similar to



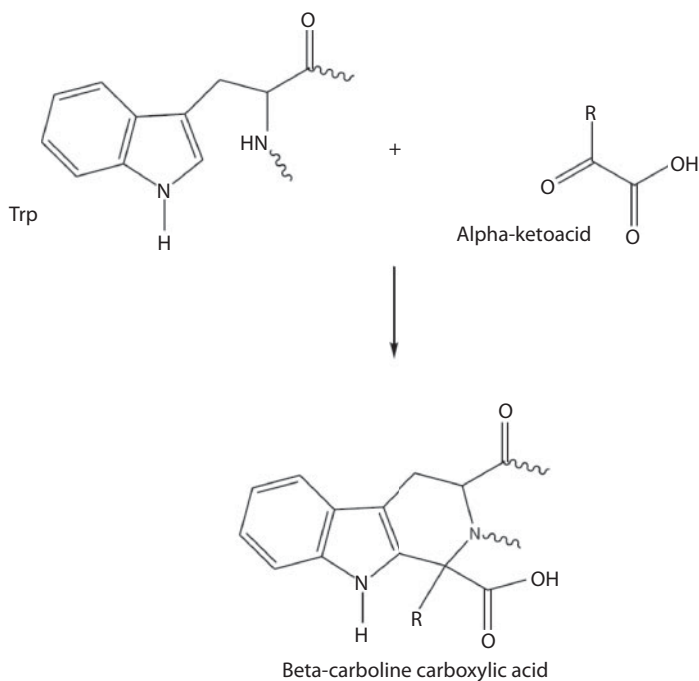
Scheme 5.1 Formation of α -carbon radicals (reprinted from Migliavacca [11]).

the known behavior of semiconductor biomaterials, such as melanin. This theory proposes that the removal of electrons from single bonds increases the level of unsaturation and conjugation in the keratin structure (e.g., dehydropeptides and conjugated imines as shown in Scheme 5.2), leading to the formation of new chromophores.

As a consequence, if the yellow chromophores in wool are due to the conjugation of unsaturated double bonds, when the conjugated protein is cleaved by mild hydrolysis, the color should be removed. It is difficult to determine whether any loss of color occurs under such conditions, but the formation of yellow solutions shows the presence of chromophores formed via other mechanisms.



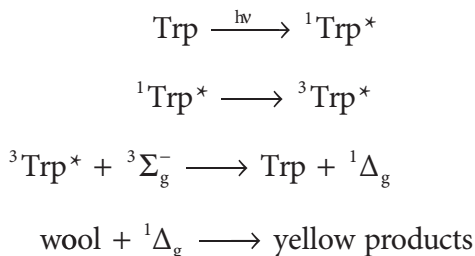
Scheme 5.2 Formation of α -ketoacids (RCOCOOH) through hydrolysis (reprinted from Migliavacca [11]).



Scheme 5.3 Formation of yellow chromophore beta-carboline carboxylic acids (reprinted from Migliavacca [11]).

5.3.2.3 Oxidation by Singlet Oxygen

According to Nicholls and Pailthorpe [48], the singlet oxygen mechanism involves absorption of the UV components of sunlight by the aromatic amino acid residues in wool protein, followed by energy transfer through the protein chain to tryptophan residues in the singlet excited state ($^1\text{Trp}^*$). These residues then undergo intersystem crossing to an excited, long-lived triplet state ($^3\text{Trp}^*$), which can react with ground state oxygen ($^3\Sigma_g^-$) to produce singlet oxygen ($^1\Delta_g$) according to the following reactions:



The major criticism of the singlet oxygen mechanism is that it fails to explain the observed increase in the photoyellowing rate of wet wool. The lifetime of singlet oxygen in water is 4.2 μ s, compared with 14 ms in the gas phase, and any singlet oxygen is therefore rapidly deactivated. A study also showed that hydroxyl radicals are produced when wet wool is irradiated with both UV-A (366 nm) and blue (425 nm) light using a fluorescent probe. Another problem for this theory arises from studies on Trp-depleted wool. Removal of 80% of the Trp from wool had surprisingly little effect on the rate of yellowing of natural or bleached wool under wet and dry conditions over short irradiation periods (2 h wet, 24 h dry).

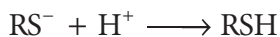
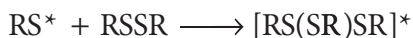
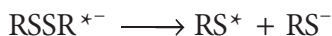
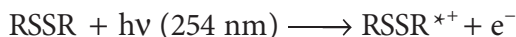
Smith [49] has detected singlet oxygen in dry-irradiated wool directly by measuring its luminescence emission at 1269 nm. He found that, when wool is irradiated at 265 and 350 nm, $^1\Delta_g$ was detected only at the higher wavelength, and therefore suggested it causes photobleaching of wool, rather than photoyellowing. He also postulated that photoyellowing of wool by sunlight is much faster in the wet state because any $^1\Delta_g$ generated by visible wavelengths, which would lead to concurrent photobleaching in the dry state, is rapidly quenched by water.

5.3.2.4 Oxidation on Sulfur Species

Millington and Church [50] suggested that the formation of both oxidized and reduced sulfur species in wool keratin after exposure to UV light is rationalized by two alternative mechanisms that are dependent on the irradiation wavelength.

Both mechanisms involve the formation of the radical anion $RSSR^{*-}$ as a key transient species, with the formation of the radical cation $RSSR^{*+}$ involved only in UV-C exposure.

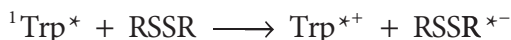
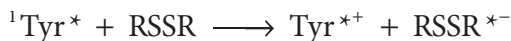
Based on the above information, the initial stages involved in the mechanism of the UV-C photolysis of cystine and wool are reported in the following reactions:



The mechanisms of the UV-B and UV-A photolysis of cystine and wool are as follows:

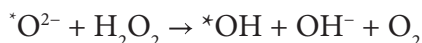


It is well known that cystine is a quenching agent for tyrosine and tryptophan in peptides and proteins. A previous work has shown that the quenching mechanism occurs via an electron transfer process with the formation of the radical anion RSSR^{*-} that rearranges to produce RS-SO_3^- :



5.3.2.5 Oxidation by Hydroxyl Radicals

According to Dyer *et al.* [51], the photo-oxidation product is consistent with mechanistic theories implicating a dominant role for the hydroxyl radical in wool; the proposed mechanism of formation is via initial production of superoxide and hydrogen peroxide, which can then generate hydroxyl radicals:



Hydroxyl radicals characteristically have an affinity for aromatic ring structures, and this photomodification is consistent with hydroxyl radical attack to the tryptophan residue.

The major pathway of tryptophan photo-oxidation results in a progression in chromophore intensity, from colorless tryptophan through to the bright yellow chromophore hydroxykynurenine (Figure 5.1).

5.3.3 Interaction between Cotton Chromophores and Radiation

In cotton, the precise origin of the UV absorption, which is not due to any of the structural groups that make up the normal cellulosic chains, is

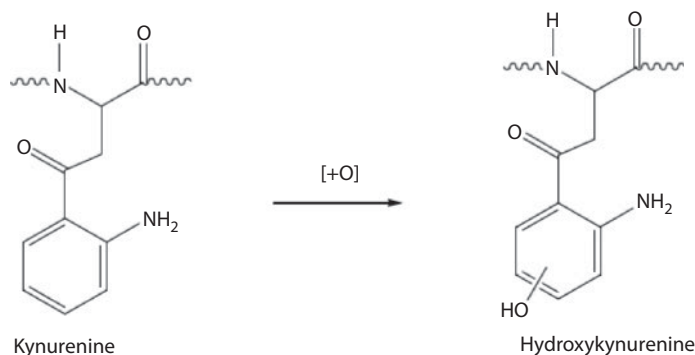


Figure 5.1 Formation of yellow chromophore hydroxykynurenine (reprinted with permission of John Wiley and Sons from Dyer *et al.* [51]).

uncertain and can only be attributed tentatively to “impurities” or “faults” bearing carbonyl and/or carboxyl groups. In fact, in cotton, the chromophores are not yet well identified, while a mechanism involving lignin impurity was proposed by Davidson [52].

Naturally pigmented green cotton derives its color from caffeic acid, a derivative of cinnamic acid, found in the suberin (wax) layer surrounding, with cellulose, the fiber. The isolated compound is fluorescent (287 and 310 nm) and it is supposed that its purpose is to absorb UV radiation in order to protect the seed. On the other hand, brown and tan cottons derive their color from tannin vacuoles in the lumen of the fiber cells. TLC analysis revealed the pigment to be a tannin precursor, catechin, and tannin derivatives (absorption near 278 nm). The brown color does not form until the fibers are exposed to oxygen and sunlight, which happens when the seed pod opens.

Naturally pigmented cottons offer better UV protection than conventional bleached or unbleached cotton; therefore, it has better UPF (ultra-violet protection factor).

On “pure” cellulose, there are two behaviors:

- $\lambda_{\text{exc}} < 300 \text{ nm}$ produces yellowing of the substrate and weight loss due to the formation of volatile photoproducts;
- $\lambda_{\text{exc}} > 300 \text{ nm}$ leads to bleaching without any weight loss following a photochromic phenomenon.

It suggests the presence in cellulose of a “family” of absorbing centers, with chromophores characterized by absorption bands that partially overlap.

The irradiation of the material with $\lambda_{\text{exc}} > 300$ nm induces the selective disappearance of the chromophores whose absorption maxima are centered at the irradiation wavelength, but also the partial bleaching of those possessing a weaker absorption cross section at this wavelength.

The reversibility of the coloration–decoloration cycles, over the whole range of studied wavelengths, demonstrates that the photochromism of cellulose is a general phenomenon [53].

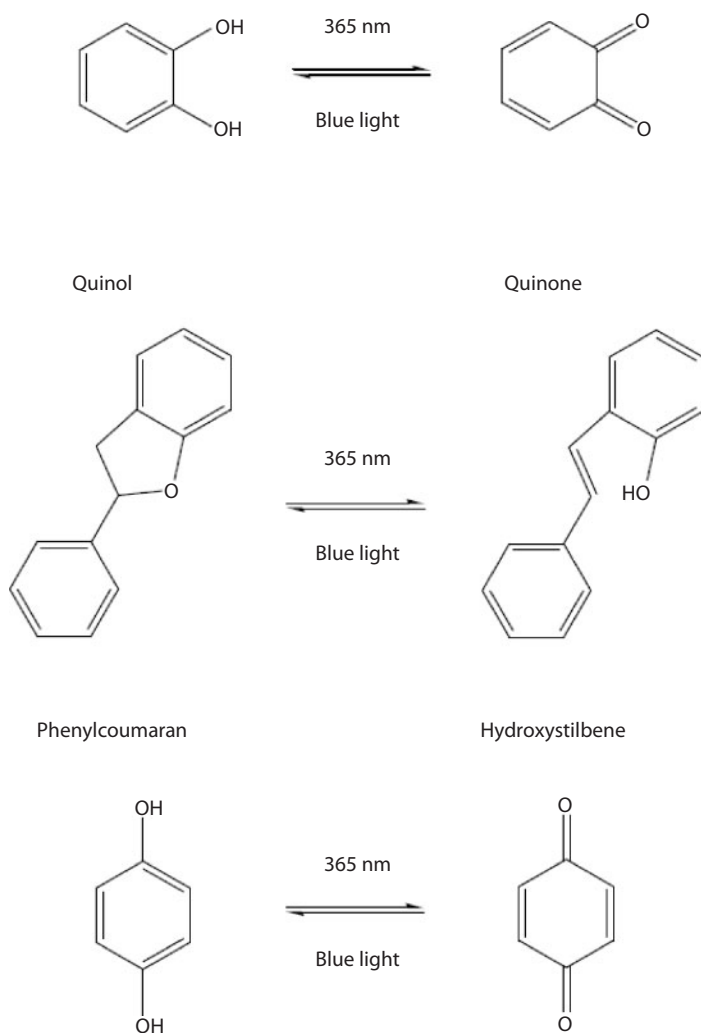


Figure 5.2 Photochromism of cellulose (reprinted with permission of Elsevier from Choudury *et al.* [53]).

This photochromism is not fully reversible, because several processes are involved during the nonradiative deactivation of excited states, only some of them being reversible during a thermal dark reaction. The origin of this behavior is tentatively attributed to the specific destruction and restoration of homologous chromophores.

The color reversion process appears to involve both photodegradation and photochromic reactions. Chemical species probably involved in this phenomenon are quinol and phenylcoumaran residues belonging to lignin impurity; some proposed mechanisms are reported in Figure 5.2.

5.4 UV Irradiation on Wool

5.4.1 Wool Dyeability Improvement

Wool and fine animal fibers are mainly composed of keratin, but show the structure of composite material formed by an assembly of cuticle cells in the form of scales and cortical cells surrounded by a keratin cell membrane and held together by an intercellular cement. The cell membrane consists of a chemically resistant protein layer and a lipidic layer that constitutes a hydrophobic barrier to the transfer of water and dye molecules from an aqueous solution [54]. Therefore, a wettability improvement of these fibers can be obtained by the removal of the hydrophobic lipidic layer and by the introduction of polar groups on the surface, both performed by chemical and/or physical means.

A chemical treatment is usually made by chlorination, which modifies the scale edges of wool and increases the critical surface tension of the fibers. In such a manner, the chlorinated fibers are made more wettable and dyeable and can be coated with polymers conferring the shrink-resist effect.

Moreover, the preparation for wool printing is an essential operation, because without this step, it is very difficult to get full colors yields, levelness, and brightness; usually, this procedure is carried out with oxidative processes: chlorination with or without polymer addition, such as chlorination–Hercosett, rarely using a “sulfitolysis” process or application of tetraethylenepentamine before printing. Then, it is necessary to modify the external fiber structure, increasing polarity and accessibility, in order to obtain a quick wettability by printing paste and easy swellability in water, preferably maintaining the original color of the fibers.

However, many research works are carried out to find alternative processes that avoid chlorination in order to remove the problem of the

formation of absorbable organohalogen compounds in wastewaters [1]. To this aim, plasma treatments have been extensively studied, but even other cheaper eco-friendly processes have been experimented, in particular for dyeability improvement, such as treatment with enzymes or UV irradiation [55].

The untreated wool fiber is little affected by the dyebath at temperatures below 70°C, while above this temperature, the dye transfer becomes important; for this reason, conventional dyeings are carried out near the boil for the time required to allow a good penetration of the dye inside the whole structure of the fiber, achieving the desired coloration intensity and fastness. If the cuticle is modified by external agents, dyes can penetrate the fiber more readily even at lower temperatures.

El-Zaher and Micheal [56] proved that UV-C radiations in air produce a photosensitized oxidation process on wool fiber surface due to atomic oxygen generated when molecular oxygen is subjected to radiation with a high intensity. In fact, when molecular oxygen is subjected to radiation at 184.9 nm, both atomic oxygen and ozone are generated, and when ozone is irradiated at 253.7 nm, atomic oxygen is generated. Hydrocarbons and ozone absorb the 253.7-nm radiation and react with atomic oxygen to form simpler volatile molecules that go away from the surface. Beneficial improvements to wool dyeability may be achieved, because after a long exposure time, the amorphous region dominates over the crystalline one, permitting an easier penetration of dye molecules. Moreover, the photo-oxidation of cystine linkage into a free-radical species promotes covalent bond formation between fiber and dye.

Gupta and Basak [57] improved the wool dyeability using a 172-nm UV excimer lamp; in this case, SEM images show ablation and etching of the surface. In case of samples exposed to oxygen atmosphere in particular, micropores can be seen on the surface. Treated wool shows increased saturation dye uptake as well as improved rate of dyeing. These changes are restricted to surface and do not affect the bulk properties. XPS analysis shows the presence of polar groups, such as cysteic acid and sulfonic acid, created by cleavage of cystine linkages. An anionic dye was chosen for dyeing and the dye uptake was significantly increased in wool fabrics UV-treated in air; at 60°C as dyeing temperature, an irradiated sample showed a dye uptake more than 95%, a good result if compared with a value of 70% for an untreated sample. Improved dye uptake by all treated samples can be attributed to the destruction of the lipid barrier layer and decrease in the number of disulfide groups in the keratin, that act as a barrier to the diffusion of aqueous solutions.

An accurate work was carried out by Millington [58] about synergic interaction between UV exposure and wet oxidation and demonstrated high degree of contrast between dyed samples UV irradiated and not irradiated; he found great dependence on the dye class and suggested that significant color differences are obtainable using 1:1 metal-complex dyes. Differences in color yields (K/S) are possible with many classes of dyestuffs: acid milling dyes, 1:2 metal-complex dyes, and 1:1 metal-complex dyes and reactive dyes, but the use of 1:1 metal-complex dyes is particularly effective.

Xin *et al.* [59] instead worked with different dyeing temperatures (45°C, 50°C, 55°C, and 60°C) using Acid Blue 7 on UV-treated wool fabrics (Hg vapor lamp Philips TUV 36 W, operating at 253.7 nm and fixed at distance of 16 cm). The UV-treated wool samples showed greater levels of dye uptake compared with those of the untreated ones. Increases in dye uptake rate and color yield, in terms of K/S , were observed on UV-treated fabrics, especially at relatively low dyeing temperature; the adsorption behavior and diffusion coefficients were also studied.

Shao *et al.* [60] confirmed the extensive fiber surface modification due to UV rays and observed increased rates of exhaustion for acid, milling, metal-complex, and reactive dyestuffs; comparison of the behavior of chlorinated wool and UV-treated wool during printing steps showed little differences related to total fixation efficiency for reactive dyes, but UV-treated fabrics showed more yellowing.

Millington [58] also faced the problem of printing and highlighted that UV-C irradiation before printing gave much better color yields on wool fabrics compared to untreated ones. To overcome the yellowing problem, he advised a mild wet oxidation with hydrogen peroxide or permonosulfate that is able, in aqueous media, to easily remove the chromophores produced by UV-C; this procedure is patented under the name of Siroflash. It was shown that the UV-C region in the medium-pressure mercury lamp spectrum is the most important component for increasing color yields in printing, mainly with reactive dyes, providing the brightest hues and the best fastness properties. Moreover, the Siroflash treatment is uniform across the fabric surface, can be limited to one fabric side, and has less impact on handle and environment than chlorination. In fact, the Siroflash method has recently been proposed for the development of inkjet printing techniques while UV irradiation has been applied to the photobleaching of wool Shao *et al.* [61].

In conclusion, a modification of the wool fiber at the cuticle level due to exposure to UV radiation undoubtedly increases its affinity toward acid dyes, even if the fiber can be damaged at some extent, but it is possible to dye at a temperature below the boil, reducing the fiber damage due to

longtime maintenance at high temperature. In general, UV irradiation enables wool fibers to absorb dyes at a greater rate than untreated ones and to obtain higher dye concentration on fiber at equilibrium. Similar effects are achieved after wool chlorination under acidic conditions.

5.4.2 Experiments on Wool Dyeing Improvement with UV Irradiation

In the work of Periolatto *et al.* [62], undyed wool yarns and fabrics were pretreated by ultraviolet radiation, in static as well as dynamic equipment, in order to obtain a modification onto fiber surface. As a consequence, UV-treated wool showed an increase in metal ion absorption and hydrophilicity, together with improved kinetics of dye absorption under the same dyeing conditions as untreated wool. Moreover, it was found that UV pretreatment can be useful to obtain the same dyeing at lower temperature (85°C) than that normally used in industrial practice (98°C). The surface modification of wool due to UV radiation was confirmed by FTIR-ATR analysis; nevertheless, the fiber morphology by SEM analysis was shown unaffected.

5.4.2.1 Static UV Irradiation

The static UV apparatus (Helios Italquartz, Milano, Italy) (Figure 5.3a and b) was a box containing a medium-pressure mercury UV lamp cooled by cold air circulation; the textile material is endorsed on a metallic support and receives the irradiation at variable distances from the UV source. The radiant exposure relative to the UV-A component resulted in an irradiance

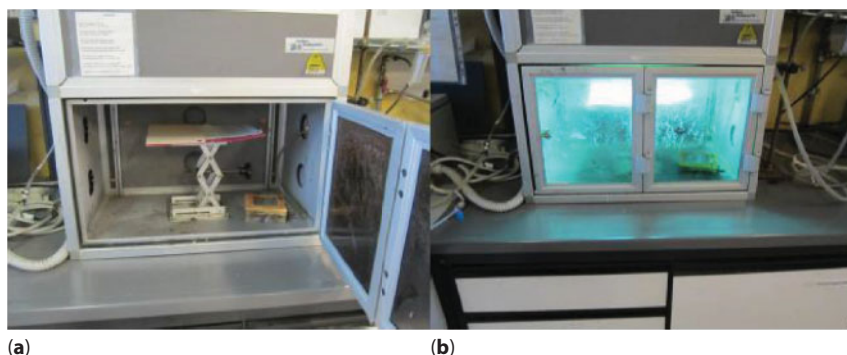


Figure 5.3 (a and b) Static UV irradiation apparatus (reprinted from Migliavacca [11]).

of about 37 mW/cm², provided the samples are positioned at a distance of 15 cm under the lamp.

Samples of pure wool knitted fabrics (292 g/m²) were half-exposed on both sides to UV light, covering the unexposed part with a paper sheet, for different times: 1, 2, 3, 4, or 5 min, respectively. In this way, the effect of UV radiation can be easily evaluated after the dyeing, simply comparing the two halves of the sample after rinsing and drying.

The immediate effect of radiation on wool fabrics was evaluated by a reflectance spectrophotometer (Datacolor Check II), on the various samples referred to the untreated ones. From obtained results, reported in Table 5.2, a color difference with respect to the untreated sample was revealed; it was mainly due to a Δb increase, related to some yellowing of the sample.

Static treatments are effective and useful for a preliminary study, also involving kinetic behavior, but they are not fully comparable to a continuous treatment, in which some parameters, such as the temperature of the irradiated material, or lamp power and, as a consequence, irradiance, differ significantly from the conditions of a static system; for example, after static treatments, the humidity of wool fabric falls as a consequence of increased temperature.

5.4.2.2 Dynamic UV Irradiation

The Sun-Wash dynamic equipment installed at Nearchimica, Legnano, Italy [63], mounts medium-pressure mercury discharge lamps irradiating a rolling carpet (Figure 5.4). The radiated area is about 120 cm × 60 cm, and the carpet speed can be modulated in order to control the exposure time.

Table 5.2 CIELab parameters for static UV irradiation on wool fabric dyed with 1% o.w.f. Acid Blue 185 (Telon Turquoise M5-G 85% from Dystar), pH 4, for 90 min at 90°C.

Irradiation time (min)	ΔL	Δa	Δb	ΔE
1	-1.56	-0.31	0.47	2.29
2	-1.70	-0.73	1.35	2.29
3	-1.85	-0.67	2.29	3.02
4	-2.00	-1.01	3.39	4.06
5	-2.44	-0.98	4.36	5.09

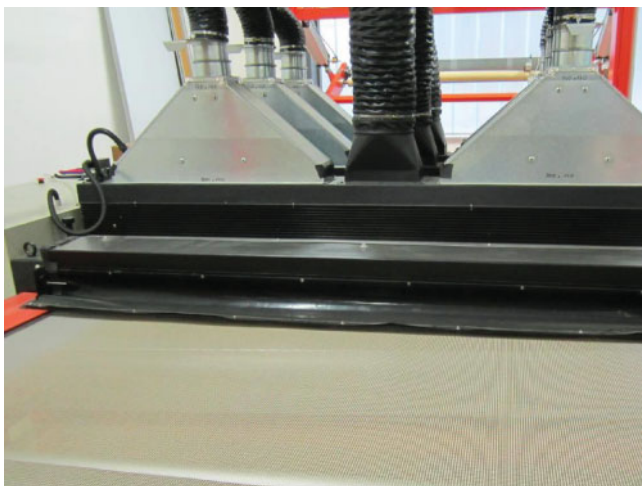


Figure 5.4 Dynamic UV irradiation equipment (reprinted from Migliavacca [11]).

Tests carried out with this equipment involved an irradiance of the order of 900 mW/cm^2 for the UV-A component, while in other similar apparatus installed at the establishment of Filidea, Biella, Italy, the lamp provided an irradiance of about 430 mW/cm^2 .

In order to compare the effects on wool fiber, the radiant exposure (J/cm^2) was considered. Static exposure for 5 min corresponded to about 11 J/cm^2 while the dynamic exposure in Sun-Wash performed with six passes for a total exposure time of 43 s provided about 39 J/cm^2 , and this was the upper limit of UV irradiation with this apparatus before having unacceptable yellowing ($\Delta b = 7.64$) compared to the same untreated wool.

5.4.3 Adjustment and Optimization of the Degree of Wool Treatment

In order to obtain good color yields, levelness, and brightness in wool fabric printing, it is essential first to modify the fiber surface by using a suitable pretreatment; in addition, in differential dyeing, it is very important to have an appropriate preparation of substrate to develop a reproducible effect. For this reason, many technicians proposed different kinds of pretreatment onto wool fibers, mainly for fabrics.

Heiz [64] points out that before the pretreatment, other steps should be considered:

- setting: useful for the relax and for the stabilization of cloth, it is usually carried out by crabbing (continuous or discontinuous steaming);
- scouring: necessary for processing oils, dirt, and size removal, it is commonly achieved with commercial detergents, sometimes by addition of suitable enzymes;
- milling: occasionally applied to impart the desired finish effect to the cloth.

Then, the preparation of wool can be performed; one of the earliest processes is oxidation, with the purpose of increasing the color yield and producing well-defined edges. The most commonly used procedures are based on chlorination while other oxidative processes, such as treatments with permonosulfuric acid or its salts, are not yet developed.

The first kind of chlorination was performed starting from sodium hypochlorite and hydrochloric or sulfuric acid, adjusting the pH to the range 1.5–2.0. An alternative way, introduced by Kroy Unshrinkable Wool Ltd of Canada and Woolmark, is the use of chlorine gas mixed to water.

Both technologies involve the production of a mixture of chlorine, hypochlorous acid, or hypochlorite; these species markedly depend on the pH of the solution.

Another alternative is based on an organic chlorine compound, as sodium dichloroisocyanurate (DCCA), which, dissolved in water, is responsible for the production of hypochlorous acid.

All these processes are carried out onto wool fibers employing a suitable wetting agent, durable in the acid/oxidizing media, in order to have a good distribution of oxidant agent on the fiber surface.

Under strongly acid conditions, a quick reaction between chlorine and wool takes place, followed by little fiber yellowing, but with poor levelness of oxidation. Under alkaline conditions, where hypochlorite ions prevail, the reaction is slower and the oxidation effect is more homogeneous, but the yellowing becomes significant. With DCCA sodium salt instead, it is possible to achieve a good levelness of treatment coupled with a middle yellowing effect even without a pH control.

The reactions happening during chlorination, the most important, as suggested by Bell [65], are:

- cystine oxidation: cystine residues are quickly oxidized to cysteic acid residues;
- peptide bond cleavage: chlorine tends to cleave peptides and proteins at tyrosine residues.

In differential dyeing techniques, these treatments are commonly used in order to increase affinity toward dyestuffs, allowing one to get color differences between treated and untreated parts of the same textile material. Since the UV irradiation is able to induce similar modifications on wool surface, it can be considered as an alternative pretreatment before dyeing, the degree of which should be optimized by means of suitable tests.

5.4.3.1 Available Tests

Different dyeing tests were proposed to evaluate the grade of the given pretreatment; Millington [58] has proposed the use of Reactive Blue 72 dyestuff (Figure 5.5). This test is based on the increased affinity of the Cu^{2+}

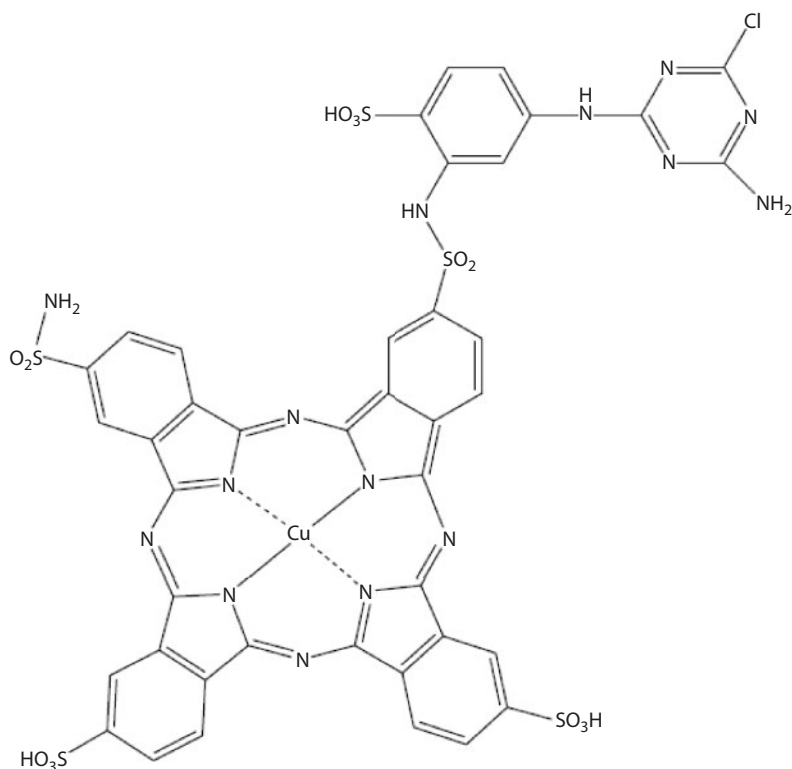


Figure 5.5 Structure of Reactive Blue 72 (reprinted from Migliavacca [11]).

phthalocyanine toward oxidized wool fibers; the new groups, mainly $-OH$ generated by an oxidant agent or by UV radiation onto cuticle, are able to form new bonds with the Cu^{2+} phthalocyanine increasing its affinity for the fiber.

It is possible that Cu^{2+} , normally with planar coordination (four ligands) inside the phthalocyanine complex, undergoes coordination 5 for admittance of a fifth ligand, changing the symmetry toward a square pyramid.

The dyeing carried out with Reactive Blue 72 (Turquoise Cibacron P-GR from Huntsman) offers a good scenario about the uniformity of the previous oxidant treatment; also, the intensity of scheduled recipes is useful for the evaluation of the intensity of oxidant action. A method for this comparison is the measurement of the K/S parameter, from the Kubelka Munch equation (Equation 5.6).

$$K/S = (1 - R\lambda)^2 / (2 R\lambda) \quad (5.6)$$

where K is a parameter related to the dyestuff, S is a parameter related to the substrate, and $R\lambda$ is the reflectance value, measured at the $\lambda_{\max}$ for the dyestuff-substrate system.

Other proposed test dyes are Lanazol Black R and Palatin Fast Black WAN (BASF); the first one is a not well-defined mix of alfa bromo acrylamido dyestuffs, while the second one is the classical 1:1 metal-complex dye Acid Black 52 (Figure 5.6), formed by an *o,o'*-azo dyestuff complexed with a Cr^{3+} ion that may be linked by oxidized groups previously mentioned.

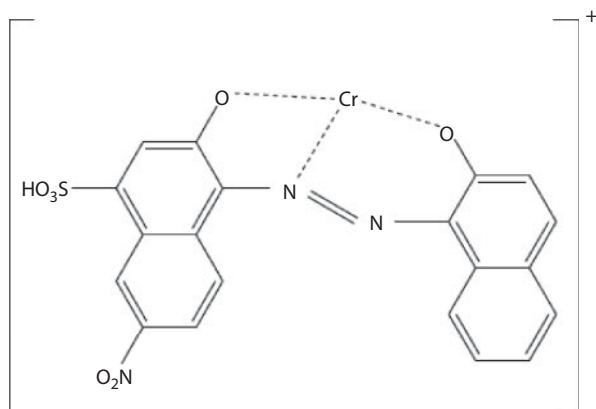


Figure 5.6 Structure of Acid Black 52 (reprinted from Migliavacca [11]).

5.4.3.2 Proposed Test

The available tests allow an assessment of the intensity of the UV treatments, but they are not very critical about the treatment uniformity; for this reason, a new test was proposed, which is able to bring together both intensity and uniformity [11].

Such new proposed test for the evaluation of degree and uniformity of UV treatments is based on Reactive Blue 38 (Brilliant Green Remazol 6B 175% by Dystar) (Figure 5.7). Even in this case, it is a phthalocyanine (metal-complex dye) but with a Ni^{2+} ion complexed in its cavity.

It has the foregoing structure of Reactive Blue 72, where the Ni^{2+} (with a coordination number of 4) is linked with two covalent bonds and two coordination covalent bonds. Likewise, it is possible that Ni^{2+} , having planar coordination (four ligands) inside the phthalocyanine complex, undergoes coordination 5 or, more easily, coordination 6 for admittance of one or two new ligands [66, 67], changing the symmetry toward a square pyramid or most probably toward an octahedral symmetry where two axial ligands differ from the others.

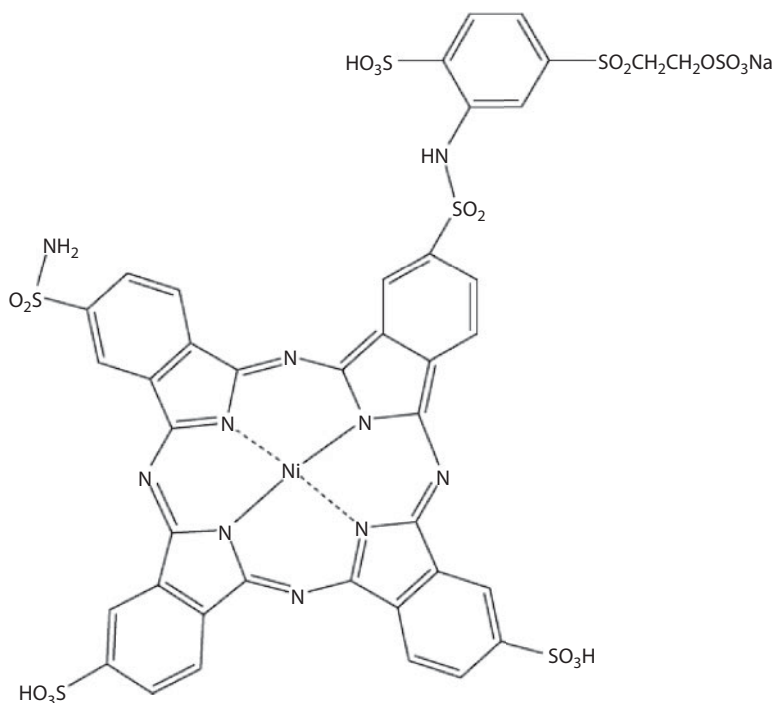


Figure 5.7 Structure of Reactive Blue 38 (reprinted from Migliavacca [11]).

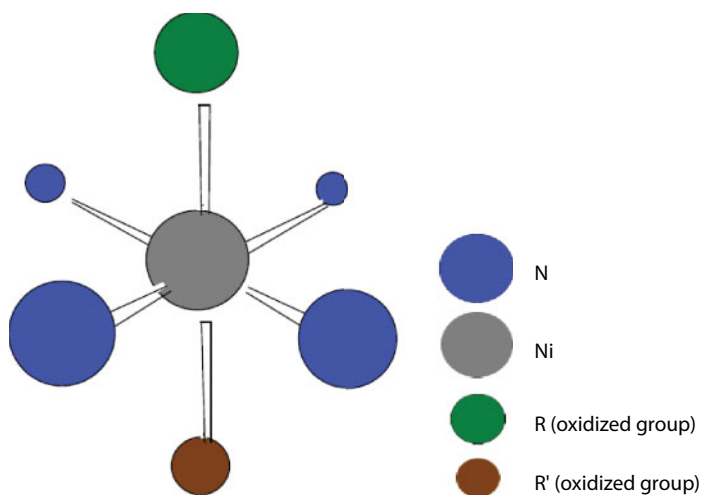


Figure 5.8 Octahedral complex (reprinted from Migliavacca [11]).

In fact, this particular dyestuff has the possibility of displacing two water molecules with more strong electron-donor groups, such as cystine oxides or cysteic acid; therefore, it can form the octahedral complex (Figure 5.8) with oxidized groups of UV-treated wool. For this reason, Migliavacca [11] suggested to use this dyestuff as a marker for the degree of UV treatment on wool.

An advantage, compared to the dye previously recommended, may be that Brilliant Green Remazol 6B 175% (Ni^{2+} -phthalocyanine) can be coordinated by two ligands instead of only one (as in the case of Cu^{2+} -phthalocyanine), and then the test selectivity could be increased.

5.4.3.3 Comparison between the Tests

The proposed test, based on dyeing carried out with 2% o.w.f. of Reactive Blue 38 at 85°C for 90 min and checked by a reflectance spectrophotometer (Datacolor Check II), shows a good result in terms of intensity evaluation of UV-treated wool.

The Kubelka Munch values are comparable with those obtained from dyeing carried out with 2% o.w.f. at 85°C for 90 min of Reactive Blue 72. The comparison between the results of the untreated wool fabric and those of the UV-treated (by a static Helios Italquartz irradiation apparatus) one is reported in Table 5.3. For both dyes, the ratio of K/S values for UV5/NT is about 2.3, showing that both are suitable to evidence the dyeability improvement due to UV irradiation.

Table 5.3 Comparison between *K/S* at 670 nm of two dyeings at 85°C for 90 min (NT untreated sample, UV5 sample subjected to UV irradiation for 5 min at 37 mW/cm²).

Sample	Dye	<i>K/S</i>
NT	Reactive Blue 38 (Brilliant Green Remazol 6B)	3.98
UV5	Reactive Blue 38	9.13
NT	Reactive Blue 72 (Turquoise Cibacron P-GR)	5.96
UV5	Reactive Blue 38	13.47

Another proposal for a test concerning both the intensity and the uniformity of the UV treatment is based on the xanthoproteic reaction [68]. This reaction involves the nitric acid that is able to develop a considerable yellow coloration on contact with proteins. In particular, there are two responsible amino acids (namely, Tyr and Trp) for this reaction in the keratin of wool. Tyr and Trp undergo, in the presence of HNO₃ of appropriate concentration, a reaction of nitration of their aromatic rings, forming nitro-derivatives intensely yellow colored in acidic media and orange colored in alkaline media.

Xanthoproteic reaction yields chromogens as a result of accessibility of Trp and Tyr to the action of nitric acid on damaged fibers, and this property can be used for assessing the degree of treatment severity: more intense yellow at higher damage of the wool cuticle.

The xanthoproteic test is carried out similarly to a dyeing, where the liquor consists of a solution of HNO₃ $\approx$ 6.0 M at room temperature and with a liquor ratio equal to 50:1; the wool fabric (both untreated and UV treated) is dipped into this solution and occasionally stirred during a period of 1 h. The acid is then dropped out and the fabric is neutralized with a 1% NaHCO₃ solution; finally, the fabric is dried in an oven at a maximum temperature of 60°C and checked using a reflectance spectrophotometer (Datacolor Check II). The Kubelka Munch values are listed in Table 5.4.

The ratios of *K/S* values of UV5/NT are about 1.1 at 410 nm and 2.2 at 490 nm. Therefore, the xanthoproteic test by reflectance measurements at 490 nm is also able to evidence modifications induced by UV irradiation.

5.4.4 Differential Dyeing Effects

In the Sun-Wash method, patented by Nearchimica with Stamperia Emiliana, Italy Sala *et al.* [63], the continuous UV pretreatment of wool

Table 5.4 Comparison between *K/S* at two wavelengths of wool samples subjected to xanthoproteic reaction (NT untreated sample, UV5 sample subjected to UV irradiation for 5 min at 37 mW/cm²).

Sample	Wavelength (nm)	<i>K/S</i>
NT	410	25.21
UV5	410	26.75
NT	490	7.17
UV5	490	15.99

fabric on one face before dyeing has been proposed to obtain different shades on the two faces or patterning effects. A careful selection of dyes is needed to obtain satisfactory tone-on-tone effects and even more to produce double-face effects with different colors. These suggestions inspired the experiments on differential dyeing of wool by UV irradiation carried out by Migliavacca [11]. In the past, differential dyeings on wool were made by pretreating part of wool fibers with a suitable accelerating agent (compared to the traditional dyeing) or by applying a retardant agent to another part of the textile material; the final effect consisted of a same-tone coloring in but with different intensity on variously treated parts. These applications, not easily controllable as a result of their intensity, however, had to be produced with accelerator agents or retarder agents against dyes; then, further addition of chemicals are needed, causing problems to the wastewaters.

The experimental results of Migliavacca *et al.* [69] showed that different kinds of dyes are able to give differential dyeing after UV irradiation, but not all members of the same dyeing class have similar behavior.

The main interests on wool fabrics were focused on two effects:

- one shade, double face with different depth, higher on the UV-treated side;
- two shades, double face with different color and depth.

Effect (a) was obtained by dyeing with a proper selection of 1:1 classical metal-complex dyes to evidence the maximum difference between irradiated and nonirradiated areas, as shown in Figure 5.9. A good final shade uniformity was obtained, with an acceptable color difference ($\Delta E \geq 5.0$) between UV-treated and untreated fabric area (double-face effect), due to an increased dye-fiber affinity of the side previously treated with UV radiation.

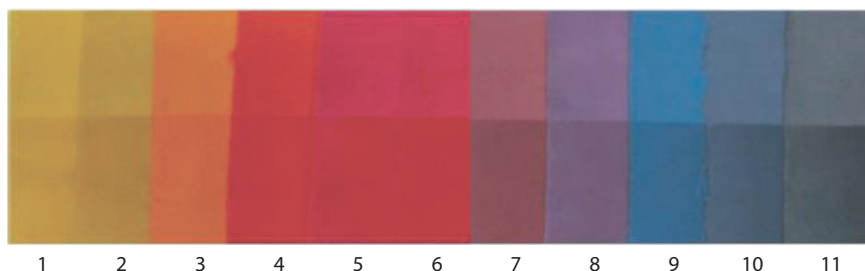


Figure 5.9 Wool fabrics dyed with classical 1:1 metal-complex dyes at 1% o.w.f. at 85°C for 90 min (upper side, untreated; lower side, UV treated). (1) Yellow Neolan RE 250%, (2) Yellow Kemalene GR 150%, (3) Orange Kemalene G, (4) Red Kemalene GRE 150%, (5) Pink Kemalene BE 600%, (6) Pink Neolan BE 200%, (7) Bordeaux Neolan RM 200%, (8) Violet Kemalene 5RL 150%, (9) Blue Kemalene 2G 250%, (10) Navy Neolan 2RLB 150%, (11) Black Kemalene BW 364% (reprinted with permission of John Wiley and Sons from Migliavacca *et al.* [69]).

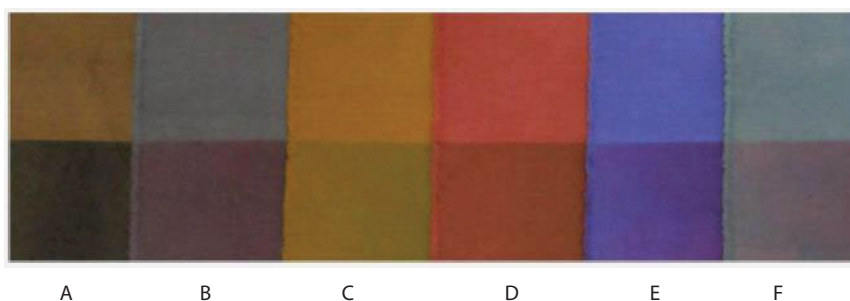


Figure 5.10 Wool fabrics dyed with 1:1 metal-complex dyes and acid dyes at 85°C for 90 min (upper side, untreated; lower side, UV treated). The composition of the recipes is detailed in Table 5.5 (reprinted with permission of John Wiley and Sons from Migliavacca *et al.* [69]).

The metal ion is not fully coordinated in the chosen metal-complex dyes; thus, they can form coordinate bonds with the oxidized groups generated by UV treatment.

Fastness evaluations toward dry rubbing and machine washing at 50°C were also carried out to confirm the feasibility of this alternative dyeing technique; in all experiments carried out with selected 1:1 metal-complex dyes, the same score of conventional premetallized 1:1 dyeings was obtained.

Effect (b) was achieved by dyeing the irradiated fabrics with mixtures of acid and metal-complex dyes, as shown in Figure 5.10, while the composition of the recipes is detailed in Table 5.5.

Table 5.5 Composition of the recipes used to dye the wool fabric samples of Figure 5.10 (reprinted with permission of John Wiley and Sons from Migliavacca *et al.* [69]).

Recipe	% Dye o.w.f.	Dye	Color index	Class
A	0.500	Farbamina Orange II	Acid Orange 7	Acid
	0.500	Kemalene Black BW 364%	Acid Black 52	1:1 Metal complex
B	0.750	Sandolan Yellow E-2GL	Acid Yellow 17	Acid
	0.500	Neolan Bordeaux RM 200%	Acid Red 194	1:1 Metal complex
	0.250	Cromacen Blue fast A	Acid Blue 25	Acid
C	0.750	Farbamina Orange II	Acid Orange 7	Acid
	0.250	Kemalene Blue 2G 250%	Acid Blue 158	1:1 Metal complex
D	0.750	Neolan Yellow RE 250%	Acid Yellow 104	1:1 Metal complex
	0.500	Cromacen Red EG	Acid Red 337	Acid
	0.250	Kemalene Blue 2G 250%	Acid Blue 158	1:1 Metal complex
E	0.600	Neolan Bordeaux RM 200%	Acid Red 194	1:1 Metal complex
	0.250	Cromacen Blue fast A	Acid Blue 25	Acid
F	0.750	Sandolan Yellow E-2GL	Acid Yellow 17	Acid
	0.500	Kemalene Pink BE 200%	Acid Red 186	1:1 Metal complex
	0.250	Cromacen Blue fast A	Acid Blue 25	Acid

Table 5.6 Chromatic differences obtained by dyeing the irradiated fabrics with mixtures of acid and metal-complex dyes (recipes detailed in Table 5.5).

Recipe	Untreated Part	UV-Treated Part
A	Dark orange	Dark gray
B	Light green-gray	Dark red-gray
C	Orange	Dark beige
D	Light red	Dark bordeaux
E	Light blue	Dark purple
F	Green-gray	Red-gray

The dye mixtures have some peculiarities; operating in fact under the well-established dyeing conditions, the 1:1 metal-complex dyes select between the UV-treated and untreated wool fabric in the manner already described for the light–dark tone effect, while the acid dyes, which, by their nature, cannot make this selection, are equally distributed between the UV-treated and untreated part of the wool fabric. This different behavior can be attributed to their relatively small molecules, and therefore, they are capable of producing dyeings that are always well leveled even in the presence of modified cuticle by UV radiation.

Many combinations of the above dyes are possible, with the ultimate goal of achieving simultaneous differences in intensity and in tone. In all color combinations proposed, the total color difference ΔE is much higher than the threshold value (5 units) established; therefore, it is a noticeable and chromatically relevant effect: the nonexposed part to UV radiation is always lighter and presents a tone considerably different from the UV-treated part, which instead appears darker and with another hue. The chromatic differences obtained are listed in Table 5.6.

5.4.5 Wool Finishing Processes

5.4.5.1 Improvement of Wool Shrinkage Resistance

Wool shrinkage resistance is a sought-after feature, especially in recent decades, when the custom is to wash and dry wool cloths by washing machines. In the mid-1960s, many chemical processes have been proposed to perform the degradation of the cuticle structure of wool to limit felting, allowing finished garments to bear ordinary washing/drying cycles.

Shrinkage resistance is often obtained using chemical oxidants, with a significant impact on wastewater treatment; for this reason, further researches were aimed to introduce alternative treatments without the use of chlorine and its compounds, but based on other oxidants, even in combination with suitable polymers.

Dodd *et al.* [70] proposed a method based on curing of a photoreactive silicon monomer onto wool fabrics by exposure to UV radiation followed by a post-cure steam treatment; the result was a machine-washable fabric obtained with low-monomer add-ons.

El-Sayed *et al.* [71] focused on a modification of wool fabric using ecologically acceptable treatments: previously UV-irradiated wool fabrics were treated with an oxidizing agent (hydrogen peroxide or sodium monoperoxyphthalate) or a protease enzyme in order to lower its shrinkage. Shao *et al.* [61] investigated the synergistic effect of UV/ozone exposure and peroxide pad-batch bleaching on wool fabrics, confirming the beneficial effect of UV/ozone treatment on wool shrinkage resistance as well.

5.4.5.2 Multifunctional Finishing

Antibacterial activity, anti-felting, anti-shrinking, antistaticity, hydrophobicity or hydrophilicity, and fire or stain resistance are just some of the many properties that are demanded from textile fabrics. A lot of studies were carried out to confer each of these properties individually; however, the possibility to confer several properties on textiles by a single product and process is gaining interest from both an economical and a technological point of view.

A recent study by Periolatto *et al.* [72] focused on the surface modification of wool fibers to confer multifunctional finishing, improving the textile value and its applications without damage to comfort properties. The attention was focused on an economical and environmental friendly process to obtain an effective treatment with good durability to washing. This was pursued by the replacement of conventional chemicals with a natural based product, such as chitosan.

Chitosan, 2-amino-2-deoxy-(1 $\rightarrow$ 4)- β -D-glucopyranan, derived from the deacetylation of the chitin component of the shells of crustaceans, is undoubtedly one of the more promising multifunctional polymers for surface modification of textiles [73]. It is a biopolymer with unique properties such as biodegradability, nontoxicity, and high antibacterial activity toward both Gram-positive and Gram-negative microorganisms, due to the combined bacteriostatic and bactericide action. In the textile field, chitosan is mainly applied as an antimicrobial finishing agent. Moreover,

fibers treated with chitosan show improved absorption of anionic dyes due to electrostatic attraction arising from the cationized amino groups of chitosan in an acidic medium. However, due to the weak interactions between chitosan macromolecules and fibers, it should stably be bonded to the fiber surface to ensure the fastness of treatment to washing. To this aim, cross-linking agents such as dialdehydes are used, although these are toxic chemicals.

The use of chitosan as an additive polymer on wool fibers was proposed by many authors, since chitosan in mild acid solution becomes a polycation with electrostatic affinity for the anionic charges of wool. However, pretreatment of wool with hydrogen peroxide is needed to increase the concentration of anionic groups on the fiber through the breaking of disulfide bonds followed by the formation of cysteic acid residues able to interact with chitosan [74, 75]. Surrounding wool fibers in the form of thin film, chitosan can significantly decrease the friction between the surface scales, reducing both felting and shrinkage. This effect was justified by a hydrophilicity increase in chitosan-treated wool due to the addition of extra hydrophilic groups, such as amine and hydroxyl; hence, the absorbed water could act as plasticizer among the surface scales. For a durable finish, cross-linkers, such as citric acid or succinic anhydride, are needed to graft chitosan onto wool with a thermal treatment to form irreversible covalent bonds.

As an alternative, an eco-friendly and low-temperature grafting of chitosan onto the fibers can be carried out by radical UV curing in the presence of a low concentration of a photoinitiator [76, 77]. Studies about the photodegradation of chitosan macromolecules due to UV exposure confirmed the formation of macroradicals on the polymer; these radicals can be involved in cross-linking and grafting processes with surface groups of the fibers.

Wool knitted fabrics were multifunctionally finished by UV grafting of chitosan, first of all to confer antimicrobial activity and to enhance the wool affinity toward acid dyes. The effect of a previous oxidative treatment of the fabric with H_2O_2 was also investigated. Moreover, the ability of grafted chitosan to give anti-felting property was tested. Then, the durability of the treatment to repeated washings was evaluated.

The chitosan and photoinitiator (Darocur 1173, 2% w/w with respect to chitosan) mixture was diluted with 2% v/v acetic acid solution and spread on the fabrics. Different impregnation conditions were investigated: contact times of 1 min, 1 h, or 24 h at temperatures of 25°C or 50°C. Samples were then dried for 10 min at 80–100°C and finally UV-cured. Chitosan add-on varied between 2% and 12% wt of the fabric.

Untreated wool showed no antibacterial activity, while tests on all treated samples revealed a reduction of microorganisms. A chitosan content of

2% grafted on the pre-oxidized wool was found enough to confer satisfactory antimicrobial activity (67% reduction of *Escherichia coli* and 50% of *Staphylococcus aureus*).

On wool chitosan coated, 2% add-on, dyeing tests carried out with Telon Turquoise M5-G 85%, C.I. Acid Blue 185, highlighted the treatment effect with a strong increase in color strength value (K/S almost double) and uniform coloration for pre-oxidized samples compared to unoxidized ones.

On the treated fabrics, it was found that the relaxation dimensional change decreased from 13.5% on the untreated wool to 1.2% on the chitosan-treated one while the total shrinkage decreased from 16.9% to just 3%.

In conclusion, besides the antibacterial effect and increased wool affinity toward acid dyes, the chitosan UV-grafted on pre-oxidized wool fibers enables conferring dimensional stability on the fabrics, strongly reducing their felting and making them wet-washable. However, the nature of surfactants chosen for washing can affect the treatment durability; in fact, cationized chitosan is able to establish strong bonds with anionic surfactants and can be partially removed by washing, whereas it cannot be removed by repeated washings with a nonionic surfactant.

5.5 UV Irradiation on Cotton

5.5.1 Cotton Dyeability Improvement

Cotton and cellulose fibers have a more homogeneous structure than wool and are richer in hydroxyl groups that confer higher hydrophilicity; hence, their finishing is mainly aimed to confer hydro and oil repellency. Moreover, the exhaust dyeing of cotton with anionic dyes (i.e., direct and reactive) demands a high concentration of electrolytes in the dyebath to reduce negative charges on the fiber surface and to promote the exhaustion of dyes. This requirement creates environmental issues due to the removal of high concentrations of salts and dyes from wastewaters. To overcome such problems, many treatments with plasma, chemicals, and polymers were experimented to impart a cationic character to the cotton fiber surface [78].

However, UV irradiation coupled with mild oxidation can improve some properties of the cotton fibers such as pilling resistance, water swelling, and dyeability.

Zuber *et al.* [79] demonstrated that UV rays have the same effect on cellulosic fibers as the alkaline treatment: irradiated cellulosic fibers showed higher swelling in comparison with untreated ones.

Bhatti *et al.* [80, 81] found that UV irradiation not only enhanced the strength of a reactive dye on irradiated fabric but also improved the dyeing properties. The reason might be that the exposure of cotton fiber to UV radiation in the presence of oxygen causes cellulose oxidation to carboxylic acids and opens spaces between the fibers, improving the dye penetration; hence, the interaction for dyeing becomes more significant.

Iqbal *et al.* [82], and more recently Adeel *et al.* [83], observed that UV radiation enhances the uptake and fastness of natural dyes on pre-irradiated cotton fabric not only with low concentrations of dye but also with a low concentration of mordant.

To overcome the environmental problems arising from the large amount of electrolyte required to reduce the repulsion between the negatively charged fibers and the anionic dyes, the cationization of cotton fiber was applied to increase the substantivity of anionic dyes by introducing positively charged sites on the fibers. Cationic polymerizable monomers, such as methacryloyl quaternary ammonium compounds, have been fixed onto cotton fabric using UV radiation to produce print patterned dyeings Shin *et al.* [84]. The dyeability of cationized cotton fiber by three classes of dyes (direct, reactive, and sulfur dyes) has been significantly improved owing to the increased ionic attraction between dyes and cationized cellulose, even in the absence of salts Jang *et al.* [85].

Dong and Jang [86] proposed the direct photografting of wool-reactive dyes themselves onto cotton fabric. This coloration utilizes the photoreactivity of certain dyes under UV irradiation, through photopolymerization, photografting, and photocross-linking processes, to form a polymerized and cross-linked dye network. Thus, a single class of dye can color almost any textile substrate, since no specific affinity of particular dyes toward individual fibers is required. Reactive dyes containing an α -bromoacrylamido reactive group are among the most successful metal-free dyes for protein fibers because of their brilliant color and high wet fastness properties. However, these reactive dyes hardly react with cotton fiber under similar conditions owing to the rather low nucleophilicity of the hydroxyl groups in cellulose compared with the thiol and amino groups in proteins. Therefore, dyes containing α -bromoacrylamido groups were employed as grafting monomers to be photografted onto cellulose under continuous UV irradiation. This novel approach may realize the photoactive coloration of cotton fiber even with dyes of low affinity for conventional reactive dyeing. Furthermore, the coloration does not require large amounts of salt, time, and energy, which makes it an alternative process of excellent environmental friendliness.

5.5.2 Differential Dyeing Effects by Fading of Dyed Cotton Yarn

On the basis of the work carried out on wool to obtain effects of differential dyeing Migliavacca *et al.* [69], the same objective was also pursued with a UV pretreatment on cotton followed by dyeing with direct dyes, but the color differences between UV-treated and untreated fabrics were found to be too low. On the other hand, differential dyeing effects were investigated by applying UV irradiation on dyed samples, just using the discoloration induced by radiation. In this case, the fading ability of the dyes on cotton yarn was exploited, and in some cases, significant color differences (ΔE higher than 5.0) were found between UV-irradiated and untreated samples.

Many samples dyed with several reactive dyes (Kayacelon React, Avitera, Levafix, Remazol) were considered. It was possible to observe that the total color difference (ΔE) was not only due to an achromatic fading (ΔL) but also attributed to a variation of chromatic parameters (Δa and Δb), because

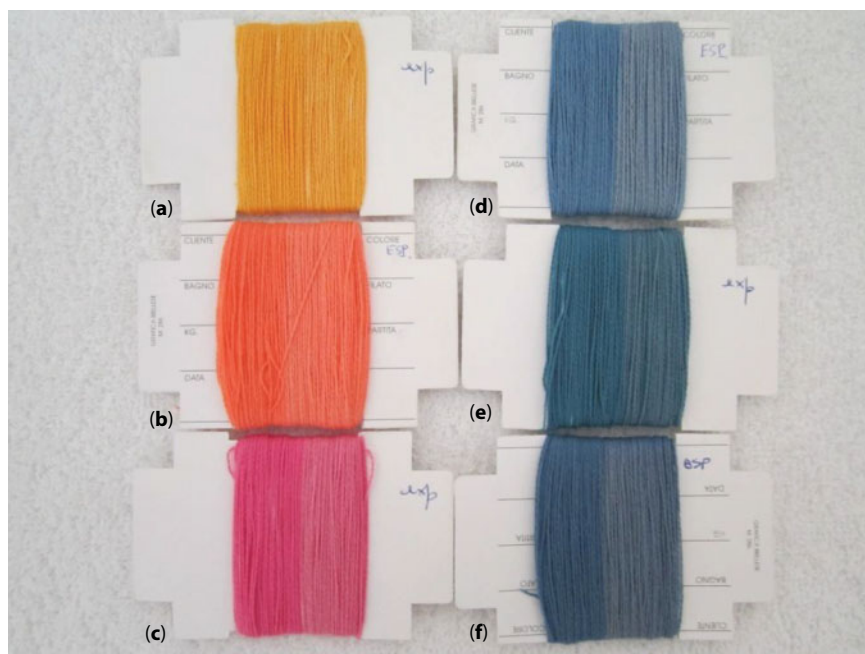


Figure 5.11 Dyeings with 0.5% selected dyes: (a) Levafix Amber CA, (b) Remazol Orange RR, (c) Remazol Red RB 133%, (d) Remazol Navy GG 133%, (e) Remazol Black B 133%, (f) Remazol Blue RR (for each shade: untreated yarn on the left side, UV faded on the right side) (reprinted from Ferrero *et al.* [13]).

a tone change after UV exposure occurred. Then, a selection of dyes sensitive toward UV-generated fade was performed, allowing one to obtain interesting differential chromatic effects Ferrero *et al.* [13].

Fading of dyed cotton yarns was carried out in two ways. The first was the UV treatment on yarn as samples wrapped on cardboard (Figure 5.11),



Figure 5.12 Cotton knitweaves made from yarns submitted to free UV treatment (reprinted from Migliavacca [11]).

where one side (right-hand side) was exposed to UV rays. Another way was the free UV treatment on yarn unwinding from a creel (where more or less a semi-cylindrical part is affected by UV rays) and then wound on a reel. Figure 5.12 represents the knitwear made from yarn treated in the latter way.

5.5.3 Cotton Finishing

Cotton fabrics often find their application in producing home furnishing, such as table linen, clothing, or work wear with high hygienic requirements. The high concentration of hydroxyl groups on cotton surface makes the fabrics water adsorbent and easily stained by liquids.

Moreover, the chemical composition and morphological properties of cellulosic fibers provide an excellent medium for bacterial growth. To overcome these limits, a finishing treatment is required on cotton fabrics to confer oil and/or water repellency and antibacterial activity.

Water and oil repellency are among the most common functional properties that need to be assessed for protective clothing. These can be conferred by the modification of the surface energy of textile fibers, possibly confined to a thin surface layer, so that the bulk properties of the textile fabric such as mechanical strength, flexibility, breathability, and softness remain uncompromised.

Ferrero *et al.* [5] proposed UV curing as an eco-friendly and cheap alternative to thermal curing of silicone and urethane acrylates onto cotton fibers to obtain water-repellent fabrics. In UV-curing processes, a suitable photoinitiator is able to interact with UV radiation, yielding radical or cationic species, which induce a rapid curing of reactive monomers and oligomers at low temperature, with lower environmental impact and lower cost than thermal processes. Moreover, if a mixture of monomer and initiator is absorbed by the fibers and subsequently UV-irradiated, the polymeric chains can form inside the textile structure, also establishing graft bonds (UV grafting) with the cellulose macromolecules and making the treatment solid and water resistant.

Fluorochemicals are organic compounds consisting of perfluorinated carbon chains, which impart water and oil repellency to the fiber surface when incorporated into a polymer backbone with perfluoro groups as side chains. The currently used fluorochemicals are based on C6 carbon chains, which have replaced the C8 fluorochemicals that can release highly hazardous and toxic substances, such as perfluoro-octanoic acid and perfluoro-octanesulfonates.

Ferrero *et al.* [6] proposed the UV curing of perfluoro-alkylpolyacrylate resins (Repellan EPF and NFC by Pulcra Chemicals and Oleophobol CP-C

by Huntsman), in water emulsions, to impart water as well as oil repellency to cotton fabrics, and the results were compared with those obtained by thermal polymerization before and after five domestic washing cycles. Yields after UV curing were quite similar, while strong water and oil repellency conferred by photografting was confirmed by static and dynamic contact angle measurements. Water repellency was practically unaffected by repeated washings regardless of curing time and finish add-on. A semi-industrial scale-up of the UV process on large fabric samples showed higher water and oil contact angles than the thermal one, even with a lower amount of finishing agent. The obtained results are encouraging and can lead the way for a real application of the UV process in industrial fields Ferrero *et al.* [8].

An antibacterial finishing, by means of a suitable surface chemical modification of fibers, is mainly required on natural fibers for furnishing, technical textiles, medical devices, hygienic textiles, food industry, and packaging. Chemicals bearing functional biocide groups are usually applied by padding, followed by a thermal treatment. Unfortunately, most of these products are toxic or carcinogenic, so the application to textiles is not advisable, also considering a possible release of the antibacterial agent, during use, upon skin contact.

For these reasons, strong chemical grafting to treated fibers is mandatory for a fast, stable, and resistant treatment. However, the finishing should not compromise the hand, appearance, and color of the fabric, considering that finishing processes are normally carried out after dyeing. In this view, the application of natural biopolymers through an eco-friendly and cheap process can be the optimal choice to develop bioactive eco-sustainable textiles from renewable sources Shahid-ul-Islam *et al.* [87].

Ferrero and Periolatto [76] proposed photocuring (UV curing and/or UV grafting) as a cheap and eco-friendly process to bind chitosan to textiles by means of radical reactions. UV-cured chitosan on cotton fabrics yielded high antimicrobial properties against *E. coli* and *S. aureus* Periolatto *et al.* [77]. A microorganism reduction of higher than 97% was found on all treated samples, regardless of the application method for chitosan. Moreover, about 2% polymer add-on was enough to confer a strong antibacterial activity on the fabrics without endangerment of hand and breathability. A prolonged contact time between chitosan solution and fabrics improved its penetration, and chitosan could graft to the fibers, showing increased washing fastness.

Semi-industrial scaled tests were carried out on large white or dyed cotton fabrics, using commercial chitosan powder dissolved in acetic acid solution with the radical photoinitiator. The chitosan add-on was

drastically lowered till 0.3% o.w.f, diluting the solution before the impregnation by padding. The as-impregnated samples, both dried in rameuse and wet, were irradiated in air by the Sun-Wash apparatus previously described [63]. Chitosan conferred a strong antibacterial activity, with the total reduction of the microorganism colonies on all the tested samples. Moreover, chitosan-treated samples showed optimum washing fastness, maintaining their antibacterial activity even after 30 washes [88] with a negligible effect on color or hand properties.

5.6 Conclusions

The chemical modifications induced by UV irradiation on wool fibers enable significant improvement on dyeing and finishing processes. The increased affinity due to structural modifications of the wool cuticle by UV rays makes it possible to obtain leveled dyeings with a fastness comparable with those carried out in the traditional manner, but with improved depth.

In particular, UV radiation can be confirmed as a valid eco-friendly pretreatment to improve the dyeability of wool fabrics by acid dyes at lower temperature than conventional dyeing, with fast kinetics, reaching the total bath exhaustion, and good fastness without damage on mechanical properties.

Moreover, with selected metal-complex dyes, it is possible to achieve considerable effects of differential dyeing between UV-irradiated and untreated areas of wool fabrics dyed at 85°C. Two different effects can be obtained on wool fabrics: one-color double face with the same shade but different depths (greater depth on the irradiated area) or two-shade double face with different colors coupling selected metal-complex dyes with acid dyes.

Among the finishing processes of wool, the anti-felting treatment with UV grafting of chitosan is an eco-friendly alternative to chlorination coupled with synthetic polymer addition and cheaper than a physical process as plasma treatment.

The UV treatment on cotton fibers can be properly utilized in dyeing and finishing processes. UV irradiation coupled with mild oxidation can improve some properties of the cotton fibers such as pilling resistance, water swelling, and dyeability. However, significant effects of differential dyeing were obtained by a UV posttreatment capable of fading dyeings with reactive dyes. UV curing and UV grafting with suitable chemicals enabled the modification of the surface of cotton fibers in order to confer oil and/or water repellency with an eco-friendly and cheap alternative

to chemical and thermal finishing treatments. Moreover, the chitosan UV grafting was found to be a valid environmental-friendly method to obtain cotton fabrics with a satisfactory washing-resistant antimicrobial activity even with low polymer add-on.

5.7 Future Perspectives

From the reported studies, it is clear that UV radiation can have great potential in textile applications as pretreatment, dyeing improvement, or finishing processes.

The present chapter deals with wool and cotton; results can be tested on other textile substrates (both natural or synthetic) in the future to evaluate similarities. It can be expected that fibers with the same chemical composition had similar behavior; hence, it is possible that protein fibers will produce the same results as wool and cellulosic fibers will produce the same results as cotton. However, other factors could influence the final results such as texture, hydrophilicity/hydrophobicity, and morphological structure of the fibers; thus, the method should be optimized for each substrate.

As reported, the chromophores are responsible for the reactions related to the UV exposure of the fibers, but UV radiation at different wavelengths can have a stronger or weaker effect on the chromophores. This aspect should be taken into account, with a deeper investigation on the desired effects and undesired drawbacks considering radiation in the whole spectrum of UV light (UV-A, UV-B, and UV-C), such as yellowing or thermal degradation of the substrate. On this last point, the use of dichroic filters to cut the infrared portion of the radiation can be useful for real applications.

In the reported studies, just a portion of dyes were considered for dyeing improvement or differential color effects. The investigation could involve specimens of all the dyeing classes, with particular interest on UV-resistant, anti-fading dyes. Moreover, the introduction of a sensitizer could be useful to enhance the rate of the reaction, thus improving the final result.

Finally, considering the finishing processes of textiles assisted by UV light, both by coating and by grafting, the range of possibilities is broad. By properly choosing the UV curable finishing agent, it is in fact possible to transfer the property of the monomer to the textile. Besides hydro and oil repellency or antibacterial activity, which are widely discussed here, fire resistance, crease recovery, conducting or insulating capacity, UV fastness, stain resistance, and self cleaning are just some of the many properties that can be conferred on fabrics by this process.

There has been an increasing consideration in nanotechnology in the present decade due to its enormous potential in applying and creating novel materials for enhanced properties and applications. Many studies were undertaken in improving textile and clothing properties and performances by applying nanocomposites [89]. Among the methods used to obtain nanocoating on textiles, plasma is reported as a suitable technique for modifying the structure and topography of the surface as well as for depositing nanocomposites onto the surfaces. Plasma has been applied as a pretreatment to improve the deposition process, to fabric nanocoatings with water repellency property, or for deposition of silver nanostructures on the fabric surface embedded within a plasma-polymerized matrix.

In this context, UV light can be explored as an alternative to plasma to replace, as for other finishing treatments, an expensive process with an economical, light, and eco-friendly one.

A lot of work has been done and more can be developed, but the results obtained are encouraging, indicating UV radiation as a promising technique to improve or confer new properties on textiles.

For further research projects, applications of the outstanding properties of some functional UV-cured polymers to fibers and fabrics can be suggested. Moreover, the investigation should be oriented in other fields than the conventional textile. In fact, the mechanical, physical, chemical and morphological properties typical of a textile, modified with target properties conferred by UV curing, could improve the performances of the basic materials. Therefore, composites in the field of electronics, biomedical, filtration, space and aeronautics are only some examples of advancing materials that can be developed with such research.

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Electroconductive Textiles

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Abstract

The chapter aims to provide comprehensive information about electroconductive textiles with special emphasis on inherently conductive polymers. Methodologies of preparation, characteristic features, and advantages and disadvantages of the conductive polymer-based electroconductive textiles are critically examined. Potential applications of conductive polymer-based electroconductive textiles, such as heating garments, cooling garments, electromagnetic interference shielding, strain/gas/humidity/pH sensors, static dissipation, and antibacterial efficacy, are discussed.

Keywords: Electroconductive textiles, graphene, carbon, metalized textiles, conductive polymer, coated textiles

6.1 Introduction

In general, textile materials used for clothing behave as insulators. The development of science and technology brought out innovation of conductive textile materials due to their demand in nonconventional and smart applications. Various approaches have been adopted for the preparation of electroconductive textiles, namely, metal coating, inserting the metal wire and metal fibers in the textile structure, blending metal fibers during spinning and weaving, application of carbon or graphene, etc. The latest

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trend is the incorporation of intrinsically conducting polymers in textile structures. These conductive polymers have conductivity in the range of 10 to 10^5 S cm^{-1} , which is more than that of the semiconductors and less than that of the metals (Figure 6.1). These polymers become conductive upon partial oxidation or reduction, a process commonly referred to as doping, similar to that with traditional semiconductors such as silicon or germanium, in which conductivity depends on the injection of electrons or holes [1, 2]. Though these polymers have remarkable electrical conductivity, they have limited real-world applications, mainly because of their lack of processability that arises from their strong interchain interaction. However, there have been some notable efforts to apply some of these electroconductive polymers on the surface of fibers, yarns, and fabrics. This is particularly the case where electroconductivity and flexibility are both important. Successful incorporation of these polymers in textile materials will yield electroconductive textiles that will possess synergistic properties of both the conductive polymer and textiles and open up many potential applications. Unlike metals, these electroconductive textiles are flexible,

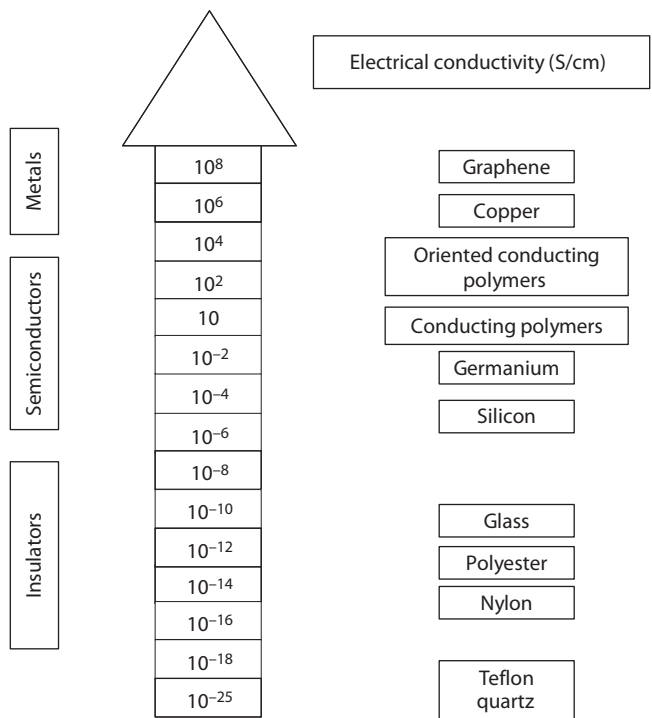


Figure 6.1 Conductivity ranges of insulators, metals, and conducting polymers.

durable, moldable, and lightweight. The most remarkable quality of these novel electroconductive textiles is the ability to customize conductivity as per the requirement to suit a specific application. Even their conductivity may be altered by various external stimuli such as strain, torsion, pH, and humidity. The resultant conductive textile is suitable for various novel applications such as sensors, heating garment, EMI shielding, etc.

6.2 Electrical Conductivity

Electrical conductivity is the ability of a material to conduct electricity. Electrical resistivity is the reciprocal of electrical conductivity. A low resistivity of a material indicates that it readily allows the movement of electric charge through it. Electrical conduction can take place in a medium depending on the charge particles such as electrons, ions, molecules, etc. present in the medium. The most familiar conducting substances are metals, in which the outermost electrons of the atoms can move easily in the interatomic spaces. Other conventional conducting materials include semiconductors, electrolytes, ionized gases, and carbon. Graphene and conducting polymers are newcomers in the group of electroconductive materials.

6.2.1 Graphene

Graphene is a single layer of carbon atoms that is tightly packed into a two-dimensional honeycomb lattice. It has good electrical conductivity, thermal conductivity, optical transparency, and mechanical properties and has great potential as a material for advanced applications. Graphene finds its application in the recent research in smart textiles due to its excellent electrical and mechanical properties. Graphene is conductive in nature due to sp^2 hybridization in which the flow of free electrons in the outermost orbital is maximum. The sp^2 hybridization is the combination of one “s” and two “p” atomic orbitals, which involves the promotion of one electron in the “s” orbital to one of the $2p$ atomic orbitals with 3 sigma bonds at 120° bond angles, which is trigonal in nature, as shown in Figure 6.2a and b.

6.2.2 The Electroconductive Polymers

Polymers that conduct electric currents without the addition of conductive (inorganic) substances are known as intrinsically conductive polymers (ICPs) or simply conducting polymers (CPs). Since the invention

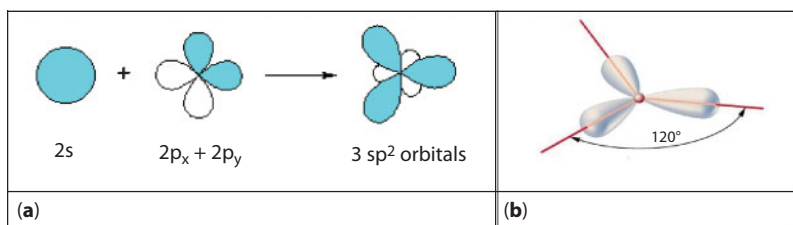


Figure 6.2 (a) Formation of sp^2 hybridization. (b) Trigonal planar structure of graphene.

of polyacetylene (PA), the first polymer exhibiting high conductivity (105 S cm^{-1}) in 1977 by Hideki Shirakawa, Alan J. Heeger, and Alan G. Mac Diarmid, different types of conductive polymers have been synthesized with a broad range of conductivities, that is, from 10^{-8} to 10^5 S cm^{-1} [3]. CPs consist of long conjugated chains formed by double bonds and hetero atoms. They can be rendered conductive by modifying the p and p - p electron systems in their double bonds and hetero atoms. Charge carriers are electrons or holes originated by adding or blending certain impurities to the polymer, called a dopant, which will serve as electron receptors or electron donors in the polymer. These holes or electrons can travel along the conjugated chain due to an application of potential difference resulting flow of electric current [1, 4, 5]. The level of conductivity achieved in conductive polymers depends on the molecular structure of the polymer, the degree of doping, and the nature of the counter ion species incorporated. Controlled doping of polymers enables engineering their conductivity values in a large range. At present, there are many CPs, such as polypyrrole (PPy), polythiophene (PTh), polyaniline (PANi), polyphenylene (PPp), polyphenylene sulfide (PPs), polyphenylene vinylene (PPv), polyfuran (PFu), poly 3-alkyl thiophene (PTh), etc. and their derivatives [6, 7]. The chemical structures of some of the conducting polymers are shown in Figure 6.3 and their electrical conductivities achieved after doping are shown in Table 6.1.

Polyacetylene (PA) is the simplest linear conjugated macromolecule and a representative of conducting polymers. It is the first polymer exhibiting high conductivity comparable with metals when exposed to oxidizing agents like iodine vapor. PA exists in two isomeric forms: trans and cis. The trans form is thermodynamically stable at room temperature [8]. Strong interchain interaction of PA gives rise to a rigid structure, which makes it infusible and insoluble in any kind of solvent. However, the double bonds in the PA backbone are susceptible to oxidation, leading to degradation of the chain and increase in electrical resistivity.

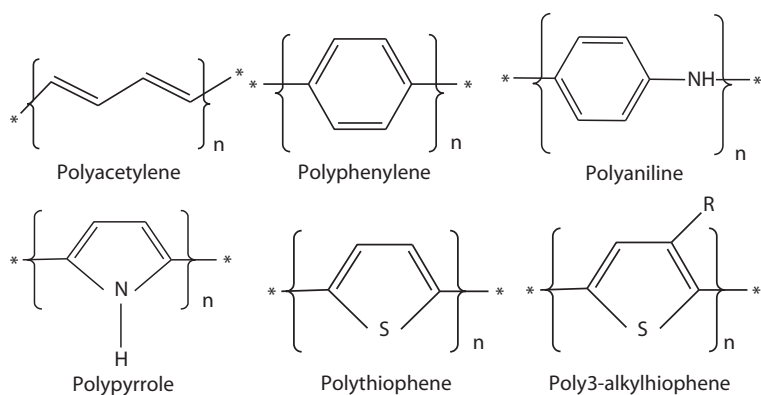


Figure 6.3 Chemical formulas of conductive polymers.

Table 6.1 Conductivities of conductive polymers with selected dopants [6].

Polymer	Doping material	Conductivity (S cm^{-1})
Polyacetylene	I_2 , Br_2 , Li, Na, AsF_5	10^4
Polypyrrole	BF_4^- , ClO_4^- , tosylate	$500\text{--}7.5 \times 10^3$
Polythiophene	BF_4^- , ClO_4^- , tosylate, FeCl_4^-	10^3
Poly (3-alkylthiophene)	BF_4^- , ClO_4^- , FeCl_4^-	$10^3\text{--}10^4$
Polyphenylene sulfide	AsF_5	500
Polyphenylene vinylene	AsF_5	10^4
Polythienylene vinylene	AsF_5	2.7×10^3
Polyphenylene	AsF_5 , K, Li	10^3
Polyiso-thianaphthene	BF_4^- , ClO_4^-	50
Polyazulene	BF_4^- , ClO_4^-	1
Polyfuran	BF_4^- , ClO_4^-	100
Polyaniline	HCl	200

Polyaniline (PANi) is one of the most widely studied CPs because of its simple preparation, relatively good environmental stability, and moderate electrical conductivity. As a common feature of all CPs, PANi has a poor solubility in most common organic solvents, which leads to the difficulty in processability. Aniline monomers have toxicological limitations.

Polythiophene (PT) has an excellent thermal stability and good conductivity. In spite of its lack of processability, the high thermal and environmental stability and high-electrical conductivity make it a highly desirable material. However, it has limitations in polymerization in water media.

Polyphenylene vinylene (PPv) has good physical, electrical, and optical properties that are important for a variety of applications. The properties of PPv can be conveniently engineered over a wide range by the inclusion of functional side groups. The optical band gap of ~ 2.6 eV and bright yellow fluorescence make PPv suitable for applications like light-emitting diodes and photovoltaic devices. This polymer can be both n- or p-doped by chemical or electrochemical means.

Poly-3,4-ethylene dioxythiophene (PEDOT) is based on a heterocyclic thiophene ring bridged by a diether. It means that it has the same conjugated backbone as PTh. It can be processed relatively easily. It can be spin-coated onto a huge variety of conductive and nonconductive substrates including glass, silicon, chromium, gold, etc.

Polypyrrole (PPy) is a widely researched conducting polymer, because of its good electrical conductivity, good environmental stability under ambient conditions, and fewer toxicological problems [9]. However, as a conjugated conducting polymer, the brittleness of PPy limits its practical uses. The processability and mechanical properties of this material can be improved either by blending PPy with some strong fiber-forming polymers or by coating it on a suitable substrate to form a composite. Thus, PPy-based composites may provide the fibers or fabrics with electrical properties similar to metals or semiconductors [10]. Therefore, in the present chapter, emphasis is on the PPy-based electroconductive textiles.

6.3 The Source of Conductivity in Conducting Polymers

The conventional insulating polymers do not possess electrons in a suitable orbital, and as a result, the valence electrons form stable σ -bonds between the adjacent atoms. However, the CPs have a common significant overlap of delocalized π -electrons along the polymer chain. These π -electrons can be made free to move either by the application of external energy (e.g., heat) or by doping. When the conductivity of CP is achieved only by application of external energy (e.g., heat), then the CP is called an intrinsically conductive polymer (ICP). The CPs can be transformed into conductors by means of doping with either an electron donor or an electron acceptor.

The doping can be done in two ways, by oxidation or by reduction. In an oxidation process, it loses an electron from the conduction band, and in a reduction process, it injects an electron into the conduction band. Typical oxidizing dopants are iodine, arsenic pentachloride, iron(III) chloride, etc. A typical reductive dopant is sodium naphthalide. The main criterion of a dopant is its ability to oxidize or reduce the CP without lowering its stability [1, 2].

6.4 Electroconductive Textiles Based on Metals

Use of metal wires or metal coating is a common practice for imparting electrical conductivity to textiles [11–15]. Metal fibers are blended with common textile fibers during spinning in order to prepare electroconductive textiles [16–19]. Those yarns are used in weaving or knitting to produce electroconductive fabrics [20–23]. However, processing of those yarns is difficult during weaving and knitting, resulting in fabrics with loose textile properties [23, 24]. Such limitations of electroconductive textiles associated with processability and poor textile properties can be successfully overcome by coating/applying CPs on textile substrates [25]. Among the CPs, PPy has been mostly used due to its high conductivity, low toxicity [26], and high environmental stability [25].

6.5 Electroconductive Textiles Based on Graphene

Graphite is the raw material of the process that is firstly converted to graphene oxide (GO) by any one of these three different methods, namely, Hummer's method, Modified Hummer's, and Improved Hummers method. Graphene oxide (GO) is used in the production of electroconductive fabric through the conventional "dip and dry" dyeing technique. The GO is made into aqueous dispersion by the application of an ultrasonicator bath for a period of 60 min. The textile materials such as fibers, yarns, or fabric are then immersed into the GO dispersed solution and soaked for 30 min at room temperature. After that, soaked textile materials are dried overnight, which leads to deposition of GO on the surface of the cotton fabric. The same soaking and drying process may be repeated multiple times in order to achieve higher GO add-on onto the textile materials. Then, GO-coated textiles are treated with the aqueous solution of $\text{Na}_2\text{S}_2\text{O}_4$ at 95°C for 30 min, which converts the immobilized GO into graphene. Surface resistivity of the acrylic fabric produced by this method is obtained in the range of

Table 6.2 Surface resistance of the GO-cotton fabric, after treatment of different reducing agents.

Sample	Surface resistance ($\text{k}\Omega \text{ cm}^{-1}$)
NaBH_4 -GO-cotton	34,600
NaOH -GO-cotton	23,300
N_2H_4 -GO-cotton	62.17
$\text{C}_6\text{H}_8\text{O}_6$ -GO-cotton	31.2
$\text{Na}_2\text{S}_2\text{O}_4$ -GO-cotton	19.4

10^2 to $10^{10} \Omega/\text{cm}$ depending on the amount of graphene add-on on the fabric surface [27]. In another study, it has been reported that the surface resistivity of polyester fabric is decreased to $23.15 \Omega \text{ cm}^{-2}$ from a value greater than $10^{11} \Omega \text{ cm}^{-2}$ by graphene coating onto the polyester fabric. It is also reported that the number of coating cycles hardly influences the electrical and electrochemical properties of polyester fabric [28, 29]. Graphene-coated knitted and woven fabric are produced with three different concentrations of GO (0.75%, 1.5%, and 2.25%) and up to 15 dipping cycles. It is reported that a coated knitted fabric performs better in terms of surface resistivity, add-on percentage, air permeability, pore size, and water vapor permeability than a coated woven fabrics [30].

The reducing agent plays a major role in enhancing the conductivity of the fabric because the conductivity of the fabric is largely influenced by the proper reduction of graphene oxide over the fabric surface. Adsorption of graphene oxide, the concentration of the reducing agent, the time duration for treatment, and the effective reduction of graphene influence the conductivity of the textile materials.

It is observed that the GO-coated fabric has a good affinity toward $\text{Na}_2\text{S}_2\text{O}_4$ as reducing agents for cotton fabric and has a better reducing potential in comparison to NaBH_4 , N_2H_4 , $\text{C}_6\text{H}_8\text{O}_6$, and NaOH . Surface resistivity for the GO-coated fabric with different reducing agents, namely, NaBH_4 , NaOH , N_2H_4 , $\text{C}_6\text{H}_8\text{O}_6$, and $\text{Na}_2\text{S}_2\text{O}_4$, is shown in Table 6.2.

6.6 Electroconductive Textile Based on PPy

A key requirement for the synthesis of PPy is that the conjugated nature of the polymer should be conserved during the synthesis process. PPy

is insoluble and does not melt due to its strong interchain interaction. Therefore, it is difficult to spin to produce filaments or fibers by melt or solution spinning. It has poor thermal stability, which makes it unsuitable for the hot molding process. Thus, there are limitations to applying it on textiles using common methodologies. In this regard, novel *in situ* polymerization methods are found to be the most suitable technique [31]. There are various approaches of *in situ* polymerization based on the reaction phase employed by various researchers, namely, *in situ* chemical, *in situ* electrochemical, *in situ* vapor phase polymerization, *in situ* polymerization in a supercritical fluid, etc. [32–36]. Other than *in situ* polymerization, the solution coating and molecular template approaches are also available. Advantages, disadvantages, and features of all these processes are described in the following sections.

6.6.1 *In Situ* Chemical Polymerization

The *in situ* chemical polymerization process is conducted in a liquid phase. One of the key requirements of this process is that the monomer should be soluble in a solvent. For chemical polymerization, solutions of monomer and a suitable oxidant (e.g., FeCl_3) are mixed together and subjected to constant stirring for a prolonged duration. As a result, oxidative polymerization occurs and polymers form in bulk. Pyrrole is soluble in water in low concentration. Therefore, the coating of different materials with PPy is possible by means of *in situ* chemical polymerization in water [37–46]. *In situ* chemical polymerization can be performed in a single-bath or a double-bath process. In the single-bath process, monomer and oxidant solutions are mixed in a single beaker, and simultaneously, the textile substrate is immersed into it, as shown in Figure 6.4. In the double-bath process, the textile substrate is treated with monomer solution first and then a monomer-enriched substrate is immersed in oxidant solution, or vice versa, as shown in Figure 6.5. As polymerization starts, some polymers deposit on the textile substrate due to adsorption and some are present in the solution in bulk. As a result, the color of the substrate and the solution changes to greenish black, which is the color of the polymer [47, 48]. In comparison to other methods, the *in situ* chemical polymerization method is the simplest. The experimental setup is very simple. It is suitable for laboratory preparation as well as for mass production of conductive textiles. The only requirement is that PPy should have some affinity to the textile substrate used.

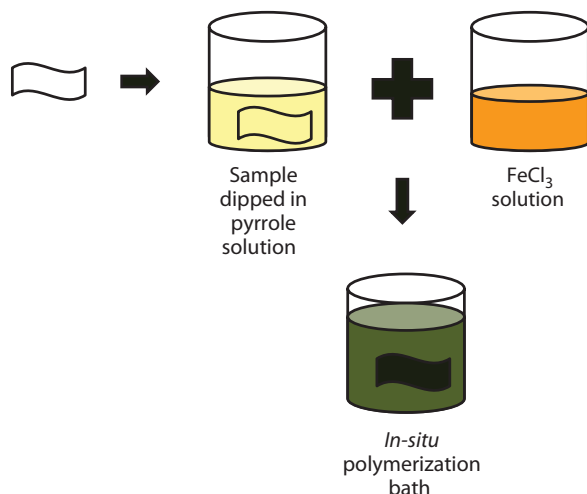


Figure 6.4 *In situ* chemical polymerization via the single-bath process.

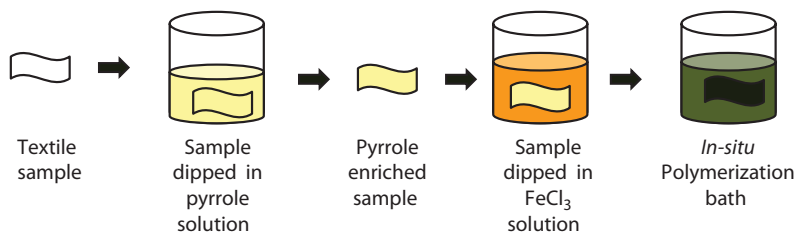


Figure 6.5 *In situ* chemical polymerization via the double-bath process.

6.6.2 *In Situ* Electrochemical Polymerization

In situ electrochemical polymerization is also conducted in a liquid phase with a soluble monomer. It is usually performed in a one-compartment cell where two electrodes such as anode and cathode are connected to an external power supply. The cell is provided with monomer solution with suitable electrolytes and dopant as shown in Figure 6.6. In most of the cases, electrolytes act as dopants as well. Electrochemical oxidation of monomer results in polymer films deposited on anode surfaces. If an anode surface is covered with a textile substrate, then polymers will deposit on it [47].

The polymerization rate and yield depend on the material of the electrode, types of solvent, electrolyte, supply voltage, temperature, time, monomer concentration, etc. [47, 49–51]. Different electrolysis techniques can be used such as potentiostatic (constant potential), galvanostatic (constant

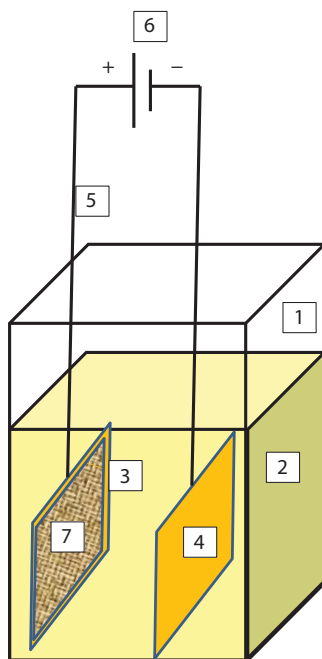


Figure 6.6 Schematic diagram of the experimental setup of electrochemical polymerization: (1) polymerization bath, (2) monomer and electrolyte solution, (3) anode, (4) cathode, (5) electrical wire, (6) power supply, (7) textile fabric affixed on anode surface.

current), and potentiodynamic (potential scanning, i.e., cyclic voltammetry) methods. Potentiostatic and galvanostatic methods are particularly suitable for mechanistic investigation nucleation and the macroscopic growth of polymers. Potentiodynamic techniques, such as cyclic voltammetry, correspond to a repetitive triangular potential waveform applied at the surface of the electrode. This method has been mainly used to obtain information about the redox processes involved in the early stages of the polymerization reaction and to examine the electrochemical behavior of the polymeric film after deposition [47, 52–58]. The main limitation of this process is the size of the sample to be prepared, which depends on the size of the anode.

6.6.3 *In Situ* Vapor Phase Polymerization

In situ vapor phase polymerization occurs in the vapor phase of either the monomer or the oxidant. It is a suitable process for producing

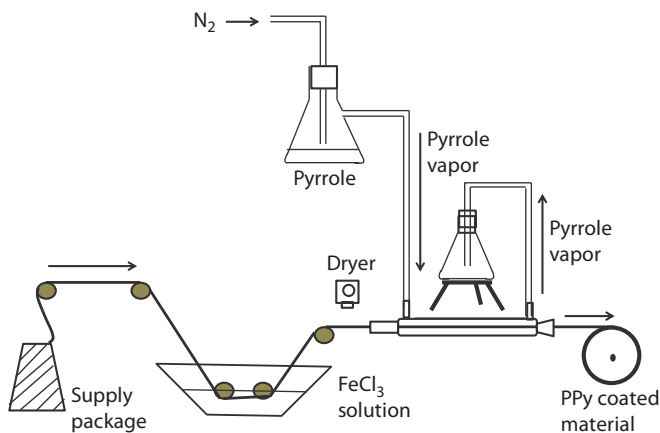


Figure 6.7 Experimental setup of *in situ* vapor phase polymerization.

electroconductive textiles in two steps. Either impregnation of textile is done in a liquid solution of oxidant and dopant at first, followed by exposure to monomer vapor for *in situ* polymerization, or vice versa [59–63]. Conducting textiles have been prepared by embedding CPs in various natural, manmade, and synthetic fibers, such as cotton, wool, viscose, aramid, polyethylene, polyester, etc. by this method [34, 64–69]. A schematic diagram of the process is shown in Figure 6.7. The vapor phase prepared fabrics to show a high uniform polymer coating on the fiber surface. As a result, variability in surface resistivity is minimized and fastness to light and washing improved. However, controlling the add-on % is difficult and the equipment setup is complicated [60].

6.6.4 *In Situ* Polymerization in Supercritical Fluid

As discussed above, textile materials can successfully be covered by conducting polymers. However, the polymers have poor affinity to most of the textile substrates, and as a result, after washing, textiles lose the polymers and resistivity increases substantially. Improved washing fastness has been achieved by using *in situ* polymerization of PANi and PPy onto polyester and polyamide fibers in the reaction medium of supercritical CO₂. The main advantage of using this approach is that the medium of supercritical fluid helps the substrate polymer to expand to create larger intermolecular spaces so that the pyrrole monomer is able to penetrate the substrate and subsequently form PPy. Upon removal of the reaction medium, the

intermolecular spaces try to retract in their original size, and as a result, the formed PPy is entrapped inside. Because of this, much durable electroconductive textiles can be prepared. However, this process is costly and the setup is complicated [70].

6.6.5 Solution Coating Process

CPs are insoluble in most common solvents. However, by grafting some functional groups in the polymer chain, they can be made soluble in some selected solvents [71]. Synthesis of soluble PPy can be possible in the form of alkyl PPys. Solubility increases with the increase in length of the alkyl chain attached to the pyrrole ring without significantly affecting the conductivity. These soluble alkyl PPys can be pre-packaged in aerosol cans or as commercially available paints and applied directly to any surface in any desired pattern for intelligent textile applications. The main advantage of soluble conducting polymers is that they can be directly applied to any substrate, which avoids exposure of the surfaces to damaging oxidizing agents and fulfills the requirements for controlled laboratory conditions [34, 72].

6.6.6 Molecular Template Approach

The molecular template approach provides a method of seamless integration of electronic functionality into textiles. This technique enables a degree of control on the level of conductivity introduced and provides improved stability to the conductive polymers incorporated into the textiles. The template stabilizes the conducting polymer and binds the systems to the fibers in the textile structure. The efficiency of the polymerization/coating process is enhanced since the template localizes the reaction within the textile. The presence of the molecular template results in the formation of an adherent, uniform, and stable conducting polymer layer [73, 74]. Conductive PPy/TiO₂ nanocomposites are successfully prepared by the surface molecular imprinting technique (MIP-PPy/TiO₂) using methyl orange as template molecule [75]. The photo-catalytic activity of MIP-PPy/TiO₂ is found twice that of Control-PPy/TiO₂ due to the introduction of the imprinted cavities on the surface of MIP-PPy/TiO₂ nanocomposites. PPy nanotubes are successfully synthesized using an aqueous solution of neutral methyl orange as soft template, and a conductivity of about 29 S cm⁻¹ has been reported [76]. In another study, the nanotubules of PPy are electrochemically synthesized using the pores of nanoporous polycarbonate (PC) membranes as templates [77].

6.7 Conductive Polymer-Based Textiles

Coating various textile substrates by *in situ* chemical polymerization of pyrrole yields new composite materials that are expected to have potential applications in various fields [78, 79]. The *in situ* chemical polymerization of PPy on textile substrate occurs via adsorption at the liquid–solid interface. This phenomenon of adsorption at the liquid–solid interface is also widely used by the textile industry in processes such as dyeing, finishing, wastewater treatment, etc. Kuhn has found no significant difference with the use of different fibers, that is, polyester, nylon, rayon, acrylics, Kevlar, Nomex, wool, and cotton; all seem to perform very similarly during *in situ* polymerization [80]. However, later on, Wang *et al.* reported that the morphology and conductivity of PPy and PANi films differ greatly according to whether the films are deposited on hydrophilic or hydrophobic surfaces of the substrate [81]. They found that the conductivity of the films deposited on the hydrophobic surfaces is at least 10^4 times higher than those deposited on hydrophilic surfaces [81]. The films on the hydrophobic surfaces consist of a continuous granular matter while the films on the hydrophilic surfaces consist of particles (spheres for PPy and rods for PANi). PPy and PANi deposition on the hydrophobic glass surface is more rapid, due to the preferential adsorption of the monomer from solution onto the hydrophobic glass surface on which it polymerizes more rapidly. Since it is formed on a covalent surface, it forms a more extended continuous morphology, covering the surface and joining the adjacent polymer chains. Various textile fibers such as cotton, wool, silk, polyester, nylon, acrylic, etc. consist of different functional groups in their polymer chain and may give rise to different levels of interaction with PPy, resulting in different levels of conductivity of the coated textiles.

6.7.1 Cotton as Substrate

Cotton fiber and its yarns and fabrics are found to be one of the most used substrates where PPy can be applied. Cotton yarns are coated with PPy by continuous vapor phase polymerization using FeCl_3 as oxidant [63]. The specific resistance obtained for cotton yarn is $1.53 \, \Omega/\text{cm}^2$ at an $80 \, \text{g L}^{-1}$ FeCl_3 solution. Optical microscopy images of uncoated and PPy-coated cotton fibers are shown in Figure 6.8. It can be seen that individual cotton fibers are coated with PPy and significant amounts of PPy are present inside the yarn structure. Significant chemical interaction between cotton fiber and PPy has been observed in terms of

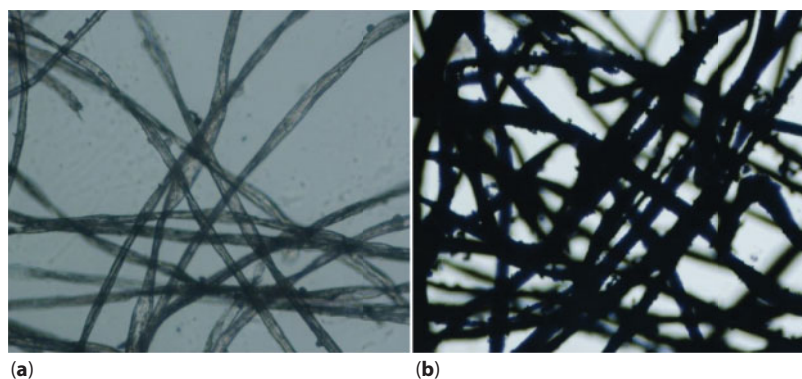


Figure 6.8 PPy-coated cotton fiber (a) before coating and (b) after PPy coating [82].

intermolecular hydrogen bonding due to *in situ* chemical polymerization [48, 80].

Electroconductive cotton fabrics are prepared by *in situ* polymerization of the aniline monomer at low temperatures [83–85]. Also, a two-step *in situ* chemical polymerization of PANi on cotton fabric is undertaken by employing the jig-dyeing principle and a minimum electrical surface resistivity of about $103 \Omega/\square$ is achieved [86]. In another study, PPy is electrochemically deposited onto cotton fabrics with the aid of a water-soluble adhesive. The mechanism for growth of the polymer appears to follow the template laid out by the yarns in the cotton fabric. This template growth has been seen to be distinctly different from that of a freestanding film in which growth appears to progress through spherical nodes. Films prepared with an added adhesive show significantly better structural uniformity than those prepared without [54]. The thermal conductivity of cotton denim fabric is also found to be enhanced significantly due to a small amount of PPy add-on [87].

6.7.2 Wool as Substrate

Wool fibers are made electrically conductive by *in situ* polymerization of pyrrole using FeCl_3 as an oxidant. The PPy-coated wool fibers are spun into yarns, and yarns are knitted to produce electroconductive fabrics using conventional industrial machinery [88, 89]. These fabrics show acceptable conductivity decay with respect to most of the stress that textile products are usually subjected to. Coating of wool fiber with PPy reduces surface roughness due to scales and reduces directional friction effects [90]. It is reported that the conductivity of PPy-coated wool yarn at a lower twist

level (400 TPM) is always more than that of wool yarn at a higher twist level (500 TPM). This is attributed to the more open and bulkier structure of wool yarn at the lower twist level, which allows the reagents to penetrate the inner layers of the yarn through its more porous structure [61, 63]. The best electrical resistivity of wool yarns obtained is $0.43 \text{ k}\Omega/\text{mm}$ [61]. It is observed that PPy is deposited on the wool fiber particularly at the exterior section of wool yarn when vapor phase polymerization is adopted as shown in Figure 6.9 [91], whereas all individual wool fibers are coated with PPy inside the yarn when *in situ* chemical polymerization is followed [45]. SEM images reveal the presence of an even 1- to $2\text{-}\mu\text{m}$ -thick PPy film coating on each wool fiber surface as shown in Figure 6.10 [45]. In another approach, soluble conducting polymers of alkyl PPy have been synthesized by polymerization of the 3-alkyl monomers, and the polymer emulsion is directly applied on the surface of wool fabrics [89].

Probable chemical bonding between the PPy to the surface proteins of the wool has been presumed in the form of hydrogen bonding between the lone pairs of electrons on the various N and O atoms in the pyrrole rings of the polymer and the amino acids of the protein [48]. It is also possible to have some N-S bonding between the S in the cysteine amino acids and the pyrrole N [89]. It has been found that the PPy coating enhances the thermal conductivity of wool fabrics [92, 93]. The thermal conductivity of the wool fabric can be increased from $0.0312 \text{ W m}^{-1} \text{ K}^{-1}$ to $1.60 \text{ W m}^{-1} \text{ K}^{-1}$

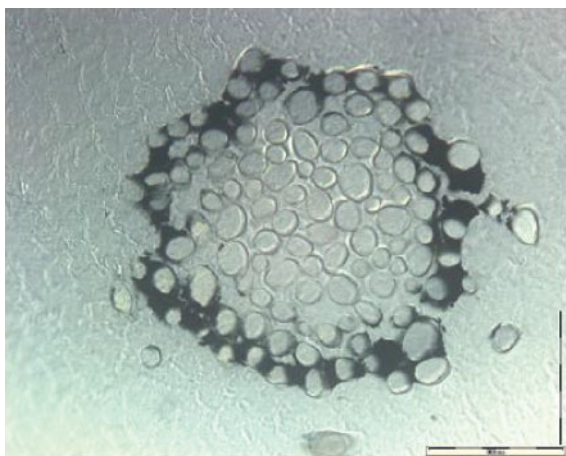


Figure 6.9 Cross sections of PPy-coated wool yarn using the continuous vapor phase method [61, 63].

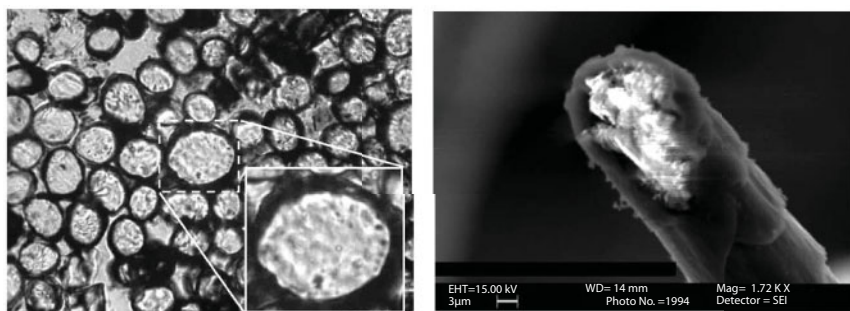


Figure 6.10 SEM picture of cross section of PPy-coated wool yarn, fibers (1000×2000 in the box). A broken PPy-coated wool fiber ($1720\times$), prepared by chemical polymerization [45].

after polypyrrole coating. PPy add-on and average surface resistivity of this sample are 8.12% and $1.337 \text{ k}\Omega/\text{Y}$, respectively [93].

6.7.3 Silk as Substrate

Different silk substrates in the form of spun silk tops, nonwoven web, yarn, and fabric are coated with PPy by *in situ* oxidative polymerization from an aqueous solution of pyrrole at room temperature using FeCl_3 [89]. These PPy-coated silk materials displayed excellent electrical properties. The PPy-coated silk tops are successfully spun into yarn either pure or in a blend with untreated silk fibers. The resulting yarns maintain good electrical properties. In other studies, silk fabrics are coated with doped PPy by *in situ* oxidative polymerization from an aqueous solution of pyrrole at room/cold temperature, by using FeCl_3 as a catalyst [94, 95].

Continuous vapor phase polymerization of pyrrole on silk (116/2 tex) and cotton (20 tex) yarns enables the production of uniformly coated yarns with an electrical conductivity of $6.4 \times 10^{-4} \text{ S cm}^{-1}$ for cellulose and $3.2 \times 10^{-4} \text{ S cm}^{-1}$ for silk after several washings [62]. In comparison to the crude fibers, the tensile strength of the coated silk fibers shows either no changes due to coating or an increase in some cases [62]. Figure 6.11 shows that the PPy layer covers the surface of individual silk fibers after *in situ* liquid phase polymerization. These findings confirm that pyrrole could diffuse into the compact texture of silk yarns and fabrics and that the polymerization proceeded smoothly, resulting in the formation of a continuous layer of polymer around the individual fibers. A significant chemical interaction

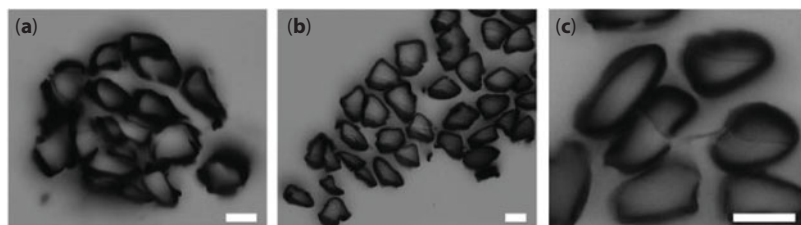


Figure 6.11 Cross sections of PPy-coated silk fibers from silk yarn and fabric; (a) silk yarn, add-on 16.8%; (b) warp thread taken from the silk fabric, add-on 13.5%; and (c) close-up of (b). The magnification bar is 10 μm [94].

between silk fiber and PPy has been observed in terms of intermolecular hydrogen bonding due to *in situ* chemical polymerization [48].

6.7.4 Viscose as Substrate

Conducting textiles are prepared to embed PPy in manmade cellulose-based fibers, such as viscose, cupro, and lyocell by means of vapor phase and liquid phase *in situ* polymerization [68, 96, 97]. The fabrics show highly uniform PPy coating on the viscose fiber surface, with a partial penetration of PPy inside the amorphous zones of fiber bulk. The vapor phase samples show a more uniform PPy layer without aggregates on the fiber surface than that of liquid phase samples. PPy penetration into the fiber bulk is almost complete for liquid phase samples, whereas only partial penetration is observed in vapor phase samples [68]. The SEM images of PPy-coated viscose fibers are shown in Figure 6.12.

Also, *in situ* synthesis of various conducting polymers in cellulose solutions and micro-cellulose dispersions and blending of pre-synthesized conducting polymers in these cellulose systems are reported [98, 99]. Significant differences have been observed between various mixing strategies as well as between the conducting polymers, namely, PANi, PPy, and PTh [99]. The best conductivity of all prepared composite materials is observed by a simple preparation of heterogeneous mixtures of PANi with a cellulose gel. Sufficient conductivity is also achieved when the percentage of PANi in the polymer mixture is reduced from 50% to 33%, while films with 17% and 9% PANi are not conducting anymore. Cellulose with its extraordinary supramolecular structure and material properties can help awaken the possibilities for conducting polymers in an interplay of the two materials [99]. In another study, conducting PANi is synthesized in the presence of dispersed pulp fibers in the polymerization reaction to

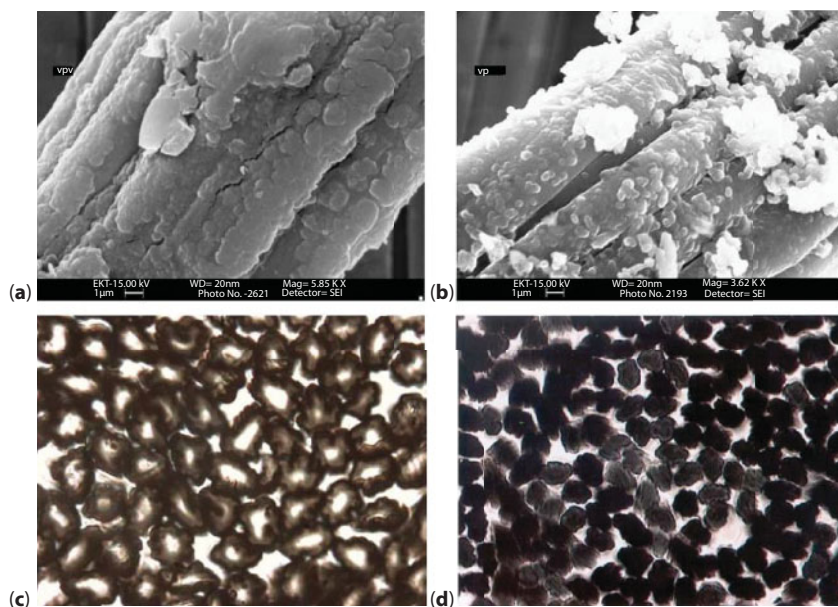


Figure 6.12 SEM images of PPy-coated viscose fiber. Longitudinal view (a) vapor phase sample, (b) liquid phase sample, cross-sectional view of (c) vapor phase and (d) liquid phase sample [68].

yield PANi/pulp composite fibers, which are then formed into a conducting paper sheet [100]. A chemical interaction has been found between the hydroxy group in the cellulose and PANi during the polymerization, which allows the formation of the spherical structure of PANi instead of a tubular structure [100]. A new conducting nanofibrous membrane composed of bacterial cellulose and PPy is obtained through *in situ* oxidative chemical polymerization of pyrrole by using ferric chloride as a catalyst. The electrical resistivity of the composites is reduced from 9.1×10^{12} to $0.33 \Omega \text{ cm}$ [101]. A strong intermolecular interaction between PPy and bacterial cellulose is found by them. Hydrogen bonding may be formed between cellulose and PPy. This would be between H of the N of the pyrrole ring and the lone pair electron of O of the $-\text{OH}$ groups of the cellulose and/or between the H of the $-\text{OH}$ group of the cellulose and the lone pair electron of N of the pyrrole [89, 97]. Ding and co-workers produced an electroconductive paper by *in situ* oxidative polymerization of pyrrole with FeCl_3 as an oxidant and PTSA as a dopant. They find no difference in the amount of PPy deposited on the outer surface and the internal wall of the paper [102]. Highly intrinsic conductive PPy/cellulose fiber composites are successfully

prepared through *in situ* chemical oxidation polymerization simply by increasing fiber concentration at the same dosage of pyrrole, oxidant, and dopant (based on the weight of dry fiber). Fourier transform infrared spectroscopy, together with XPS, certified that the PPy with a longer conjugation length and a higher doping level across the conductive fiber is obtained at higher fiber concentrations. The resulting composite shows the lowest surface resistivity of $0.433 \text{ k}\Omega/\square$, as well as improved stability toward electrical conductivity and thermal stability [103].

6.7.5 Polyester as Substrate

Conductive polyester fibers are prepared by coating and melt mixing followed by the spinning of conductive polyesters [104, 105]. It is observed that coated fibers have much better electrical properties than conductive fibers obtained by the melt spinning method. The conductivity of fibers obtained by melt mixing is very low due to structural inhomogeneity and the aggregation of conductive polymers [104, 105]. Many types of research followed the *in situ* polymerization route for the preparation of electroconductive polyester textiles. PPy is chemically [106–108] and electrochemically [35, 58, 109–111] synthesized on polyester textiles to produce conducting textiles.

Macasaquit and Binag have optimized the *in situ* chemical polymerization method of producing conducting PPy/polyester composite textile and the least conductivity achieved was 0.10 S cm^{-1} [113]. It has been reported that a smooth and coherent film of PPy can be achieved by encasing individual polyester fibers via chemical polymerization, which does not affect the tactile properties of the host substrate [114]. PPy is also polymerized chemically and electrochemically in sequence on a polyester woven fabric that has a high electrical conductivity of $0.2 \text{ }\Omega \text{ cm}$ [115]. The thermal stability of the PPy-coated polyester prepared by sequential chemical and electrochemical methods is found to be much higher than that prepared only by the chemical process [115]. The thickness of the PPy on the polyester textile surface could be controlled by adjusting the monomer concentration, but these deposits are found to be not adherent to the textile surface and can be washed off easily [42]. Polyester/Lycra fabric is made electrically conductive by *in situ* chemical polymerization of pyrrole using FeCl_3 and AQSA as additives [116]. It is found that PPy particles remain mainly in yarn crossover, and as a result, they are difficult to remove by rinsing [116]. Vapor phase polymerization is used to coat polyester yarns with PPy in the presence of ferric chloride as an initiator [112]. In this case, at least 0.6 mol/L concentration of the FeCl_3 solution is required to achieve

a uniform coating of PPy on the polyester surface as shown in Figure 6.13. In another study, PTh is successfully coated on a polyester fabric by *in situ* chemical polymerization [117]. The electrically conductive polyester/PANi composite fabrics are prepared by a novel two-step process, and the surface resistivity of the polyester substrate is decreased to $103 \Omega/\square$ from an initial value of 10^{11} – $10^{12} \Omega/\square$ [118].

6.7.6 Nylon as Substrate

The nylon 66 yarn is coated with PPy by vapor phase polymerization, which shows an electrical resistivity of $2.59 \Omega\text{g}/\text{cm}^2$ [63]. The cross section of the PPy-coated yarn is shown in Figure 6.14. It can be seen that a uniform coating of PPy is achieved on the yarn surface, which is also earlier reported by Kuhn, as shown in Figure 6.15 [80]. Nylon 6 fibers/fabrics coated with PPy by *in situ* vapor phase polymerization exhibit sensing capacities for external stimuli such as strain, temperature, relative humidity, etc. [67, 119]. PPy-coated nylon/Lycra fabrics are prepared using an aqueous solution containing 0.015 M pyrrole, 0.04 M FeCl_3 oxidant, and 0.005 M NDSA dopant at room temperature for 2 h [41]. An ultrathin

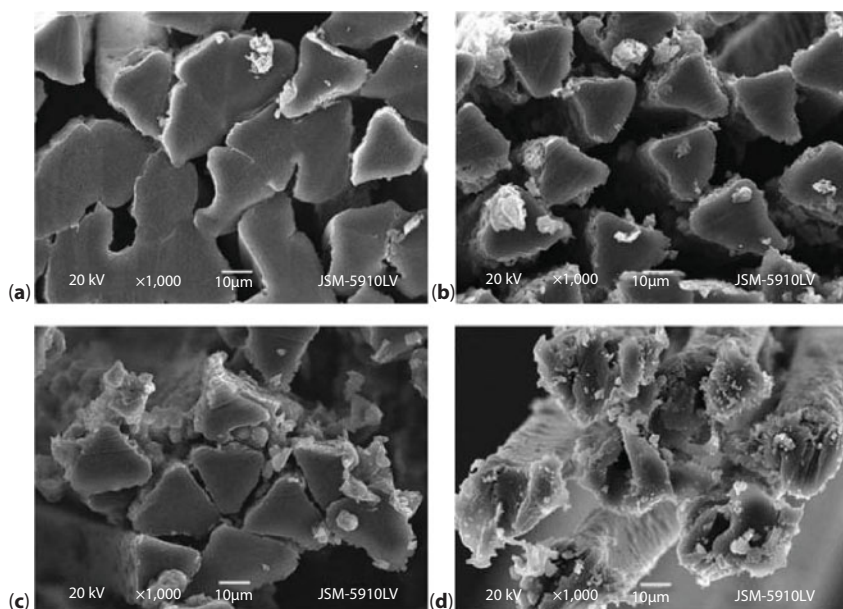


Figure 6.13 Cross section of PPy-deposited polyester fibers at various FeCl_3 concentrations: (a) 0.2 mol/L, (b) 0.4 mol/L, (c) 0.6 mol/L, and (d) 0.8 mol/L [112].

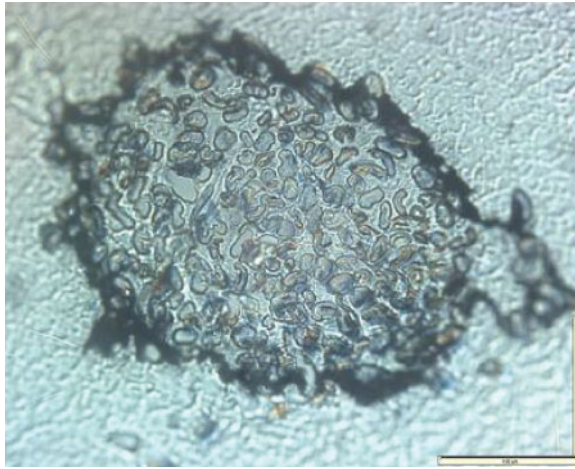


Figure 6.14 Cross section of PPy-coated nylon 66 yarn using the continuous vapor phase method [63].

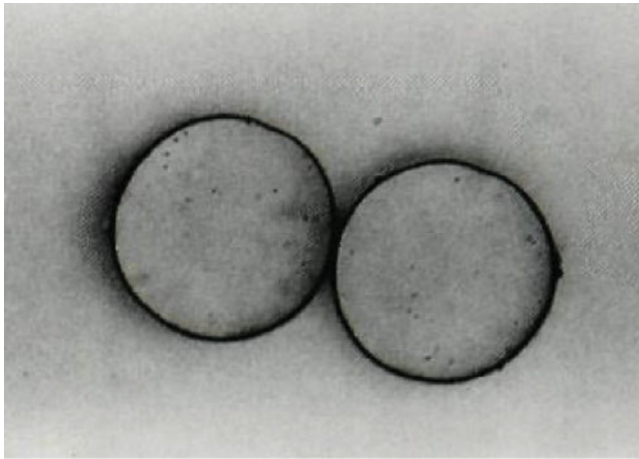


Figure 6.15 Cross section of nylon 6 fiber treated with PPy. The dark area shows the PPy coating. Magnification, 960× [80].

and coherent PPy layer is formed on each individual nylon and Lycra fiber. In another study, a surface resistance of a PPy-coated nylon Lycra fabric of $149 \Omega/\square$ is obtained [120]. Such a conductive fabric shows outstanding flexibility and stretchability and demonstrates strong adhesion between the PPy and the fabric of interest. A PPy-coated nylon fabric with an electrical resistance of $5 \Omega/\square$ is successfully prepared by using sequential HTHP

chemical and electrochemical polymerizations [121]. The adhesion of the PPy layers is so excellent that even ultrasonification cannot separate the PPy coating from the fabric. Highly stretchable and highly conductive fabrics are prepared by *in situ* chemical polymerization of PPy on a nylon/Spandex stretch fabric in aqueous solutions with 0.5 M pyrrole, 1.165 M FeCl_3 , and 0.165 M benzenesulfonic acid at 5°C for 1 h [122].

6.7.7 Polypropylene as Substrate

The chemical polymerization of pyrrole in the presence of polypropylene (PP) particles yields composites with conductivities in the range 10^{-10} to $10^{-2} \text{ S cm}^{-1}$ depending on the PPy content [123]. Another article describes the synthesis and properties of PPy layers by vapor phase oxidative polymerization on the surface of a microporous polyethylene (PE) film [66]. A polypropylene nonwoven with a conductive PPy coating using iron (III) chloride as an oxidant, water as a solvent, and 5-sulfosalicylic acid as a dopant exhibits good coating consistency, material durability, and low resistance of about 55Ω [124]. The surface coating on the polypropylene fibers is found to be smoother than the coating on the nylon fibers [124]. However, no chemical interaction has been found between ultrahigh molecular weight polyethylene (UHMWPE) fiber and PPy as evidenced by FTIR results [125].

6.7.8 Glass as Substrate

Cohesive high-quality PPy films are successfully synthesized on a glass surface with different doping anions by various researchers [126, 127]. They found that the nature of the substrate greatly influenced the nature of the *in situ* deposited films. It is reported that the films deposited on a hydrophilic glass surface have much higher resistivity than those deposited on a hydrophobic glass surface [66, 126]. Glass fabric coated with PPy by vapor phase polymerization exhibits reasonable electrical conductivity and electrical stability, and is effective in heat generation [12].

6.7.9 Other Fibers

A conducting polymer composite is prepared by the *in situ* polymerization of pyrrole on a polyacrylonitrile (PAN) matrix [128]. Also, PPy is successfully coated on aramid fibers [65] and Lycra fibers [69] by vapor phase polymerization, and a conductivity of the order of $10^{-3} \text{ S cm}^{-1}$ is obtained in the case of the aramid fiber. It is shown that when chitosan is coated with

PPy, the electrical and thermal properties of the resulting composite are improved [129]. PPy is successfully coated on individual palmyra fibers, which show an average electrical resistivity of $2.96 \text{ k}\Omega \text{ cm}^{-1}$ with good electrochemical response [130]. Composite films and nanofibers of polyurethane (PU)/PPy are successfully prepared for the purpose of combining the properties of PU with PPy [119]. The conductivity of the resulting composites increases with an increase in PPy content. The conductivity of the order of $10^{-5} \text{ S cm}^{-1}$ is obtained in a PU/PPy film containing 20 wt.% of PPy. It has been reported that CP/CCG (chemically converted graphene) composites can be prepared by *in situ* polymerization and solution mixing. The hybridization of CPs with CCGs provides composites with unique properties of both CPs and CCGs and also induces new properties and functions based on synergetic effects [131].

The chemical interaction between PPy and different fibers (e.g., cotton, wool, silk, polyester, etc.) leads to improved fixation of PPy on these fibers. It is evident that the adsorption of PPy on the textile surface is a complex phenomenon, which is governed by various substrate parameters such as hydrophilicity/hydrophobicity of the fiber, intermolecular interaction with PPy, and surface texture of the fiber [48].

6.8 Effect of Various Yarns and Fabrics as Substrate

Chemical oxidative deposition of conductive polymers onto different kinds of fibers, yarns, or fabrics yields new composite materials that are expected to have potential use in various fields [48, 78, 132]. An attempt is made to prepare electroconductive yarns by *in situ* chemical and electrochemical polymerization of pyrrole onto cotton, polyester, and cotton/polyester blended ring spun yarns [82, 110, 133, 134]. The cotton yarn shows less resistance than the polyester yarn. It is reported that the physical properties of yarns such as hydrophilicity, surface morphology, shape factor, yarn twist, and linear density influence the thickness of the coating [48, 63]. Najar *et al.* found that porous and bulky wool yarns having less twist show better conductivity than wool yarns having a compact structure with a higher twist [61]. This result is attributed to the more open and bulkier structure of wool yarn at lower twist levels, enabling better penetration of the FeCl_3 and pyrrole between the fibers, hence giving rise to a more extensive polymerization. Continuous *in situ* vapor polymerized PPy-coated electroconductive cotton rotor yarn exhibits lower resistivity than the ring wool yarn and the nylon 66 continuous filament yarn [63]. It is suspected that this lower electrical resistance of cotton yarn is due to

the lower resistance of uncoated cotton yarn than wool yarn. However, information on the *in situ* chemical polymerization of cotton rotor yarn is lacking, although rotor yarn has significant potential in various applications. The electrical resistivity of PANi-coated fabrics is greatly influenced by the nature of the fabric structure and the number of yarns in the fabric [135, 136]. The structure that has a number of interlacement points can take only a fewer number of polymers and results in poor conductivity. On the other hand, a lesser number of interlacement increases yarn float length, which increases the conduction path in the fabric. Also, the increase in pick density reduces the surface resistivity by increasing more conduction path for the flow of electric charge. The change in surface resistivity with the increase in thread density of plain, twill, and satin fabrics is shown in Figure 6.16 [135]. The twill fabric shows lower electrical resistivity than the satin fabric, although it has higher interlacement points. This may be due to the firmness of the twill fabric structure compared to the satin structure, which helps in better conduction. In another study, a knitted fabric treated with PPy is used as a fabric resistor and the effect of stitch parameters on the quality of the intra-fabric connection is investigated [137]. In another study, conductive fabrics are prepared by weaving PPy-coated polyester yarns by Romero *et al.* [138]. They found that the untwisted yarns and satin fabrics that have a porous and open structure give the most satisfactory results with higher conductivity. Regarding fabric substrates, most of the studies are carried out on woven and knitted fabrics [112, 116, 137, 139]. It has been concluded that nonwovens fabrics such as needle punched and

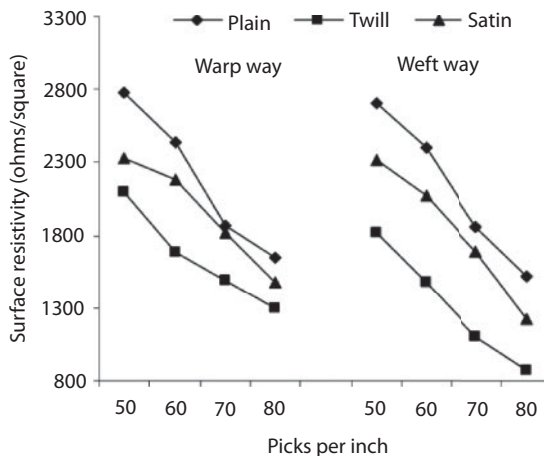


Figure 6.16 Surface resistivity of PANi-coated fabrics [135].

spunlaced might give superior conductivity compared to woven and knitted fabrics due to their porous and bulky structure [140, 141].

6.9 Applications of Electroconductive Textiles

Although there are plenty of reports on the preparation of various types of conducting textiles and their applications, in practice, very little has been achieved as far as the real application of the conductive textiles is concerned. However, some of the important applications of textiles will be discussed here, which have not been reported in the literature until now.

6.9.1 Application of Electroconductive Textiles for Heat Generation

A resistor can generate heat when it is connected to an external voltage supply. This phenomenon of heat generation is well explained by Joule's law. An electroconductive textile material can act as a resistor with a certain level of electrical conductivity to generate heat through Joule's effect.

An electrical conductor requires a moderate electrical resistivity for effective Joule's effect on heat generation. A highly conductive metal with very low resistivity does not produce heat during the passing of electric current through it. That is why metal is blended with insulating textile fibers by various means to develop resistive electroconductive composite yarns or fabrics for heat generation [11–13]. A stainless steel multifilament blended carbon yarn is produced with moderate resistance for a suitable application of heat generation [18, 19]. It is found that this kind of electroconductive yarn/wire exhibits particularly brittle characteristics and poor bending properties that are not suitable for textile applications [24]. In this regard, a flexible knitted fabric made of silver and elastomeric yarn can generate sufficient heat to warm the body. This fabric can be used to manufacture personal heating garments that can generate heat by applying external voltage [15].

Conductive polymers such as PPy, PANi, PPy, PTh, etc. are coated/applied on the surface of textile yarns/fabrics by various means to prepare electroconductive composites. These non-metallic polymeric composites are found to be suitable for potential application of heat generation. Compared to other heating materials, the advantages of these heating fabrics are their temperature homogeneity, low power density on a large surface area, lightweight, and their suppleness and fineness. They can be

sewed up, cut off, or pasted on substrates for a large range of applications [142, 143].

Dall'Acqua *et al.* have prepared textile composites by embedding PPy in natural and manmade cellulosic fibers, such as cotton, viscose, cupro, and lyocell, by *in situ* vapor phase polymerization, and they are found to be suitable for application of heat generation [68]. In another study, PPy is incorporated in cotton woven fabrics, and various properties such as anti-static, antimicrobial, and heat generation are investigated [84]. A possible application of the PPy-coated composite fabric is demonstrated as heating devices, as shown in Figure 6.17 [139]. A square-shaped fabric (6 cm $\times$ 6 cm) is positioned between two pressed electric contacts. The temperature rise is measured using an Omega infrared thermometer, placed at the center of the sample.

The temperature–current (T – I) and voltage–current (V – I) characteristics of this textile composite are shown in Figure 6.18. The T – I characteristic follows an exponential trend and the V – I characteristic follows a power law. According to the power law, the maximum theoretical power achieved from the fabrics is $P = VI$, where P is the power developed and V and I are the voltage and current, respectively. In Figure 6.19, the power and the impedance as a function of current are shown.

In another study, when a constant voltage of 9 V is applied to a cotton/PPy fabric for 10 min, its surface temperature rises up to 90°C, and for many numbers of repeating cycles, the performance of the fabric does not deteriorate [84]. Similar observations are also made by Maity *et al.* in the case of PPy-coated polyester woven and nonwoven fabrics prepared by *in situ* chemical polymerization [140]. The voltage–temperature (V – T) characteristic of the PPy-coated needle punched nonwoven fabric is shown in

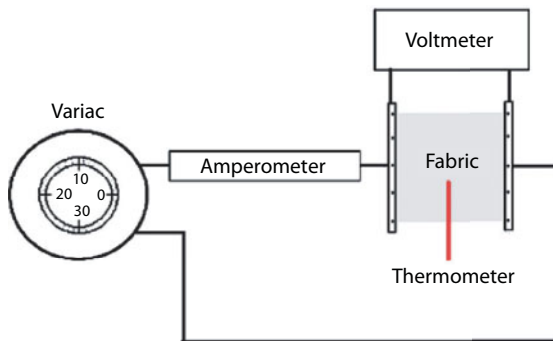


Figure 6.17 Experimental setup diagram for measuring the heating effect of a textile composite [139].

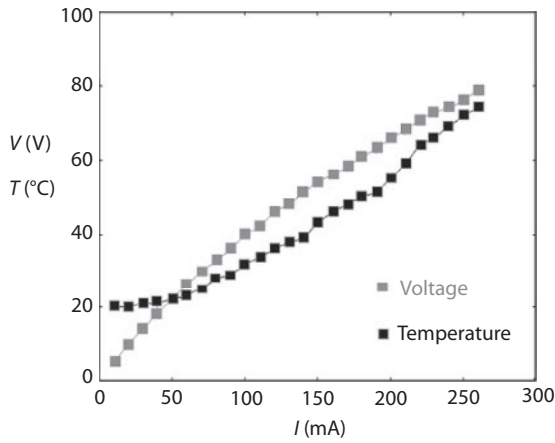


Figure 6.18 Behavior of the voltage and temperature of the PPy-coated sample as a function of the current [139].

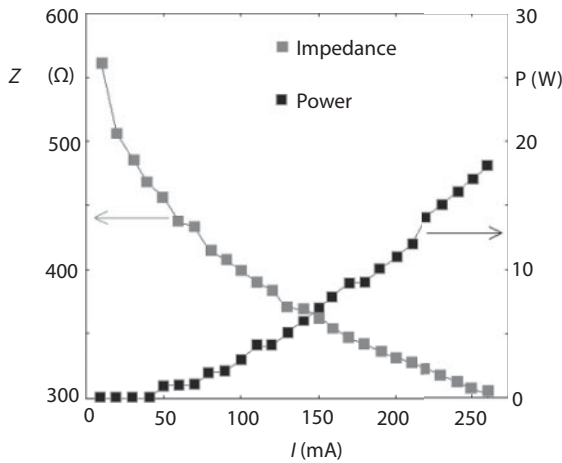


Figure 6.19 Behavior of the impedance and power developed by the PPy-coated textile composite as a function of the current [139].

Figure 6.20. Initially, the temperature increases sharply with time at a fixed applied voltage and then levels off at a particular temperature. These conductive fabrics can be used as heating pads, which are more comfortable to wear than metal-incorporated fabrics.

The V - T characteristics of the fabrics follow an exponential trend in the form of $T = ae^{bV} + C$, where T is the measured temperature and a , b , and c are coefficients, exponent, and constant, respectively [140]. The

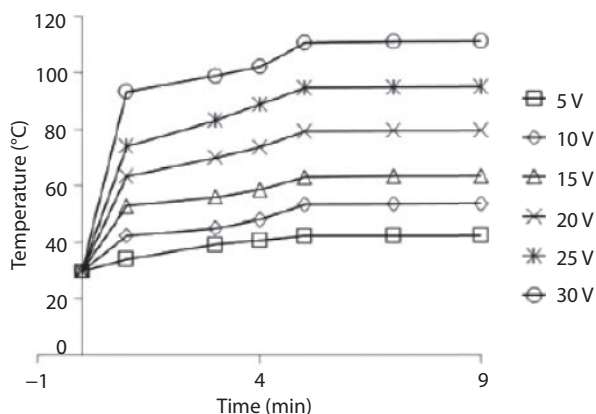


Figure 6.20 Voltage–temperature characteristics of PPy-coated polyester needle punched nonwoven fabric [140].

V – T characteristics of viscose/PPy fabrics prepared by *in situ* vapor phase polymerization with different FeCl_3 concentrations are fitted with exponential trend of the equation $T = T_0 + ae^{-kV}$, where V is the applied potential, T_0 is the initial temperature, and T is the final temperature.

The resulting current–voltage characteristic of the viscose fabric prepared by *in situ* vapor phase polymerization depends on FeCl_3 concentration. It shows a linear trend until the FeCl_3 concentration of 9 g L^{-1} and an exponential trend for higher FeCl_3 concentrations as shown in Figure 6.21 [68].

It is suggested by Sparavigna *et al.* and Macasaquit and Binag that 100% polyester/PPy conductive fabrics are practically useful for many applications, including flexible, portable, surface-heating elements for medical or other applications [112, 139]. PPy-coated polyester/Lycra woven composite fabrics exhibit reasonable electrical conductivity, and effective heat generation reaches 40.55°C at 24 V [91, 116]. For all these composites, the rate of change of temperature has two distinct phases, an initial sharp rise followed by a leveling-off to plateau, similar to cotton/PPy composites [144]. Rodriguez *et al.* have observed that the electrical resistivity and heating effect of PPy composites depend on the doping anion present, whether it is chloride (Cl^-) or other [145]. A nylon/PPy composite fabric with an electrical resistance of $5 \text{ } \Omega/\square$ is prepared by sequential HTHP chemical and electrochemical polymerizations [121]. The surface temperature of this fabric is increased very quickly from room temperature to about 55°C within 2 min by the application of a commercial battery of 3.6 V. The

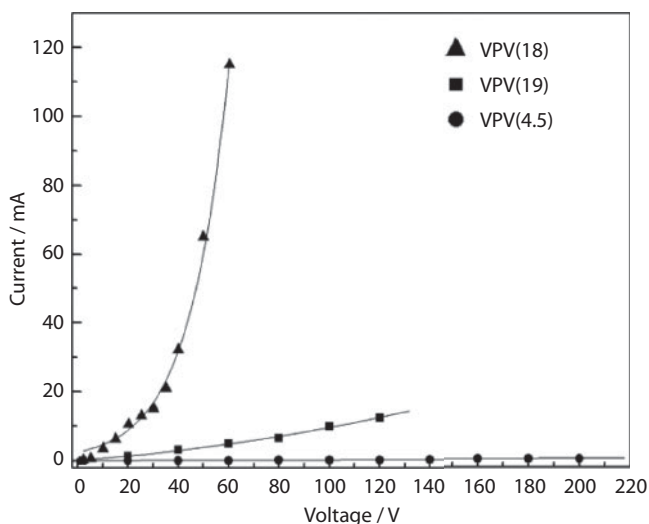


Figure 6.21 Plot of temperature versus applied voltage for different vapor phase polymerized samples [68].

heat-generating property of fabric is stable for at least 10 repeated cycles [121]. A PPy-coated E-glass fabric exhibits reasonable electrical stability and is found to be effective in heat generation. By application of a constant voltage across the fabric, the surface temperature increases whereas power consumption is found to decrease [146]. Silk/PPy electroconductive composites are also prepared for the application of heat generation [95, 147]. The PPy-coated polyester woven, spunlaced, and needle punched nonwoven fabrics displayed an exponential rise of surface temperature on application of voltage, and the rise of temperature was found to be related to the time duration of the applied voltage [140]. The electroconductive fabrics would heat up quickly and reach a stable temperature that was very suitable for application as a heating garment or heating pad.

6.9.2 Applications of PPy-Based Electroconductive Textiles as Sensor

CPs have attracted interest in their applications due to their special properties (e.g., tailoring electronic properties, controllable electrical conductivity, low cost, and high-yield synthesis). Their sensitivity toward various exterior stimuli, such as strain, pH, humidity, temperature, etc. opens up many possibilities of sensory applications such as investigating applied

structural strain, pH, organic molecules, pollutant gas, and low concentrations of metals in water [148].

6.9.2.1 Strain Sensor

Electrically conductive fibers/yarns/fabrics are promising materials for flexible conductive sensors because of their sensitivity to strain. According to Wang *et al.*, electrical resistance of PPy-coated Lycra fibers increases nonlinearly with the strain, up to a strain of 0.5. At the beginning, the resistance increases slowly; after a strain of 0.2, there is an obvious change in electrical resistance, as shown in Figure 6.22 [69]. A PPy- and PEDOT-coated textile composite prepared by sequential chemical and electrochemical polymerization exhibits a monotonic increase of the electrical resistance with an elongation of up to 50%. This elastic textile composite can be used as a strain sensor for large deformation [149]. In another study, changes in conductivity of PPy-coated Spandex/nylon fabrics with repeated fabric extension are investigated to improve the properties of conductive pad material used for electrotherapy when it is subjected to various movements of the human body [122]. The electrical resistivity of four different PPy-coated yarns of different liner densities responds dissimilarly upon application of tensile strain as shown in Figure 6.23 [82]. The yarns also responded well due to the application of twist in the yarn structure. The strain sensitivity is found to be better in the case of the finer yarn for both strain and twist applications. In another study, the fabric conductivity

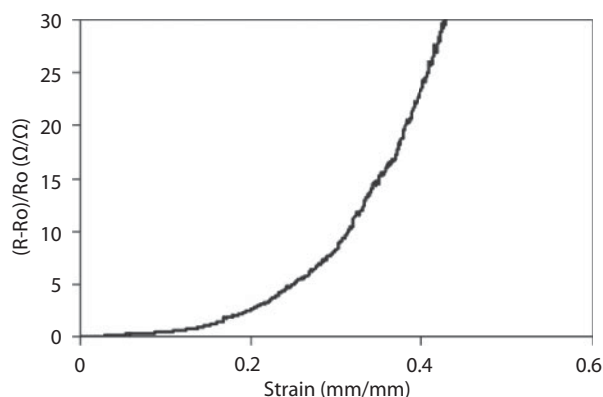


Figure 6.22 Typical resistance versus strain curve of PPy-coated Lycra fibers [69].

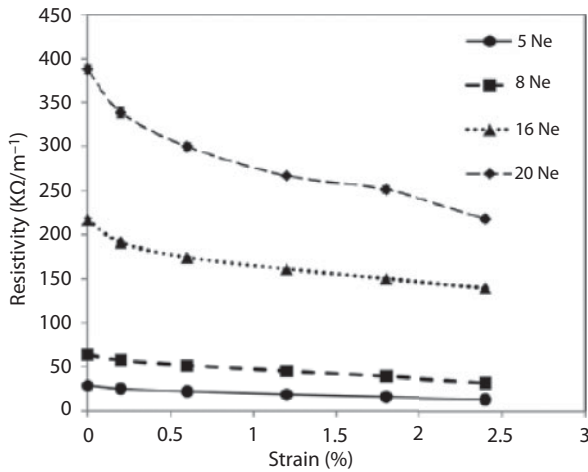


Figure 6.23 Effect of tensile strain on electrical resistance of PPY-coated cotton yarns [82].

increases as the fabric is stretched up to 50% extension and then leveled off as shown in Figure 6.24. An initial increase in conductivity is obtained based on the fact that the surface interval between two electrode probes is reduced by de-crimping and de-twisting of covering yarns with fabric extension. Moreover, it is probably due to a progressive increase in the number of contacts and the area contacting the bundles of fibers since fibers are closely rearranged as the applied load increased.

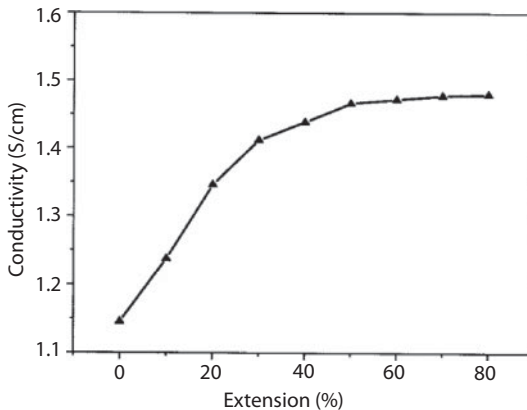


Figure 6.24 Change of PPY-coated Spandex/nylon fabric conductivity with extension [122].

As the number of repeated extension cycles is increased, the fabric conductivity is hardly decreased and well maintained at 40% extension [122]. A PPy-coated nylon fabric is demonstrated to measure urine volume in patients with urinary bladder dysfunction. This fabric, when placed around a phantom bladder, produced a reproducible change in electrical resistance on stretching. The resistance response to stretching is linear in 20%–40% strain variation [150]. Another strain sensor is fabricated on a natural rubber substrate coated with a very thin layer of PPy, using the vapor phase polymerization technique in a vacuum environment. This sensor can measure large strain with a gauge factor of up to 1.86 [151]. Wu *et al.* suggest that conducting polymer-coated Lycra fabrics can be integrated into truly wearable clothing and garments to create strain sensors with a wide dynamic range [41].

PPy-coated PA-6 fibers exhibit an increase in electrical resistivity as strain increases and even at a higher rate of increment of electrical resistivity observed at higher strain rate as shown in Figure 6.25 [67]. Also, the conductive polymer-based sensor is used to measure the strain deformations of a lightweight nylon fabric [152, 153].

6.9.2.2 Gas Sensor

The active layers of conductive polymers and their derivatives have been explored as gas sensors since the early 1980s [154]. The conductive polymers or polymer-coated substrates show rapid changes in electrical conductivity upon exposure to various gases/vapors at room temperature. This behavior of the polymer makes them suitable for application as a gas sensor.

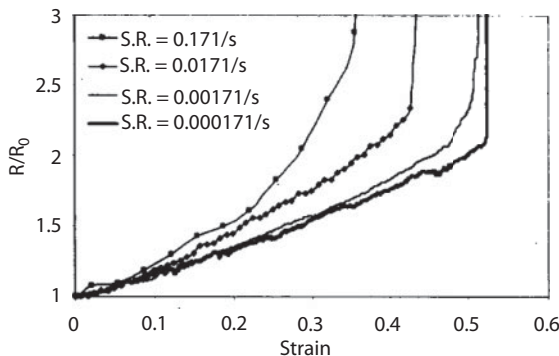


Figure 6.25 Effect of strain and strain rate on electrical resistivity of PPy-coated PA-6 fibers [67].

In comparison with most of the commercially available sensors, which are usually based on metal oxides and operate at high temperature, the sensors made of conductive polymers have many advantages. Their conductivity is highly sensitive to many chemical vapors at the parts per million levels or less through several different mechanisms including doping/dedoping, reduction/oxidation, and hydraulic conductivity [155–159].

PANi is a promising polymer for detecting chemical agents that produce strong acids upon hydrolysis. Conversely, the protonated emeraldine salt of PANi can be used to detect basic vapors (e.g., NH_3 or organic amines). These gases/vapors can deprotonate the polymer and decrease its conductivity [160, 161]. Nicho *et al.* reported that the PANi-coated PMMA substrate is sensitive to even very low concentrations of NH_3 gas of less than 10 ppm [161]. Acrylic acid doped PANi is also explored as an ammonia-vapor sensor over a broad range of concentrations of 1–600 ppm [162]. PANi films are also used as NO_2 sensors [163]. Amine-PANi nanofibers are prepared by Virji *et al.* for the detection of H_2S gas [164]. Also, PANi nanofibers that are deposited on gold and platinum electrodes are used as resistive sensors for the detection of H_2 gas [165]. The sensitivity of the platinum-PANi nanofiber sensor to hydrogen (<10 ppm) has been found to be much greater than that observed for the gold-PANi nanofiber. Boron trifluoride etherate doped PTh has a highly sensitive response to NH_3 of 50 mmol/L sensor [166].

Real-time detection of explosives [e.g., 2,4,6-trinitrotoluene (TNT)] in a complex environment containing various interferents has been a great challenge. Many gas sensors have been developed, including fluorescence and electrochemical sensors. Yang and Swager explored poly(phenylene ethynylene) for detecting TNT [167]. This process involves electron transfer from the photo-induced excited state of the electron donor poly(phenylene ethynylene) to the electron acceptor TNT. Amplifying fluorescent polymers show very high sensitivity to quenching TNT via a photo-induced electron-transfer quenching mechanism. This sensitivity of fluorescence quenching is due to a combination of interchain and intrachain excitation transport in thin films [167]. Some other CPs have also been used to detect TNT and other nitro-aromatic explosives [168, 169]. PPy also stands out as an excellent gas sensor due to its high conductivity and good environmental stability [170, 171]. PPy thin films are synthesized *in situ* by chemical polymerization for investigating their sensing behavior toward NH_3 and NO at room temperature. For reducing gases like NH_3 , the resistance of the films increases upon exposure to the gas and decreases for oxidizing gases such as NO. It is reported that these films are selective for NH_3 , and the sensitivity exhibited a linear response in the 4–80 ppm range [172], as

shown in Figure 6.26. The response/sensitivity of the PPy film is defined by Equation 6.1.

$$\text{Response / Sensitivity} = \frac{\text{Resistance}_{\text{gas}} - \text{Resistance}_{\text{air}}}{\text{Resistance}_{\text{air}}} \times 100\% \quad (6.1)$$

The higher response toward NH_3 as compared to NO and humidity can be explained on the basis of different interactions between an active layer and adsorbed gas. PPy is a p-type material, and when it interacts with reducing gases such as NH_3 , there is a reduction in the charge carrier density. Since the majority carrier (holes) density is decreased due to the electron-donating nature of NH_3 it results in decreasing the conductivity of the material. In the case of oxidizing gases such as NO, there is an increase in charge carrier concentration, since NO is electron-accepting in nature and the conductivity of the material increases. Chitte and co-workers synthesized PPy in the pure form and doped with LiClO_4 , PTSA, and NSA for NH_3 sensing. The NH_3 sensitivities reported by them are 0.54, 1.28, 2.08, and 2.86 for pure PPy, PPy/ LiClO_4 , PPy/PTSA, and PPy/NSA, respectively [173]. In another work, the sensitivity of the pristine/PPy film and PPy/ Fe_3O_4 composite films to NH_3 is investigated. It is found that the improved sensing stability and reduced response time can be obtained through the addition of Fe_3O_4 particles into the PPy [174]. Highly functionalized PPy films have been produced by incorporating phenylalanine in the PPy backbone by emulsion polymerization for detection of NH_3 gas [175]. Thin PPy films are produced on glass and ITO surface and characterized for sensing

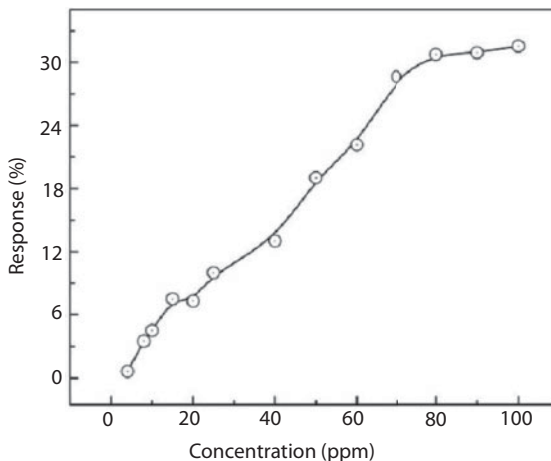


Figure 6.26 Sensor response as a function of NH_3 concentration [172].

various volatile compounds [127, 176]. PPy-coated textile fabrics are prepared with varying surface resistivities and are studied for their gas sensing capabilities by monitoring conductivity changes. A reversible change in conductivity is observed when these fabrics are sequentially exposed to NH_3 and HCl gases. When HCl is replaced with CO_2 , a twofold decrease in conductivity is observed [177]. Water-soluble PPy is synthesized and found suitable for trimethylamine and other gas sensors [178].

It is revealed that PPy-ZnO nanocomposites with different ZnO weight ratios (10%, 20%, 30%, 40%, and 50%) could detect NO_2 at low concentration with very high selectivity and sensitivity at room temperature. The sensing mechanism of PPy-ZnO nanocomposites to NO_2 is presumed to be the effects of the p-n junction between PPy and ZnO [179].

In another work, PPy is used as a sensitive membrane for detecting aerosol particles optically. A polymer optical fiber reflectance probe is constructed by depositing the PPy nanofilm at the end face of the fiber. The sensor principle relies on the change in the refractive index of the PPy nanofilm upon its interaction with aerosol nanoparticles and on the electrostatic induction between aerosol particles and the PPy nanofilm, which leads to a change in the reflected intensity. The fabricated fiber optic reflectance probe using the PPy nanofilm shows distinct variations in the reflected light intensity depending on the type of aerosol particle, such as NaCl, black carbon (BC), polystyrene latex (PSL), etc., and its properties. The proposed sensing approach may promote the use of conductive polymers in optical techniques for the detection of atmospheric aerosols [180].

6.9.2.3 *pH Sensor*

Conductive polymers possess acidic and/or basic groups that can be protonated or deprotonated. Deprotonation of these polymers results in a decrease of charge carriers along the polymer chains and is accompanied by changes in electrical and optical properties [159]. The protonation enhances the conductivity of PPy, whereas deprotonation leads to a lower conductivity. The sensitivity of PPy-coated PET fabric toward pH has also been reported [109, 133]. An increase in the pH of the environment causes a decrease in the doping level due to the release of a part of the counter ions and an increase in the surface resistivity. Therefore, as basicity of the environment increases, the resistivity of PPy-coated textiles increases. However, after a certain level of basic pH, the resistivity of the fabrics increases drastically [133]. In another study, the change in optical property of the PPy film with pH is studied and results are shown in Figure 6.27 [181].

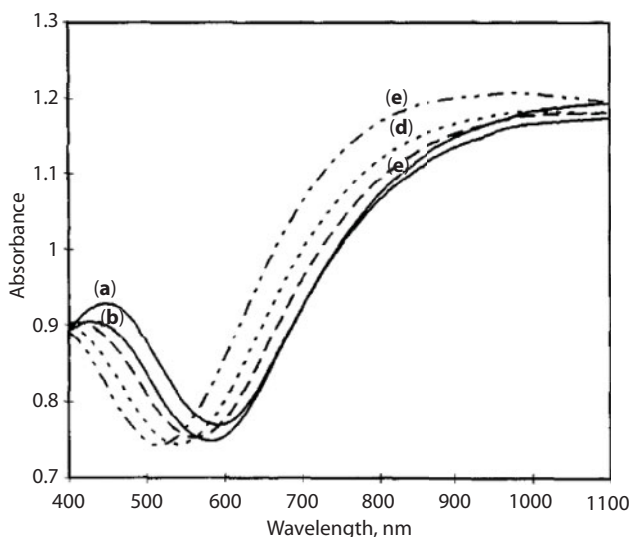


Figure 6.27 pH dependence of the absorption spectra of a PPy film: (a) pH 3.0, (b) pH 6.0, (c) pH 7.0, (d) pH 9.0, and (e) pH 11.0 [181].

On increasing the pH from 6 to 12, the absorbance between 600 and 900 nm increases, while the minimum is shifted from 600 nm (at pH 6) to 500 nm (at pH 12). In the same wavelength range (600–900 nm), a slight decrease in absorbance but no shift in the spectrum is observed when going from pH 3 to pH 6. The maximum which appears at around 400 nm is also shifted to shorter wavelengths when the pH is increased from 6 to 12. Lakard *et al.* compared five potentiometric pH sensors based on thin CP films, which are obtained from electropolymerization of their respective monomers (i.e., 1,3-diaminopropane, diethylenetriamine, pyrrole, *p*-phenylenediamine, and aniline) [182]. They chose these monomers since they contained amino groups, which are sensitive to proton-concentration changes. Their potentiometric responses appear to be linear in the range of pH 2–11. These sensors present good reversibility and good stability over a period of 1 month [182]. Chatterjee *et al.* proposed that PPy-coated palmyra fibers are good enough for possible application as a pH sensor [130].

6.9.2.4 Humidity Sensor

Humidity affects the conductivity of the PPy-coated fibers. The electrical resistance of PPy-coated PA6 fibers increases gradually when the relative

humidity increases from 40% to 85% at 25°C. A linear relationship with a small slope can be assumed between the electrical resistance and the relative humidity within this range [67]. Moisture sensitivity of different kinds of PPy-coated textile fabrics is shown in Figure 6.28. It can be seen that surface resistivity decreases as the moisture content of the fabrics increases, and sigmoid curves have been obtained for all kinds of fabrics [133].

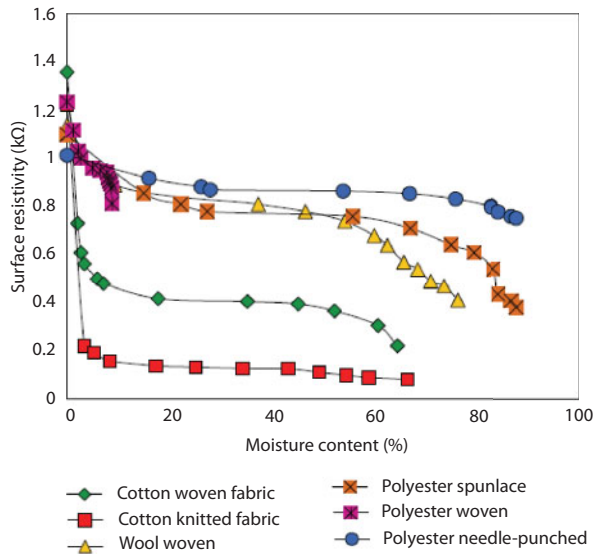


Figure 6.28 Effect of moisture sensitivity of PPy-coated textile fabrics [133].

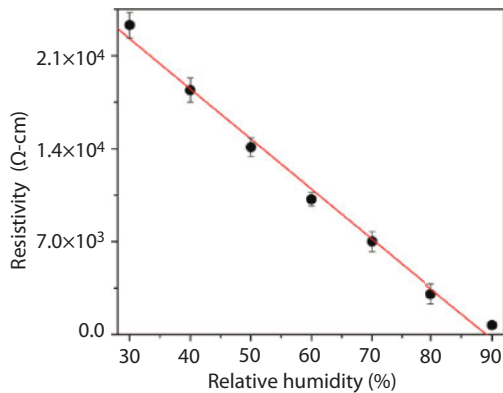


Figure 6.29 Resistivity of a PPy-coated cellulosic film as a function of humidity [98].

In another study, it has been observed that the resistivity of a PPy-coated cellulose film decreases linearly from 23.3 to 700 Ω cm as the relative humidity increases from 30% to 90%, as shown in Figure 6.29 [98].

6.9.3 Applications of Electroconductive Textiles for EMI Shielding

Electromagnetic interference (EMI) shielding is a process of restricting the penetration of electromagnetic waves into a medium or object by blocking them by a barrier made of electroconductive material. It is a very popular method of protecting electronic and electrical equipment and even humans against electromagnetic radiation. The barrier or protector that protects a body, environment, or a circuit from harmful electromagnetic radiation is called a shield. It is well known that exposure to long-term or acute electromagnetic radiation can have harmful effects on human tissue [181–188]. Furthermore, electromagnetic radiation can interfere with certain bio-electronic devices, such as pacemakers [189] and affects the lives of people. The recent proliferation of electronic devices, such as cell phones and computer equipment, which emit low levels of electromagnetic radiation, or interference, has significantly increased the problem and created a need for everyday shielding garments. In this regard, a variety of electromagnetic shielding composites have been produced to prevent electromagnetic radiations [190–193].

6.9.3.1 *Textile/Metal Composites for EMI Shielding*

Various approaches are available in the literature regarding the preparation of textile/metal composites for effective EMI shielding such as a surface coating of textile fabrics with metals, coating with ferromagnetic materials, inserting metal wires in textile structure, etc.

Textile fabrics have been coated with metals such as aluminum, copper, nickel, and silver, and a combination of them on an industrial scale to prepare electroconductive composites [190, 194, 195]. The coating methods used are electroless plating, laminating with aluminum foils, dying with copper sulfide, vapor deposition, etc. Electroless metal plating is a non-electrolytic method of deposition of metal from solution by oxidation and reduction [196]. This method has some advantages such as coherent metal deposition, excellent conductivity, and shielding effectiveness. It is also applicable to complex-shaped insulating textile materials [196]. Coated thin-film composites based on woven or nonwoven fabrics with

different surface properties have been prepared to have varied surface properties by varying the evaporation conditions during vapor deposition coating [197]. The shielding efficiency of these metalized textile fabrics mainly works via the principle of energy reflection and not its absorption. In many cases, such a phenomenon is not satisfactory, which leads to the search for materials with a greater capability of absorbing electromagnetic radiation. Also, different compositions of Cu/Zn/Sn-coated polyester nonwoven (CNW) and Ni/Cu-coated polypropylene nonwoven (SNW) show various EMI SE depending on incident frequency as shown in Figure 6.30. Coated CNW fabrics show higher EMI SE due to their higher thickness compared to coated SNW fabrics [198].

In recent years, some patents have appeared that deal with the production of textile composites with ferromagnetic properties. Such products can be applied as flexible screens for attenuating electromagnetic radiation, to produce cores in transformers, motors, generators, etc., and to produce filters to remove substances showing magnetic properties from air and water [190]. Nonwoven materials with ferromagnetic coating showed EMI SE of about 30 to 35 dB for a frequency range of 1000 to 2000 MHz [190]. Such materials are proposed for applications of camouflage in military objects, restricting the range of fields emitted by devices such as shortwave and microwave diathermy.

Textile materials embedded with metallic wires and fibers are also explored as EMI shield. Knitted fabrics form a good conductive network that can better stop electromagnetic radiation and achieve shielding

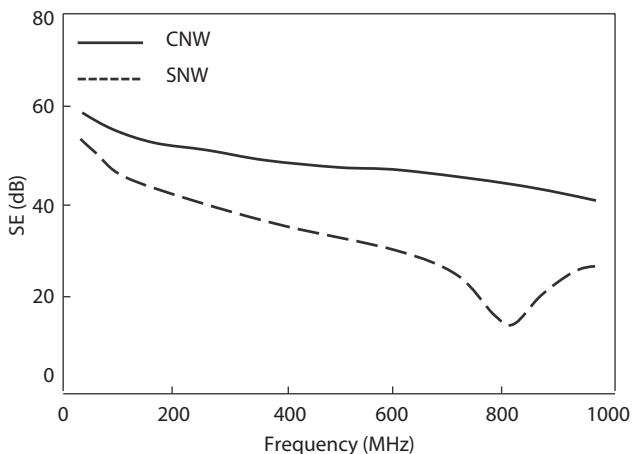


Figure 6.30 Shielding effectiveness of various metalized nonwovens [198].

effectiveness [199]. They have good impact energy absorption characteristics. Electroconductive composites are prepared by using polypropylene (PP) matrix and knitted glass fibers as reinforcements [200]. Copper wires are incorporated as conductive fillers into a knitted structure to provide the desired EMI SE in the composite structure. The EMI SE of these knitted composites is greatly influenced by the amount of copper, which can be varied by changing the knit structure, stitch density, and linear density of yarns used for knitting [21, 22, 200]. The copper and stainless steel wires are wrapped with polyamide filaments to produce a hybrid conductive yarn that is co-woven–knitted to produce fabrics for EMI SE [198]. The effect of single-layer and multilayer fabrics made of stainless steel/polyester (40/60) spun yarn on shielding effectiveness has been investigated and the results are shown in Figure 6.31. Here, a multilayer structure of various thicknesses and stainless steel (SS) fiber content are responsible for blocking the electromagnetic interference in a different frequency.

Also, polypropylene and polyamide filaments are wrapped in copper wire to produce conductive yarn. This yarn is utilized as warp and weft identically for manufacturing woven fabric to obtain isotropic shielding behavior [201]. It is observed that the EMI SE of these woven fabrics increases with the increase of copper wire content as well as with the density of warp or weft at all frequencies of incident radiation. The shielding effectiveness of these fabrics of a single layer is barely sufficient for general applications and the multilayers provide adequate shielding effectiveness (20–55 dB) when the wave is normally incident on the fabric of thickness

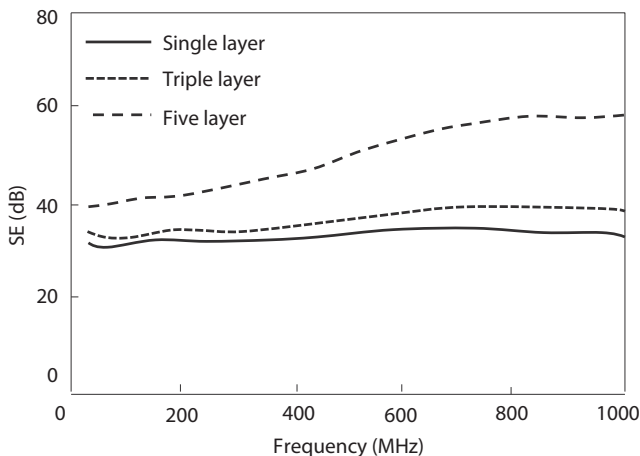


Figure 6.31 Shielding effectiveness of laminated SS/PET (40/60) woven fabrics [198].

higher than 1.6 mm. The EMI SE increases with an increase of fabric thickness as the number of conductive layers increases, as shown in Figure 6.32 [201].

6.9.3.2 Conductive Polymer-Coated Textiles for EMI Shielding

Coating of conducting polymers on insulating fabrics produces novel composites for potential applications of EMI shielding [115, 141, 193, 202–207]. Various composite textiles are prepared by coating different textile substrates, such as cotton, wool, viscose, cupro, lyocell, polyester, nylon, etc. with conducting polymers by means of *in situ* polymerization [34, 61–63, 65–69, 86, 113, 149, 208]. These composite textiles show better performance than metal fiber and filler composites, which are susceptible to galvanic corrosion or loss of conductivity due to friction [194]. The conducting polymers reflect less and largely absorb electromagnetic radiation [194]. It has been reported that textile fabrics coated with PPy by chemical polymerization are suitable for EMI shielding [25, 63, 193, 202, 208]. It is found that the electrical resistivity of an effective electromagnetic shield should be less than $100 \Omega/\text{cm}^2$ [209–211]. Muthukumar and Govindarajan reported that a PANi-coated polyester fabric of resistivity $5 \text{ k}\Omega/\square$ is suitable for EMI shielding [212].

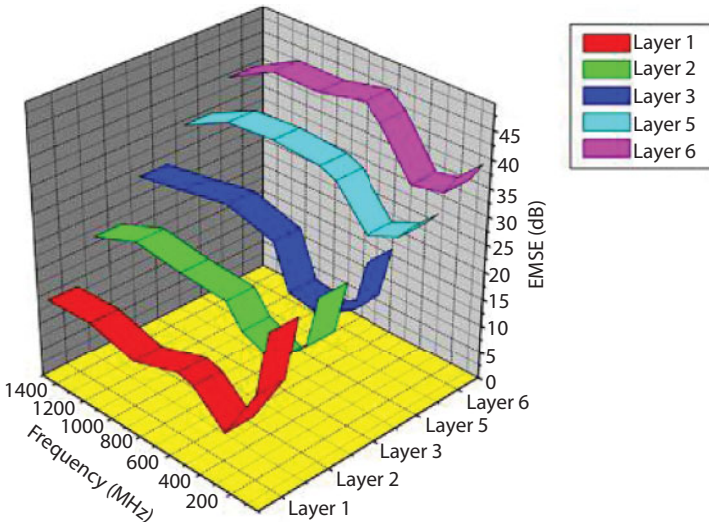


Figure 6.32 EMI SE of a woven fabric at various layers [201].

6.9.3.3 Conductive Polymer-Coated Woven Fabrics for Electromagnetic Shielding

The polymerization of aniline pyrrole and thiophene on insulating fabrics such as polyester, glass, and high silica cloth is carried out by *in situ* chemical polymerization [210]. In the radiofrequency range from 100 to 1000 MHz, conducting PANi-coated polyester fabrics show a shielding effectiveness in the 30–40 dB range as shown in Figure 6.33. The reflectance studies show that the PANi-coated polyester fabrics can absorb about 98% and can reflect only about 2% of the energy. In the case of PPy-coated polyester fabrics, 96% of energy is absorbed and 4% is reflected back, whereas in the case of the PTh-coated polyester fabric, 82% of the energy is absorbed and 18% is reflected back [210]. An effective shield should absorb all the energy and nothing should reflect back. The shielding effectiveness of the PPy-coated nylon/Lycra fabric prepared with an anthraquinone-2-sulfonic acid (AQSA) dopant is reported as 89.9% at 18 GHz [213]. In another study, PPy is polymerized chemically and electrochemically in sequence on a polyester woven fabric, for preparation of a composite with a very low electrical resistivity of $0.2 \Omega \text{ cm}$. The EMI SE of this composite is about 36 dB over a wide frequency range of up to 1.5 GHz, as shown in Figure 6.34. It can be seen that the composite restricts electromagnetic waves largely by absorption rather than by reflection. Overall, EMI SE increases with the decrease of electrical resistivity [115].

PPy films with high conductivity and good adhesion are prepared on the surface of insulating epoxy resin substrates using chemical polymerization.

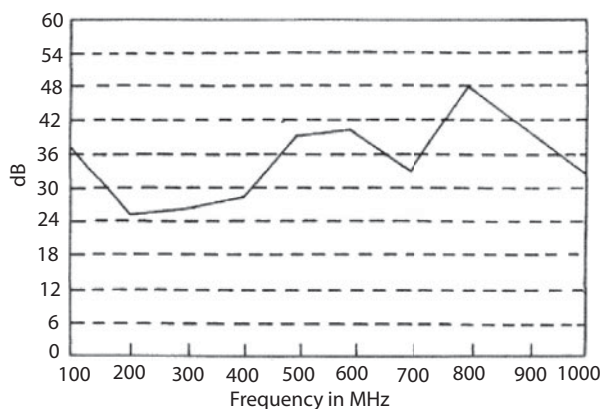


Figure 6.33 Shielding effectiveness of PANi-coated fabrics in the frequency range 100–1000 MHz [210].

Those films show EMI SE values of about 30 dB over a wide frequency range from 30 to 1500 MHz, as shown in Figure 6.35 [214]. PPy-coated polyester and silica fabrics show EMI SE values of 21.48 and 35.51 dB, respectively, at a frequency of 101 GHz [215]. PPy-coated glass fabrics having resistivity below $500 \Omega/\square$ exhibit 98.67% to 99.23% signal loss in the frequency range of 800–2400 MHz [208]. As the resistivity of these PPy-coated glass fabrics decreases, EMI SE increases, as shown in Figure 6.36. These fabrics are proposed for applications such as a shield for household appliances, FM/AM radio broadcast sets, wireless phones, cellular phones, computers, buildings, secret rooms, and various electronic gadgets that operate up to 2.4 GHz frequency [208].

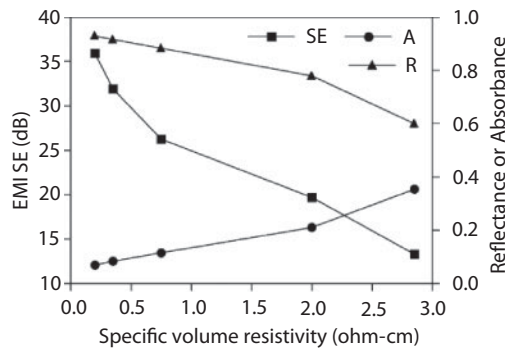


Figure 6.34 EMI SE absorbance (A) and reflectance (R) of PET fabric/PPy composites with various specific volume resistivities [202].

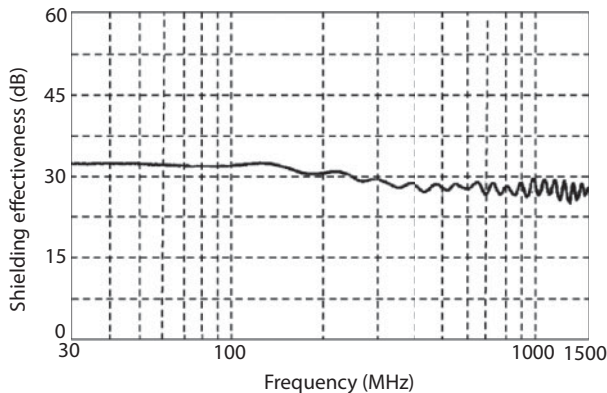


Figure 6.35 Shielding effectiveness of the PPy film [214].

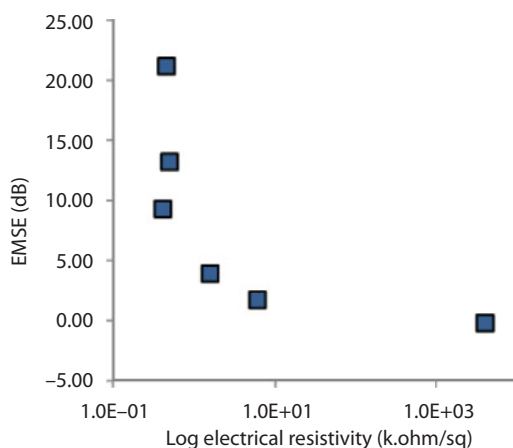


Figure 6.36 EMI SE of a PPY-coated glass fabric as a function of electrical resistivity [208].

In another study, silver (Ag) is thermally vacuum evaporated on the surface of PPY-polyester complexes. The EMI SE of fabric complexes increases as the area of Ag evaporation layer increases. When the Ag is partially (approximately 37%) evaporated on one side of fabric complexes, the EMI SE is 29 dB at 0.5 GHz, and while Ag is evaporated on the total area of the sample, the EMI SE obtained is 33 dB at the same frequency range [216]. The EMI shielding efficiency of the PPY-coated fabric prepared by the combined chemical and electrochemical method has been found to be about 98% [217]. In another study, PPY and Ag-coated nonwoven composites exhibit an EMI SE of 13–15.5 dB within the frequency range of 15–3000 MHz [218].

6.9.3.4 Conductive Polymer-Coated Nonwoven Fabrics for Electromagnetic Shielding

The EMI SE of PPY-coated hydro-entangled polyester nonwoven textiles is studied in the frequency range 100 to 800 MHz [107]. A positive correlation between the SE and the surface conductivity of these nonwoven textiles is found. An EMI SE of 37 dB was found for the sample with the lowest surface resistivity of $3 \Omega/\square$. In another study, PPY-coated polyester nonwoven composite fabrics show effective an EMI SE of 20 dB at 1 GHz frequency [219]. For these nonwoven fabrics, coating with Ag particles enhances the EMI SE up to 55 dB, and for multilayer complexes of these fabrics, EMI SE is about 80 dB. PPY-coated nonwoven fabrics are proposed

as an excellent radiofrequency and microwave absorber because of their high absorbance and low reflectance [69]. It is reported that PPy-coated textile fabrics with high conductivity showed reflection-dominant EMI SE and those with low conductivity showed absorption-dominant EMI SE [215]. The EMI SE of the PPy-coated polyester needle punched nonwoven fabric is reported as 20.07 dB at 4 GHz frequency. The surface resistivity of the coated needle punched fabric is found to be as low as $18 \Omega/\square$ with 16.28% PPy add-on [141]. The EMI SE values of some conductive textile materials proposed as an effective shield, as cited in the literature, are tabulated in Table 6.3.

6.9.3.5 Effects of Different Process Parameters on EMI Shielding

EMI SE values of the PPy-coated cotton fabrics at different FeCl_3 concentrations can be seen in Figure 6.37. For each concentration, the highest value is achieved at a frequency of 200 MHz. A remarkable decline in shielding values can be seen in the frequency range of 200–800 MHz. The shielding behavior of the samples shows an almost linear shielding effect between 800 and 1800 MHz. Afterward, a slight increase to 1800–2500 MHz and then a slight decrease to 300 MHz are observed [113].

The effects of the concentration of *p*-toluenesulfonic acid (PTSA) as dopant and polymerization time on the EMI SE of conducting polymer-coated textiles in the frequency range 1–18 GHz are investigated and results are shown in Figure 6.38. The levels of absorption are higher than the levels of reflection in all the tested samples and absorption is relatively even throughout the frequency range for different concentrations of dopants and polymerization times. Reflection increases with an increase in dopant concentration and polymerization time due to the increase in conductivity. The reflection values are more dispersive than the absorption, and at the long polymerization times, the reflection increases throughout the frequency range [204]. It is reported that the shielding effectiveness of the PPy samples prepared in the presence of surfactants markedly increases with surfactant concentration [223].

Chitosan (CHI), when used as an additive, can improve EMI SE, electrical conductivity, and thermal diffusivity of the PPy film [129]. The optimum concentration of chitosan for the best conductivity is 0.7% (w/v), but after that, the conductivity decreases with further increase in chitosan concentration. This is due to the fact that in the concentrations, more than 0.7% (w/v) of chitosan is a highly viscous solution, and for that, the rate of polymerization becomes very slow and the amount of deposited polymer is much lower, which led to low conductivity, as shown in Figure 6.39.

Table 6.3 Shielding effectiveness of various conductive textiles.

Material	Resistivity	Testing frequency	EMI SE (dB)	References
Metalized fabrics				
Metalized fabrics	–	100 kHz to 1 GHz	75–80	[190]
Copper and stainless steel wire Co-weaved/ knitted fabrics	–	100 kHz to 1 GHz	40–50	[198]
Metalized nylon	Surface resistivity $0.09 \Omega/\square$	800 MHz	67.04	[107]
Conductive polymer-based fabrics				
PPy blended hot melt adhesives	Linear resistivity $0.2 \Omega \text{ cm}^{-1}$	300 MHz	30	[220]
PPy-coated fabrics	Surface resistivity $3 \Omega/\square$	800 MHz	37.02	[107]
PPy-coated glass fabrics	Surface resistivity $460 \Omega/\square$	800 MHz	18.75	[208]
PPy-coated Twill fabric	Surface resistivity $40 \Omega/\square$	800 MHz	16.8	[107]
PPy/chitosan composite film	Linear resistivity $0.0145 \Omega \text{ cm}^{-1}$	1200 MHz	32.15–35.66	[129]
PPy-coated polyester fabrics	Volume resistivity $0.2 \Omega \cdot \text{cm}$	1500 MHz	36.6	[202]
PPy-coated polyester fabrics	Volume resistivity $0.3 \Omega \cdot \text{cm}$	1500 MHz	35 dB	[215]

(Continued)

Table 6.3 Cont.

Material	Resistivity	Testing frequency	EMI SE (dB)	References
PPy-coated polyester needle punched nonwoven fabric	Surface resistivity 18 $\Omega/\square$	4 GHz	20.07 dB	[141]
PPy or poly[3,4-ethylenedioxythiophene]-coated polyester woven fabric	Volume resistivity 0.3 $\Omega\cdot\text{cm}$	1500 MHz	36	[208]
PPy-coated cotton fabric	Surface resistivity 1.18 M $\Omega/\square$	2500 MHz	01	[113]
PPy-coated glass fabrics	Surface resistivity 460 $\Omega/\square$	2.4 GHz	21.16	[208]
Ag/PPy-coated fabric complex	—		80	[221]
PANi-coated polyester fabrics	Volume resistivity 10–60 $\Omega\cdot\text{cm}$	101 GHz	21.48	[210, 211]
PANi-coated silica fabrics	Volume resistivity 10–28 $\Omega\cdot\text{cm}$	101 GHz	35.61	[210, 211]
Boron and carbon fabrics	—	1200 MHz	30	[222]

6.9.4 Thermoelectric Effect of Conductive Polymer-Based Textiles

The thermoelectric effect is the direct conversion of heat energy to electric energy or vice versa. A thermoelectric device generates emf upon the creation of a temperature gradient. Conversely, when a voltage is applied to it, it creates a temperature gradient. A thermoelectric device consists of two wires of dissimilar materials connected together to form a closed

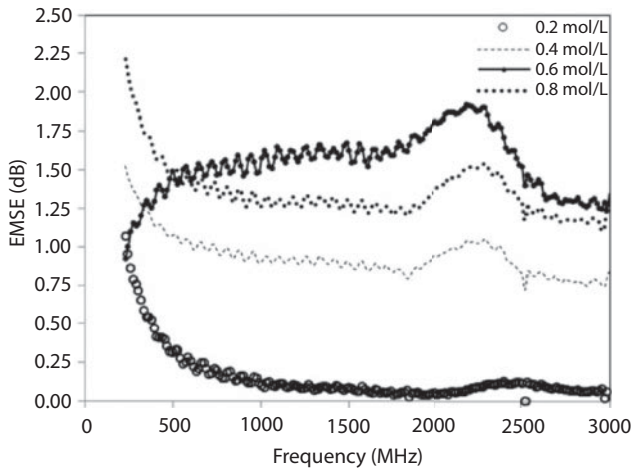


Figure 6.37 EMI SE of PPY-coated fabrics with various FeCl_3 concentrations [113].

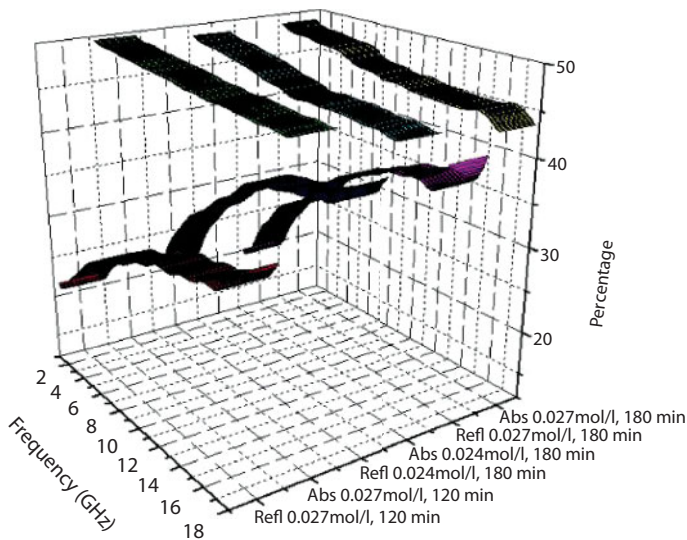


Figure 6.38 Reflection (bottom three) and absorption (top three) percentages for three selected samples. PTSA concentrations and polymerization times are indicated [204].

circuit, as shown in Figure 6.40. The thermoelectric device is also called thermocouple.

This phenomenon was discovered by Seebeck in 1821 and hence was called the Seebeck effect. He found that if two wires of dissimilar metals are connected, so as to form a closed circuit, then an emf is developed on

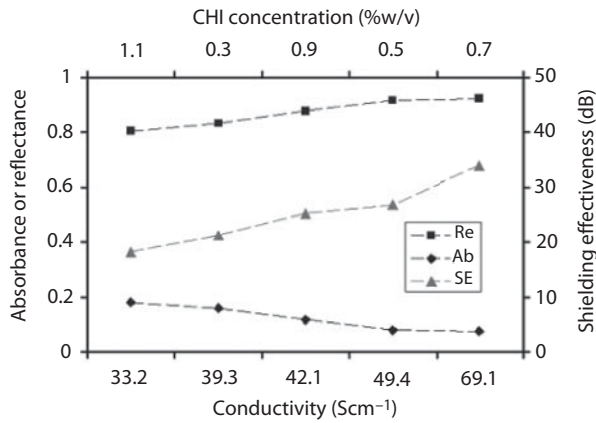


Figure 6.39 The shielding effectiveness (SE), absorbance (Ab), and reflectance (Re) of PPy-chitosan composite films with various electrical conductivities and different concentrations of chitosan [129].

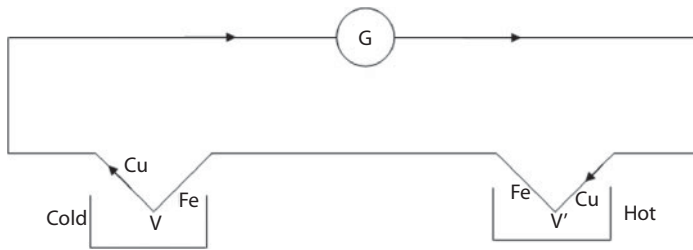


Figure 6.40 Fe-Cu thermocouple.

it and hence a current flows through it when junctions of two dissimilar metals are maintained at two different temperatures. The magnitude and direction of this current depend on the nature of the two materials used and on the difference of temperature between the hot and cold junctions. The emf generated in a thermocouple is called thermoelectric emf and the current is called thermoelectric current. Thermoelectric emf will exist and thermoelectric current will flow as long as there is a temperature difference between the two junctions.

Research on organic materials for thermoelectric applications has not been so attractive, probably because of their poor electrical conductivity, until the discovery of CPs. Some of these electrically conducting polymers have gained attention because of their considerable thermal stability. These materials, such as polyaniline and PPy, are considered suitable for

applications to electronic devices and sensors. For thermal sensors, a systematic investigation of thermoelectric performances of polyaniline and PPy is interesting. PPy is chemically synthesized on PET fabrics, giving rise to textiles with a low DC surface resistivity of $306 \Omega/\square$. PPy shows extremely low thermal diffusivities regardless of the electrical conductivity. The low thermal conductivity gives a significant advantage to the thermoelectric figure-of-merit ZT , comparable with that of some traditional inorganic thermoelectric materials [139]. The figure of merit is defined by Equation 6.2.

$$ZT = \left(\frac{S^2 \sigma}{k} \right) \quad (6.2)$$

where, S , σ , k , and T are the Seebeck coefficient, electric conductivity, thermal conductivity, and absolute temperature, respectively.

Thermoelectric Seebeck coefficient (S) and its temperature dependence are determined by fabricating a thermocouple connecting a strip of PPy/PET fabric with a copper wire [139]. The two materials are electrically connected by the pressure of a very small silver clip, insulated from the junction. The hot junction is placed in the thermostat with a reference chromel–alumel thermocouple, and the cold junction between PPy/PET strip and copper wire is thermally anchored at room temperature (26°C). The same anchoring is used at the cold junction of the chromel–alumel thermocouple. A diagram of the experimental setup is shown in Figure 6.41 [139].

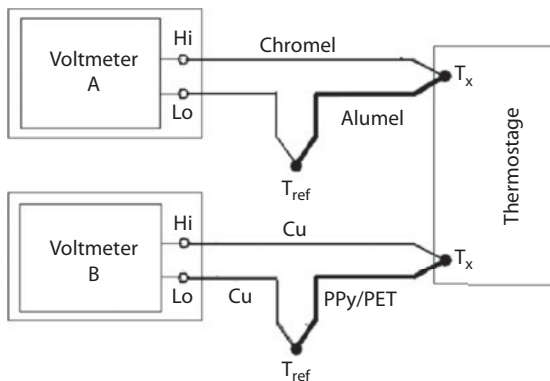


Figure 6.41 Diagram of the experimental setup for measuring the Seebeck effect of the PPy/PET-Cu thermocouple [139].

In Figure 6.42, the behavior of the electromotive force measured for two such PPy/copper thermocouples is given as a function of temperature difference ΔT between the actual hot junction temperature and room temperature.

In another study, the Seebeck coefficient and the electric conductivity of polyaniline and PPy at different doping levels are measured. It is found that at 300 K, the logarithm of the electrical conductivity varies linearly with the Seebeck coefficient as shown in Figure 6.43 [224].

According to Kelvin relations between Seebeck and Peltier coefficients, an evaluation of the Seebeck effect allows the estimation of the cooling power of a material. A study demonstrates that both the Seebeck and Peltier

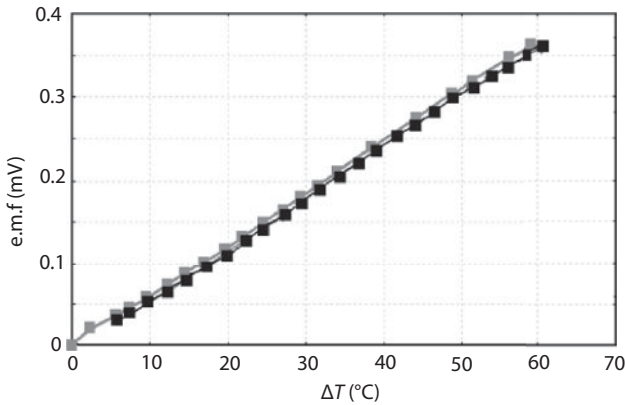


Figure 6.42 Electromotive force measured for a PPy-PET/copper thermocouple as a function of the temperature difference between the actual hot junction temperature and room temperature. The figure reports two different scanning in temperature [139].

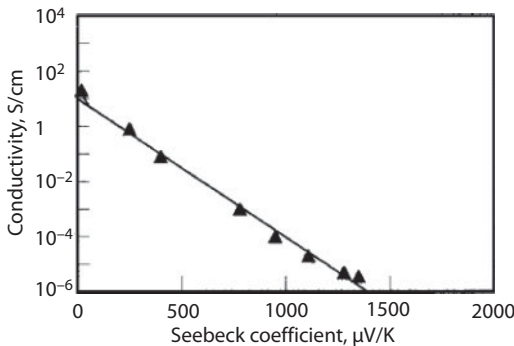


Figure 6.43 Log(conductivity) versus Seebeck coefficient [224].

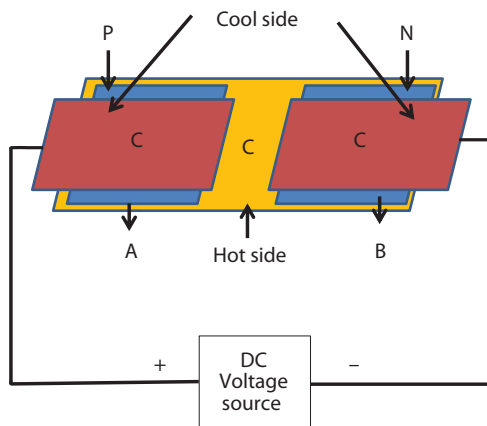


Figure 6.44 An experimental setup for cooling effect; (a) P-type conductive polymer fabric, (b) N-type MWNT composite material, and (c) copper metal plates [226].

effects can be achieved by using conducting polymer materials, so that it is possible to make a cooling fabric from conducting polymer-coated fibers.

The thermoelectricity effect between two conducting polymer-coated fabric samples is only about 10 V/°C. A cooling effect by conductive polymer powder is achieved but performance is unsteady due to electrical degradation of the conducting polymer [225]. Lee *et al.* fabricate active cooling e-textiles. P-type and N-type conducting polymer-coated textiles are used to study the Peltier effect. PPy is used as a P-type conducting polymer whereas a carbon nanotube is used as an N-type conducting polymer [226]. The experimental setup is shown in Figure 6.44.

A temperature difference of about 5°C has been achieved between the upper side and the lower side, as shown in Figure 6.45. The difference of temperature is quite low (about 5°C) because the thermal insulation between the layers is not operating well. To improve cooling effect, the potential energy between two materials should be elevated and heat transfer between the sides should be blocked by high insulation. In addition, if a higher conductive N-type and P-type material is developed, the cooling function by Peltier effect will be elevated.

6.9.5 Corrosion Protection by Conductive Polymers

Corrosion is the result of chemical reactions that occur between a metal or a metal alloy and its environment. Conductive polymers have been explored for corrosion-inhibiting coatings on metals. The conducting polymer coatings may be used as a component blended with conventional coatings

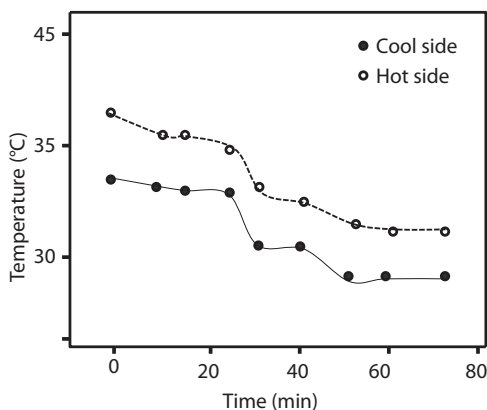


Figure 6.45 Peltier effect experiments with temperature versus time [226].

(nonconducting polymers, paints) or as primer coatings. Conductive polymer coatings exhibit more positive redox potentials than iron and aluminum. Thus, conductive polymer coatings protect these metals against corrosion [40]. PANi is electrodeposited on passivated steel in a strong acid environment, which enhances corrosion protection of the metal. PANi performs well in retarding corrosion of carbon steel [227]. PPy has also been studied for its corrosion protection. Poly(3-methylthiophene) is electropolymerized onto stainless steel and shows significantly improved corrosion protection in 1N sulfuric acid solutions [227].

6.9.6 Wastewater Treatment by Conductive Polymers

The composite of a conducting polymer shows considerable potential in the removal of heavy metals, color, and anions from paper mill wastewater and has the ability to reduce Chemical Oxygen Demand (COD). These composites have good repeatability in the performance of removing color, anions, heavy metals from waste water and reduce COD. [228].

6.9.7 Antistatic Properties of Conductive Polymer-Based Textiles

PANi and PPy can be used in industrial textiles to make them antistatic [25, 84, 85]. A PPy-treated polyester fabric gives better antistatic properties compared to a PANi-treated fabric [45, 84, 128]. The graphene-coated cotton fabric has been found to have excellent antistatic properties with 1.5 wt.% of graphene add-on, whose surface resistance and volume resistance were on the order of 10^5 and $10^3 \Omega$ [229].

Table 6.4 Antimicrobial properties of PPy-treated cotton fabrics [84].

Sample	Microbial reduction (%)		
	<i>Staphylococcus aureus</i>	<i>Escherichia coli</i>	<i>Candida albicans</i>
Cotton + PPy	64.86	59.14	73.07
Cotton + PPy + CuCl ₂	92.53	97.60	100.00

6.9.8 Antimicrobial Properties of Conductive Polymer-Based Textiles

A PPy-treated cotton fabric showed a 65% reduction of gram-positive bacteria, 59% reduction of gram-negative bacteria and 73% for a fungal culture, which are boosted by the addition of another antimicrobial agent, namely, CuCl₂, as shown in Table 6.4.

The mechanism of antimicrobial activities is suggested to be a due attack on the cell wall of the bacteria by the charged nitrogen and chloride ions of PPy. This is in accordance with the mechanism of antimicrobial activity of known agents such as quaternary ammonium salts and halamines due to the similarity in structure. However, an advantage of using PPy is that it is insoluble in water unlike quaternary ammonium salt and halamines; hence, its durability and regeneration ability are good [84]. The good antibacterial activity against *S. aureus* and *E. coli* has been observed by polypyrrole-coated cotton fabrics [230].

6.10 Durability Properties of Conductive Polymer-Based Textiles

6.10.1 Tensile Property

The mechanical properties (such as drapability, flexibility, and strength) of electroconductive polyester, polyamide, and cotton fabrics coated with a thiophene derivative (PEDOT) monomer are not significantly affected by the treatment. Polyester and polyamide showed almost no change in tensile strength (<1%). No significant reduction in tensile strength of PANi-coated PET fabrics is observed [118]. Also, the polymerization process does not affect the overall tensile performance of silk fibers, as shown in Table 6.5 [147]. However, in the case of cotton, a decrease in maximum

Table 6.5 Mechanical properties of untreated and PPy-coated silk yarn [147].

Parameters	Untreated yarn	PPy-coated yarn
Tenacity (g/den)	3.99 ± 0.16	4.09 ± 0.15
Elongation (%)	13.7 ± 1.3	13.2 ± 1.1
Modulus (g/den)	90.3 ± 4.9	85.5 ± 6.3
Energy ($\text{g} \times \text{mm}$)	6536 ± 1015	6222 ± 703

strength of about 20% is observed [9], and a slight increase in both the tenacity and elongation of the PPy-coated wool yarns is observed [61].

6.10.2 Launderability

Laundering of PPy-coated textiles causes a reduction in the conductivity of the textiles. Laundering conditions have a large effect on the level of deterioration caused. It has been reported that the best laundering conditions are low temperatures (40°C), low pH (less than 4), and in the presence of a sequestering agent. The use of detergents containing sodium carbonate and bleaching agents and/or working at neutral or alkaline pH should be avoided [231]. Fastness performances to washing, light exposure, and dry rubbing are found consistent for textile uses, while poor fastness has been observed to moist rubbing tests in the case of PPy-treated cellulosic fibers prepared by vapor phase polymerization [68]. Domestic washing of PPy-treated silk fabric causes a large decrease in conductivity, which dropped to about 30% of that of the control samples. The conductivity of the sample subjected to dry cleaning with CCl_4 remained essentially unchanged [147]. It has been reported that the fabrics made of PPy-coated wool fibers have an excellent resistance to organic solvents that are used during conventional dry cleaning treatments. However, the resistivity of the fabrics increases significantly after domestic laundering due to alkali doping of conducting PPy coating, as shown in Figure 6.46 [88].

6.10.3 pH Stability

The stability of electrical conductivity of PPy-coated polyester fabrics have been tested in a wide range of pH [1, 7, 13]. It has been found that the treatment with higher pH causes a decrease of the doping level as well as the release of part of the counter ions from the polymer matrix leading to increase in resistivity. In alkaline aqueous solutions, $-\text{OH}$ plays a key role

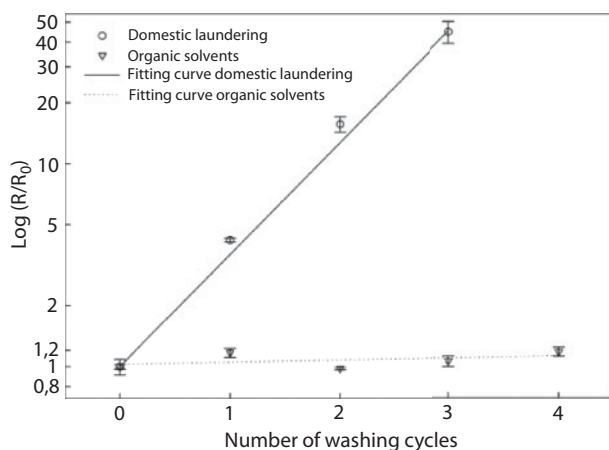


Figure 6.46 Logarithmic normalized resistivity ratio versus number of washing cycles [88].

in the dedoping process of PPy. Higher $-OH$ concentrations result in more dedoping. The $-OH$ ion exchanges with doping anions and the electrochemical activity decreases [232].

6.10.4 Environmental Stability

The scope of applications for these strong and flexible CP-based electroconductive textiles is somewhat limited by their instability due to conductivity loss upon exposure to the environment for a long time. The environmental stability of such electroconductive textiles depends on their exposure time, environmental condition, synthesis conditions, type of dopants, substrates, etc. [25, 80].

The conductivity of PPy-coated silk fabrics decays upon exposure to environmental conditions over a long period of time. Only about 10%–20% of the loss of original conductivity is observed after 2 years [147]. The resistivity of PPy-coated polyester fabrics is found to be increased by 12.56% after 18 weeks of atmospheric aging [140]. The atmospheric stability of PPy-coated fabrics prepared with low-temperature synthesis is found to be remarkably higher than that of the fabric prepared at room temperature [233]. The conductive PPy-coated nylon Lycra fabric is less stable in the air due to its reactivity with a variety of atmospheric chemicals, especially oxygen. The surface resistivity of this PPy-coated nylon Lycra-coated fabric is increased by 10-fold when stored in the air for 54 days. However, in the desiccator, it is more stable, with its surface resistivity

increasing by less than twofold in the same period, as shown in Figure 6.47 [41]. Figure 6.48 shows the resistance changes in PPy-coated polyester fabrics over a period of 120 days at room temperature. Although both samples display a resistance decrease in the first 7 days of aging, the resistance of the sample containing the DHBP additive decays significantly slower than the control sample containing AQSA only [234]. It is also observed that when the sulfonic acid salts are used as dopant anions, it improves atmospheric

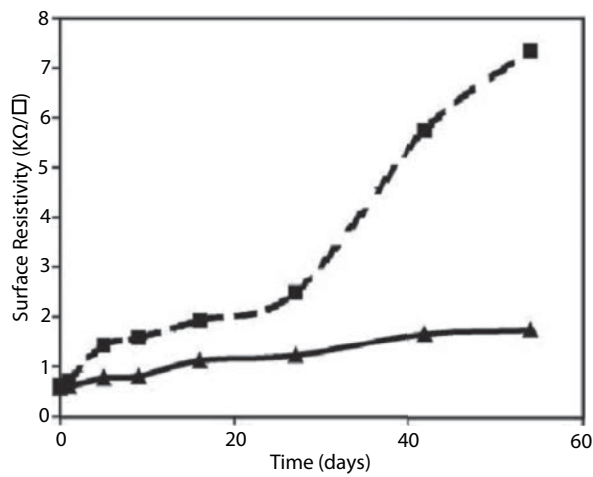


Figure 6.47 The changes of surface resistivity versus storage time of PPy-coated nylon Lycra. Broken line: stored in open air; bold line: stored in a desiccator [41].

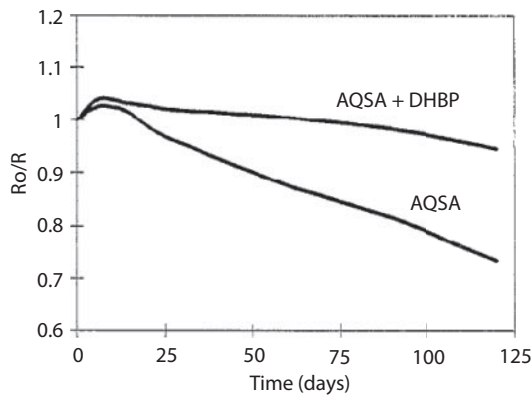


Figure 6.48 Room temperature stability curves of PPy-coated polyester fabrics with and without DHBP [234].

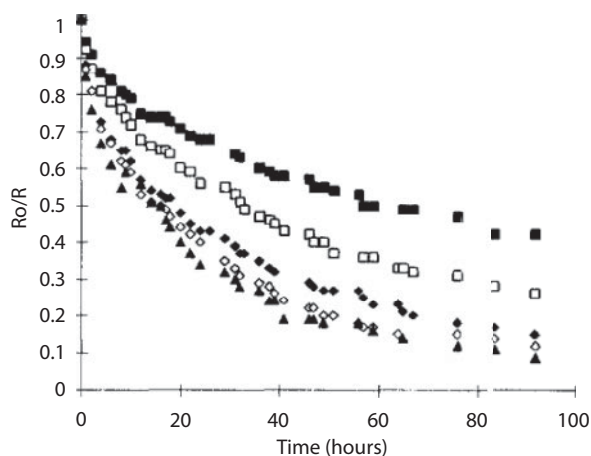


Figure 6.49 Conductivity decay of PPy-coated fabrics at 100°C. (■) AQSA, (□) N2SA, (◆) NDSA, (◇) PTSA, and (▲) Cl [25].

aging of PPy-coated cotton fabrics [232, 235]. An effect of doping anions on atmospheric aging has been studied by Kuhn *et al.* [25]. The surface resistivity of these coated textiles is measured at intervals while undergoing accelerated aging in a forced air oven. The results are shown in Figure 6.49. It can be seen that the relative conductivity decreases as a function of time. Investigations concerning the mechanism and kinetics of the conductivity loss have revealed that it proceeds by two sequential steps: the diffusion of oxygen into the film and the reaction of the oxygen with the polymer backbone. The diffusion of oxygen through the polymer film depends on the polymer morphology. The smooth surface morphology restricts the diffusion process and hence shows better stability.

However, few researchers reported that PANi- and PPy-coated fabrics have a good tolerance for all tested conditions such as intensive water shower, humidity, cold, and ultraviolet light, and electrical resistance is not significantly affected by weathering [78, 236].

6.10.5 Thermal Stability

An important limitation of CPs is their thermal stability. The degradation kinetics of PPy has been studied extensively by Child *et al.* [234]. The degradation is significantly more rapid in the air, indicating that oxidation of the organic polymer backbone, thus reducing the conjugation length, is the primary cause of the conductivity loss [42]. The stability depends on the polymerization conditions, dopant ion, and aging conditions.

Low temperature during polymer synthesis (273 K) and higher pyrrole concentrations (2 g/L) lead to a stable polymer [237]. Kim *et al.* have found that fabrics prepared using the electrochemical method have superior thermal stability than fabrics prepared by chemical polymerization [115].

The selection of the dopant ion is a critical factor in the thermal stability of the resulting PPy film [234, 238]. The incorporation of aromatic dopants, such as anthraquinone-2-sulfonic acid, results in an improvement in the thermal stability of PPy coatings on a textile substrate. Further dramatic increases in the thermal stability have been realized by the incorporation of small quantities of benzophenone-based stabilizing agents such as 2,4-dihydroxybenzophenone (DHBP). During thermal aging, the conductivity of PPy-coated textile produced with these stabilizing agents initially increases and then decreases at a significantly lower rate than that of the control samples as shown in Figure 6.50. The level of stability enhancement is dependent on the additive/pyrrole ratio in the reaction bath and on the coating thickness.

The heat treatment of PPy-coated polyester textiles doped with anionic surfactant below 80°C does not significantly change the final resistance of the conducting textiles [91]. It has been observed that the PPy/NDSA-coated nylon Lycra fabric is thermogravimetrically less stable than the uncoated fabric as shown in TGA thermographs in Figure 6.51 [41].

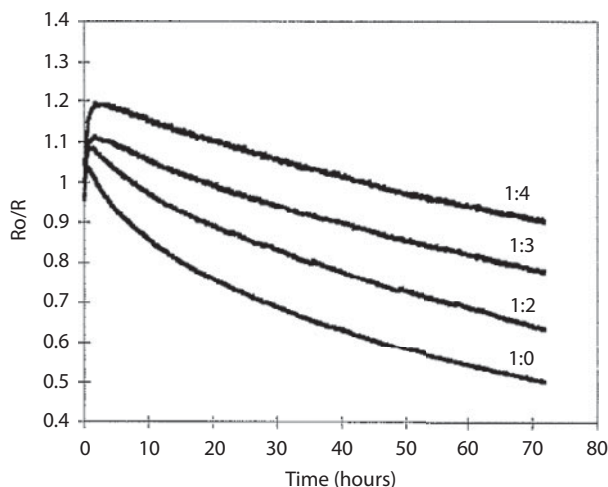


Figure 6.50 Thermal aging plots of PPy-coated polyester fabrics at 100°C with varying pyrrole/DHBP ratios [234].

Varesano *et al.* studied the degradation behavior of PPY-coated woolen knitted fabric by light exposure and temperature separately. Figure 6.52 shows resistance changes in samples exposed to artificial light with respect to those left in the heater. Both series of samples show a moderate increase in resistance after 100 h of treatment. The PPY coating is oxidized upon environmental exposure to atmospheric oxygen, and the degradation process is enhanced by the effect of sunlight [88]. Other researchers also observed that heat treatment of PPY causes increases in resistivity [42].

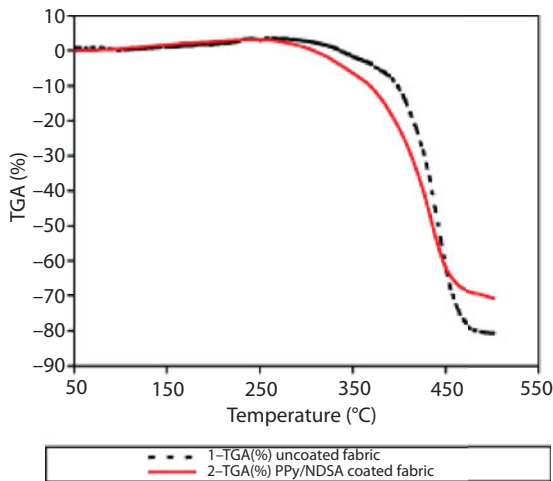


Figure 6.51 TGA analyses of uncoated and PPY-coated nylon Lycra fabrics [41].

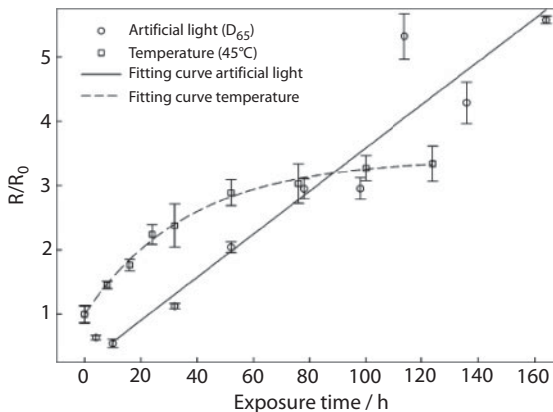


Figure 6.52 Resistivity ratio (R/R_0) versus exposure time to light and temperature of PPY-coated wool textiles [88].

After PANi coating, the heat of fusion, melting temperature, and degree of crystallinity of nylon 6 fabrics slightly decrease and the decrement is more prominent at higher aniline concentrations, as shown in Figure 6.53. It is suspected that the diffusion of aniline into the nylon 6 fabric, to some extent, may disturb the crystalline region and decrease its thermal properties. At high aniline concentrations over 0.2 M, the endothermic peaks have a shoulder. This is supposed to be caused by hydrogen bonding between nylon 6 and PANi [122]. However, the thermal stability of the silk fabric increases after PPY coating, as shown in Figure 6.54 [147].

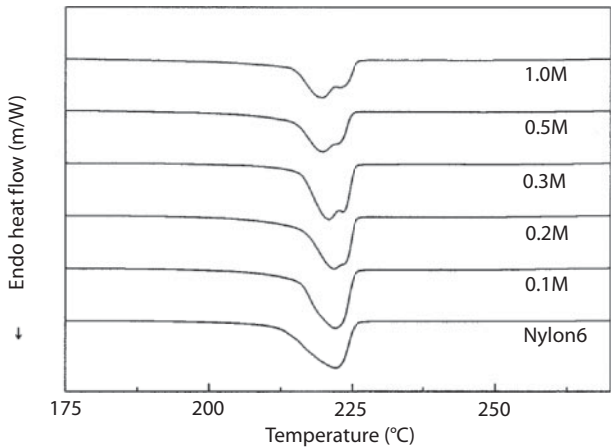


Figure 6.53 DSC thermograms of nylon 6 and PAN-nylon 6 fabrics [122].

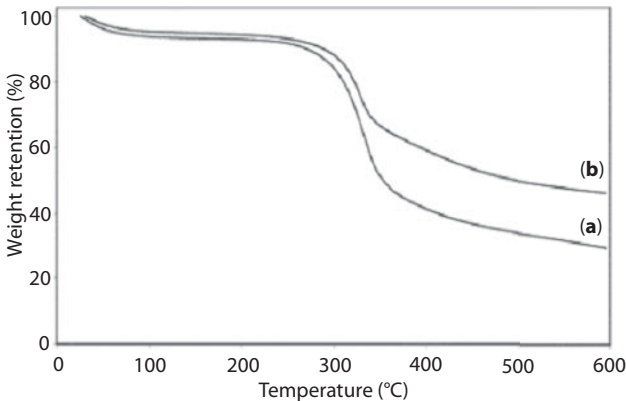


Figure 6.54 DSC curves of (a) untreated silk yarn and (b) PPY-coated silk yarn [147].

6.11 Future Scope and Challenges

Although these conductive polymer-based textiles possess excellent electrical conductivity that is suitable for many potential applications, their main limitation is their poor consistency and stability of electrical conductivity in many working atmospheres, and as a result, they gradually lose electrical conductivity over time. Also, the substantivity of PPy toward textile fibers is not very good. It is now a challenge for current researchers to obtain consistent, stable, and durable electroconductivity into textiles through the coating of conductive polymers.

6.12 Conclusions

Textiles as polymeric materials are inherent insulators with their electrical resistivity in the range of $10^{12} \Omega$ or higher. Imparting electrical conductivity to textile materials can improve the functionality of textiles. Conventionally, for this purpose, metallic fibers, or fibers coated with a metal, are used. Metal fibers are blended during staple spinning to manufacture electroconductive yarns. These metallized yarns are used in weaving or knitting to produce electroconductive fabrics. However, processing these yarns is difficult; they lose their textile properties. These metallic fibers are not fit for practical use due to their poor recovery from bending and breakage. Also, it is difficult to mix spin, mix weave, or mix knit the metallic fibers with conventional textile fibers. In the case of textile fibers, yarns, or fabrics coated with a metal layer by electroplating, forming a uniform and continuous layer on the textile surface is necessary. In order to satisfy this requirement, the surface of the fiber needs to be smooth and highly polished. Also, intensive care is required during the coating operation to coat a continuous layer of metal with uniform thickness. As a result, the cost of the coating operation is very high. Also, the metal-coated fiber has a disadvantage in that the coating is easily peeled off during processing or use. The fiber coated with a conductive dope containing an electrically conductive material, such as carbon black, silver particles, etc. is also unacceptable because the coating operation is expensive and the coated layer is easily peeled off from the fiber during processing. If carbon black is used in dope mixed with polymer to spin a conductive filament, then at least 15% (o.w.f.) of carbon black loading is required. This large amount of carbon black makes the fiber-forming process difficult, complex, and expensive. Many such limitations associated with processability, flexibility, durability,

etc. could be successfully overcome by coating/applying conducting polymers such as polyaniline, polypyrrole, and polythiophene, to name a few, on textile substrates. These conductive polymer-coated textile materials, owing to their flexibility, durability, ease of preparation, and application, show great potential for various applications, including shielding of electromagnetic radiation, heating garments, cooling garments, strain/gas/humidity/pH sensors, static dissipation, antibacterial efficacy, etc. There are different approaches for coating textile materials with conductive polymers based on the reaction phase employed by various researchers, namely, *in situ* chemical, *in situ* electrochemical, *in situ* vapor phase polymerization, *in situ* polymerization in the supercritical fluid, etc. Almost all textile fiber substrates are used to coat conductive polymers, and most of them show satisfactory results. The conductive polymer-based electroconductive textiles are found suitable for potential application in heat generation. Compared to other heating materials, the advantages of these heating fabrics are their temperature homogeneity, low power density on large surface area, lightweight, suppleness, and fineness. They can be sewed up, cut off, or pasted on substrates for a large range of applications. The custom-made electronic property, controllable electrical conductivity, low-cost and high-yield synthesis, and sensitivity toward various exterior stimuli such as strain, pH, humidity, temperature, and so on enable their potential application as sensors. It is found that these conductive polymer-coated textiles are efficient shielding materials for electromagnetic radiation as they work based on the principle of absorption of electromagnetic rays rather than reflection. These materials are also found to exhibit a thermoelectric cooling effect, antibacterial properties, wastewater purification, static charge dissipation, etc. Although the mechanical properties of the textiles are not greatly affected by the polymer coating, maintaining environmental stability, thermal stability, and launderability remains a challenge to current researchers.

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Coated or Laminated Textiles for Aerostat and Stratospheric Airship

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Abstract

Aerostat and airship are lighter-than-air (LTA) systems that are mainly used for defense applications such as military surveillance, detecting aerial threats, etc. and also for many other purposes. Significant challenges are faced in developing materials for LTA systems, especially for stratospheric airships, which require balancing all the required properties. The material should be lightweight, strong, flexible at low temperature, capable of containing helium gas for a long time, and weather resistant (i.e., provides protection from intense UV rays, ozone, etc.) and should provide a long service life. Generally, multilayered coated or laminated fabrics are used to fulfill all the requirements for this particular application, where a specific layer executes a specific functionality.

This chapter discusses the basic structure of a multilayered envelope for airship or aerostat, requirements for each layer, challenges, and different potential materials (polymers, fibers, and fabrics) for different layers. The case studies of different coated or laminated fabrics developed by leading competitors that prepare LTA systems have also been included. It also highlights the potentiality of advance polymeric nanocomposites, especially polyurethane nanocomposites, for this particular application. The future possibilities of extensive usage of polymer nanocomposites and their challenges have also been discussed. Finally, the different models that have been developed by researchers for predicting the performance and service life of coated/laminated envelopes of an aerostat/airship have also been explored.

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Keywords: Coated or laminated fabric, gas barrier, weather resistance, high-performance fiber, polymer nanocomposite

7.1 Introduction

In recent years, high-altitude LTA systems operating 20 km above sea level have been receiving great attention. The altitude is chosen depending on many factors such as the jet stream or wind speed, severe weather, and Federal Aviation Administration (FAA) air-traffic layer [1, 2]. There are mainly two types of LTA systems: aerostat (tethered system) and airship (untethered system). The tethered aerostat is operated from a fixed location and lift is provided solely by a lifting gas such as helium or hydrogen that is contained in the envelope. It requires no power for station keeping or for controlling the altitude and it is also easily recoverable for payload maintenance [2]. In contrast, an untethered high-altitude airship is a power-driven, unmanned, and free-flying vehicle system where lift is provided by a combined effect of lifting gas and aerodynamics. The conventional airships can be further classified on the basis of (i) hull configuration (rigid, semi-rigid, and flexible), (ii) the way vertical force is produced (lighter-than-air, heavier-than-air, and hybrid), and (iii) payload capacity (heavy lift and medium lift). Due to its very simple structure, light weight, easy fabrication, and lower cost for fabrication and maintenance, the non-rigid type of airship is preferred over others [3–6]. Figure 7.1 shows different types of conventional airships and their different components.

The LTA systems are generally used in defense applications such as military surveillance, homeland defense, detecting aerial threats, etc. Besides this, it can also be used in network monitoring, multimedia and 3G/4G services for mobile phones, broadcasting, weather forecasting, disaster management, and many other purposes [7, 8]. A stratospheric airship can offer a cost-effective alternative to earth-orbit satellites for acquiring unique data sets related to telecommunications and science. Some advantages of high-altitude airship over satellites are as follows [2, 4, 9]:

- i. Cheaper access and low cost for launching
- ii. Rapid reconstitution of capabilities
- iii. Persistent 24/7 capability

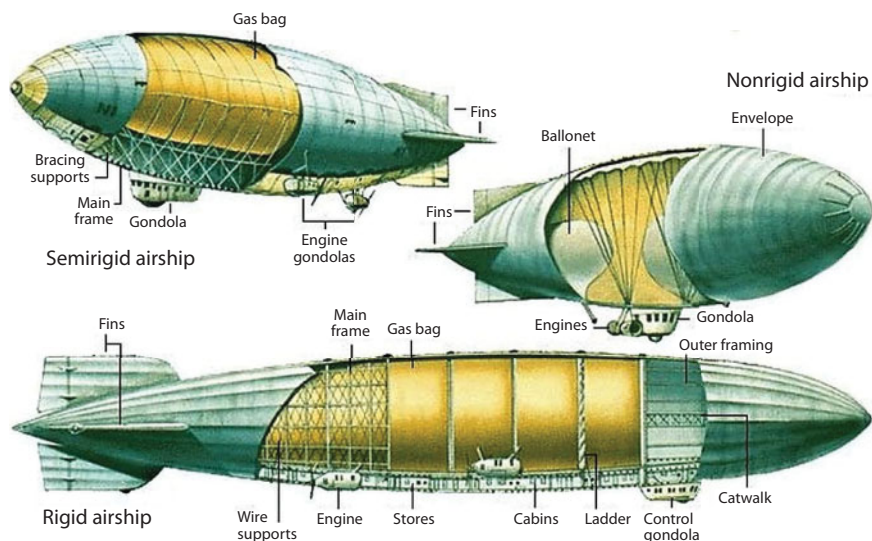


Figure 7.1 Different types of airships and their components [5].

- iv. Multi-mission, repairable/exchangeable/upgradable payloads
- v. Relocate-ability
- vi. Long duration aloft (≥ 1 year)

In LTA systems, the envelope is one of the major structural parts and contains lifting gas such as helium, maintaining its aerodynamic shape. During their service life, the LTA systems are exposed to various environmental conditions such as UV rays from sunlight, ozone, temperature variation (heat or cold), atmospheric pressure variation, rain, moisture, pollutants, etc., causing degradation of the materials used in the envelopes. Hence, the material should have good weather resistance property to withstand such harsh environments. Moreover, for lifting any LTA system, helium or non-flammable hydrogen gases are generally used. Therefore, the envelope material should have good barrier property against these gases, so that gases do not leak, thus securing a long service life. Besides these, there are many other requirements for LTA envelopes such as high strength-to-weight ratio, lower creep, good abrasion resistance, and excellent low-temperature flexibility. Any single-layered material cannot fulfill all these requirements. Hence, multilayered coated or laminated fabrics are generally used to withstand such harsh environments and to fulfill all other requirements [2, 8, 10].

7.2 Global Competitors for Making Aerostat/Airship at Present

The history of airship invention began in 1784 when Jean-Pierre Blanchard first recorded a flight of a non-rigid dirigible (the French word for airship) and fitted a hand-powered propeller to a balloon for propulsion [11]. After that, many things/specifications have been added and many modifications have been made in the structure and shape of aerostats/airships by different research organizations from all over the world.

Recently, research agencies in many developing countries such as the United States, UK, Korea, Canada, Germany, and Japan have launched various programs for the design and development of an unmanned stratospheric airship for different communications-related applications. Different organizations and laboratories in various countries are working on the development of high altitude airship (HAA) systems. Among these, the current key players dominating the market of global LTA systems are TCOM, L.P. (Columbia), Lockheed Martin (USA), ILC Dover (USA), Raven Aerostar (USA), Raytheon (USA), RosAeroSystems (Russia), and RT (Israel) [12]. In India, some organizations such as Aerial Delivery Research and Development Establishment (ADRDE, Agra), Defence Research and Development Organization (DRDO), National Balloon Facility (NBF, Hyderabad), Tata Institute of Fundamental Research (TIFR), and Indian Space Research Organisation (ISRO) are actively working in this area.

Some recently developed advanced models of aerostat/airship are HAATM (Lockheed Martin, USA), MAAT FP7 (European Commission, Aeronautics and Air Transport), Zeppelin LZ NT-07 (Zeppelin Luftschifftechnik GmbH, Germany), SkyFreighter (Millennium Airship Inc., Canada/USA), DynaLifter PSC-3 (Ohio Airships Inc., USA), Skycat-20 (ATG/World SkyCat, UK), etc. [3, 7, 13]. In India, ADRDE, Agra (DRDO) has also launched two new aerostats in recent years, which were named “Akashdeep” and “Nakshatra.” Among these, “Nakshatra” has a bigger payload capacity and better surveillance functionality [14, 15].

7.3 Working Atmosphere of Aerostats and High Altitude Airship (HAA)

Aerostats or airships fly based on the principle of the Archimedes law of buoyancy, while they are filled with a suitable lighter-than-air gas such as helium, for lifting and floating purposes. The low-altitude aerostat

generally flies at a height of about 1–5 km (maximum, 10 km), while in the case of HAA, it may vary in the range of 17–55 km. Hence, the hull of the aerostat/airship is exposed to intense UV radiation (coming from the sun), humidity, rain (at the troposphere level), temperature variation (50 to -50°C), lower and varied pressure due to varying altitudes (5475 to 110 Pa), pollutants, etc. Moreover, high-altitude stratospheric airships also face concentrated ozone (in the ozone layer), cosmic radiations, etc. These harsh conditions cause deterioration of aerostat/airship material, resulting in loss of strength and increase of helium gas permeability through the hull [2, 16]. Moreover, at the stratospheric level, the temperature may be as low as -50°C , making the material brittle, which may lead to cracks in the material surface. It also increases helium gas leakage through the material, causing a loss in crores [8, 10]. Hence, material development for the outer envelope or hull of the aerostat is quite challenging, especially for HAA.

7.4 Materials Used in LTA Envelopes

Aerostats or airships are made based on a “balloon-within-a-balloon” concept where the envelope of the inner balloon is called “ballonet” and the outer envelope is called “hull.” Ballonet is frequently filled with air during inflation or releases air during deflation, for maintaining the proper altitude as per requirement.

7.4.1 Requirements for Hull Materials

The aerostat/airship hull should have the following properties for providing a long service life [2]:

- i. Good weather resistance especially against intense radiations (UV, ozone, etc), temperature, and rain/moisture
- ii. High barrier properties against helium gas to reduce the loss of filled gas and also to maximize the station time
- iii. Flexibility at a wide range of temperatures, especially at subzero temperature, to avoid brittleness of the material and loss of gas barrier property
- iv. High tensile strength as it determines the maximum possible size of the aerostat
- v. Low weight and high strength-to-weight ratio to increase the payload capacity

- vi. High tear strength to prevent catastrophic failure, which is very common
- vii. Good abrasion resistance or wear resistance for better handling
- viii. Low creep to avoid the change of aerodynamic shape with time and surrounding conditions
- ix. Good bondability or sealability for obtaining good joint strength, avoiding leakage of gases
- x. Long service life

In fact, any single fabric or film could not fulfill all these requirements. Therefore, multilayered laminated or coated fabrics are used. Figure 7.2 shows the typical multilayered coated and laminated structures for a hull, where the individual layer performs a specific task, and in combination, the structure can fulfill all the requirements.

7.4.1.1 Strength Layer

A suitable single-layered textile fabric is generally used in the strength layer or load-bearing layer of a hull. The main requirements for a layer are as follows:

- i. High tensile and shear strength to sustain the high pressure experienced by the system
- ii. High work of rupture
- iii. Good tear resistance
- iv. Lighter in weight for taking higher payloads
- v. Good bondability or sealability
- vi. Lower creep

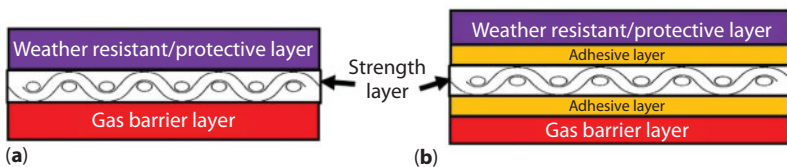


Figure 7.2 Different layers of typical multilayered coated (a) and laminated (b) structures for LTA systems.

7.4.1.1.1 Fabric Structure Used in Strength Layer

A single-layered or multilayered woven fabric is commonly used as the structural layer. Moreover, among different weave designs, the plain weave is the most common for this purpose for obtaining a high-strength fabric that allows many variations. The common variations of plain weave are basket weave or “rip stop” weave (“1-2-1 rip stop” or “1-3-1 rip stop”), which improves tear resistance [17]. Figure 7.3 shows different fabric structures that are commonly used in strength layer.

Besides woven fabric, researchers have also taken trials using non-woven fabric. Cubic Tech Corp. has developed flexible multilayered composite laminates for the HAA system using non-woven fabric. The main technical and performance advantages of non-woven over woven fabric are as follows [18]:

- i. Significant weight savings over the woven fabric of similar strength
- ii. Eliminate strength and modulus loss and other structural deficiencies caused by crimping of yarns during the weaving process
- iii. More flexibility
- iv. Better long-term fatigue and creep fracture

7.4.1.1.2 Potential Fibers Used in Strength Layer

The most challenging aspect in designing a strength layer is the identification of a suitable high-performance fiber. In the early stage of development in this area, polyester and nylon fabrics were used commonly in the

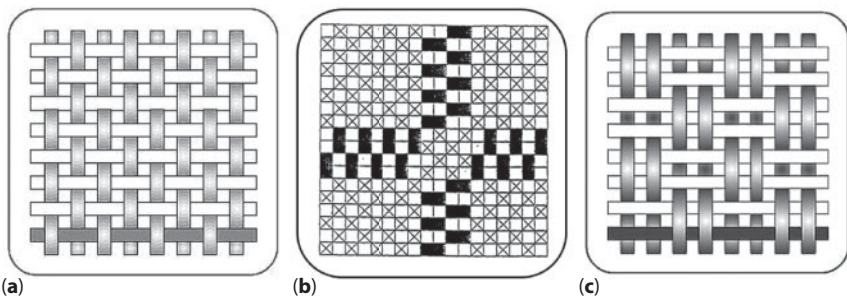


Figure 7.3 Different fabric construction: (a) plain weave, (b) “rip stop” weave, and (c) basket weave.

strength layer of hull. The combination of moderate strength (≈ 10 g/den) and moderate extension ($>10\%$) of commercial polyester and nylon fibers results in good work of rupture, making them suitable for aerostat envelopes. Especially, high-tenacity polyester fabrics are extensively used for making aerostat envelopes due to the following advantages [2]:

- i. High strength-to-weight ratio
- ii. Good weather resistance property
- iii. Low creep
- iv. Low moisture regain and hydrolysis resistance
- v. Lower cost than high-performance fibers

In the late 20th century, high-performance fibers (high tenacity: 20 g/den and high modulus: over 300 g/den) became available. Examples of some of these high-performance fibers are Zylon[®], Spectra[®], Vectran[®], Kevlar[®], M5[®], etc. (Figure 7.4) [19]. With the invention of these new high-performance fibers, the performance of airships also increased in terms of longer service life, higher payload, and higher altitude of floating of an airship. Table 7.1 highlights the comparative properties of different commodities and high-performance fibers.

Aramid[®] fibers such as Kevlar[®], Nomex[®], Technora[®], etc. are aromatic amide fibers having much superior mechanical properties than steel and glass fibers. However, their folding and abrasion resistance is not good [2]. Zylon[®] (PBO) fiber has superior mechanical properties, creep resistance,

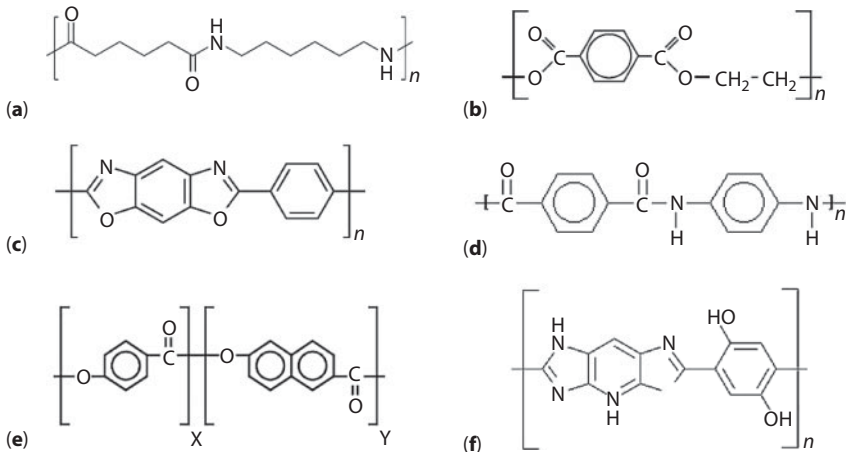


Figure 7.4 Chemical structure (repeat unit) of some commercial and high-performance fibers: (a) Nylon 6,6, (b) polyester, (c) Zylon[®], (d) Kevlar[®], (e) Vectran[®], and (f) M5[®].

Table 7.1 Properties of some commercial and high-performance fibers [18–21].

Fiber	Tensile properties			Moisture regain (%)	Density (g/cm ³)	T _d (°C)
	Tensile strength (GPa)	Young's modulus (GPa)	Breaking extension (%)			
Polyester (Kosa®)	1	15	20	0.4	1.38	>300
Nylon 6,6	0.91	9.57	20–25	4	1.14	>300
Zylon® AS	5.8	180	3.5	2	1.54	650
Zylon® HM	5.8	270	2.5	0.6	1.56	650
Spectra® 900	2.4	70	4	–	0.97	150
Spectra® 1000	3.1	105	2.5	–	0.97	150
Dyneema®	3.4	111	–	–	0.97	–
Vectran®	2.85	65	3.3	<0.1	1.4	400
Kevlar® 49	3.6–4.1	130	2.8	4.5	1.44	550
Kevlar® 149	3.4	185	2	3	1.47	550
Technora®	3.4	71	4.5	3.5–5	1.39	550
M5® (PIPD)	3.5–4.5	330	2.5	4.5	1.7	500

T_d decomposition temperature.

and thermal stability than p-Amide[®] fibers. Also, the abrasion resistance of Zylon[®] is higher than that of p-Amide[®] fiber under the same load, but much lower than that of nylon or high-molecular-weight polyethylene fiber [22].

M5 or PIPD (polyhydroquinone-diimidazopyridine) fiber is based on a rigid-rod polymer having very high strength and modulus as good as PBO fibers (such as Zylon[®]). M5 fiber shows excellent UV stability, having a capability of retaining strength just like virgin fiber even after 100 h exposure to a xenon lamp, whereas Zylon[®] fibers lost over 35% of original fiber strength after exposure for the same duration. Additionally, M5 fiber shows much better stability than Zylon[®] fiber at elevated temperatures and at high relative humidity [23].

Dyneema[®] and Spectra[®] are ultrahigh molecular weight polyethylene (UHMWPE) fibers that are manufactured by patented “gel spinning technology.” These two fibers possess extremely high strength and modulus, high impact strength, high durability, low density, and excellent light and chemical stability, which make them a potential material for the load-bearing layer of airship envelopes. Moreover, these fibers show excellent abrasion resistance and fatigue resistance [24].

Vectran[®] is an aromatic polyester fiber having excellent mechanical properties and retention of properties at a wide range of temperatures, high thermal stability, excellent chemical resistance, and low moisture regain. In many lab-scale trials or prototype heavy-lift spherical balloon systems, Vectran[®]-based hull laminates showed promising results. In comparison to polyester-based material, this material exhibited much higher strength-to-weight ratio as well as excellent tear resistance [4, 25–27].

Recently, these high-performance fibers are attracting substantial attention in the LTA industry. However, the main disadvantages of the high-performance fibers that limit their applications for making aerostat/airship hull are as follows [2]:

- i. High cost of production
- ii. Limited availability
- iii. Lower extension
- iv. Higher creep (for Spectra[®])
- v. Lower moisture and UV resistance (for Zylon[®])

7.4.1.2 Weather-Resistant or -Protective Layer

This layer protects the system from harsh atmospheric conditions such as ozone, UV radiation, temperature variation, humidity, and rain. The main requirements for this layer are as follows:

- i. Good weather resistance property
- ii. Excellent low-temperature flexibility
- iii. Good bondability or sealability

Generally, high weather-resistant polymers such as polyvinyl fluoride (PVF, Tedlar®), polyvinylidene fluoride (PVDF), etc. are used in this layer. Very frequently, an aluminized top coating is used to give a better weather resistance property [4, 26].

7.4.1.3 Gas Barrier Layer

This layer serves as a gas barrier to retain helium gas inside the hull for a longer duration, which increases the service life of the aerostat/airship. The main requirements for this layer are as follows:

- i. High helium gas barrier property
- ii. Excellent low-temperature flexibility
- iii. Good bondability or sealability

Generally, a polymer having good helium gas barrier properties such as polyvinylidene chloride (PVDC), polyester (Mylar®), and ethylene vinyl alcohol copolymer (EVOH) are used in this layer [2, 26].

7.4.1.4 Adhesive Layer

During the preparation of multilayered laminated composite materials for LTA systems, adhesive layers are often used to bind various layers (protective layer and strength layer or gas barrier layer and strength layer), as shown in Figure 7.2. A very thin adhesive layer is important to provide enough bonding strength and flexibility while controlling the total weight of the composite material. Therefore, selection of the appropriate polymeric material is very vital for the adhesive layer. Very frequently, thermoplastic polyurethane is used for this purpose. Sometimes, various formulating agents, like plasticizers, cross-linkers, gas-impermeable nanomaterials, etc., are added in the adhesive formulation to modify the base polymer [28]. The following are the main properties required for this layer:

- i. Good compatibility with both substrate
- ii. Good bondability or adhesion power
- iii. Excellent low-temperature flexibility

This layer may not be required for adhering two substrates having good compatibility or bondability under application of heat. Sometimes, the surface of layers that have to be joined is functionalized by grafting or by treating it with plasma or e-beam to avoid the additional layer of adhesive and also for the reduction of weight of the composite laminate [29].

7.4.2 Requirements for Ballonet Materials

Ballonet is the other important component of LTA systems such as aerostats and airships. It acts as an internal barrier that separates air (present inside the ballonet) and helium gas (present inside the hull). During the descending or ascending of the aerostat/airship, the ballonet is continuously flexed as inflated or deflated, respectively. Therefore, the main requirements for ballonet materials are as follows [2]:

- i. Good flex fatigue resistance
- ii. Excellent low-temperature flexibility
- iii. Lightweight
- iv. Good gas barrier property to minimize lifting gas loss and purity decay
- v. Good abrasion resistance
- vi. Good bondability or sealability

Ballonet is generally prepared by using a lightweight fabric made of fine denier polyester or high-performance fibers, and both sides of the fabric are coated or laminated with a polymer that has good gas barrier properties and low-temperature flexibility. In this context, a lightweight polyester fabric coated with thermoplastic polyurethane-based formulation that has fair gas barrier properties, good abrasion resistance, and good low-temperature flexibility is very common.

7.4.3 Different Polymers as Potential Candidates for Protective/Gas Barrier Layer

There are a series of polymeric systems that are being used in the gas barrier and protective layer of the laminated or coated fabric envelope of an aerostat/airship. Fluoropolymers such as polyvinyl fluoride (PVE, Tedlar®), fluorinated ethylene-propylene copolymer (FEP, DuPont), polytetrafluoroethylene (PTFE, Teflon®), and polyvinylidene fluoride

(PVDF) films have been used for most of the large LTA hull material applications. These fluoropolymers, especially Tedlar® film, are well known for their excellent weather-resistance property, outstanding mechanical properties, good gas containment properties, inertness toward a wide variety of solvents/chemicals/staining agents, and low-temperature toughness, which make them potential candidates for LTA systems [2]. Pigmented Tedlar® film or Tedlar® film with UV absorber additives blocks more than 99% of the UV radiation in the wavelength range of 290–350 nm [4]. However, the main concerns associated with these fluoropolymers are adhesion problems, and some of them are not heat sealable.

Because of an excellent barrier property, EVOH and Mylar® (DuPont, biaxially oriented polyester) are two potential candidates for the gas barrier layer of a laminated envelope for aerostats/airships. Plasticized polyvinyl chloride (PVC) is commonly used for coating on fabrics due to its good weathering property and ozone resistance, good low-temperature flexibility, heat sealability and low cost. Low-density polyethylene (LDPE) is a heat-sealable and a very flexible polymer, which is normally coextruded with other polymeric films to improve its gas barrier property. A lightweight LDPE/Mylar®/polyester fabric laminate can be potentially used in a super-pressure balloon application [30]. Lin and Tan studied the effect of ozone aging on the PE-EVOH (ethylene-vinyl alcohol copolymer) films, which showed great potential for making envelopes for near-space vehicles (NSVs) [31].

The vinylidene chloride/vinyl chloride copolymer-based Saran® film is an excellent gas barrier material, which is extensively used in packaging. However, due to its poor low-temperature flexibility, it is not recommended for use in the envelope of LTA systems [2].

Polyurethanes are a unique class of polymers that are available in many formulations and possess versatile and excellently balanced properties such as outstanding overall toughness, excellent low-temperature flexibility, good tear strength, good abrasion resistance, fair gas permeability, and fair to good weatherability. Therefore, polyurethane-based coated fabrics have many applications, and the most important one is for aerostat/airship envelopes. Moreover, thermoplastic polyurethane can also be adhesively bonded, heat sealed, and laminated onto other substrates to make a laminated structure for aerostat/airship envelopes. Among all polymeric systems, silicone rubber has the best low-temperature flexibility. However, its low toughness, high gas permeability, and low abrasion resistance are problematic for this particular application [2].

7.4.4 Coating and Lamination: Processing Techniques, Advantages and Disadvantages

Coating is a process in which a polymeric layer (solvent/water-based coating formulation or hot polymer melt) is applied directly to one surface or to both surfaces of the fabric. There are many coating techniques such as solution coating, melt coating, and transfer coating. Solution coating on textile/fabric can be done by various methods such as knife coating (knife-over-roll or floating knife), roll coating (direct-roll, kiss-roll, and gravure-roll coating), rotary screen coating, etc. [29]. Among these different coating techniques, the floating knife technique is preferred for applying tie-coat on the fabric, while the knife-over-roll coating technique is used for giving more uniform successive coatings on the tie-coat. Melt coating has mainly two types: extrusion coating and power coating. The hot-melt extrusion-based Zimmer process is very much popular for making coated fabric for inflatables [32].

In contrast, lamination is the process of joining two or more layers into one structure where generally at least one layer is a textile material. During lamination, different layers are joined by using an adhesive or by heat treatment utilizing the adhesive properties of one or more of the component layers. In lamination, the laminas (fabric and films) are generally hot-pressed between two Teflon-coated nip rolls or a series of heated calendar roll [29]. Different types of lamination methods are used for the application of a polymeric film layer on a substrate: adhesive lamination, heat lamination, flame lamination, and hot-melt lamination. Among these, adhesive lamination is commonly used for the preparation of laminated structures for inflatables, where a polyurethane-based adhesive is generally used. During lamination, few process parameters need to be controlled [32]:

- i. Nip pressure
- ii. Nip-zone temperature
- iii. Speed of the machine
- iv. Drying time and temperature
- v. Curing time and temperature
- vi. Knife setting in adhesive lamination
- vii. Openness of roller in hot-melt lamination
- viii. Pressure on winding and unwinding roller

Both processes (coating and lamination) have some advantages and disadvantages, which are discussed below. In coated and laminated textiles, the polymeric layer interacts differently with textile fabric. Figure 7.5a

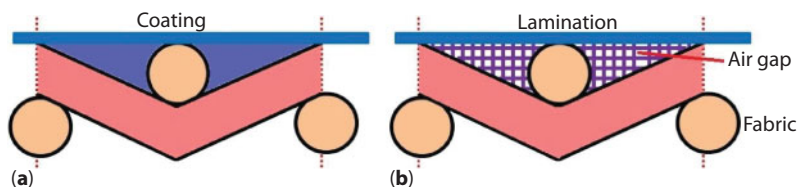


Figure 7.5 Schematic of coated (a) and laminated (b) textiles.

demonstrates how a coating formulation covers the surface of the fabric and how it is able to penetrate the fabric structure, filling the air pockets and bridging the interstices. However, in the case of a laminate (Figure 7.5b), the polymeric film sits on the fabric surface and the fabric retains most of its air pockets, showing fewer points of contact [33]. Therefore, in coating, a better interaction is generally obtained between polymer and fabric compared to lamination.

Obtaining good interlaminar adhesion strength is a great challenge in the case of laminated structures showing delamination tendency. Therefore, adhesive lamination is preferred mostly over other lamination techniques for manufacturing laminated fabric for aerostat/airship envelopes. However, selection of a suitable adhesive controlling the balance between proper bond strength and flexibility is a very challenging task. Sometimes, the fabric or film is treated with plasma or electron beam for surface functionalization, resulting in improved interlaminar adhesion [29]. In the case of adhesive lamination, the interlaminar adhesion strength depends on the surface properties of films and adhesive as well as the process conditions. For proper bonding among different layers, the surface tension of film/fabric should be higher than the surface tension of the adhesive. For example, the surface tension of virgin Tedlar® film is about 30 dynes/cm, which is lower than the surface tension of commonly used adhesive (~40 dynes/cm), resulting in improper adhesion strength. Corona treatment of PET fabric and Tedlar® film increases the surface tension to about 44–48 dynes/cm, showing a significant improvement in adhesion strength [32].

In lamination, there is a chance of crease formation on the laminated fabric if the film is not fed properly. However, there is no such problem in coating. In coating, there is always a chance of bubble formation in the coating formulation, causing faulty coating and a scratchy surface. Additionally, maintaining the required viscosity in coating formulation is a very challenging task; otherwise, faults may occur on the coated surface. There is no such type of problems in lamination.

In coating, bonding occurs either through the drying process (evaporation) or through a curing process, which is required to provoke

cross-linking. In lamination, curing is generally not required. Most of the coating formulation is prepared by using toxic solvents, and a huge amount of solvent is used for making coating formulation, causing environmental pollution, whereas in lamination, solvent is generally not required. Though solvent coating is sometimes used as an adhesive layer during lamination, there is less requirement for solvent. Moreover, nowadays, solvent-free hot-melt adhesive is becoming popular. In many cases, adhesives are not required because of their self-adhering property and they can be laminated only by hot pressing.

Oftentimes, different additives are incorporated in the coating formulation or in the film for the improvement of polymer properties, mainly weather resistance and gas barrier properties, by retaining all of their other inherent properties. For example, the weather resistance property of a polymer can be improved by incorporating a suitable combination of UV additives such as UV absorber, hindered amine light stabilizer (HALS), antioxidant, carbon black, and inorganic nano UV additives (TiO_2 , ZnO , CeO_2 , etc.), whereas, the gas barrier property of a polymer can be improved mainly by incorporation and proper dispersion of layered structure nano-materials or nanoplatelets such as nano-clay, graphene, etc. [34].

7.5 Case Studies on Different Coated or Laminated LTA Envelopes

The defense organizations of different countries have designed and patented many coated or laminated structures that are the potential materials for aerostat/airship envelopes [4, 26, 32, 35, 36]. Some of the reported structures are presented below.

KARI, Korea (2006), in collaboration with two other Korean organizations developed a film-fabric laminate for a stratospheric airship envelope that consists of an outer layer of Tedlar® film (for environment protection and gas leakage protection) and an inner layer of TPU film (for sealing and helium gas barrier) that were laminated on a plane fabric weave made of Vectran HT fiber. The fabric was impregnated in PU-adhesive before lamination. Carbon black was added to the inside TPU film as the black color (see Figure 7.6a) and is good for fabric inspection. The detail specification of the different layers is mentioned in Figure 7.6b [4].

Jet Propulsion Laboratory, NASA, and ILC Dover Inc., USA (2008), designed, fabricated, and tested a prototype balloon for long duration performance in the upper atmosphere of Venus (altitude of 55 km). The balloon

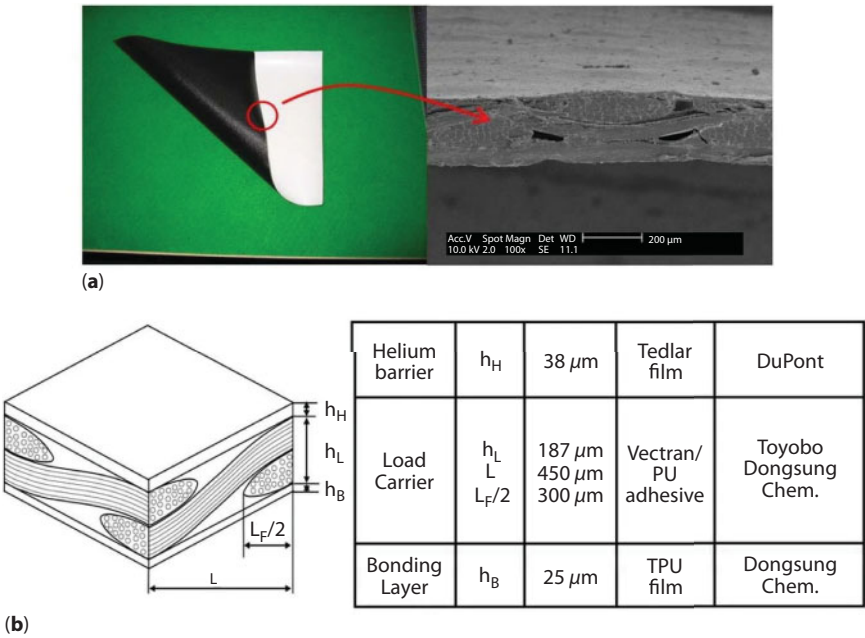


Figure 7.6 Microstructure of film-fabric laminate developed jointly by Lighter-Than-Air Vehicle Group (Korea Aerospace Research Institute), Department of Structural Systems and CAE (Chungbuk National University, Korea), and Department of Aerospace Engineering (Korea Advanced Institute of Science and Technology): (a) SEM image of the cross section and (b) schematic of CAD modeling and detailed specification of each layer [4].

was made of a multicomponent laminated structure of less than 180 g/m², composed of layers of (top to bottom) Teflon film, aluminized polyester (Mylar®) film, Vectran fabric, and polyurethane coating (Figure 7.7). This structure provided good sulfuric acid resistance, low gas permeability, and high strength for working under super-pressure conditions [26].

ADRDE, Agra, India (DRDO), studied and developed some unique coated and laminated structures for aerostat envelopes. Some details of these structures are given below [32].

- i. The weather resistance property of a PVC-coated fabric improved significantly with a top coating of PVDF. However, application of a thin coating in the outer layer was not easy as proper adhesion of PVDF with PVC was very challenging, and sealability of the coated fabric was reduced significantly due to the presence of PVDF in the outer layer.

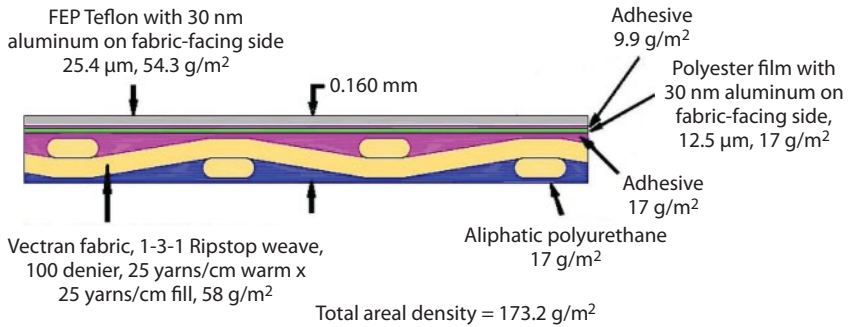


Figure 7.7 Multicomponent laminate material for a high-altitude balloon developed by Jet Propulsion Laboratory, California, USA [26].

A significant number of trials were taken to overcome these problems.

- ii. A comparison was made between Tedlar®/polyester laminated fabric and PU-coated fabric, where the laminated fabric showed better results in terms of enhanced life, better gas impermeability, and desired strength in lower mass. However, in terms of flexibility, the PU-coated fabric performed better.

In another study, Pal *et al.* studied the effect of outdoor exposure and accelerated aging on PU-coated nylon and polyester woven fabric. The degradation behavior of the coated fabric was studied in terms of loss in gas barrier properties, breaking strength, breaking extension, and work of rupture. Although the polyester fabric showed less reduction in tensile strength compared to the nylon fabric, reduction in work of rupture was higher in the case of the polyester fabric. A better weather resistance property was obtained for both fabrics by giving a weather-resistant finish on the fabric, prior to coating [12].

7.6 Advanced Polymer Nanocomposites as Potential Material for LTA Envelopes

Nowadays, by virtue of nanotechnology and using the potential of nanomaterials, polymer nanocomposite-based high-performance coated or laminated fabrics are being developed, which might be potential materials for preparing envelopes of futuristic LTA systems.

7.6.1 Why Nanocomposites?

Recently, nanocomposites have gained much interest in almost all technical fields. Significant efforts are devoted to the process and control of the nanostructure via innovative approaches. Due to the nanoscale dimension and very high surface area-to-volume ratio, the nanomaterials have a potential to enhance the properties of the polymer when dispersed properly in polymeric matrix [37, 38]. Extensive research is being carried out to explore the potential of different nanomaterials to improve specific properties of the polymer. In this regard, we will discuss those nanomaterials that have a potential to improve the helium gas barrier and weather resistance property of the polymer as these two properties are very crucial in developing aerostat envelopes.

The nanomaterials that have a plate-like structure, such as nano-clay and graphene, have great potential to improve the gas barrier properties of polymer. These nanoplatelets, which have a very high aspect ratio, have the capability to enhance the barrier property of polymers against different gases even at very low filler loading. Actually, with proper exfoliation of these nanoplatelets in the polymer matrix, gas permeability is reduced significantly by increasing the tortuous path length for diffusing the gas molecules through polymer nanocomposites [39, 40], as explained in Figure 7.8.

Except for gas barrier properties, the nano-clay and graphene also have good potential to increase mechanical strength and modulus, thermal stability, flammability, etc. There are some inorganic nanomaterials such as nano- TiO_2 , nano- ZnO , nano- CeO_2 , etc. that have the potential to significantly increase the weather resistance property. Most of these nanomaterials are semiconductors, and they can absorb UV light by “band gap exciton theory,” converting the harmful UV radiation to harmless infrared

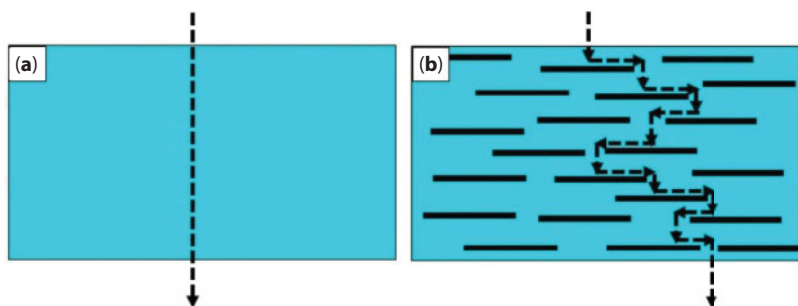


Figure 7.8 Gas diffusion through (a) neat polymer without any restriction and (b) polymer nanocomposites where “tortuosity” is increased by nanoplatelets.

radiation [41]. Moreover, these nanomaterials can also reflect UV light if a continuous top coating is applied. Graphene can also act as a UV absorber, resulting in improvement of the weather resistance property of polymers as reported in the literature [42]. A good synergistic weather resistance property can be obtained by choosing a suitable combination of inorganic nano-additives and some organic UV additives [43, 44].

7.6.2 Some Case Studies and Applications of Polymer Nanocomposites in Inflatables

The use of polymer nanocomposites in this field has not formally started, although there is a strong potential for polymer nanocomposites to improve material properties. Due to the high breaking elongation, excellent elastic recovery and low-temperature flexibility, good abrasion resistance, and excellent adhesion property or bondability, the thermoplastic polyurethane (TPU)-based films, coatings, and adhesives are potential materials for making envelopes of LTA systems. However, the weather resistance and gas barrier properties of neat TPU are moderate and need to be improved for this special application. The properties of polyurethane can be controlled by controlling its structure and chemistry via changing the raw materials, their composition, and reaction conditions. Generally, aliphatic grade polyurethane shows better weather resistance compared to aromatic grade polyurethane [45]. Many studies reported the increase in weather resistance of polyurethane-based coatings or films by reinforcing them with different nanoparticles such as TiO_2 [46, 47], ZnO [43, 44, 48], and CeO_2 [43, 44, 49, 50]. Similarly, an enormous number of studies have been reported for investigating the effect of polyurethane structure on gas permeability [51–53]. The gas barrier property of polyurethane generally increases with the increase in the ratio of hard and soft segments, T_g and crystallinity of soft segments, and cross-linking density [54, 55]. As already discussed, nano-clay and different derivatives of graphene have great potential to improve the gas barrier property of polymers. A significant number of investigations on the improvement of the gas barrier property of polyurethane by incorporation of nano-clay [56–58] or graphene [59–61] have been carried out and some are ongoing.

These weather-resistant and gas barrier TPU nanocomposite films and coatings have a great importance for manufacturing aerostat/airship envelopes in the near future. Table 7.2 shows some polyurethane nanocomposite-based helium/hydrogen gas barrier films and coatings that can be potential materials for the preparation of aerostat/airship envelopes.

Table 7.2 Helium or hydrogen gas permeability through polyurethane nanocomposite-based flexible films or coated fabrics.

Class of polyurethane	Nanofiller	Filler concentration	Process	Film or coating	Gas	% Reduction in permeability	Reference
Third-generation hyperbranched PU	Nano-clay (Cloisite 30B)	8 wt%	Solution casting	Film	Helium	76%	[56]
Polyester-based TPU	GO	1 wt%	Solvent casting	Film	Helium	80%	[60]
Aliphatic polyether grade TPU	Nano-clay (Cloisite 30B)	3 wt%	Solvent coating	Coating on polyester fabric	Helium	58.5%	[62]
Polyester grade TPU	Nano-clay (Cloisite 30B)	3 wt%	Solvent coating	Coating on Nylon 6,6 fabric	Hydrogen	36%	[63]

TPU, thermoplastic polyurethane; Cloisite 30B, organomodified montmorillonite clay modified by methyl tallow bis-2-hydroxy ethyl ammonium chloride; GO, graphene oxide.

Joshi *et al.* developed a polyurethane/clay nanocomposite-based coated fabric with improved hydrogen gas barrier, mechanical, and thermal properties for inflatables. A nylon fabric was coated (coating thickness, 0.25 mm) with a polyurethane/DMF solution containing 3 wt% clay, and about 36% reduction in hydrogen gas permeability was observed [63].

In a very recent study, Chatterjee and coworkers coated a polyester fabric with a series of TPU nanocomposite-based coating formulations by varying the concentration of nano-clay (Cloisite 30B), graphene, and organic UV stabilizers (a mixture of 40% UV absorber, 40% HALS, and 20% antioxidant). There was a significant reduction in 'loss of gas barrier property' after 100 h exposure to accelerated weathering, with incorporation of nano-clay and graphene in coating formulation. The optimized concentration was decided by the desirability function approach using Design Expert® software. The layout of the "9-run" design mixture is shown in Figure 7.9a. An optimum result (minimum loss of helium gas barrier property and UPF value) was obtained with the formulation containing 3.03 wt% graphene, 1.36 wt% nano-clay, and 0.61 wt% organic UV stabilizer, showing no significant degradation of surface coating (Figure 7.9d) [8]. The optimized coated fabric has a good potential to be used in aerostat hulls [8].

Wang *et al.* developed several weather-resistant polyurethane nanocomposite coatings utilizing the synergistic effect of nano UV additives (ZnO/CeO₂) and organic UV additives (UV absorbers and antioxidants). The weather resistance performance of the coatings was analyzed by exposing them to UV radiation and the ozone atmosphere. The polyurethane

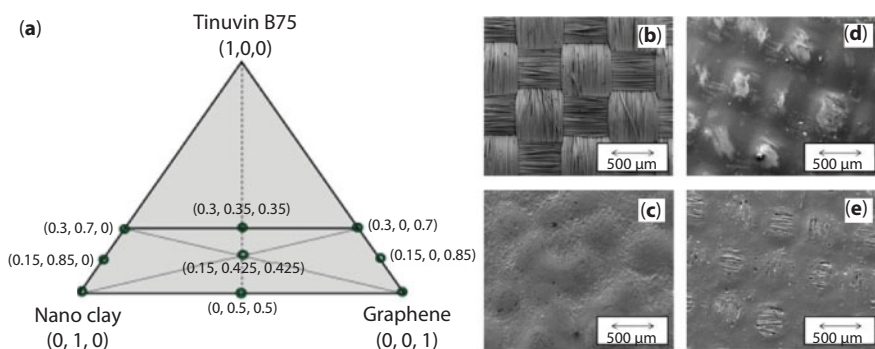


Figure 7.9 (a) Layout of the mixture design with an upper bound constraint for one component (values in brackets define the weight proportion of each component at that specific point); SEM images of (b) the base fabric, (c) the coated fabric with optimized formulation, (d) the coated fabric with optimized formulation and exposed under artificial weathering for 100 h, and (e) the coated fabric that performed worst [8].

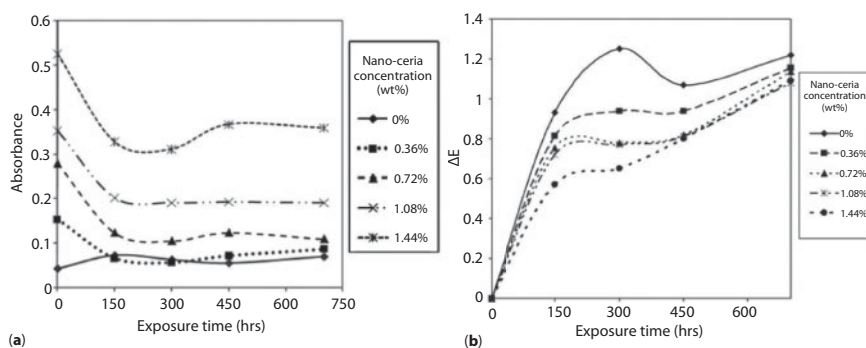


Figure 7.10 (a) Total absorbance at 340 nm and (b) color change (ΔE), as a function of exposure time for the PU-based clear coats containing different amount of nano-ceria [48].

modified by composite stabilizer systems showed much better UV/ozone resistance property than neat PU [43, 44]. Some studies reported improvement in the weather resistance property of polyurethane films or coatings by using TiO_2 [PU-UV-5,9], ZnO [48], and CeO_2 [43, 44, 49, 50].

Saadat-Monfared *et al.* observed that nano-ceria have a very good UV absorbency, resulting in the gradual increase in UV absorbency of PU-based coating with increasing concentrations of nano-ceria (Figure 7.10a). For the same reason, there was a significant reduction in 'change in color' was observed after exposure to accelerated artificial weathering, with increasing concentrations of nano-ceria (Figure 7.10b) [49]. These types of weather-resistant PU nanocomposite-based coatings and films may be potentially applied in the outer layer of the aerostat/airship envelope.

7.6.3 Difficulties and Future Challenges for Polymer Nanocomposites

Obtaining desired properties such as excellent weather resistance, gas barrier, low-temperature flexibility, high strength, abrasion resistance, easy bondability, etc. in a full package is the main challenge for stratospheric airship envelope materials. Despite being surrounded by ambitious ideas, nanotechnology faces the huge challenge of replacing typical or commercialized technologies or products. Although the different polymer nanocomposites have a huge potential in preparing coated and laminated fabrics with improved weather-resistant, gas barrier, and many other desired properties, there are many challenges in their preparation, due to some disadvantages of nanotechnology itself. The main challenges are highlighted below:

- i. At present, nanotechnology is one the most expensive technologies. Hence, implication of nanotechnology in this area may increase the production cost. However, if the material's performance increases significantly by using polymer nanocomposites in place of neat polymers, the increase in cost will not be a barrier.
- ii. Some recent studies highlight the fact that some nanomaterials have negative effects on the environment as well as on human health [64].
- iii. The final properties of polymer nanocomposites are solely dependent on the dispersion and orientation of nanomaterials in the polymer matrix. However, obtaining proper dispersion and distribution of nanomaterials in the polymer matrix is a very challenging task.
- iv. Currently, most of the research and development in nanotechnology are limited at the lab-scale level. Therefore, application of these lab-developed process technologies in bulk, such as for creating the envelope of LTA systems, is a big challenge. The bulk production of nanomaterials such as graphene or metal oxide nanoparticles (TiO_2 , ZnO , etc.) is also very challenging due to very high production cost. Currently, many researches face the task of overcoming this. However, due to their great effectivity and requirement of very less amount of nanomaterials to obtain similar or better properties in comparison to bulk materials, may compensate the expenses marginally.

Although there are many challenges encountered when using polymer nanocomposites in preparing coated or laminated aerostat/airship envelopes, it is expected that polymer nanocomposites will attract the attention of researchers, considering their great potential as materials for making such envelopes in the near future.

7.7 Models for Predicting the Performance and Service Life of Aerostats/Airships

Many studies have focused on predicting and analyzing the mechanical performance of aerostat/airship envelopes using different analytical

models and testing the materials under varying conditions, while considering many factors [4, 35, 65, 66].

Development of a suitable model for predicting the life of an aerostat or airship is a very difficult task. Shallow observed a significant difference between exposure to a xenon arc lamp and to sunlight and was not able to estimate a particular relationship between weather-o-meter and outdoor test results [67]. Using a controlled accelerated atmosphere and making some assumptions during estimation, a proper correlation may be derived from artificial weathering, outdoor test, and actual field test data. However, the task is very difficult and the correlation may not be valid for all locations. To date, literature is scarce in this area.

In a very recent study, Chatterjee *et al.* proposed a systematic approach for predicting the service life of an aerostat envelope made of polyurethane-coated polyester fabric. For this, a reliability model was used where two main stresses—UV radiation and temperature—were considered. A life–stress relationship was obtained by testing the samples in accelerated aging where the stress level was higher than the actual level. The proposed model was validated using the actual field test data. This type of model is quite helpful to predict the service life of a newly developed LTA system before their commercialization in the practical field [68].

7.8 Challenges and Future Scopes

There are many challenges in developing flexible, weather-resistant, and helium gas barrier coated/laminated material for hulls and ballonets of LTA systems, especially for stratospheric airships. The first challenge is the selection of an appropriate fiber in making a high-strength and lightweight fabric that is suitable for stratospheric environment. High-performance fibers such as Vectran®, M5®, Zylon®, and Spectra® are the potential candidates for providing a high-strength fabric at lower weight, compared to conventional fibers such as polyester or nylon. However, there are some concerns for such fibers, such as creep, moisture resistance, UV resistance, fatigue, and high cost.

The second key challenge is the selection of suitable polymers that would protect the load-bearing layer from UV/ozone degradation, restrict the permeation of helium gas, and also maintain flexibility in the structure even at subzero temperatures in the long term. Fluoropolymers such as PVF (Tedlar®), PVDF, Teflon®, etc. are the best potential candidates for protective layers, although they have some limitations such as adhesion problem

with other substrates. EVOH, Mylar®, etc. are potential candidates for the gas barrier layer, but they also have some issues. Polyurethane is a unique polymer that can be used in all layers (protective layer, gas barrier layer, adhesion layer, and sealing layer) due to its versatile properties; only its gas barrier property and weather resistance property need to be improved for a better, long-term performance of aerostats/airships. Therefore, for overcoming some current minor difficulties, nanotechnology, nanomaterials, and nanocomposites have a bright future in this field. However, there are additional challenges with nanotechnology-based approaches as discussed earlier.

The third key challenge is the selection of an appropriate processing technique, be it coating or lamination. It mainly depends on the raw materials to be used, the frequency of the inflating/deflating operation required (for ballonets), and the expected life of the LTA system. There are many factors to be controlled during coating or laminating the fabric to obtain the desired sustainable properties. Many trials have been undertaken by different organizations in developing coated or laminated textiles to make prototypes or large-scale balloons/aerostats/airships.

The fourth challenge is designing LTA systems. Development of a “structurally efficient joint” is very much needed, because the service life of LTA systems is totally dependent on the joint strength. Proper selection of joint design, adhesive, and seaming technology is a major factor for obtaining a good joint strength. Finally, estimation of the performance of an aerostat/airship by different models developed by different researchers is very important to have a prior idea of its performance before exposure in the actual field.

7.9 Conclusion

LTA systems such as aerostats and high altitude airships have huge potential for telecommunication, broadcasting, weather monitoring, and defense applications. The materials of these LTA systems must have the following properties: weather resistance (against UV radiation and ozone), low gas permeability, light weight, low-temperature flexibility, high strength, abrasion resistance, and good bondability, among others. Therefore, the challenge for materials scientists is to develop suitable materials for aerostat/airship envelopes that can provide the right balance of these desirable properties. Generally, multilayered coated or laminated textiles are used for making envelopes for LTA systems, where a specific layer executes a specific functionality. However, there are many challenges for the materials (fibers, fabrics, and polymers) to be used in different layers. The development and

use of high-performance fibers such as Vectran[®], Zylon[®], M5[®], Kevlar[®], Nomex[®], Spectra[®], and Dyneema[®] have a potential to fulfill almost all the requirements which are beyond the capabilities of conventional fibers like polyester and nylon. However, it can be obtained by compromising with the high cost and limited availability of these high-performance fibers. In addition to this, advanced polymer nanocomposites have great potential of improving the properties of coated/laminated textiles, much better than neat polymers. In particular, polyurethane nanocomposites containing different additives such as gas-impermeable fillers (nano-clay, graphene), inorganic/nano UV additives (nano-TiO₂, nano-ZnO, nano-CeO₂, etc), and organic UV additives (UV absorbers, antioxidant, HALS etc) are capable of producing the next generation's aerostats/airships with longer service life.

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Woolen Carpet Industry: Environmental Impact and Recent Remediation Approaches

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Abstract

Woolen carpets have been considered as the most suitable textile floor covering due to various reasons. Unfortunately, the production of woolen carpets, their use, and final disposal are directly or indirectly associated with many environmental issues. Raw wool production and various stages of conversion of raw wool to carpet demand a series of operations and involve a lot of chemicals and energy. Environmental issues are associated not only with the production of a carpet but also with the usage and final disposal of the carpet.

This chapter aims to provide comprehensive information about the causes and origins of environmental problems that arose in the cleaning of raw wool, manufacturing of carpet, its use, and final disposal. The feasible methods to reduce the impact of these environmental problems are part of this chapter as well. Application of advance technologies and adoption of good practices aimed at reducing effluent load shall also be discussed.

Keywords: Scouring, pesticide, dyeing, wool, carpet, dyeing, effluent

8.1 Introduction

Wool has been the fiber of choice in the manufacture of carpet and other floor coverings for centuries. The early carpet makers were nomadic sheep herders. Since then, carpet making has been associated with the technology of wool industry. The tradition of using wool in carpet has been the benchmark for other textile fibers to be utilized in carpet manufacture [1].

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Wool is one of the most appropriate renewable source of raw material for making carpets. It is a biodegradable fiber extracted from the body of a sheep, which exists in the form of a protective coat. Wool protects the sheep from adverse climatic conditions, especially against extreme cold weather. Due to the good thermal insulation and resilience property of wool fiber, the carpet made of wool has a huge demand in cold countries. However, wool fiber is one of the dirtiest fiber in its raw form. It requires several mechanical and chemical cleaning steps before its actual use in carpet application. The operations required in cleaning raw wool especially using chemical methods entail a large number of environmental issues.

In the process of making a carpet, dyeing plays an important role. Compared with other textile fibers, dyeing of wool is relatively easy. Dyeing of wool with a suitable class of dyes imparts brilliant colors to it. Due to the availability of a wide gamut of colors, the dyed woolen yarn used in carpet makes it more attractive.

Conversion of wool from its raw fiber stage to a decorative carpet is a lengthy process. In the process of converting wool to carpet, there are a number of steps involved that adversely affect the environment. Environmental regulations on processing of wool are stringent. Therefore, environmental legislations associated with effluent generation in the course of manufacturing of a product, consumer safety during its use, and its after-use disposal product have become a great deal.

8.2 Flowchart of the Manufacture of a Woolen Carpet, Its Use, and After-Use Disposal

Carpets are one of the most useful floor coverings due to their aesthetic and functional attributes. Different fibers are used to provide the piled surface in a carpet. Among them, carpets made up of woolen piled surface have a huge demand in both residential and commercial settings.

A flowchart describing the manufacture of a woolen carpet, its use, and after-use disposal is shown in Figure 8.1.

8.3 Wool Fiber Production and Related Environmental Issues

Wool fiber production requires significantly less energy as compared to the synthetic fibers used in carpet manufacture. Wool fiber production

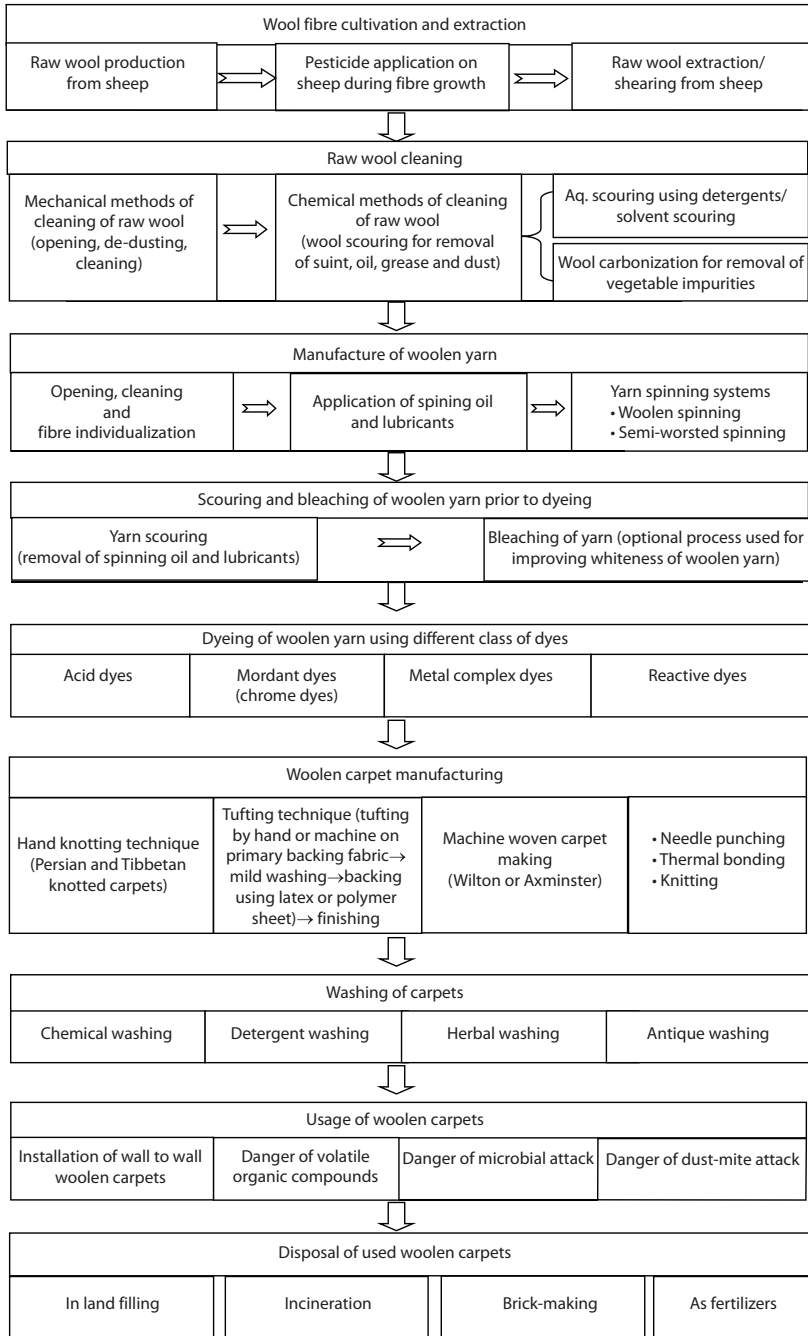


Figure 8.1 Flowchart describing the manufacture of a woollen carpet, its use, and after-use disposal.

consumes only 38% of the total energy requirement of polyester fiber production. Similarly, with respect to acrylic and nylon, the energy requirement of wool fiber production is only 27% and 19%, respectively [2].

In general, the weight-wise percentage of wool fiber in a woolen carpet is more than 60% irrespective of the technique used for the manufacture of the carpet. Therefore, while studying the life cycle assessment (LCA) of a woolen carpet, the role of wool as a raw material has a great technical importance. Wool fiber production in terms of cultivation and extraction has been studied with respect to its impact on the environment.

Commercial sheep farming requires a huge tract of grassland for grazing of sheep to take place. However, sheep meant for wool production are seldom grazed on land that could be used for food crops. Therefore, sheep are generally grazed in the hilly areas [3].

Farming of sheep is very close to a self-sustainable system with minimum damage to the environment (Figure 8.2). Grazing animals eat clover and grass. In return, they give a high proportion of nitrogen back to the soil in their dung and urine. A huge amount of nitrogen is also returned back through decay of plant materials. The nitrogen returned to the soil in this way keeps the soil nitrogen level intact and ensures its supply to the grass through the action of microorganisms in the soil.

Besides, sheep farming needs regular application of fertilizers to the grassland. Application of fertilizer is useful to maintain a required level of grass growth and forage yield. But of course, injudicious use of fertilizer may result in adverse environmental effects. A long-term impact on surface water and groundwater quality may be seen in terms of increase in phosphorus and nitrate concentrations [4].

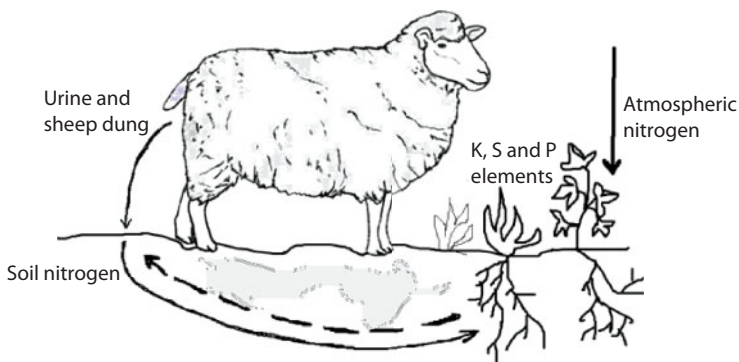


Figure 8.2 Sheep farming: an environment-friendly self-sustainable system.

However, the green reputation of wool fiber production has been questioned from time to time. It has been claimed that sheep farming is one of the biggest producers of greenhouse gases in wool-producing countries like New Zealand and Australia. A sheep produces huge amount of methane during the digestion of its food.

Even then, as compared to synthetic fiber, the production of wool fiber can be considered a relatively “cleaner and greener” process [3].

8.3.1 Pesticides in Raw Wool

Use of pesticides in sheep is another serious environmental concern as far as wool cultivation and extraction are concerned. The sheep meant for production of fiber is treated with pesticides to prevent it from infestation by parasitic insects. Without such treatment, the blowflies are prone to lay their eggs in the fleece of the sheep. In absence of proper preventive measures, the fly maggots may attack the flesh of a live sheep. This can be a painful infection, and in some cases, the sheep may even die [5]. Table 8.1 shows different types of pesticides used in wool.

Table 8.1 Different types of pesticides used in wool.

Type of pesticides	Examples
Organochlorine (OCs)	γ -Hexachlorocyclohexane (lindane) Dieldrin DDT
Organophosphorus (OPs)	Diazinon Propetamphos Chlorfenvinphos Chlorpyriphos Dichlorfenthion
Synthetic pyrethroids (SPs)	Cypermethrin Deltamethrin Fenvalerate Flumethrin Cyhalothrin
Insect growth regulators (IGRs)	Cyromazine Dicyclanil Diflubenzuron Triflumuron

All commercially available pesticides are poisons and therefore are toxic to a living organism beyond a particular dose. They adversely affect the normal biochemical reactions necessary for metabolism by inhibiting the enzymatic activities. In the past, pesticides based on organochlorines (OCs) were used to protect sheep from the attack of these parasites. These OC-based pesticides were cheap and effective. However, the major wool-growing countries have officially banned the use of OC-based pesticides due to the irreparable damage they cause to the environment. Instead, some of the pesticides such as lindane (gamma-hexachlorocyclohexane), camphechlor, and toxaphene are still used by several other wool-producing countries in a limited quantity. Nowadays, the main classes of pesticides used on sheep are the organophosphates (OPs) and synthetic pyrethroids (SPs). Both these classes have lower mammalian toxicity and are less persistent than the OCs. However, their use is also not free from danger. Therefore, many plant-based pesticides are now being investigated as a replacement due to their safe use and less polluting effect [6].

The commercially available pesticides have a lipophilic (fat-loving) nature. They have a strong association with wool oil and grease. After scouring, these pesticides are almost removed from the fiber and become part of the scouring effluent. In this way, carpet as an end product carries a very small concentration of this pesticide. This helps in the safe disposal of the carpet after its use.

The presence of pesticide in the scouring effluent brings problems to the scourer. In the scouring effluent, wool grease is a valuable by-product and every attempt is made to recover the grease from the scouring effluent. Centrifugation is the most commonly used method. However, this method is capable of extracting only about 40% of the total grease present in scour liquor. Acid cracking is another method to recover wool grease, which can recover as much as 90% of the total grease present in scour liquor, but the disadvantage of the acid cracking method is that the quality of grease recovered is not as good. Therefore, the recovered grease by the acid cracking method is not suitable for the preparation of cosmetic cream and pharmaceutical-grade lanolin.

Although lanolin refiners have developed techniques for reducing total pesticide levels to 1 ppm or less, improvements are still required to meet the norms of German specifications. Concurrently, efforts have been made to optimize the usage of pesticide on sheep. This may help in reducing the amount of pesticides in wool at the time of shearing. Some specific biological treatments of scouring effluent have the ability to remove pesticides [7].

8.4 Wool Fiber Cleaning and Related Environmental Issues

8.4.1 Mechanical Opening and Cleaning

Raw wool fiber extracted from sheep cannot be used directly for the preparation of yarn. In fact, it requires several stages of opening and cleaning before the actual yarn spinning. A first stage of opening and de-dusting of greasy raw wool is carried out prior to scouring. This is a mechanical process designed to shake out dirt from the wool and to open the fleeces in order to improve the efficiency of the scour in removing contaminants. Therefore, the basic objective of this step is to remove dust, dirt, and other vegetable contaminants. The severity of opening and de-dusting processes varies depending on the characteristics of the greasy wool being processed. Such pre-opening and cleaning of fiber help in reducing the effluent load in the subsequent stage of fiber cleaning, that is, scouring. However, a third stage of mechanical opening and cleaning of scoured wool is also required before yarn spinning operation. A wide range of machinery is used for the pre-opening and cleaning of greasy wool, depending on the quality and characteristics of the wool.

The dirty raw wool requires preliminary opening in a double drum opener as shown in Figure 8.3. The double drum opener offers self-cleaning to remove the accumulated grease and dirt present in the raw wool. After the double drum opener, the wool fiber is passed through a step blender. The step blender has an air exhaust to encourage dust removal.

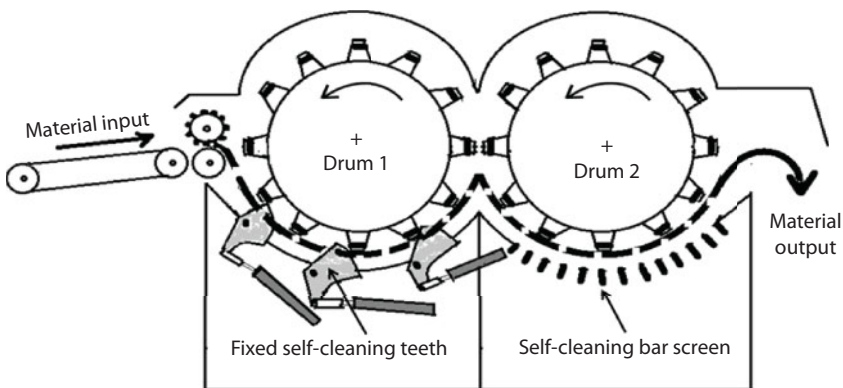


Figure 8.3 Double drum opener with self-cleaning ability.

It also has a screw conveyor with perforated screens to remove dirt particles through it [8].

8.4.2 Wool Scouring

Wool is regarded as a high-quality, environmental friendly fiber. But raw wool contains a substantial amount of impurities. These impurities are classified in terms of natural, added, and acquired impurities. Wool wax and suint (water-soluble material) are the natural impurities present in raw wool. Vegetable matters such as burrs, grass, urea, animal dander, dust, and dirt are in the category of acquired impurities, which they carry in their fleece while grazing. Some color staining (used for identification of sheep) and pesticide residues (from the treatment of the sheep to prevent disease), although in a very small proportion, exist in raw wool in the form of added impurities. During the scouring process, the impurities are either removed or digested in the wool-scouring chemicals. But this process results in the discharge of a highly polluting effluent. The organic effluent load from a typical wool-scouring plant is approximately equivalent to the sewage from a town of 50,000 people [7].

The main objective of a wool scour is to remove all non-wool contaminants such as wax (or grease), suint (or sweat), dirt, and vegetable matter at maximum efficiency and with minimum pollution of the environment.

Wool scouring involves washing the greasy wool in hot water and detergent to remove wax, suint, dirt, and loose vegetable matter. After scouring, rinsing and drying of cleaned wool are carried out.

The WRONZ mini-bowl system is a popular wool scouring system used worldwide. It typically consists of six in-line bowls. The first three bowls contain a non-ionic detergent to scour the wool at 60–65°C. The fourth and fifth bowls are usually cold rinse bowls, whereas the sixth one is a hot rinse bowl [8, 9].

The raw wool is passed through these bowls. A pair of squeeze rollers is installed in between any two bowls to extract the water and other contaminants from wool. Finally, after scouring, the wool is dried up to a specified moisture content value, before its packaging in bale form.

Initially, detergent is added into the first three bowls of a typical wool scour, but with time, concentration of the detergent is to be maintained in the second and third scouring bowls only. In wool scour, the liquor flow is in a counter-current direction, opposite to the direction of the flow of wool. Therefore, from time to time, addition of fresh detergent in the scouring system goes from bowl 3 to bowl 2 to bowl 1.

The amount of detergent in the wool scouring liquor should be optimum. Too much detergent in the scouring liquor can result in squeeze roller slippage, particularly in bowls 1, 2, and 3. Excess detergent can be deposited onto the fibers and is lost from the scouring liquor. The problem of squeeze roller slippage also arises when insufficient amount of detergent is present in the scouring liquor. In fact, in this case, liquor becomes very greasy and tends to cause squeeze roller slippage. This in turn hampers the wool grease recovery and exerts burden to the effluent. Therefore, it is advisable to use the optimum quantity of detergent in the scouring liquor.

In recent developments, a WRONZ Comprehensive Scouring System has been designed, as shown in Figure 8.4. It has the following advantages: improved energy efficiency, water saving, grease recovery, and effluent removal. Detergent is introduced in bowl 3 and the liquor flows back through bowls 2 and 1. Cold water flows back from bowl 5 to bowl 4 and the flow direction of clean hot rinse water is from bowl 6 to bowls 3, 2, and 1. The scour liquor is taken continuously from bowls 1 and 2 and passed to a settling tank where the heavy particles settle out as sludge and are automatically discharged. The liquid then passes to a centrifuge where wool grease is recovered and the clean liquid continuously returned

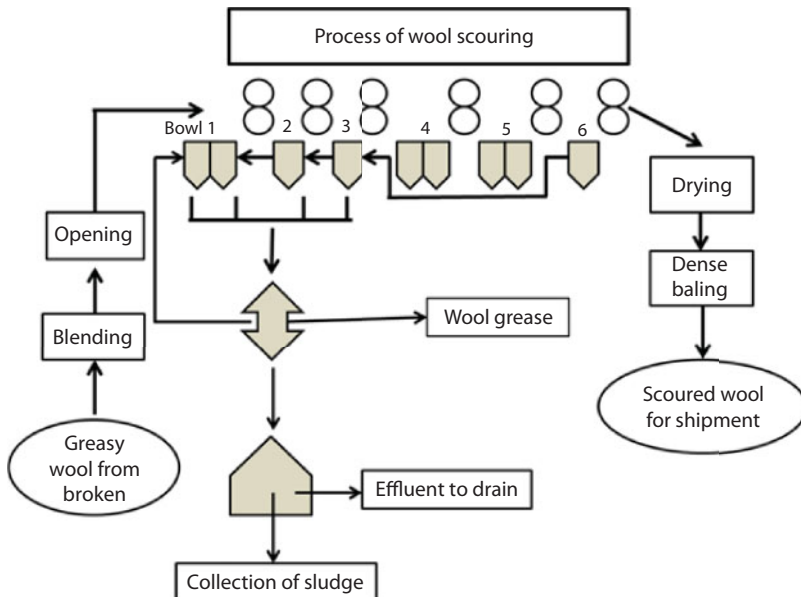


Figure 8.4 WRONZ comprehensive wool scouring system.

to bowl 1. For energy conservation, the dirty liquor is discharged via a heat exchanger that heats the incoming fresh make-up water for bowl 6.

8.4.3 Role of Detergent in Wool Scouring

The primary role of detergent in wool scouring is to remove the grease and dirt contaminants present on the surface of the raw wool fiber. In addition to this, the presence of detergent in a scouring bath helps in removing the water-soluble suint from fiber.

Depending on the level of impurity present in the wool, different wool types require different amounts of detergent to maintain the emulsion in the scouring liquor. Clean wools need less detergent than dirty wools. Scouring the crossbred-type greasy wool requires only 1 kg of detergent for almost 1000 kg of greasy wool. In contrast, the greasy wool obtained from slipe wool blends needs at least 1 kg of detergent for 80 kg of greasy wool. Therefore, it is very important to recognize the wool type to ensure the correct requirement of detergent in the scouring bowls. This can avoid the undesirable load of the scouring effluent.

Most of the detergents used in wool scouring are synthetic in nature. These are alkyl phenol and ethylene oxide-based non-ionic detergents. For ease of use, these detergents are normally in liquid form. However, some scouring detergents form gels when mixed with small volumes of water. This happens with pure nonylphenol polyethylene oxide-type wool scouring detergents. The tendency of formation of gels by these detergents can be a problem, when pumping is done through pipes. Therefore, care should be taken during addition of such detergents into scouring bowls. Proper mixing and agitation can prevent the possibility of formation of gels and subsequent precipitation of these detergents.

Nonylphenol polyethylene oxide (NPEO) has been used as detergent in the wool scouring industry for quite a long time (Figure 8.5). But, use of NPEO is now banned in most countries due to its limited biodegradability. It generates short-chain ethoxylated phenols during biodegradation, which are known to be endocrine disrupters.

The other types of detergents commercially used in wool scouring are fatty alcohol ethoxylate-type surfactants, which are generally considered to be biodegradable. In New Zealand, there are two popular detergents of this category, namely, Dobanol 91/6 and Teric G9A6. These detergents contain a C_9 – C_{11} linear fatty alcohol in combination with six moles of ethylene oxide. However, these types of detergents are not good for scouring of difficult-to-scour wools. A significant amount of these detergent residues remain in the recovered wool grease [9–11].

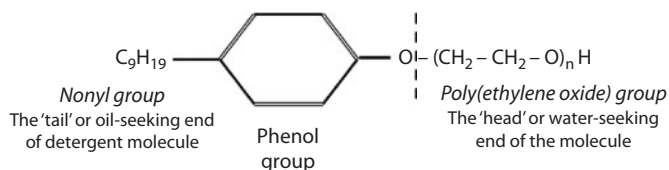


Figure 8.5 Nonylphenol polyethylene oxide detergent molecule.

8.4.4 Carbonization of Wool

Raw wool is also contaminated with vegetable impurities. These vegetable impurities are mainly burrs, seeds, twigs, and straw. These impurities are acquired by the sheep during grazing. The wool scouring process is not able to remove these vegetable impurities and therefore a separate carbonization process is included in overall wool cleaning operations. The carbonization process is composed of acidizing, drying, baking, crushing, beating, neutralizing, and final drying of wool fiber. Depending on the temperature of treatment and the resident time given, sulfuric acid used in the carbonization process has a concentration in the range of 4.5% to 7.5%. During drying and subsequent baking, the vegetable matter present in wool becomes brittle and charred under an acidified environment of concentrated sulfuric acid. Further, crushing and beating of wool separate the brittle and charred vegetable matter from fiber. In the last step, neutralization is carried out in the scour train in the presence of sodium carbonate and non-ionic detergent. Prior to final drying, proper rinsing is done to ensure that the wool is free from any residual chemical [9].

8.5 Woolen Carpet Yarn Manufacturing and Related Environmental Issues

The scoured wool meant for carpet yarn manufacture is first passed through an opener known as a fearnought opener, as shown in Figure 8.6. This fiber opener resembles a crude single-stage card having feed rollers, a swift, two to four sets of workers, and strippers. The swift is clothed with coarse curved metal teeth (20–30 mm long) and rotates at around 200 rpm. The workers and strippers rotate much slowly in the opposite direction to the swift. Proper opening and blending of wool fiber occur when it passes from swift to worker and back to the swift. The opened wool is ejected by a rapidly revolving doffer (600 rpm). A mesh is installed just under the swift,

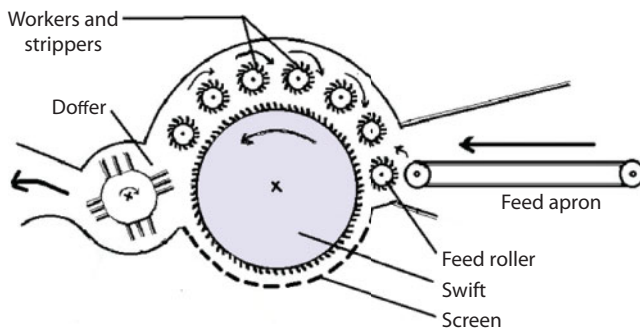


Figure 8.6 Fearnought.

which allows dust and dirt to fall out. A fearnought is generally used in blending line of a woolen spinning plant.

Before the commencement of actual yarn spinning operation, opening, cleaning, oiling, and mixing are carried out as an integrated fiber preparation sequence. Oils and lubricants are applied at the stage of fiber mixing to reduce electrostatic charge buildup. This also helps in the minimization of fly waste, reduction of fiber breakage, and improvement of fiber cohesion. However, such oils and lubricants have to be removed in the process during the second stage of scouring in yarn form prior to dyeing [8].

Lubricants are basically fiber processing aids, which have been originally derived from fat-based products like tallow. These lubricants are used to provide required cohesiveness in the fiber to form web. However, due to their high cost and environmental damage, these products have recently been replaced by mineral and synthetic lubricants. Polyalkylene glycols, ethoxylated esters, and complex phosphoric esters are some of the examples of such synthetically produced lubricants. The controlled synthesis of these lubricants allows imbining any desired combination of properties in the final product. Although these synthetic lubricants are more expensive than their mineral oil-based substitutes, they are applied at varying concentrations (typically 0.5%–4%) to solve the purpose. In this way, they are economical to use [12].

Most recently, the increasingly stringent regulations on effluent disposal have led to the development of biodegradable lubricants. Some blends of synthetic lubricants and emulsifiable mineral oils are also available in the market, claiming to have excellent antistatic, lubrication, and cohesion properties. These lubricants can be removed from the fiber by aqueous scouring in the yarn stage with generation of less toxic effluents. In addition to this, some lubricants that are compatible with dyeing auxiliaries

have also been identified. Using such types of lubricants can even avoid the second stage of scouring (in yarn stage) and thus yarn can directly be dyed. Omitting the scouring process in the yarn stage can be helpful in reducing the scouring effluent load.

Woolen and semi-worsted spinning systems are commonly used to convert fiber into carpet yarn. Depending on the quality of input material and its preparation before spinning, the characteristics of the yarn produced from both the systems are different. Both of the systems utilize carding as the first major step to separate and mix the fibers. During spinning, the fibers are drafted and twisted to achieve a desired level of fineness and strength in the yarn. Woolen processing is the simplest production route, in which three basic stages—blending, carding, and spinning—are involved. It is a comparatively inexpensive route for converting scoured wool into heavier count yarns.

In comparison to the woolen system, the semi-worsted system produces yarn of better quality. The yarn produced is particularly used for making carpet of superior quality. The semi-worsted system involves blending, carding, gilling, and spinning steps for the preparation of yarn. Wool with a relatively low level of contamination is suitable for the semi-worsted system [8].

Dust and noise are associated with the woolen carpet industry as occupational hazards. Consistent efforts have been paid to mitigate and control these hazards to protect the workforce. Dust is a common air pollutant generated by different sources. Microscopic organisms, vegetable impurities, and dander (dead skin cells shed by animals) are common causes of dust in the environment. Dust particles vary in size from visible to invisible. The smaller the particle, the longer it stays in the air and the further it can travel. Large dust particles fall out of the air relatively close to where they are created. Large dust particles tend to be trapped in the nose and mouth and can be readily breathed out or swallowed harmlessly. Fine dust particles are more likely to penetrate deeply into the lungs while ultrafine particles can be absorbed directly into the bloodstream. The type and size of a dust particle determine how toxic the dust is. The inhaled dust particles may be the cause of irritation to the eyes, coughing, sneezing, or asthma.

Additionally, airborne contamination can also occur in gaseous form (gases and vapors) or as aerosols, which include sprays, mists, smokes, and fumes. Airborne contaminations are of particular concern because they are associated with classical widespread occupational lung diseases such as pneumoconiosis. There is also increasing interest in other dust-related diseases, such as cancer, asthma, allergy, and irritation.

Therefore, compliance to the regulations during operations like opening, carding, gilling, spinning, twisting, and winding can reduce the dust and noise level of the working environment.

Workers who are exposed to industrial noise have a danger of suffering from hearing impairment. Precautions are required to be taken to control the noise below the prescribed limit of 90 dB. The noise level can be controlled by properly designing the layout of the plant in which the noisy machines can be segregated (e.g., compressor). Proper maintenance of the machines and adoption of sound absorbers and silencers are also helpful in reducing the noise level. Incorporation of an individual spindle drive in place of a belt drive in spinning, use of improved bearings, reduction in vibrating parts, elimination of cams, and use of electronic controls for noise damping are some of the possibilities to reduce the noise level of a carpet production house [13, 14].

8.6 Bleaching of Woolen Yarn and Related Environmental Issues

Bleaching is an optional process, and it is carried out essentially for yarns that have to be dyed with light or pastel colors. The natural color of wool is creamy white to a deep yellow white. Bleaching of wool is carried out to improve its whiteness. However, bleaching can be omitted for yarns to be dyed with dark shades. Bleaching of wool can be carried out by using reductive- or oxidative-type chemicals. Earlier, reductive bleaching of wool was carried out by using sulfur dioxide gas. This method of bleaching was known as “stoving.” In this method, the woolen substrate is placed in an environment of sulfur dioxide gas. However, the whiteness produced in the substrate after bleaching was not permanent. The other method of reductive bleaching is bisulfite bleaching, in which an aqueous solution of sodium metabisulfite was used. The environmental issue associated with such bleaching methods is the escape of sulfur dioxide gas into the atmosphere.

Bleaching of wool can also be performed using hydrogen peroxide. Hydrogen peroxide is an oxidative bleaching agent, which manifests its bleaching action under acidic conditions. This is one of the reasons why hydrogen peroxide is the preferred bleaching agent for wool. Other than these bleaching agents, woolen yarns and carpets are also bleached using hypochlorite or bleaching powder. However, due to the emission of free chlorine, they are known to be extremely toxic to the environment. Some

mills have started using ozone bleaching, a comparatively new technology for bleaching of woollen substrate [15].

8.7 Dyeing of Woollen Carpet Yarn and Related Environmental Issues

Dyeing is an essential step of the entire process of carpet manufacture. A carpet can be saleable only if it has attractive color and design. While selecting the dyestuff and related auxiliaries for dyeing the woollen pile yarn, one should always keep into consideration the environmental impact. Accordingly, focus should always be on such application techniques, machinery, and chemicals, which may help in reducing the effluent load after dyeing. Strict environmental regulations and awareness among the users have restricted the application of carcinogenic azo dyes in carpet yarn dyeing. However, the use of mordant dyes in wool yarn dyeing is still a concern.

Woollen carpet yarn is generally dyed in hank form. However, developments are taking place to dye the yarn in package form as well. The dyeing machines used for dyeing carpet yarn hanks are mainly front loaded cabinet type and top loaded carrier type. In these machines, the dye liquor is circulated over a weir and through the yarn by means of a reversible impeller.

In the case of the front loaded cabinet hank dyeing machine, a hank carrier is mounted on a trolley that is loaded outside the dyeing cabinet. The other hank carrier is utilized inside the dyeing cabinet, in which dyeing takes place. Therefore, at one point in time, two hank carriers are required for each cabinet. This helps in minimizing the time to load and unload the material in the machine. This machine is suitable for woollen yarn hanks, which can be dyed at temperatures below 98°C. The machine is equipped with an automatic reversal device for better control of the liquor flow direction [16].

Most of the wool dyeing is still carried out with the use of heavy metals, mainly chromium. Almost half of this production employs the after-chrome process and the remainder uses metal complex dyestuffs.

After-chrome dyes are used predominantly for blacks and, to a lesser degree, for navy blues. Replacement of chrome blacks and navies with environmental friendly alternatives has been thought for wool dyeing. But alternative dyestuff, capable of giving the same level of fastness and richness of shade, remains a challenge [5].

Chromium in its hexavalent form (Cr^{+6}) is a serious environmental hazard, since it may enter the food chain easily. Woolen yarn dyed by after-chrome dyeing procedure requires a minimum quantity of chromium to produce the desirable shade. To fulfill this need, about 300 mg/L of chromium must be supplied in the form of 1 g/L of hydrated sodium dichromate. This high level of chromium demand of over 300 mg/L for dyeing should come down eventually to 1 mg/L in the dye bath effluent. Special application methods have been developed involving reduction of Cr^{+6} to Cr^{+3} and facilitating the formation of complex of chromium with carboxyl end groups of wool substrate. Looking into the serious effects of chromium, various eco standards have prescribed the norms of extractable heavy metal limits on woolen goods as below 2 ppm level [17].

Modification in dyestuff chemical structure has also led to achieve metal complex dyes with high level of exhaustion for reducing the load of effluent to a specified limit.

A summary of the most common dyestuffs used for dyeing of wool is shown in Table 8.2 [18].

Another environmental issue related with wool yarn dyeing is the use of formaldehyde. During dyeing at high temperature and high pH conditions, there may be a significant damage in the wool structure. Therefore, formaldehyde-based compounds are used as protective agents for wool in high-temperature dyeing, especially when the wool–polyester blends are dyed. These protective agents facilitate the cross-linking of wool by replacing the broken cystine disulfide links by more stable $-\text{S}-\text{CH}_2-\text{S}-$ groups. However, use of formaldehyde has the disadvantage of toxicity and allergy. It also gives a harsher handle to the processed wool yarn [19].

However, the damage of wool during dyeing can be reduced if wool is dyed at low temperatures (usually 85–90°C). In order to achieve a satisfactory exhaustion and a good level of wet fastness properties, low-temperature dyeing of wool is carried out for a comparatively longer time. It is also possible by the addition of various reagents to the dye bath or by modifying the surface of the wool substrate. Use of a non-ionic or amphoteric surfactant as dye bath additive facilitates the dyeing of wool at low temperatures. The most common non-ionic surfactants used are linear alkyl polyethylene glycols and glycol ethers. But it is found that the biodegradation of these surfactants are not easy and they produce hydrophobic metabolites. They are sometimes more toxic than even the parent compounds [20]. Therefore, modification of wool fiber surface using proteolytic enzymes or polar solvents is preferred. These enzymes have the ability to enhance the rate of dye uptake in the fiber. These modifications partially digest the non-keratinous

Table 8.2 Summary of common dyestuffs used in dyeing of wool.

Sr. no.	Dyestuff class	Chemicals and auxiliaries	Features
1.	Acid dyes (metal-free)	10% Na_2SO_4 or $(\text{NH}_4)_2\text{SO}_4$ is generally used as leveling agent for level-dyeing. - The sulfate ions compete with dye anion to react with protonated cationic sites of wool. - A broad range of acidic pH can be applicable.	Three types: - Equalizing dyes (strongly acidic conditions by formic acid) - Half-milling dyes (moderately acidic conditions by acetic acid) - Milling dyes (almost neutral conditions by acetic acid and sodium acetate or ammonium sulfate) - Brilliant shades - Variable fastness properties - Dye anion links to amino groups of wool
2.	Chrome dyes (mordant)	- pH = 3 to 4.5 - Organic acids like acetic/tartaric/lactic acid can be used - Reducing agent: sodium thiosulfate - Sodium sulfate	- After-chrome method using sodium or potassium dichromate - High wet fastness - Good light fastness - Good dry-cleaning fastness - Precipitation of formed complex in dye bath or surface of the fiber results in poor rubbing fastness and effluent load

(Continued)

Table 8.2 Summary of common dyestuffs used in dyeing of wool. (*Continued*)

Sr. no.	Dyestuff class	Chemicals and auxiliaries	Features
3.	1:1 metal complex dyes	• pH = 1.8 to 2.5 using sulfuric or formic acid (pH 2.5 in the presence of auxiliary agents such as alkanol-ethoxylates) • Salt: sodium sulfate • Ammonia or sodium acetate can be added to the last rinsing bath for neutralization	• Excellent migrating and penetrating properties • Good light fastness • Ease of application • Moderate wet fastness property • High acidic pH is harmful to wool
4.	1:2 metal complex dyes	• pH = 4.5 to 7 • Ammonium sulfate or acetate • Leveling agents (non-ionic, ionic and amphoteric surfactants)	• Weakly acidic to neutral dyeing conditions • Good wet fastness property
5.	Reactive dyes	• pH = 4.5 to 7 using formic or acetic acid • Leveling agent • After-treatment with ammonia for highest fastness	• Good wash and light fastness • Formation of covalent bonds with wool

scaly surface of the fiber. This significantly increases the dyeing rate at temperatures below the boiling. Depending on the cost of the processing and the environmental issues associated, different pretreatment methods are used to improve the dyeing of wool at low temperatures [21].

Pyridine and anionic surfactant-based compounds are used in dyeing of highly twisted woolen carpet yarns. Woolen yarns having a very high twist level often face the problem of penetration of dye solution in the yarn structure. This problem can be mitigated to a large extent by the use of acid leveling dyes, which have strong migrating behavior at boiling temperature. Further, to improve the wet fastness properties of these dyes, pyridine and anionic surfactant-based disaggregating compounds (lyocol PDW-S) are used. Unfortunately, these compounds have an unpleasant odor and toxicological issues. Therefore, Lyocol FDW-S has been nowadays replaced by a powerful wetting agent such as Lyogen WPA-S [19].

In dyeing of wool with reactive dyes, it is desired to have a very high degree of dye-fiber bonding tendency. This enables the minimization of dyestuff loss in the subsequent step of clearing treatment and thus reduces the effluent load. This also results in achieving maximum wet fastness. It is also desirable to have a high rate of adsorption of dye on substrate in comparison to the reaction rate of dyeing with substrate. This helps to achieve a level dyeing. Leveling agents are used to overcome the problem of tippy dyeing of wool. These leveling agents form dye-surfactant complexes on the surface of the wool evenly at low temperatures. With the increase in dye bath temperature, the dye-surfactant complexes start breaking down and thus the dye molecules are allowed to penetrate and react with the substrate to form covalent bonding. Around 1%–1.5% (of the mass of fiber) of auxiliary with amphoteric or weakly cationic nature is used in reactive dyeing of wool to promote dye uptake at low temperature.

Exhaustion of dye in reactive dyeing takes place in slightly acidic pH (around 5–6). If the starting pH of the dye bath is kept high, it will result in poor exhaustion of the dye. On the other hand, if the starting pH is kept too low, the problem of unlevelness will occur due to rapid dye uptake. Darker shades can be achieved by dyeing at boiling temperature for a period of 1.5–2.0 h (prolonged). After dyeing, an alkaline clearing treatment is essential to achieve maximum wet fastness. This alkaline treatment is generally carried out in the presence of ammonia at pH 8.5 to 9.0 for a period of 15 min at 80°C. Use of ammonia in place of any other alkali in the clearing treatment is a better option to reduce the dye effluent load [22].

8.8 Manufacture of Woolen Carpets and Related Environmental Issues

Woolen carpets are manufactured using a variety of techniques. Each of these techniques has some distinct features in terms of manufacturing setup and productivity. Majority of the carpets are made by weaving, tufting, or knotting. Other than these, there are two more production methods known as needlepunching and bonding, but they are less common as far as woolen carpet manufacturing is concerned.

In countries like India, China, Nepal, and Iran, hand-knotting, hand-tufting, and hand-weaving techniques are the most preferred techniques for production of a woolen carpet. With growing demand and competitiveness in the market, nowadays relatively high-speed processes such as tufting and weaving by machines have taken over a big market share worldwide. Carpet weaving by using Wilton or Axminster processes is used for making high-quality carpets in relatively short production runs [23–25].

In a woven carpet, the entire structure of pile and backing is assembled simultaneously in a single operation. Unlike a woven carpet, tufted carpet is a sandwich of the pile structure, primary backing, and secondary backing. As compared to woven carpet manufacturing, tufting is more productive and less labor intensive. Therefore, tufted carpets are less expensive than woven carpets. However, all types of carpets have their market demand. Different carpet types and their special features are given in Table 8.3.

8.8.1 Environmental Issues Related to Carpet Manufacture

Manufacture of a carpet using knotting or weaving does not create any serious environmental problem. However, carpet produced by tufting or thermal bonding involves the use of various chemicals and volatile substances. Unlike woven carpets, tufted woolen carpets need complex finishing treatment to achieve good dimensional stability. In tufted carpets, the tufts are inserted in a pre-woven fabric called “primary backing fabric.” This is done with the help of a tufting machine or gun. Latex pre-coat is necessary on the back face of the duly tufted structure to anchor the tufts and to impart a stiffer handle. A secondary backing fabric, generally a leno fabric, is used along with a formulated latex solution to impart this dimensional stability. Recently, hot melt adhesive or a ready-made polymer backing sheet is used to laminate the pre-tufted structure from its back face by applying a fixed amount of heat under pressure [26].

Table 8.3 Carpet fabric construction.

Carpet type	Special features
Tufting	
600–2000 rows of pile yarn simultaneously stitched through carrier fabric (primary backing)	• Most prevalent method for carpet production (over 90%) • Flexibility achieved with varying colors, surface textures, various types of yarns, etc.
Cut pile: Carpet pile surface with all of the yarn tufts of the same height	• Patterned effects created in cut-pile constructions using different colors of yarn • Geometric designs created by shifting needle bar attachment
Loop pile: Level loop Multilevel loop	• All loops have the same height from row to row • Patterning attachment used to achieve different pile heights in a pattern repeat
Cut and loop: A combination of cut and loop pile	• Varying levels of pile height and pile textures create interest
Weaving	
Colored pile yarns and backing yarns woven simultaneously into fabric	• Primarily used in commercial installations (except hand-knotted) • Heavy, firm handle; highly durable • Often used in hospitality locations
Wilton: Woven on Wilton loom, can have various pile heights (level or multilevel) and either loop or cut	• Capable of intricate patterning, styling and coloration versatility • Withstands heavy traffic; mostly used in commercial installations and area rugs • Weaving process contributes to durability, firmness, and flexibility • Face-to-face version weaves two carpets (or rugs) simultaneously

(Continued)

Table 8.3 Cont.

Carpet type	Special features
Axminster: Cut pile only, woven on an Axminster loom. Most are single level, but may be multilevel too	• Offers huge range of patterns and colors • Withstands heavy traffic, mostly used in commercial installations and area rugs • Weaving process contributes to durability, firmness (bends only in one direction) • Three different machine types: spool, gripper, spool-gripper
Knitting	
Warp-knitted fabric made on face and back simultaneously. Pile, backing and stitching yarns are looped together by three sets of needles	• Similar to woven carpet, but less stiff, bends only in one direction • Mostly solid shade or tweed effect • Quality depends on amount of pile yarn and strength of attachment of face, chain, and backing yarns
Needlepunching	
Web of fibers moves through machine. Barbed felting needles penetrate web and entangle fibers into durable, felt-like products	• Usually made with solution-dyed polypropylene • Diverse range of designs—ribs, sculptured effects, patterns • Only used in glue-down installations
Bonding	
Yarns are implanted into vinyl or thermoplastic coated backing	• Often die-cut for tiles • Cut pile formed by slitting two parallel sheets of face-to-face carpet

Application of latex is generally carried out during the manufacture of tufted carpets. A concentrated solution of coating paste is made using natural or synthetic latex and other additives. The application of latex solution on the back face of the carpet is done by hand using a rectangular metallic strip. An optimization in terms of latex recipe formulation and its consumption for a particular quality of carpet is an important area to study upon. The homogeneity and viscosity of the latex solution are also important to decide its consumption in the carpet.

8.9 Washing of Carpets and Related Environmental Issues

The woolen carpets are thoroughly washed prior to application of various mechanical and chemical finishes to them. Manufacture of a carpet, specially using hand-weaving techniques, takes a long time. During the course of weaving operation, a lot of dust, dirt, and other impurities are acquired and accumulated by the carpet. The objective of carpet washing is to remove dirt, dust, loose cut fiber, tufting grease, stains, etc. from the piled surface of the carpet. Additionally, washing enhances sheen, luster, and handle properties of the carpet. In order to achieve satisfactory results, pile yarn of carpet must be opened or raised with the help of a steel tooth comb. The raising of pile structure enables good penetration of washing chemicals, thus ensuring efficient washing. In traditional chemical washing of handmade woolen carpets, bleaching powder solution plays a major role. It works as an oxidizing agent to react with undesirable organic impurities present on the surface of the carpet. But nowadays, it has mostly been replaced by sodium hypochlorite and hydrogen peroxide. The optimization of the washing recipe ensures the intended properties in the carpet with minimum damage to it. The optimized recipe is described in Table 8.4.

There are several steps involved in the washing of a carpet:

Step I: Initially, after rolling the carpet, it is allowed to soak in a tank containing water of slightly alkaline pH. The soaking is carried out for a period of about 24 h.

Step II: The carpet is then spread on a flat washing platform. The fresh water is now forcefully pushed under the carpet and wiped off using a wooden scraper with sharp edge. The mechanical action of the scraper removes dirt, dust, and other organic matter from the carpet surface. This is done for several numbers of cycles.

Step III: In the next step, carpet is impregnated with aqueous sulfuric acid for 10 min at 30°C. It is further rinsed with fresh water with continuous mechanical scrapping. Until this point, the pH of the carpet is kept below 3.

Step IV: Further, impregnation of carpet in sodium hypochlorite solution is done for 10 min at 30°C. This is followed by impregnation of sodium hydroxide solution for a period of 10 min.

- Step V: After this, washing with fresh water is carried out with continuous scrapping.
- Step VI: Finally, the pH of the carpet is ensured to be neutral. If required, dilute acetic acid is used for neutralization of pH.
- Step VII: The carpet is now rolled and allowed to drip off the water for 24 h.
- Step VIII: Subsequently, after unrolling, the carpet is allowed to dry either under sunlight or by the use of a stenter.

Typical washing of a woolen carpet is shown in Figure 8.7. The process standardization in washing eliminates the possibility of use of excess sodium hydroxide in washing, which may otherwise damage the wool present on the carpet surface. The standardization helps in the reduction

Table 8.4. Optimized recipe for chemical washing of woolen carpets.

Independent variable	Concentration
Sulfuric acid	10–20 g/L
Sodium hypochlorite	1–3 g/L available chlorine
Sodium hydroxide.	10–15 g/L
Temperature	30°C



Figure 8.7 Washing of a woolen carpet.

of the load of effluent treatment. The process also curtails the use of water in the washing process.

Initially, sulfuric acid impregnation is carried out to acidify the carpet, which is a prerequisite for reaction with hypochlorite. When bleaching powder solution is added, nascent chlorine is evolved and de-scaling of wool surface takes place. The further addition of sodium hydroxide neutralizes excess acid and helps weaken the surface projected scales. During washing, the mechanical action helps in the removal of the weakened scales from the fiber surface.

The concentration of chemicals used in the washing of a carpet depends on the constructional parameters of the carpet and varies widely with pile height, pile density, etc. The amount of sulfuric acid used varies in the range of 10 to 20 g/L. The concentration of calcium hypochlorite varies from 1.0 to 3 g/L of available chlorine. Caustic soda (sodium hydroxide) concentration used in the process is kept within the range of 10–15 g/L.

8.9.1 Disadvantages of the Process

After washing, the shade depth of dyed yarn reduces to some extent. This is mainly due to the removal of scales in which dye particles were entrapped prior to washing. The presence of residual chemicals such as active chlorine may give wool a yellowish color. Therefore, care should be taken to ensure the neutralization of the material after washing; otherwise, residual alkali hydrolyzes wool. This results in damage of the carpet in terms of fiber shedding during its use. Nonuniform distribution of chemicals during washing also damages the carpet. For example, uneven distribution of caustic soda solution in carpet in the final stage of washing may cause damage to wool, resulting in huge wear and abrasion loss of fibers [27, 28].

A large volume of water is consumed during the washing-off stage of a carpet. Approximately 200 L of water is used in washing 1 square yard of carpet, which is too high.

For reducing carpet washing effluent, the following steps may be followed:

1. Transfer from a long chemical washing process to detergent and softener wash.
2. Go for machine washing for hand-tufted and flat woven products instead of the existing traditional manual wash.
3. The water from hydro-extractors can be recycled and used for carpet washing.

8.10 Environmental Issues Related to the Usage of Woolen Carpets

8.10.1 Microbial and Dust Mite Generation in an Indoor Environment

Woolen carpets can be a good platform for microbes to grow upon. Microbes can damage woolen carpets by attacking the disulfide linkages of amino acid chains present in the wool. The presence of sufficient moisture in an ambient temperature environment is a good facilitator of microbial growth. An accelerated microbial growth in carpet may adversely affect human health. It can be a cause of skin rashes, fungal infections, and allergies in the human body.

Dust mites are the major cause of allergic conditions such as asthma. They exist in close association with dust in dwellings. In an indoor environment, dust mites are airborne and feed on dead human skin flakes. Wool is a keratinous protein fiber, and it has often been alleged that dust mites can live on woolen carpets. Thus, for people suffering from asthma, it is advisable not to use wall-to-wall woolen carpets to avoid the danger of dust mites [5, 29].

8.10.2 Emission of Volatile Organic Compounds

There are serious concerns with the emission of volatile organic compounds, while using tufted carpets in an indoor environment. The volatile organic compounds are those compounds that can be vaporized at ambient temperature. The origin of toxic and volatile substances in tufted carpets is mainly due to the backing used in tufted carpets. Isocyanates are generally used in polyurethane resins, which is one of the main components of carpet backing. Similarly, 4-vinylcyclohexene is produced as a by-product during curing of butadiene copolymers, the synthetic latex used in carpet backing. 4-Vinylcyclohexene is classified as a group 2B carcinogen [30–32].

Sometimes, the biocides used in carpet backing to protect the backing materials from biological deterioration create undesirable fumes in the environment. Pentachlorophenol (PCP) was once a popular biocide used in woolen carpets. However, application of PCP in carpets is now banned in most of the developed countries.

A similar issue regarding the release of volatile chemicals is sometimes encountered during installation of wall-to-wall carpets. The existence of volatile chemicals in adhesives used for installation purposes may pollute the indoor environment. Therefore, during the installation of such carpets, the doors and windows should be kept open to keep the environment full

of fresh air. The ventilation system should also be kept operational for at least 72 h after the installation. This ensures the exhaust of toxic fumes from the indoor environment [33].

8.11 Environmental Issues Related to the Disposal of Used Woolen Carpets

The disposal of used carpets has become a serious concern nowadays. Billions of pounds of waste are generated every year due to the disposal of used carpets. Therefore, use of biodegradable fiber in carpet making is being promoted. With the stringent legislative norms for disposal of any product at the end of its working life, manufacturers are considering measures to avoid the use of prohibited chemicals during the manufacturing of the product. The problem of disposal of used products has become more severe in countries that are more densely populated. Looking at the seriousness of the problem, provisions have been made in most of the developed countries by which the consumer may return a worn carpet back to the retailer for arrangement of its disposal. The disposal of the used carpets contributes to the large volume of waste in landfills. Here, the problem arises more with carpets that contain non-biodegradable substances. Another practical difficulty associated with the disposal of used carpets in landfills is the cost of transportation of used products to landfill sites.

However, unlike carpets made of synthetic fibers, wool carpets have the potential of close-loop recycling. A study was conducted by the research team of WRONZ to investigate the effect of disposal of used woolen carpet (containing small amount of backing material) on dry matter yield of grasslands after using it as landfill. The growth of grass was monitored after a period of 10 weeks, and it was found that there was a significant improvement in the elemental composition of the soil of that landfill area. The growth rate of the grass was also found to be significantly high [3].

8.12 Some Remediation Approaches to Combat Environmental Issues of Wool Carpet Industry

8.12.1 Adoption of Alternative Techniques

8.12.1.1 Eco-Efficient Wool Dry Scouring (WDS)

Cleaning of raw wool is generally carried out by hot aqueous scouring. However, this is a complicated process that involves the use of detergents

and alkali. The process also generates large quantities of wastewater with a high organic content.

In cleaning 1 kg of wool by aqueous scouring, almost 17 L of effluent with a high chemical oxygen demand (COD) value (0.3–2.4 kg) is generated. Therefore, aqueous scouring of wool has a high environmental impact. On one hand, it consumes large amounts of water and energy, and on the other hand, it generates large quantities of highly polluted effluents. Moreover, the wastewater requires several treatment stages before disposal, thus consuming additional resources.

Scouring of wool in dry form has been demonstrated as an innovative process of cleaning the raw wool, based on closed-loop processing and total waste recovery. In this process, greasy wool is compressed with powdered polystyrene beads at a slightly higher temperature of 65°C. In a laboratory scale, it has been shown that an average micron of 21 wool fibers with 7.6% grease content, 16.2% suint, and 35.1% dirt could be cleansed to residual grease and suint levels of 0.5% and 4.5%. In this process, polystyrene could be regenerated by solvent extraction for its reuse. After this process, cleaner wool can be obtained easily just by a simple rinsing process with low water and energy consumption. In comparison to the aqueous scouring, the cleaning of wool using this process gives better wool quality. In this process, wool grease and wool dust can be easily recovered. The wool grease recovered as by-product is used in the cosmetic industry. In addition, the wool dust finds its application in agriculture as fertilizer.

The new dry scouring process resulted in several environmental benefits:

- Reduction of 70% in water consumption;
- Reduction of wastewater effluents in the rinsing water process by 70%;
- Wastewater produced through this process has better quality as it has 75% lower chemical oxygen demand (COD);
- The need for detergents and chemicals was reduced by 70%;
- Reduction of 30% in energy consumption mainly from the wastewater management system (reduction of amount of wastewater and improved quality of the effluent);
- Carbon footprint reduced by 96 kg of CO₂ eq. per functional unit with the WDS technology compared to traditional wool scouring processes.

WDS technology has a lower environmental impact than the traditional wool scouring process. The low fugitive emission of solvent has been

measured at the pilot plant. Mechanization and automation can further reduce the environmental impact significantly at industrial scale [34].

8.12.1.2 *Wool Scouring Using Natural Ingredients*

Nowadays, studies have been focused on finding out some eco-friendly alternatives of the detergent-based scouring of wool. One such alternative has been cow urine and ritha (*Sapindus saponaria*). The wool scouring using cow urine and ritha has the potential to reduce the consumption of chemicals, water, and energy used in wool scouring. Cow urine works as an alkaline medium while the ritha works as a natural detergent. The cow urine mainly contains urea, which helps the fiber to swell, and the ammonia present in the urine maintains a pH of 8–9. The enzyme present in the urine helps break the bond between the wool fiber surface and grease. Since ritha works as a detergent, it takes out the loosened grease along with it [35].

8.12.1.3 *Energy-Efficient Wool Scouring*

A typical wool scouring plant can be made energy efficient by recognizing and monitoring the areas where energy can be saved. Proper installation of pipe work at the time of plant erection and good housekeeping can help save energy in the boiler house area by proper reticulation of steam pipes.

By installing close-fitting bowl covers in the scouring bowls, at least 15% of the heat loss can be saved in scouring. Introduction of the WRONZ comprehensive scouring system with provisions of regulation of flow of effluent using the FLOCOM technique has been able to efficiently recover the heat from effluent on one hand and the reduction of effluent volume discharge on the other hand.

After scouring, the wool stock is required to be dried. Drying is a highly energy-intensive process, which consumes almost 30% of the total energy requirement of a wool scouring plant. Radiofrequency drying, high-intensity drying, and microprocessor-based control systems have been developed with the goal of achieving a cost-effective, energy-efficient drying with even supply of dry heat. Direct firing of dryers with natural gas promises efficient use of energy and ensures almost 30% energy savings as compared to drying using steam boilers and steam reticulation [36].

8.12.2 **Treatment of Wool Scouring Effluents**

The major components of wool scour liquor are suint, wool grease, and dirt. Suint is mainly the sodium and potassium salts, soluble in cold water.

Wool grease is an organic mixture of unoxidized and oxidized grease. The dirt component present in wool scour liquor is in the form of fine clay particles to coarse groats. The minor components left in the scouring liquor are vegetable matter, wool fiber, and detergents. Wool scour liquor may also contain a very small percentage of pesticide, generally in the ppb level, which can be toxic to aquatic life. In the case of alkaline scouring using soap and soda, the scour liquor has to be made near neutral pH of around 6 to 8 before the effluent treatment.

The discharge of effluent cannot be carried out at elevated temperatures since the higher temperature of discharge might kill aquatic life. The excess heat in the effluent discharge can be recovered using heat recovery equipment.

Eventually, the discharge of any industrial waste is collected by the local authorities. Based on the quantity of wastewater and suspended solid present in the waste, charges are decided and paid to the authorities. This is also dependent on the amount of oxygen needed to oxidize the waste in the effluent liquor.

The amount of oxygen required to completely oxidize 1 L of waste is calculated in terms of BOD_5 and COD values. BOD_5 is the *biochemical oxygen demand*. It is the amount of oxygen needed to oxidize 1 L of waste under similar conditions to the natural water into which the waste is disposed. In BOD_5 , 5 indicates the number of days for which the effluent sample is incubated before testing. This test simulates the natural process of oxidation of the waste in the river or stream into which it will be discharged. The amount of oxygen is measured in milligrams. The BOD indicates the amount of decomposable organic matter in the waste and therefore shows the concentration of the waste.

COD is the *chemical oxygen demand*. It is the amount of oxygen needed to chemically oxidize 1 L of the waste under specified conditions. Determination of COD requires much less time as compared to the BOD test.

It is pertinent to mention that centrifuging the effluent before discharge greatly reduces the pollution level of the effluent. In addition, the recovery of wool grease can be profitable. During effluent discharge, the 20/30 standard is generally followed. The 20/30 standard indicates that the discharge should have a maximum of 20 mg/L of BOD_5 and 30 mg/L of suspended solids (SS) values. Generally, after primary treatments, the load of wool scour pollutants is reduced up to 50%. After secondary treatment, the pollutant load is reduced by at least 65%–75%. The tertiary treatments are meant to reduce the pollutant load to achieve the norms of the 20/30 standard.

There are several types of treatment systems, some of which are available in New Zealand.

8.12.2.1 Primary Treatments

The primary treatments are aimed to reduce the amount and variability of the discharge. They also remove settle-able solids and recover wool grease and heat of the system.

In the WRONZ liquor handling loop, different methods are used to remove different types of pollutants. The removal of waste fiber from scour liquor takes place in wedge wire screens as shown in Figure 8.8.

The screens require cleaning at regular intervals to avoid blockage due to other impurities present in the scour liquor. Removal of SS is done by gravity in a settling tank. About 50% of the SS are removed by this method. Addition of flocculent in the liquor aids the removal of SS by combining the small dirt particles with larger particles, which settle to the bottom of the tank. The flocculent causes the small particles to coagulate into larger particles. The major component of wool scouring liquor is grease. About 45%–50% of the total grease present in the scour liquor can be removed by centrifuging. Heat exchangers are used to reduce the heat of the primary effluent before it is discharged [37].

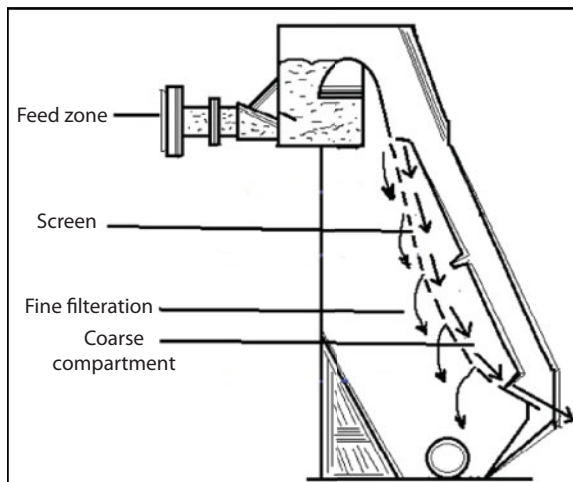


Figure 8.8 Wedge wire screen.

8.12.2.2 *Secondary Treatments*

After primary treatment, the effluent still contains suint and reduced amounts of grease and dirt. Most of the secondary treatments remove the grease and dirt, leaving a suint solution. The treatments of the effluent include chemical destabilization by acid cracking, chemical flocculation, biological processes, and ultrafiltration.

8.12.2.3 *Tertiary Treatments*

After the secondary treatments, further processes may be used including the following:

1. Biological treatments, such as adding nutrients to the grease-free liquor obtained from acid cracking,
2. Incineration of the sludge left after the secondary treatment, and
3. Solvent extraction of sludge, where a solvent is used to extract the grease and water from the effluent.

However, mixing of clay with wool scour sludge has shown to impart excellent properties in brick-making. Therefore, consumption of wool scour sludge as an additive for brick-making can be thought as a good option and this could work side by side with other existing waste management options like land filling, composting, and incineration [18].

8.12.3 **Treatment of Dye Wastewater Effluents**

Primary treatment of dye wastewater is composed of various steps. These steps include coarse and fine screening, stabilization/equalization, sedimentation, and primary sludge dewatering.

Secondary treatment is composed of anaerobic pretreatment (wherever $\text{COD} > 3500 \text{ mg/L}$), aerobic treatment (like activated sludge process), secondary sedimentation, thickening (centrifuging/decanting), sun-drying (sludge drying beds), etc.

In tertiary treatment, a wide range of processes are covered. These processes include polishing pond (to even out discharge variations), coagulation and flocculation, microfiltration (to achieve low TSS levels), activated carbon filtration, and/or ozonization (for reducing odor and color).

In a wool dyeing plant, the wastewater has to be passed through a number of treatment chambers before the final disposal. In a typical effluent

plant meant for dye wastewater treatment, the wastewater is initially passed through many coarse and fine sieves to separate fibrous and other macro-sized impurities. It is now brought to the oil and grease chamber, where the floating oil/grease is removed. Now, this water is brought to a collection tank, where cooling is done. The required temperature for proper functioning of ETP is 40°C. For cooling, spray cooling arrangements are generally made. Plate-type heat exchangers are also used to recover the heat of wastewater and utilize it in preheating of the process water.

From the collection tank, the cooled wastewater moves to the equalization tank. The objective of the equalization tank is to thoroughly mix the wastewater. The mixing is done through air purging. The wastewater from the equalization tank is now pumped into the reaction tank, where the dosing of coagulants (alum/ferrous sulfate and lime) is done. The pH of water is maintained between 7 and 8.5. Here, the wastewater containing small particles in the suspended form is allowed to combine with larger particulates to settle down. The dosage of coagulant per liter of wastewater is maintained in between 0.5 and 1 g depending on the quality of inlet wastewater. This water now flows into the flocculation tank, where the high-molecular-weight flocculent (generally starch and multiple charged ions) is dosed. The flocculent attracts or traps the coagulated particulates and converts them into flocs, which can be quickly settled. The dosage of the flocculent may vary between 3 and 5 g per 1000 L of water.

The flocculated water now moves into the primary clarifier. In this tank, the flocs settle down at the bottom and clear water flows from the top to the aeration tank. In order to collect settled flocs, the scrapper arrangement is installed in the clarifier. The scraper moving at the bottom of the tank collects the sediments in a pit at the center of the tank. This sediment (sludge) is taken out from the bottom to sludge drying beds. After proper drying, the sludge is finally collected in HDPE bags and disposed off as per the norms of pollution controlling authorities. The size of the primary clarifier must be large enough to provide a minimum of 4 h retention period to water for proper settling.

In the next step, a bacteria culture is prepared in a separate tank. Bacteria consume the organic compound as food and convert it into simple molecules like water and CO_2 in the presence of oxygen. The supply of O_2 is ensured through air purging by means of air blowers. For efficient biological degradation of organic compounds, the level of dissolved oxygen should be kept between 4 and 5 mg/L of water. The level of mixed liquor suspended solids (MLSS) should also be kept below 35%. A regular dosing of urea and DAP is required to maintain consistency of bacterial count in the tank. The water from the aeration tank flows into the secondary

clarifier. The sludge settled in the secondary clarifier is sent back to the aeration tank. Since sludge remains activated and contains bacteria, this process is known as the activated sludge process. In case the MLSS level goes beyond 35%, the sludge settled in the secondary clarifier is taken to sludge drying beds and is disposed off as per environmental disposal norms. The clear water from this clarifier flows down to the final sump [20, 38, 39].

8.12.4 Adoption of Best Practices to Reduce Effluent Generation

To reduce effluent generation, the following actions may be taken:

1. Dyeing machineries with low material-to-liquor ratio may reduce the consumption of water in dyeing. Industries currently use machines with an M:L ratio of 1:20 to 1:50. Package dyeing in place of hank dyeing can reduce the M:L ratio to as low as 1:8.
2. Re-processing/re-dyeing and color addition during dyeing lead to increase in effluent generation. Efforts should be made to achieve the right shade the first time by proper use of technology. Use of color-matching instruments like spectrophotometer and proper lab trials are necessary to minimize re-dyeing and lot-to-lot variations.
3. Dyeing machines with two different passages for drain are preferred. One passage should be for dye effluent and the other should be for discharge of washing effluent. The washing effluent collected can be reused for dyeing after its treatment with sequestering agent.
4. The steam condensate should be recovered from dyeing and drying machines to save both energy and water.
5. The drains of hydro-extractor, carpet washing, etc. should be managed properly to reduce the load on ETP.
6. In the case of acid dyes with high exhaustion, the following steps can be followed to reduce the effluent load:
 - a. Save the exhausted dye bath—this can be done by pumping it to a holding tank and returning it to the machine for use in the next dyeing procedure.
 - b. Analyze the dye bath for residual chemicals—most auxiliaries do not exhaust in the dyeing process.
 - c. Unexhausted dyestuffs need to be analyzed to determine the concentration remaining in the dye bath. Dye bath

- analysis can be performed using a spectrophotometer and specific guidelines for such a procedure.
- d. Reuse of dye bath is possible to repeat the same shade. However, the dye bath reuse is limited by impurity buildup due to substrate quality, salt buildup, steam contamination, and surfactants. This practice is generally adopted for products where high-quality dyeing is not essential.
 7. Installation of improved machinery with better controls.
 8. A number of finishing operations are carried out in a carpet prior to its final packaging. These finishing operations are done mechanically or by the use of chemicals. In tufted carpets, proper design of the primary/secondary backing fabrics can minimize the consumption of latex and other chemicals.
 9. Use of low add-on methods like spray or foaming can reduce the consumption of desired finish/chemical in the carpet.
 10. Use of volatile chemicals in the preparation of latex solution for back coating of a carpet should be avoided.
 11. Proper training of employees and good housekeeping practices are helpful in reducing the pollution-causing factors in the carpet manufacturing unit.
 12. Use of formaldehyde-free cross-linking agents should be ensured in back coating of carpets.
 13. Solid waste generation can be reduced in the finishing of carpets by proper planning and control of the processes.

Wastage of water can be minimized in carpet washing by closed-loop recycling. During carpet manufacture, much of the wet processing is conducted in aqueous medium using water. Therefore, the amount of wastewater generated after wet processing is huge. It is important to identify the processing steps in which potential water savings can be made. It is equally important to think over those steps in which the wastewater can be reused. By reducing the use of water and its recycling, huge amounts of water can be saved. It has been suggested that most companies can save 20%–50% of water expenditure and effluent treatment charges by reducing the consumption of water and promoting its recycling during any operation. This consists of washing the carpet in a series of tanks containing relatively cleaner water [8]. The rinse water is reused by moving it progressively from the last rinse tank to the first. Wash water may also be suitable for reuse elsewhere on the site such as for floor washing, rinsing containers, etc. [40].

8.13 Conclusion

The present study gives an insight into the various processing steps used in woolen carpet manufacture starting from wool as raw material to its final disposal as used carpet. Attempts have been made to cover the information about different sources of pollution during processing of raw wool to carpet. The effects of pollution problems caused by different cleaning and processing treatments and the methods to deal with such problems have also been thoroughly discussed. Setting up good housekeeping practices, possibilities of recovery of used water, and its reusability may be utilized to minimize effluent volume. The possibility of cleaning raw wool involving dry techniques should be thoroughly studied. It is suggested that the wool scouring effluent and dye house waste be handled separately to achieve better efficiency in waste treatment plants.

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Intensification of Textile Wastewater Treatment Processes

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Abstract

The effluents from the textile processing industry cause great environmental and human health concerns; development of an eco-friendly and energy-efficient technique to treat such effluents has been a major challenge. The conventional wastewater treatment methods have been ineffective to remove textile pollutants, due to the high toxicity and chemical stability of such pollutants. Advanced oxidation processes have been proven to be the most appropriate and most efficient techniques for the treatment of textile pollutants because of their cost-effectiveness, high performance, and lower consumption of materials and reagents. The main objective of this chapter is to provide effective treatment methods based on process intensification (PI), which consists of chemical and process design approaches that lead to substantially smaller, cleaner, safer, and more energy-efficient processes. This chapter mainly focuses on the application of novel process technologies to achieve significant size reduction in individual unit operations, or the complete removal of process steps by performing multiple functions in fewer steps. These should lead to overcome the problems that restricted the practical applications of wastewater treatment and cause significant reductions in capital and running costs, and improvements in process efficiency and safety.

Keywords: Process intensification, advanced oxidation processes, textile pollutants, treatment, degradation

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9.1 Introduction

The textile industry is one of the major sources of wastewater pollution, which consumes immense amounts of process water and chemicals [1]. Researches indicate that for the production of 1 ton of textiles, about 21–377 m³ of water is consumed and chemical consumption varies from 10% to over 100% of the weight of the cloth [2, 3]. Environmental studies reveal that approximately 7×10^5 tons of dyestuffs are produced annually and 280,000 tons of textile effluents are discharged into water resources, which makes textile effluents a great danger to human health and the environment [4, 5]. In a typical dye processing unit (Figure 9.1), approximately, 80 L of water is consumed per kilogram of product, which generates different types of wastewater in various magnitudes and qualities [6].

The minimization of the impact of wastewater discharges on humans and the environment is a big challenge [7, 8]. Although the improvement in conventional methods such as simple coagulation and biological processes has been a topic worthy of research, in the last quarter of the 20th century, application of novel technologies started to overcome the limitations attributed to conventional treatment methods [9, 10]. Application of novel equipment and/or processes was even more important in the treatment of wastewater produced in industry, because the complex molecules of the anthropogenic pollutants are hardly attacked by the microorganisms in biological processes [11]. The inefficiency of conventional treatment technologies led the scientific community to use alternative novel processes

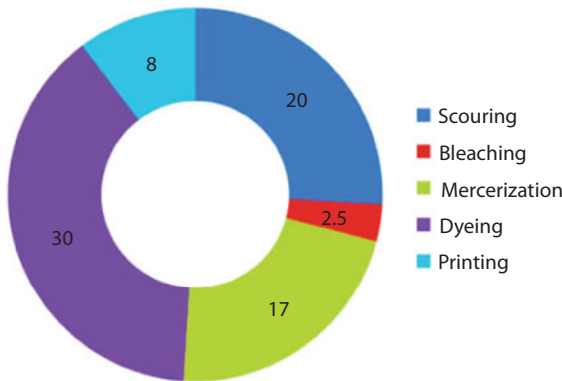


Figure 9.1 Typical amount of water consumed (in m³/1000 L of product) in a conventional continuous process [6].

and search for operating conditions to improve wastewater treatment efficiency [4, 12].

Since the textile industry effluent consists of various dyes, chemicals, and sizing materials, the selection of a suitable treatment technology for effective treatment depends on several factors listed in Figure 9.2.

The advanced oxidation processes (AOPs) based on the production of very reactive hydroxyl radicals are novel techniques that can be used as a practical method for textile effluent removal [14, 15]. AOPs include various methods such as heterogeneous and homogeneous photocatalysis; Fenton and Fenton-like processes; ozonation; the use of ultrasound, microwaves, and g-irradiation; electrochemical processes; and wet oxidation processes [16]. Compared to conventional technologies, AOPs degrade pollutants without generating a secondary waste stream as is the case for membrane processes; hence, the investment and operational costs reduced dramatically [17]. The combination and integration of AOP methods led to the introduction of synergistic processes, which can intensify the textile wastewater treatment [17–19]. This chapter covers the latest developments in

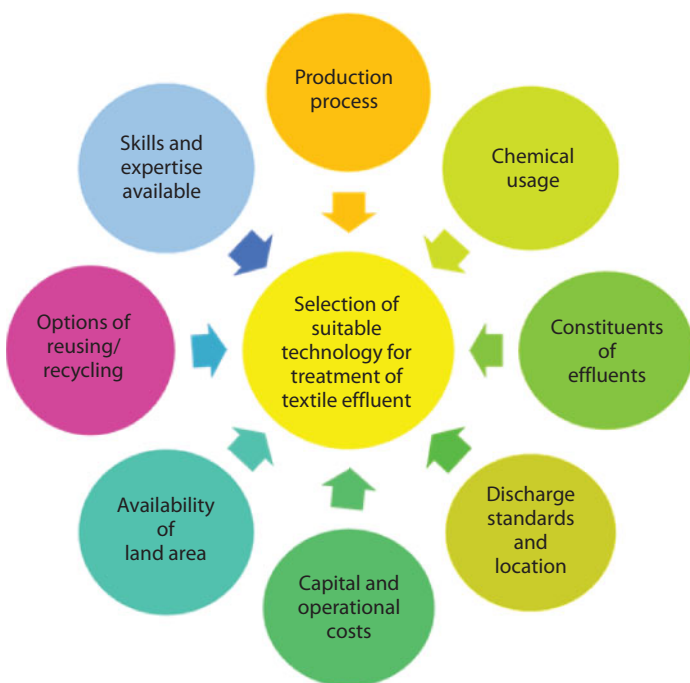


Figure 9.2 Selection criteria of suitable methodology for effective treatment of textile effluent [13].

advanced oxidation processes (AOPs) as alternative methods for the degradation of textile pollutants based on process intensification (PI). Based on the researches, publications regarding textile wastewater treatment rose continuously in the past decade (Figure 9.3), which indicates that much attention has been paid to the development of AOP wastewater treatment techniques [20].

The principal objective of this chapter is to discuss the combined and integrated AOP systems for the intensification of textile wastewater treatment. The focus is on the PI technologies including processes and equipment, and a number of combined or hybrid systems are introduced for the degradation of textile pollutants [21]. Application of cost-effective and environment-friendly processes is also highlighted in this chapter, which is intended to be a useful resource for practicing engineers and chemists alike who are interested in applying PI technologies for the removal of a wide range of pollutants, especially textile effluents [22]. The compact photocatalytic rotating packed bed reactor, one of the PI equipment addressed in this chapter, is a good example of an intensified AOP that was applied for the degradation of pollutants. Another highlight of this chapter is the application of novel metal organic frameworks (MOFs) as visible-light

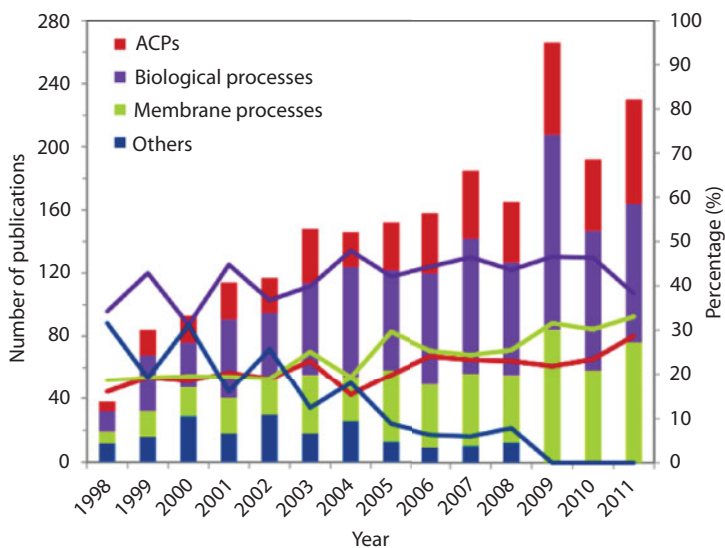


Figure 9.3 Number of research articles appearing on textile wastewater treatment technologies per year [20].

drive photocatalysts, which have unique properties such as large specific surface area, high pore volume, and excellent stability compared to conventional photocatalysts [23].

Toward the end of the chapter, we have included several sections to emphasize the industry relevance of PI, with particular focus on its energy-saving potential, process economics, and environmental impact [24]. The introduction of this chapter provides general information on process-intensifying equipment and methods and gives some examples of their application on degradation processes. The succeeding sections of the chapter describe the technology, design, and application of compact and cost-efficient equipment in various scales. The final section focuses on the industrial and large-scale application of AOPs. The PI clean technologies as novel approaches introduced in this chapter can be considered an essential step for large-scale application.

9.2 AOP Techniques

AOPs are classified into two categories: homogeneous and heterogeneous processes.

9.2.1 Homogeneous Process

The homogeneous process, which corresponds to the single-phase system, uses UV, ozone, and H_2O_2 for the treatment of contaminants [25]. The application of UV light for the degradation of contaminants can be classified into two categories [26]:

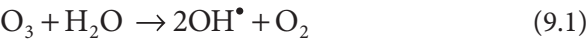
- Direct photodegradation, which proceeds following direct excitation of the pollutant by UV light.
- Photo-oxidation, where light drives oxidation processes principally initiated by hydroxyl radicals.

The latter process involves the use of an oxidant to generate radicals, which attack organic pollutants to initiate oxidation. The following are the three major oxidants used [27]:

- Hydrogen peroxide
- Ozone
- Photo-Fenton system ($\text{Fe}^{3+}/\text{H}_2\text{O}_2$)

9.2.1.1 O_3/UV

The combination of UV radiation and ozone is known as photodecomposition of ozone, which leads to two hydroxyl radicals [28]. The current system applied three components for the production of OH radicals and/or to oxidize the pollutant: UV radiation, ozone, and hydrogen peroxide.



Applications of O_3/UV systems for the degradation of different textile pollutants are summarized in Table 9.1.

9.2.1.2 H_2O_2/UV

The H_2O_2/UV system is essentially decomposition of H_2O_2 due to absorbance of UV irradiation of 254 nm; the mechanism of this process is represented as follows [32]:



Applications of the UV/H_2O_2 system for the degradation of different textile pollutants are summarized in Table 9.2.

9.2.1.3 $O_3/H_2O_2/UV$

In this process, again $HO^\bullet$ radicals are considered to be the most important intermediates, initiating oxidative degradation of organic compounds [37]. In such process, the addition of hydrogen peroxide causes more production of $HO^\bullet$ radicals, which leads to more degradation efficiency.

Table 9.1 Performance of the O_3/UV system for the degradation of textile pollutants.

Industrial application	Pollutants	Efficiency	Reference
Textile industry	Reactive Red	99.80%	[29]
Textile industry	C.I. Acid Black 1	95%	[30]
Textile industry	Reactive Red 2	99.80%	[31]

Table 9.2 Performance of the UV/H₂O system for the degradation of textile pollutants.

Industrial application	Pollutants	Efficiency	Reference
Textile, dyeing, and finishing process	RB5	99.82%	[33]
Textile, dyeing, and finishing process	C.I. Acid Black 24	100%	[34]
Textile, dyeing, and finishing process	RY14	34.2%	[28]
Dye industry	Reactive Orange 4	88.68%	[35]
Textile and dye industries	Reactive Red 2	98.60%	[36]

Table 9.3 Performance of the O₃/H₂O₂/UV system for the degradation of textile pollutants.

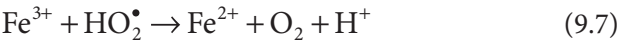
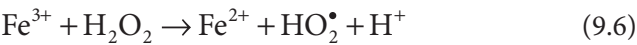
Industrial application	Pollutants	Efficiency	Reference
Textile industry	Reactive Red	97.60%	[29]
Textile and dye industries	Reactive Red 2	97.20%	[38]
Textile, dyeing, and finishing process	C.I. Direct Black 22	99%	[39]
Acetate and polyester fiber dyeing effluent	Dye	99%	[40]



Applications of the O₃/H₂O₂/UV system for the degradation of different textile pollutants are summarized in Table 9.3.

9.2.1.4 Photo-Fenton (Fe²⁺/H₂O₂/UV)

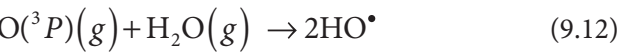
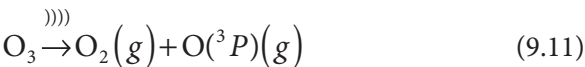
In the photo-Fenton process, the OH radicals are produced via reaction between Fe²⁺ and H₂O₂ as follows [41]:



Applications of the $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$ system for the degradation of different textile pollutants are summarized in Table 9.4.

9.2.1.5 O_3/US

The mass transfer and decomposition of ozone can be intensified using ultrasound radiation, which causes more generation of free OH radicals [46]. The mechanism of OH generation using the US/O_3 system is presented as follows [47]:



Applications of the US/O_3 system for the degradation of different textile pollutants are summarized in Table 9.5.

Table 9.4 Performance of the $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$ system for the degradation of textile pollutants.

Industrial application	Pollutants	Efficiency	Reference
Textile and dye industries	RY 14	94.80%	[28]
Dye industry	Reactive Black B	93%	[42]
Textile and dye industries	Reactive Black 5	98%	[43]
Dye industry	DASDA	89%	[44]
Textile industry	Methylene blue	80%	[45]

Table 9.5 Performance of the US/O_3 system for the degradation of textile pollutants.

Industrial application	Pollutants	Efficiency	Reference
Textile industry	CI Direct Red 23	98%	[48]
Dye industry	CI Reactive Blue 19	65%	[49]
Textile industry	Yellow 145	80%	[50]

Table 9.6 Performance of the $\text{H}_2\text{O}_2/\text{O}_3$ system for the degradation of textile pollutants.

Industrial application	Pollutants	Efficiency	Reference
Textile industry	C.I. Reactive Yellow 15	96%	[52]
Dye industry	Reactive Brilliant red	94%	[53]
Textile industry	C.I. Reactive Blue 28	91%	[52]
Dye industry	C.I. Basic Brown 4	68.5%	[54]
Dye industry	Orange 39	83%	[55]

9.2.1.6 $\text{H}_2\text{O}_2/\text{US}$

The combination of ultrasonic irradiation with H_2O_2 leads to enhancement of degradation efficiency [51]. Applications of the $\text{H}_2\text{O}_2/\text{O}_3$ system for the degradation of different textile pollutants are summarized in Table 9.6.

9.2.1.7 *Electrochemical Oxidation*

In this process, the textile contaminants are degraded using direct electron transfer to the anode and/or mediated oxidation with OH produced from water discharge at the anode surface at high current [56]. Applications of the electrochemical oxidation system for the degradation of different textile pollutants are summarized in Table 9.7.

9.2.1.8 *Plasma-Based Oxidation Methods*

Plasma-based oxidation methods are known as an efficient degradation technique due to their complexity, versatility, and high oxidant capacity, which are used for the treatment of various wastewaters [60]. These

Table 9.7 Performance of the electrochemical oxidation system for the degradation of textile pollutants.

Industrial application	Pollutants	Efficiency	Reference
Textile industry	Azo dyes	15.80%	[16]
Dyeing industry	Azo dyes	99.40%	[57]
Textile and dye industries	Azo dyes	43.20%	[16]
Textile industry	Disperse and acid dyes	>90%	[58]
Textile industry	Alizarin Red	93%	[59]

processes consist of various methods such as electrohydraulic discharge, corona discharge, dielectric barrier discharge (DBD), microwave discharge, and radiofrequency [61]. Among the plasma-based oxidation methods, DBD is one of the most promising and most interesting technique, because it allows having various reactor configurations, such as axial with metal-glass/quartz electrodes, axial with glass electrodes, and DBD falling liquid [62]. Furthermore, operation at low temperature as well as atmospheric pressure is another benefit of the DBD method. DBD does not require additional chemicals, and no dangerous chloro-organic by-products are generated compared to, for example, chlorination. The DBD technique, depending on conditions, can produce large amounts of ozone and UV radiation, in which oxidant radicals are generated directly inside the plasma and during dissolution of ozone in water [63–65]. Overall, strong electric fields applied to water (electrohydraulic discharge) initiate both chemical and physical processes [65]. The electrohydraulic discharge method types differ primarily by the amount of energy deposited in the system, in which results reveal that the corona or corona-like system applies discharges of ~ 1 J/pulse, whereas the pulsed arc discharge uses energy of ~ 1 kJ/pulse and larger [65, 66]. Applications of plasma-based oxidation methods for the degradation of different textile pollutants are summarized in Table 9.8.

9.2.1.9 Electro-Fenton

The electro-Fenton process benefits both Fenton's reaction in the bulk and anodic oxidation at the anode surface [68]. H_2O_2 and Fe^{2+} can be continuously generated by simultaneous electrochemical reduction of O_2 and Fe^{3+} , respectively, on the cathode surface:

Table 9.8 Performance of plasma-based oxidation methods for the degradation of textile pollutants.

Industrial application	Pollutants	Efficiency	Reference
Textile industry	Astrazon Yellow (AY)	>95%	[63]
Textile industry	Anthraquinone dyes	>95%	[63]
Textile and dye industries	Reactive Black 5	97%	[67]
Textile industry	Orange I	92%	[64]
Dye and food industry	Azo dye	81.24%	[61]

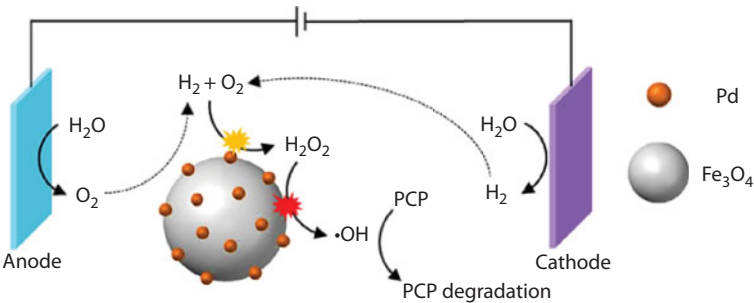
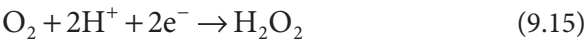
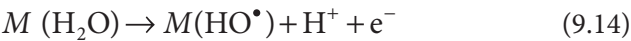


Figure 9.4 The mechanism of the electro-Fenton process [69].



where M is the anode. The mechanism of the electrochemical–heterogeneous Fenton process for the degradation of pentachlorophenol (PCP) using nanoparticles $\text{Fe}_3\text{O}_4\text{-Pd}$ is shown in Figure 9.4.

The experimental results for the degradation of a synthetic solution containing 190 mg L^{-1} of Novacron Blue (NB) dye using the electro-Fenton process revealed that after 4 h of electrolysis, chemical oxygen demand (COD) removal was only 34% when no ferrous ions were added to the

solutions, while the presence of ferrous ion greatly improved COD removal to more than 90% (Figure 9.5), depending on operating conditions [70].

Applications of the electro-Fenton process for the degradation of different textile pollutants are summarized in Table 9.9.

9.2.1.10 O_3 in Alkaline Medium

Intensification of degradation rate in alkaline media is attributed to the presence of hydroxyl radicals that have higher oxidation potential than molecular ozone [75]. Applications of O_3 in alkaline medium for the degradation of different textile pollutants are summarized in Table 9.10.

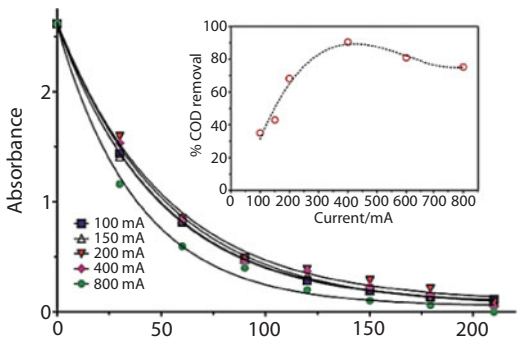


Figure 9.5 Removal and COD decay during electrolysis of Novacron Blue (NB) dye [70].

Table 9.9 Performance of the electro-Fenton process for the degradation of textile pollutants.

Industrial application	Pollutants	Efficiency	Reference
Dye industry	Sunset Yellow	100%	[71]
Textile and dye industries	Acid Yellow 36	98%	[72]
Textile industry	Novacron Blue dye	90%	[70]
Textile, printing, cosmetic industries	Methyl red Azo dye	80%	[73]
Textile industry	Acid red 97 dye	95%	[3]
Textile and dye industries	Dispersed Red	83%	[74]

Table 9.10 Performance of O_3 in alkaline medium for the degradation of textile pollutants.

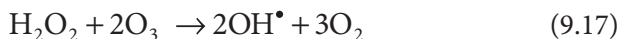
Industrial application	Pollutants	Efficiency	Reference
Textile industry	Direct Pink 3B	98%	[76]
Textile industry	Reactive Violet SH-2R	98%	[76]
Textile industry	Textile	43%	[77]

Table 9.11 Performance of the O_3/H_2O_2 system for the degradation of textile pollutants.

Industrial application	Pollutants	Efficiency	Reference
Textile industry	Reactive Red	99%	[29]
Textile and dye industries	Reactive Red 2	99.40%	[36]
Textile industry	Dyes	70%	[14]

9.2.1.11 O_3/H_2O_2

The mechanism of the O_3/H_2O_2 system is defined as follows [47]:



Applications of the O_3/H_2O_2 system for the degradation of different textile pollutants are summarized in Table 9.11.

9.2.2 Heterogeneous Processes

9.2.2.1 Catalytic Ozonation

So far, various mechanisms have been proposed for catalytic ozonation [78]:

- Ozone decomposition on oxidized/reduced form of metal deposited on the surface of a solid support.
- Decomposition of ozone on Lewis centers of metal oxides.
- Ozone decomposition takes place on non-dissociated hydroxyl groups of metal oxides.
- Ozone decomposition of activated carbons takes place on basic centers of the catalyst.

Applications of the catalytic ozonation process for the degradation of different textile pollutants are summarized in Table 9.12.

9.2.2.2 *Photocatalytic Ozonation*

The combination of UV radiation and ozonation, which is known as photocatalytic ozonation, is an efficient method for the complete degradation of various textile contaminants [75, 84]. Applications of the photocatalytic ozonation process for the degradation of different textile pollutants are summarized in Table 9.13.

9.2.2.3 *Heterogeneous Photocatalysis*

The reaction mechanism of the photocatalysis process is explained as follows [88]:

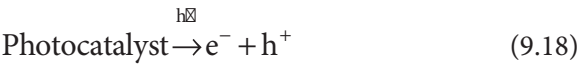


Table 9.12 Performance of the catalytic ozonation process for the degradation of textile pollutants.

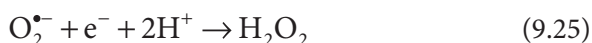
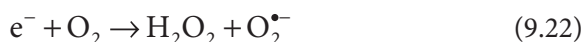
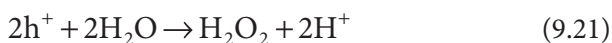
Industrial application	Pollutants	Efficiency	Reference
Textile and dye industries	Remazol Brilliant	90%	[79]
Textile industry	Blue R	90%	[80]
Dye industry	Methylene blue	100%	[81]
Dye industry	RR194	80%	[82]
Textile industry	C.I Reactive Red 2	>95%	[83]

Table 9.13 Performance of the photocatalytic ozonation process for the degradation of textile pollutants.

Industrial application	Pollutants	Efficiency	Reference
Textile industry	Reactive dyes	>95%	[85]
Textile industry	Reactive Red 198	100%	[86]
Textile industry	Reactive Red 120	100%	[86]
Textile and dye industries	Reactive dyes	97%	[87]

Table 9.14 Performance of the photocatalysis process for the degradation of textile pollutants.

Industrial application	Pollutants	Efficiency	Reference
Textile and dye industries	Azo and disperse dye	99%	[89]
Textile industry	Mixture of dyes	98%	[90]
Textile industry	Methyl orange	84%	[91]
Textile and dye industries	Reactive dyestuffs	99%	[25]



Applications of the photocatalysis process for the degradation of different textile pollutants are summarized in Table 9.14.

9.3 Process Intensification

One of the difficult steps in treatment operations is the selection of the best technique for removal of specific industrial wastewater. The selection of one or more treatment processes that operate simultaneously or in series depends on the quality standards to be met and the most effective treatment with the lowest reasonable cost [92]. Hence, the main parameters that must be considered in the material selection and equipment and/or process design to achieve maximum treatment efficiency are summarized as follows [11]:

- The quality of the original wastewater
- Removal of parent contaminants
- Conventional treatment options
- Treatment flexibility
- The facility decontamination capacity
- Final wastewater treatment system efficiency
- Economic studies
- Life cycle assessment to determine environmental compatibility of the wastewater treatment technology
- Potential use of treated water

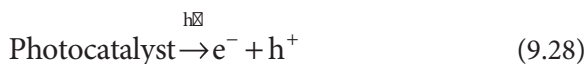
The coupling of two or more AOPs is a great idea toward enhancement of process efficiency due to the cumulative effect and the synergistic effect, which refer to the increased production of reactive oxygen species and positive interactions among the individual processes, respectively [93]. The synergy can be quantified as the normalized difference between the rate constants achieved under the combined method (k_{combined}) and the sum of those obtained under the individual methods (k_i) as shown in Equation 9.27, where a positive value stands for a synergistic effect, a negative value stands for an antagonistic effect, and zero stands for a simpler cumulative effect [94, 95].

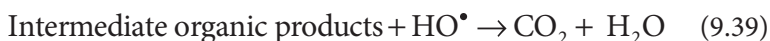
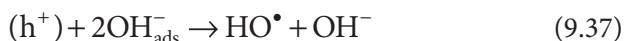
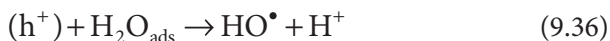
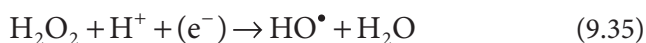
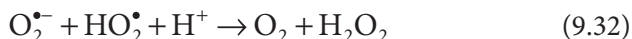
$$S = \frac{k_{\text{combined}} - \sum_1^n k_i}{k_{\text{combined}}} \quad (9.27)$$

The combination of different AOP systems typically results in a synergistic effect due to the wider spectrum of oxidants involved in the processes.

9.3.1 Sonophotocatalysis

The combination of ultrasonic irradiation with the photocatalytic process (i.e., sonophotocatalysis) leads to the cleavage of dissolved oxygen molecules and water molecules, which subsequently generates more oxidative free radicals, thereby improving degradation reaction rates. The mechanism of this process is presented as follows [51, 96–99]:





where e^{-} , h^{+} and OH^{-} are the electron, hole, and the hydroxide ion adsorbed on the photocatalyst surface, respectively, and)))) represents ultrasound.

Generally, the operational details and performance of the sonophotocatalytic process for the degradation of textile effluents are described as follows [100]:

- The rate of degradation reaction follows pseudo-first-order kinetics.
- The rate of degradation mainly depends on the initial textile concentration as well as photocatalyst dosage.
- The pH is a key factor that affects the process efficiency.
- The nature and the structure of the pollutants are very important.
- The nature of the catalysts (size, shape, surface area, and other morphologies) is an effective parameter.
- The nature and intensity of the light source and the reactor configuration are very important factors in case of economics.

- The intensity of ultrasound source should be considered and optimized during the degradation process.

Applications of the sonophotocatalysis process for the degradation of different textile pollutants are summarized in Table 9.15.

9.3.2 Sono-Fenton (Fenton/Sonolysis)

The degradation of contaminants using Sono-Fenton method is carried out via active species generated by the reaction of hydrogen peroxide with ferrous and ferric ions in acid solution [104]. The main reaction pathway for the degradation in solution is the oxidation by HO[•], which during the process sonolysis increases the yield of HO[•] from Fenton's reagent. Applications of Sono-Fenton process for the degradation of different textile pollutants are summarized in Table 9.16.

Table 9.15 Performance of the sonophotocatalysis process for the degradation of textile pollutants.

Industrial application	Pollutants	Efficiency	Reference
Textile industry	Naphthol-Blue-Black	94%	[101]
Textile industry	Bismarck Brown G dye	98%	[102]
Textile industry	C.I. Acid Orange 7	100%	[66]
Textile and dye industries	Basic Brown 1 dye	99%	[9]
Textile industry	Acid Yellow 23	98%	[103]

Table 9.16 Performance of the Sono-Fenton process for the degradation of textile pollutants.

Industrial application	Pollutants	Efficiency	Reference
Textile industry	Remazol RGB reactive dye	96%	[105]
Textile industry	Reactive Black 5	98%	[106]
Textile industry	Direct Orange 39	97%	[55]
Textile industry	Reactive Black 5	100%	[12]

9.4 Equipment and Processes

The challenges related to the scale-up for AOP equipment are considerably more complex than those of conventional devices. Any development that leads to a substantially smaller, cleaner, safer and more energy-efficient process can be used to overcome limitations [107]. Designing new equipment based on the PI will permit us to approach high-efficiency as well as low-cost processes. One such equipment is the photocatalytic rotating packed bed reactor, which has been made for intensifying degradation of different pollutants especially dyes and textile pollutants [108].

Conventional photocatalytic reactors have some limitations such as poor light distribution and low surface areas for photocatalyst per unit volume of reactor, whose large-scale application is a great problem due to these limitations. Process intensification simply overcomes the mentioned limitations by designing novel equipment such as rotating packed bed (RPB) [110]. Rotating packed bed (Figure 9.6) improves mass transfer, micro-mixing, and reaction rate via centrifugal force emerging from the high rotational speed in a porous domain, and because of which, under this condition, improvement of mass transfer between phases leads to high operational

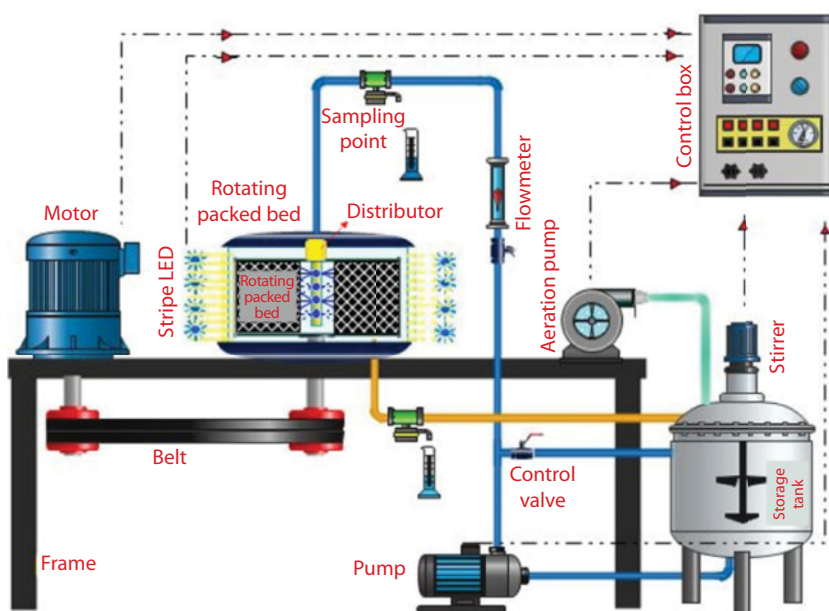


Figure 9.6 Photocatalytic rotating packed bed reactor [109].

The performance of the RPB photocatalytic reactor for the degradation of mixture dyes was evaluated by comparing its degradation efficiency with a conventional reactor, the results of which revealed that under the same conditions, the conventional reactor not only consumes more photocatalyst but also needs more irradiation time compared to the RPB [109]. These facts mean that the RPB photocatalytic reactor is more economic. Based on the results, the RPB photocatalytic reactor operates at a higher flow rate, which is very important from the point of view of economics for large-scale application [113].

Another evaluation of the application of the RPB photocatalytic reactor for simultaneous degradation of a mixture of dyes [111] including methylene blue (MB), auramine-O (AO), and erythrosine (ER) showed that the

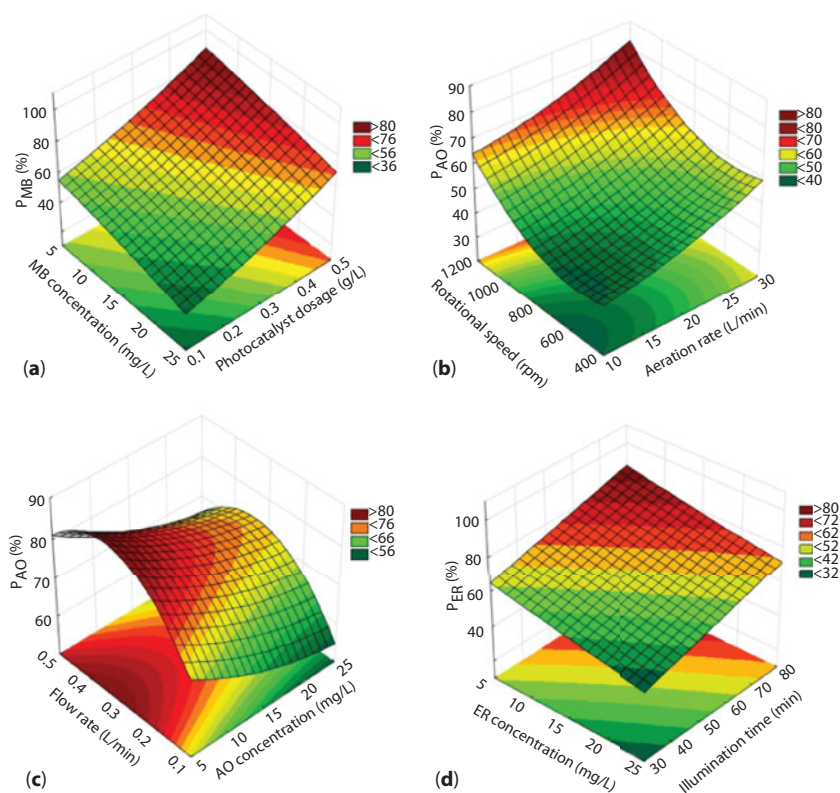


Figure 9.8 Response surface (3D) plots for photocatalytic degradation process versus between independent variables. (a) MB concentration with photocatalyst dosage, (b) rotational speed with aeration rate, (c) flow rate with AO concentration, (d) ER concentration with illumination time [124].

Table 9.17 Comparison of different reactors' performance for photocatalytic degradation process [115].

Reactor type	Light source	Dye	Concentration (mg/L)	Catalyst	Catalyst loading (g/L)	Time (min)	Efficiency
Conventional reactor [116]	Hg lamp	MB	10	CuO	0.100	120	4%
Conventional reactor [117]	Halogen	MB	10	CuO	0.020	360	27%
Conventional reactor [118]	UV lamp	MB	10	CuO	0.014	150	83%
Conventional reactor [119]	Hg lamp	MB	7	CuO	0.200	180	61%
Conventional reactor [120]	UV lamp	MB	10	CuO	0.500	210	33%
Microreactor [121]	UV lamp	MB	10	Cu/CuO	0.04	50	15%
Conventional reactor [122]	Xenon lamp	MB	20	Cu/Cu ₂ O	0.280	120	67%
Microfluid reactor [123]	UV lamp	MB	10	Cu@Cu ₂ O	0.100	50	4.7%
Rotating packed bed [115]	Blue LED	MB	10	CuO/Cu ₂ O/Cu	0.300	90	91.91%

maximum efficiency (92.01%, 89.57% and 89.96% for MB, ER, and AO, respectively) was achieved under optimum conditions: irradiation time of 75 min, 15 mg/L of each dye, 0.4 g/L of photocatalyst, rotational speed of 1000 rpm, solution flow rate of 0.3 L/min, and aeration rate of 25 L/min (Figure 9.8).

The performance of the RPB photocatalytic reactor for the dye degradation process compared to other reactors (Table 9.17) indicates that conventional reactors not only have less efficiency but also require more irradiation time, which means that the RPB photocatalytic reactor is more efficient and cost-effective [111]. The superior advantages of this equipment are related to the high interfacial surface area generated by the rotational speed, which enhances mass transfer and mixing processes [114].

Another compact device that utilizes the benefits of PI is the sonophotocatalytic reactor, which applies both photocatalytic and sonolysis methods simultaneously for the treatment of wastewater (Figure 9.9). Among AOP techniques, sonophotocatalytic degradation is one of the best combined processes, which has the ability to degrade various organic pollutants such as dyes and textiles [125].

In fact, cavitation, which was generated by ultrasonic waves, leads to more immersion of the catalyst in the bulk solution that subsequently increases the interfacial surface between pollutants and catalyst particles. Under this condition, mass transfer resistance decreases, and after the cleanup procedure, the catalyst surface regenerates during the acoustic microstreaming process [126]. During sonication, H_2O_2 is produced, which can convert into OH radicals, which then causes an increase in the mineralization rate of contaminants. Aside from photocatalytic degradation, the sonophotocatalytic process has some unique benefits such as lower toxicity, lower cost, and the non-requirement of a cooling system [127].

The performance of the sonophotocatalytic degradation process was evaluated for the treatment of mixture dyes including trypan blue (TB) and vesuvine (VS); investigations showed that high degradation efficiency was achieved using a designed reactor system [94]. Based on the obtained results, the maximum sonophotodegradation percentages were found to be 98.44% and 99.36% for TB and VS, respectively (Figure 9.10). The optimum conditions were as follows: 25 mg/L of each dye, a solution flow rate of 70 mL/min, an irradiation/sonication time of 25 min, a pH of 6, and a photocatalyst dosage of 0.25 g/L.

The synergy index was used for evaluating the contribution of each individual process. For a combined AOP process such as the sonophotocatalytic process, the synergy index is defined as the ratio of the sonophotocatalytic

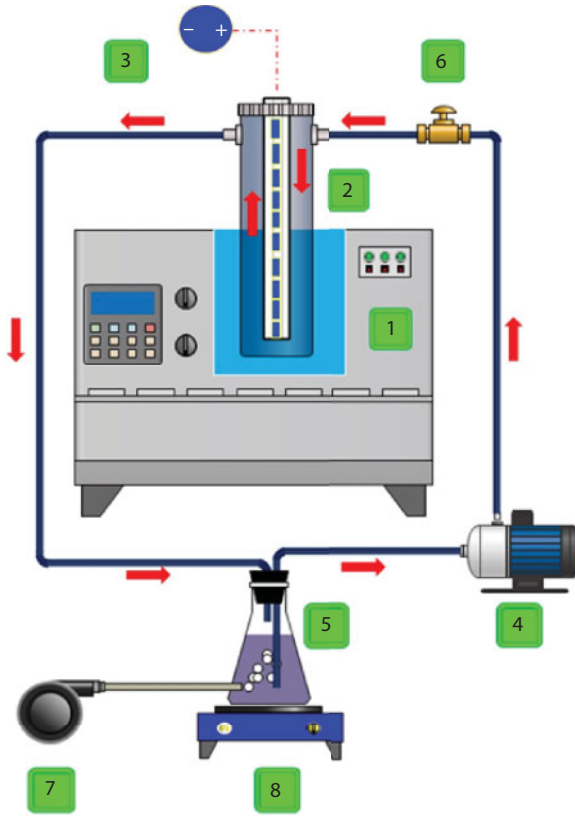


Figure 9.9 Sonophotocatalytic reactor setup: 1, ultrasonic bath; 2, reactor vessel; 3, LED source; 4, peristaltic pump; 5, reservoir; 6, sampling valve; 7, aeration pump; 8, magnet stirrer [94].

rate constant to the sum of the rate constants of the individual processes [128]:

$$\text{synergistic effect } (S) = \frac{k_{\text{sonophotocatalytic}}}{k_{\text{sonocatalytic}} + k_{\text{photocatalytic}}} \quad (9.40)$$

where $k_{\text{sonophotocatalytic}}$, $k_{\text{sonocatalytic}}$, and $k_{\text{photocatalytic}}$ are the apparent rate constant of sonophotocatalytic, sonocatalytic and photocatalytic processes, respectively. The synergistic effect values greater than 1.0 indicate a positive effect on the obtained efficiency. The evaluation of synergy effect for the degradation of TB and VS revealed that combined processes have a positive effect on degradation efficiency compared to individual processes

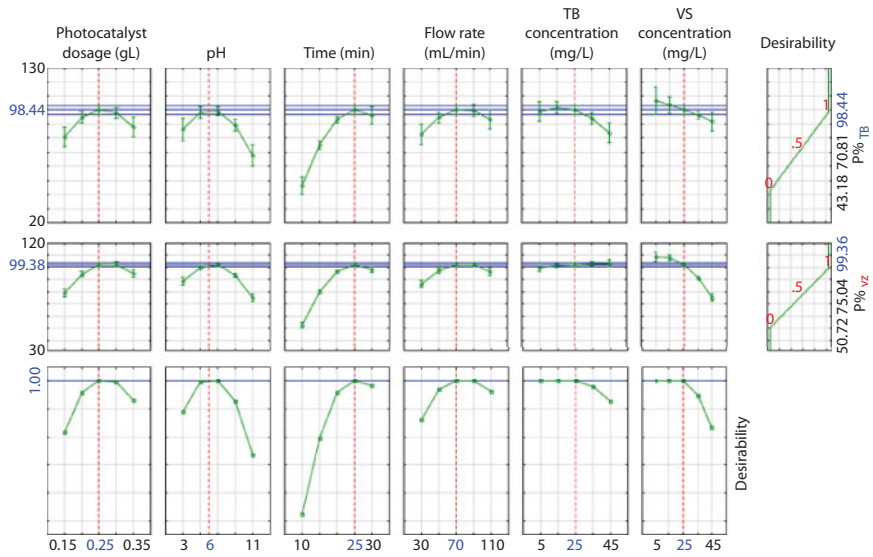


Figure 9.10 Profiles for predicated values and desirability function for sonophotocatalytic degradation. Dashed line shows optimum values [94].

Table 9.18 Synergy index for hybrid system and individual processes [94].

Photocatalyst dosage (g/L)	k (1/min)			Synergy index
	Sonocatalysis	Photocatalyst	Sonophotocatalyst	
0.15	0.013	0.042	0.108	1.96
0.20	0.016	0.051	0.162	2.41
0.25	0.023	0.077	0.253	2.53
0.30	0.019	0.068	0.214	2.46
0.35	0.011	0.035	0.081	1.76

(Table 9.18). This can be attributed to the role of ultrasonic waves in de-aggregating the catalyst particles, which leads to an increase in the interfacial surface area between pollutants and catalyst particles, causing an increase in the mass transfer and reaction rate [129]. The formation, growth, and collapse of bubbles in liquid, which are a known chemical effect of ultrasonic field, lead to faster degradation rate and enhancement of degradation efficiency [130].

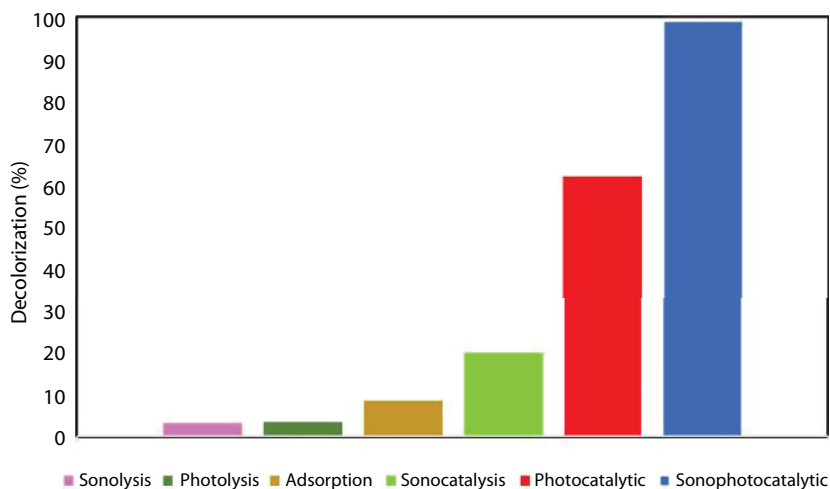


Figure 9.11 Decolonization efficiency under different processes under optimum conditions: 25 mg/L of each dye, solution flow rate of 70 mL/min, irradiation and sonication time of 25 min, pH 6.0, and photocatalyst dosage of 0.25 g/L [94].

The comparison of degradation rates obtained using different treatment processes including sonocatalysis, photocatalysis, and sonophotocatalysis indicated that, under optimum conditions, the reaction rate constant of the sonophotocatalytic process is greater than the sum of the rate constants of the individual processes, that is, $K_{\text{sonophoto}} > K_{\text{photo}} + K_{\text{sono}}$ (Figure 9.11), which represents the synergistic effect of combined AOP methods [94].

Other studies for the degradation of different dye effluents such as disulfine blue (DB) and rose bengal (RB) (Figure 9.12) show that high degradation percentages were obtained for DB (99.98%) and RB (98.76%) [131].

9.5 Catalyst Design and Modification

The performance of the catalyst has a significant effect on the reactor/process efficiency. Improvements in catalyst activity and selectivity can enhance process economics as well as reduction in greenhouse gas emissions through better feedstock utilization [132]. The following catalyst properties can be considered for PI [133]:

- Secondary catalytic function
- Enhanced transport characteristics
- Novel catalyst morphologies

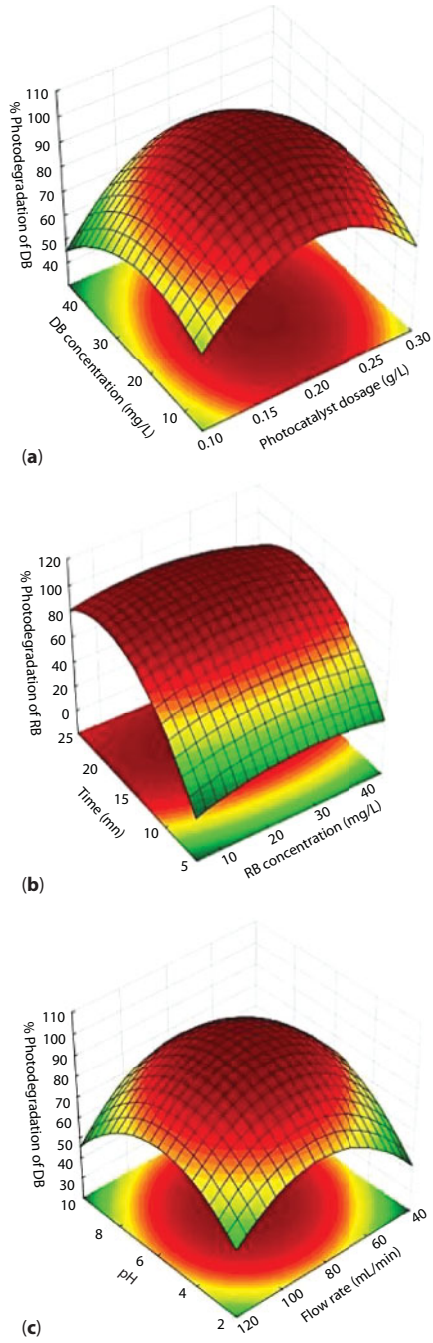


Figure 9.12 Response surface plots of central composite design: (a) DB concentration–photocatalyst dosage; (b) illumination time–RB concentration; (c) pH–flow rate [131].

- Energy transfer properties
- Reactant transfer properties

The synergy through combining two processes in a single catalyst particle can lead to significant process advantages.

9.5.1 Development of New Efficient Photocatalysts

Conventional photocatalysts have low efficiency for the degradation of pollutants due to the following [134]:

- Quick recombination of the photogenerated electron–hole pairs (within 10–100 ns), which releases thermal energy or unproductive photons;
- High reactivity that leads to fast backward or secondary reactions with the formation of undesirable by-products;
- A low absorption in the visible region, which determines their inability to use solar light (less than 5% is used in the case of TiO_2 anatase).

Therefore, the synthesis and development of novel photocatalysts that could overcome the above limitations is one of the main research topics [135].

9.5.2 Metal Organic Frameworks Photocatalysts

Metal organic frameworks (MOFs) are known efficient photocatalysts due to their optical transition and electrochemical and photochemical activity [136]. However, when using MOF photocatalysts, the degradation is performed in a very limited subset of materials due to their special structures. Although these photocatalysts have low conductivities, when they are exposed to light irradiation, electrons and holes are generated, resulting in reductive and oxidative power, respectively [137]. According to the mentioned properties, MOFs should be considered as an array of self-assembled molecular catalysts and not as conventional photocatalysts. Furthermore, the HOMO–LUMO gap terminology should be used in order to describe the discrete character of the light-induced transitions in these coordination compounds [138]. The application of MOF photocatalysts for the degradation of various textile effluents was reported [137, 139–143], the results of which indicate that, compared to conventional photocatalysts, MOFs have many advantages [144]:

- Preparation via various methods including solvothermal, vapor diffusion, emulsion-assistant precipitation, ultrasonication, and even post-synthesis modification allows a high degree of crystalline quality and morphology [145].
- The well-defined crystalline structures are beneficial in the characterization and study of the structure–property relationship of these solid photocatalysts.
- The modular nature of the MOF synthesis allows the rational design and fine-tuning of these catalysts at the molecular level, making the electronic structure of the MOF catalysts to be easily tailored.
- The structural features of tunable active sites (i.e., metal-Oxo clusters and organic linkers) in MOFs lead to more efficient solar harnessing [146].
- The intrinsic porosity and high surface area of MOFs can facilitate the diffusion of the pollutant and product molecules through their open channels, where active catalytic sites are located, thereby reaching a high efficiency of the catalytic reaction.
- Different from typical TiO_2 -based catalysts, the visible light photocatalytic activity can be easily introduced via the linker substitutions of organic chromophores in MOF structures, such as with an amino group.
- The combination of the conventional semiconductor properties with the strong adsorbing properties of some MOFs can generate composite materials with enhanced catalytic efficiency and better visible light response [147].

The applications of MOF photocatalysts for photocatalytic degradation of different dyes and textiles are summarized in Tables 9.19 and 9.20, the results of which show that MOFs are efficient photocatalysts for the degradation of many various textiles. Table 9.19 shows the results for degradation under UV irradiation, while Table 9.20 shows MOF applications under visible-light irradiation.

9.6 Economic Evaluation/Justification of AOPs

One of the important indicators in the application of novel methods for textile effluents treatment is economic productivity. Therefore, the economic justification of a method should be considered and capital fixed

Table 9.19 Photocatalytic performance of various MOFs for the degradation of different dyes under UV irradiation.

MOFs	Dye	Dye concentration (mg L ⁻¹)	MOF concentration (mg L ⁻¹)	Time of degradation (min)	Degradation (%)	Reference
(<i>n</i> -Bu ₃ Sn) ₄ Fe(CN) ₆ H ₂ O	MB	32	42	180	100	[148]
[NiL ₄ V ^{IV} W ^{VI} ₁₀ O ₂₄₀ (V ^{IV} O) ₂]	MB	10	100	180	96	[149]
[PhBiS ₂ CN(C ₂ H ₅) ₂ Cl] _{<i>n</i>}	RhB	6	250	50	93	[150]
[Pb(ttbt)(1,4- <i>b</i> -doa)] <i>n</i> ·2 <i>n</i> H ₂ O	RhB	10	200	120	99	[151]
[Ag ₇ (pytz) ₄ [(PW ₁₂ O ₄₀)]	MB	18.7	100	80	98	[152]
[Mn(phen) ₂ (H ₂ cpb)]	MB	10	250	120	100	[152]
[Mn(phen) ₂ (H ₂ cpb)]	MO	30	250	120	100	[152]
[(Pb(Tab) ₂)(PF) ₆] _{<i>n</i>}	AO7	100	250	120	100	[153]
[(Pb(Tab) ₂ (bpe)) ₂ (PF) ₆] _{<i>n</i>}	AO7	100	250	90	100	[153]
[(Pb(Tab) ₂)(PF) ₆] _{<i>n</i>}	OI	100	250	100	100	[153]
[(Pb(Tab) ₂ (bpe)) ₂ (PF) ₆] _{<i>n</i>}	OI	100	250	120	100	[153]
[Cu ₂ (4-atrz) ₆ (SiW ₁₂ O ₄₀)(H ₂ O)]·6H ₂ O	MB	6	1667	60	98	[154]
(Me ₂ DABCO) ₅ (Cu ₁₅ Br ₂₄)Br	KR	6	500	150	99	[155]

Table 9.20 Photocatalytic performance of various MOFs for the degradation of different dyes under visible-light irradiation.

MOFs	Dye	Dye concentration (mg L ⁻¹)	MOFs concentration (mg L ⁻¹)	Time of degradation (min)	Degradation (%)	Reference
[Cu ₂ (L ₂) ₂ (CrMo ₆ (OH) ₅ O ₁₉)(H ₂ O) ₂].2H ₂ O	RhB	5	1111	350	92	[156]
[(MV)((UO ₂) ₂ (TDC) ₃)] _n	RhB	10	500	180	100	[157]
[W ₅ Cu ₄ (CN) ₂ (pyridine)] _{4-n}	MB	4.9	750	60	98	[158]
HKUST-1	MG	10	250	85	98	[159]
[Zr ^{IV} O(OH) ₄ (CO ₂) ₁₂]	MB	100	667	180	100	[160]
Cd ₈ S(SPh) ₁₄ (DMF) ₃	RhB	20	2000	180	92	[161]
[Cd ₈ S(SPh) ₁₄ (DMF)(bpy)] _n	RhB	20	2000	180	95	[161]
[(CH ₃) ₂ NH ₂] ₃ [ZnL ₂ (BW ₁₂ O ₄₀)]·4DMF·4H ₂ O	CV	10	750	24	100	[162]
rGO/MIL-125(Ti)	RhB	50	400	50	96	[163]
Pd/MIL-101(Cr)/rGO	BG	25	250	15	100	[164]
20%-rGO/NH ₂ -MIL-125(Ti)	MO	20	750	30	100	[165]

costs as well as operating costs should be calculated and optimized. The fixed capital costs are including the sum of all equipment's purchase, installation, piping, instrumentation, insulation, electrical facilities, buildings, yard improvements and auxiliary facilities while operating costs are including as the sum of raw materials, lab, consumables, and utilities. The fixed and operation costs for the treatment of pollutants was investigated using UV/H₂O₂ as AOP system and adsorption using activated carbon as conventional method which estimated fixed costs of different treatment technique according to the depreciation period (40 years) are provided as follow [32, 166]:

Treatment via photoreactor:

$$FC_C = \left(\frac{85.000 + (40 \times 1500)}{(40 \times 24 \times 365) \times \left(\frac{V_C}{\theta_C} \right)} \right) \times \left(\frac{1 \text{ m}^3}{1000 \text{ L}} \right) \quad (9.41)$$

where FC_C (\$/L), V_C (m³), and θ_C (h) are typical UV/H₂O₂ fixed cost, the volume of the photoreactor, and the residence time of the wastewater in the photoreactor, respectively. The fixed cost for treatment using the UV/H₂O₂ process is usually \$58,000 plus the cost of UV lamp, which is \$15,000 per year. The maximum allowable useful life estimate under U.S. income tax regulations is 40 years, which can be considered as depreciation time [32].

Treatment using the adsorption method (activated carbon):

$$FC_P = \left(\frac{58.000}{(40 \times 24 \times 365) \times \left(\frac{V_P}{\theta_P} \right)} \right) \times \left(\frac{1 \text{ m}^3}{1000 \text{ L}} \right) \quad (9.42)$$

where FC_P (\$/L), V_P (m³), and \$58,000 are related to the fixed cost of typical adsorption column, the volume of the column, and the capital cost a for typical activated carbon column, respectively.

Treatment using a biological reactor:

$$FC_B = \frac{\left((72 \times 40 \times 24 \times 365) \times \left(\frac{V_B}{\theta_B} \right) \right) + 368.403}{(40 \times 24 \times 365) \times \left(\frac{V_B}{\theta_B} \right)} \quad (9.43)$$

where FC_B (\$/L), V_B , and θ_B are typical activated sludge capital cost, bio-reactor volume, and the residence time, respectively. \$368,403 corresponds to the capital cost for a typical biological treatment and \$72 is also required for the treatment of 1 m^3 wastewater [32].

The optimization of fixed and operating costs is a key step for commercial application. The operating cost of AOP methods is high because of the continuous addition of some reagents such as H_2O_2 and Fe^{+2} . Physical treatment methods utilizing an adsorbent are considered to be an additional expense for regeneration. The operating and maintenance cost for the treatment of pollutants using typical UV/ H_2O_2 , adsorption (activated carbon), and biological processes is defined as follows [32, 166, 167]:

$$\text{OMC}_C = \left(\frac{2000}{(24 \times 365) \times \left(\frac{V_C}{\theta_C} \right)} \right) \times \left(\frac{1 \text{ m}^3}{1000 \text{ L}} \right) \quad (9.44)$$

where OMC_C and \$2000 are the operating and maintenance cost for the UV/ H_2O_2 treatment system and the operating cost estimated for 40 years, respectively. The maintenance and operating cost (OMC_p) for treatment using the adsorption column (activated carbon) is defined as follows [32]:

$$\text{OMC}_p = \left(\frac{1200 + 0.29V_p}{(24 \times 365) \times \left(\frac{V_p}{\theta_p} \right)} \right) \times \left(\frac{1 \text{ m}^3}{1000 \text{ L}} \right) \quad (9.45)$$

where \$1200 is the operating and maintenance cost estimated for 40 years and $0.29 \text{ [$/m}^3\text{]}$ is the cost for the regeneration and reactivation of the carbon bed. The maintenance and operating cost of a typical biological treatment (OMC_B) is defined as follows:

$$\text{OMC}_B = \left(\frac{4.58 \times (24 \times 365) \left(\frac{V_B}{\theta_B} \right) + 36.295}{(24 \times 365) \times \left(\frac{V_B}{\theta_B} \right)} \right) \times \left(\frac{1 \text{ m}^3}{1000 \text{ L}} \right) \quad (9.46)$$

where \$36,295 is the operating and maintenance cost predicted for 40 years plus the $4.58 \text{ [$/m}^3\text{]}$. Equations 9.41 to 9.46 can be applied for optimizing the cost of various integrated processes containing AOPs [32].

9.6.1 Power Consumption and Cost-Effectiveness

Degradation of methomyl via ultrasound cavitation (US) and its coupling with H_2O_2 , Fenton, and the photo-Fenton process were investigated to evaluate the synergistic effect of combination AOPs on the degradation efficiency [92]. Results proved that a combination of US and the photo-Fenton process is the most effective process with maximum degradation corresponding to 78.8% efficiency. Energy efficiency and cost-effectiveness were evaluated for different treatment processes, and results revealed that the electrical cost of 79,892.34 Rs./m³ for ultrasonic degradation of methomyl has drastically reduced to 2277.00 Rs./m³, 1518.00 Rs./m³, and 807.58 Rs./m³ by using ultrasound cavitation in combination with H_2O_2 , Fenton, and the photo-Fenton process, respectively (Table 9.21). These calculations were performed based on the cost of electricity in India (Rs. 5.06/kWh). The cost analysis results showed that the combination of US and the photo-Fenton process was the most energy-efficient and most cost-effective process for the degradation of methomyl.

The treatment time for complete degradation is used as the standard for power consumption (kWh/m³) during individual ultrasound cavitation and hybrid processes. In the case of an individual US process, the requirement of high power consumption makes it too expensive, mainly due to the low degradation rate, which translates into a very long treatment time [92]. The combination of US with H_2O_2 or Fenton or the photo-Fenton process makes the process economically attractive, and less treatment time is needed for complete degradation. The hybrid processes are more economical because of an increased generation of hydroxyl radicals, which subsequently increases the rate of degradation [168].

Although hybrid systems require additional energy, a combination of processes has proved to be the most cost-effective one due to the high degradation rate, which caused complete degradation of pollutants. As shown in Table 9.21, the cost of methomyl degradation of 79,892.34 Rs./m³ incurred during US has been reduced by almost 98 times, that is, to 807.58 Rs./m³, when ultrasound cavitation was coupled with the photo-Fenton process [92].

Although most researches on water pollution control for the textile industry focused on the qualitative explanation and the related scientific methods, it is necessary to focus on the textile treatment cost analysis as well [169, 170]. The key factors that affect the cost of textile treatment are the pollution-control technique, regional distribution, and the type of textile industry. Table 9.22 shows the possible operating cost for textile wastewater treatment methods, which indicates that cost analyses have been done on very few treatments [171]. Results indicate that the combined

Table 9.21 Comparison of power consumption and cost-effectiveness of various processes [92].

Treatment process	Power supplied (W/l)	% Degradation	Treatment time (min)	Power consumption (kWh/m ³)	Cost of electricity (Rs./m ³)
US	1000	28.70	72	15,789.00	79,892.34
US + H ₂ O ₂	1000	100	27	450.00	2277.00
US + Fenton	1000	100	18	300.00	1518.00
US + Photo-Fenton	1064	100	9	159.60	807.58

Table 9.22 Cost of textile wastewater treatment techniques [171].

Process for the treatment of textile wastewater	Treatment cost (US\$/m ³) ^a	Color/COD removal	Reference
Color removal by Fetons process followed by COD removal by activated sludge	0.4	Complete decolorization. Final COD of 80 ppm after activated sludge process.	[8]
Fetons oxidation for the color and COD removal from biologically pretreated textile wastewater (textile factory in Turkey)	0.59	For the Fenton process, 78% and 95% COD and color removal efficiencies, respectively.	[177]
Fe ³⁺ /H ₂ O ₂ for the color and COD removal from biologically pretreated textile wastewater (textile factory in Turkey)	0.57	For the Fenton e-like process, 64% and 71% COD and color removal efficiencies, respectively.	[177]
Ozonation for the color and COD removal from biologically pretreated textile wastewater (textile factory in Turkey)	4.94	43% COD and 97% color removal by ozonation.	[177]
Ozonation and H ₂ O ₂ (peroxone) for the color and COD removal from biologically pretreated textile wastewater (textile factory in Turkey)	5.02	54% COD and 99% color removal by ozonation.	[177]
Fetons process followed by coagulation (polyaluminum chloride) followed by ion exchange process applied to textile wastewater	3.5 (cost of sludge disposal, 1.5 US\$/m ³)	In this study, chemical coagulation (8% COD removal) and ion exchange processes (51% COD removal and final COD 50 mg/L) were applied after pretreatment by Fenton oxidation process (29% COD removal) to the textile wastewater.	[10]

^aThe sludge disposal cost and labor cost are excluded.

Fenton and biological treatment method has lower cost as compared to the combined ozone and biological treatment, while the Fenton-based treatment produces more sludge as compared to the ozone-based treatment, and its disposal will also need the additional cost. It should be considered that the wastewater for the treatment methods is different and hence these two methods should not be compared [172]. To obtain a lower operating cost in the case of a combination process, the mineralization percentage should be minimum in the pretreatment or posttreatment stage to reduce the needless spending of chemicals and energy [173]. Costs optimization can be performed by categorizing the treatment processes into two parts: an expensive treatment part and a cheap treatment part. First, the most expensive treatment parts should be identified and then those parts should be minimized or substituted with cheaper or more effective solutions. Reusability of catalyst and exploitation of the hydrogen peroxide in the bleaching effluent can be considered for optimization of costs [174]. The cost of the possible combinations and the toxicity of intermediates achieved after treatment should be compared with each other to choose the best combination system [175]. Finally, the combined process that yields low

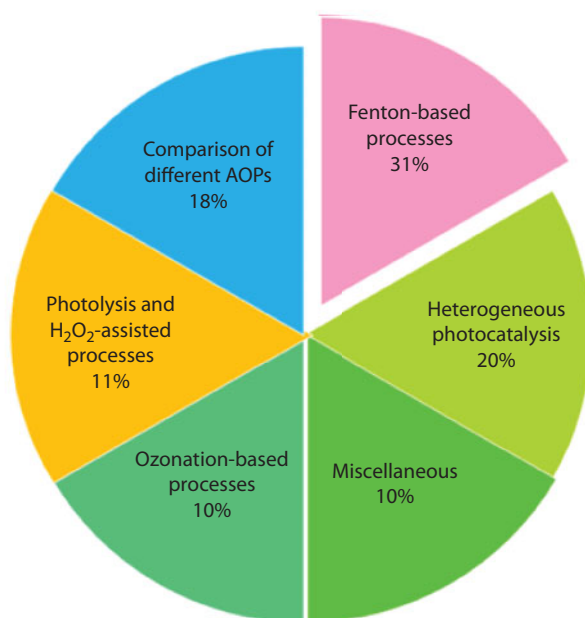


Figure 9.13 Performance of different types of AOPs for treatment of Directive according to 2013/39/EU [178].

cost and low toxicity should be selected as the treatment method, although the components of the wastewater should be considered [176].

Application of different AOP systems for treatment of Directive according to 2013/39/EU (Figure 9.13) indicates that Fenton-based processes are the most applied AOPs (31%) in compounds defined in Directive 2013/39/EU, followed by heterogeneous photocatalysis (20%), while an important fraction is related to the comparison of different AOPs (18%) [178].

9.7 Industrial and Large-Scale Applications

Various combinations of AOP systems have been applied for the treatment of different textile pollutants at pilot- and large-scale applications, which indicate that AOPs (specially combined and integrated systems) have a significant effect on treatment performance [169]. The performance of pilot-scale combined processes (Figure 9.14), consisting of the fluidized biofilm process, chemical coagulation, and electrochemical oxidation, was evaluated for textile wastewater treatment, the results of which indicated that the current system could treat textile effluents successfully [179].

Scaling-up of a slurry reactor for the photocatalytic oxidation of cyanide has been successfully carried out using commercial TiO_2 and a silica-supported TiO_2 , which reveals that the current system performed well [180]. Experimental results for the degradation of contaminants using a novel bench-scale reactor system, which consists of a cylindrical vessel (diameter, 0.056 m) with 54 hollow quartz glass tubes (diameter, 0.006 m) coated on its peripheral surface with catalyst within, indicated that the designed reactor can degrade various pollutants [181]. A pilot-scale system for the treatment

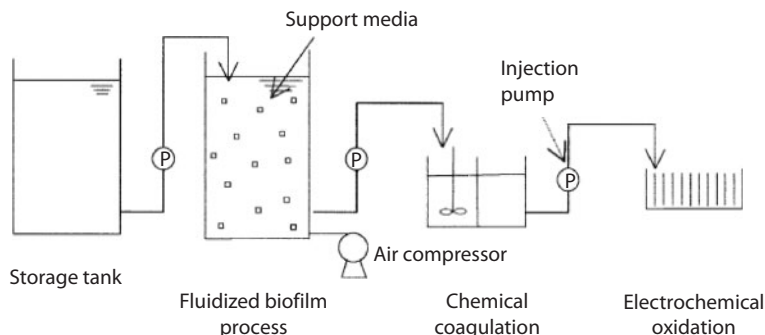


Figure 9.14 Flow diagram of a pilot-scale combined process for textile wastewater treatment [179].

of textile wastewater was designed to evaluate pre-ozonation efficiency for the removal of color and soluble COD, the results of which indicated that the current system is efficient in removing textile effluents [182]. An efficient photoreactor for the treatment of industrial dye effluents was fabricated based on the solar energy for environmental cleanup. Treatment of dye industry effluent revealed that this reactor could degrade dye effluents from industries with high efficiency [183]. Since, the adaptation of AOPs methods towards industrial applications faces several challenges such as energy consumption, operation costs, and up-scaling, more investigation of operational parameters such as energy source, pressure drop, holdup, residence time, power and cost analysis can be beneficial for optimization of the process which consequently leads to overcoming risks of AOPs equipment scale-up for commercial applications.

9.8 Application of Nanostructures in Wastewater Treatment

In the last two decades, nanotechnology has emerged significantly with its applications in almost all branches of science and technology [184]. Nanostructures with many benefits including large surface area, pore volume, and proper functionalities are categorized into different porous materials such as activated carbon, pillared clays, zeolites, mesoporous oxides, polymers, and metal-organic frameworks, which have varying extents of effectiveness in removing the toxic pollutants from wastewater [185, 186]. For example, carbon nanotubes (CNTs), which are well-known nanostructures for wastewater treatment, have two types (Figure 9.15):

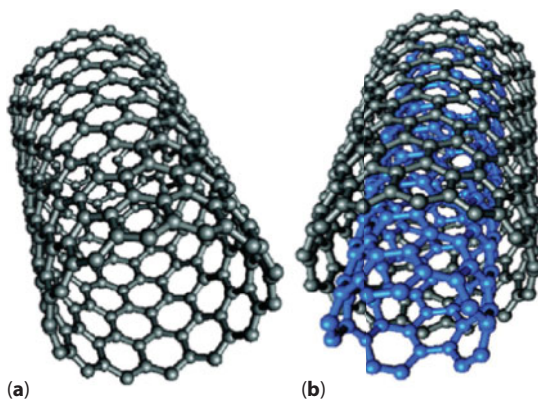


Figure 9.15 Structure representations of (a) SWCNTs and (b) MWCNTs [184].

Table 9.23 Examples of nanomaterial applications for drinking water treatment [188].

Nanoscale property	Opportunities in water purification systems	Comparison with current technology for drinking water treatment
Magnetism	Separation of small reactive particles used as catalysts or sorbents	Replaces gravity separation or high-pressure filtration
High surface area and selective surface reactivity	High ratio of reactive atoms on the outside of nanomaterials relative to their total mass improves unit efficiency; achieves highly selective sorption of singular or multiple contaminants	High surface area can be attained using nanoporous materials but have internal mass transport limitations; high surface area materials can be precipitated <i>in situ</i> by continuous addition of chemicals (e.g., alum)
Surface catalysis	Allows for multiple elements to be placed in close proximity; allows use of small quantities of costly elements	Catalysis is not currently used in drinking water treatment
Ion delivery	Localized deposition of antibacterial nanomaterials to prevent biofouling	Practices chemical disinfection of the entire water body rather than localized surface release of antibacterial agents
Photocatalysis	New materials allow for controlled production of different reactive oxygen species or aqueous electrons	Titanium dioxide with low-pressure Hg lamps are only commercialized technology
Photo-thermal	Super-heating via light to enable solar membrane distillation	Thermal membrane distillation heats entire body of water rather than localized surface heating

Dielectric properties	Heating induced by microwaves for self-cleaning surfaces or regeneration of sorbents	Self-cleaning surfaces are not currently available, and reactivation of granular activated carbon occurs ex situ to packed beds in large gas fired kilns
Electrically conductive	Functionalized MWCNT electrodes in capacitive deionization processes	Metallic electrodes have low adsorption capacity compared with MWCNTs
Super hydrophobic	Controlling hydrophobicity of surfaces with graphene can reduce biofouling or improve membrane flux	A narrow range of polymers exist to modulate hydrophobicity of membrane or other surfaces
Strength	Electrospinning of nanofibers offers new opportunities to synthesize polymers and metal (hydr)oxide composites	Hydraulically rigid ion exchange beds, activated carbon agglomerates or other porous sorbents are used in packed beds; thin film polymeric membranes are supported on more rigid supports; cationic polymers added to strengthen metal hydroxide flocs

single-walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs), which have shown excellent performance for the treatment of various pollutants [184].

Nanomaterials offer engineers a unique array of properties that are difficult to obtain using traditional chemicals or bulk materials (Table 9.23). Nanostructures that are used for wastewater treatment include four main classes: (1) nano-adsorbents such as activated carbon, carbon nanotubes, grapheme, manganese oxide, zinc oxide, titanium oxide, magnesium oxide, and ferric oxides are usually applied for removal of heavy metals from the wastewater; (2) nano-catalysts like photocatalyst, electro-catalyst, Fenton-based catalyst, and chemical oxidant have the potential for removing both organic and inorganic contaminants; (3) nano-membranes have been used for effective removal of dyes, heavy metals, and foulants using carbon nanotube membranes, electro-spun nanofibers, and hybrid nano-membranes; and (4) the integration of nanotechnology with biological processes such as algal membrane bioreactor, anaerobic digestion, and microbial fuel cell for wastewater purification [187]. Rather than adding bulk chemicals to the entire flow stream, the localized surface reactions allow treatment at targeted locations, greatly enhancing treatment efficiency [188].

9.9 Challenges and Future Directions

Although, the high fixed capital and operating costs of AOPs methods could limit large-scale industrial application, designing the equipment and or processes based on the process intensification can be considered as an alternative approach to overcome such limitations [191, 192]. The design of hybrid processes as innovative technologies based on the process intensification (PI) can play a key role in reducing energy consumption and may lead to smaller, cleaner, and safer processes [193, 194]. The development of clean and renewable energy source such as solar energy is among the most interesting alternatives in the near future, which can help PI technologies to be economical for large-scale applications [195, 196].

Still in the development stages, AOP systems face several technical and economic issues such as high operational costs and complexity in scale-up, especially in continuous mode, and considering the efficiency and economic feasibility of the membrane technology, it is a viable option to overcome existing limitations [197–199]. The combination of AOP systems with membrane technology can be considered as an alternative process for reducing the energy requirement, which is known as a major obstacle for common applications [175, 200, 201].

Since some AOPs require chemicals/catalysts, another major concern of AOP treatment methods is toxicity from the applied chemicals/catalysts, which can act as contaminants or can interact with natural elements, transforming them into a more hazardous form because of their reactivity [15]. Therefore, developing novel catalysts such as biodegradable nanostructure materials based on the nanotechnology can be a solution [202–204]. Furthermore, reduction of catalysts' toxicity can be carried out via surface modification using biodegradable or biocompatible materials [205]. Overall, with ongoing research, more advancements and more conclusive findings can be achieved based on the PI in the coming years, which may lead to establishing the most efficient and most cost-effective treatment methods for industrial-scale systems [206].

9.10 Conclusion

In this chapter, the different types of advanced oxidation processes were reviewed and their application for the degradation of textile pollutants was described. After a brief discussion on AOP combination methods for intensification of the degradation process, this chapter illustrated recently developed equipment/processes as well as materials for process design problems involving reaction and separation. Successful technologies that were introduced in this chapter will allow the examination of similarities and differences among high-performance candidates in order to select the most practical novel designs. The fixed and capital costs of AOPs compared to other treatment methods were investigated, the results of which indicated that AOPs can be used as an efficient and cost-effective method for the degradation of textile pollutants. Overall, the PI clean technologies as novel approaches introduced in this chapter can be considered as an essential step for large-scale application.

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Visible-Light-Induced Photocatalytic Degradation of Textile Dyes over Plasmonic Silver-Modified TiO_2

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Abstract

Textile industries are considered as major users of various dyes. These industries release wastewaters containing approximately 1 million kg of dyes into the natural water ecosystem each year. Such organic compounds possess high chemical stability and low biodegradability in aqueous environment due to their complex aromatic structure and synthetic origin, which is potentially harmful to the environment. In addition, most of them are toxic and carcinogenic. Therefore, treatment of effluents containing textile dyes has now become an important environmental issue. Various physical, chemical, and biological techniques such as ion exchange, photocatalysis, oxidation, precipitation, adsorption, ultrafiltration, and reverse osmosis have been developed to remove dyes from aqueous systems. Among these techniques, photocatalysis technology, an advanced oxidation process, has recently gained considerable attention for the degradation of dyes as it uses renewable and pollution-free solar energy and produces minimal secondary wastes (the concept of green chemistry). Visible-light-induced photocatalytic degradation of dyes is usually carried out by employing semiconductor photocatalysts. TiO_2 is preferred over other semiconductors because of its nontoxicity, highly abundant nature, low cost, and high oxidizing power. Doped TiO_2 has extensively been studied as it shifts the absorbance from UV to visible range. Recently, plasmonic TiO_2 -based photocatalysts are gaining huge attention owing to their surface plasmon resonance properties. Ag, among other noble metals, is cost-effective and has high utility in environmental applications. Thus, in this chapter, we have discussed visible-light-induced photocatalytic degradation of textile dyes over silver

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(Ag)-modified TiO_2 . Optimal reaction conditions for degradation and active species responsible for dye degradation were also discussed.

Keywords: Plasmonic photocatalyst, Ag- TiO_2 , photodegradation, textile dyes, doping

10.1 Introduction

Water pollution has become an important environmental issue across the globe [1–3]. Effluents from textile industries containing many toxic pollutants including dyes are being discharged into the aqueous environment to a considerable extent [4]. The total worldwide consumption of dyes by the textile industries is in excess of 10^7 kg per year and approximately 1 million kg of dye are discharged into rivers and streams by textile industries each year [5–7]. The major problem associated with the discharge of large quantities of these organic compounds in wastewater is their chemical stability and low biodegradability in water due to their complex aromatic structure and synthetic origin, which is potentially harmful to the environment. Moreover, many of them are known to be toxic to aquatic life and to be carcinogenic [8–11]. Therefore, it is highly essential to treat these effluents before their discharge into bodies of water.

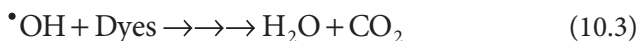
Various physical, chemical, and biological techniques, such as ultrafiltration, reverse osmosis, ion exchange, and adsorption on various adsorbents, have been developed for wastewater treatment to remove dyes from aqueous solutions [12–14]. Advanced oxidation processes (AOPs) are considered a good alternative for wastewater treatment because of their ability to destroy toxic organic effluents completely without converting pollution to another form [15]. This method is very adaptable in small scales and is suitable for developing countries whose marginalized sectors are major victims of water pollution. The following are some of the AOP techniques: (1) photolytic technique, (2) Fenton process, (3) photo-Fenton process, (4) ozonation process, (5) sonolysis, (6) photocatalysis, and (7) biodegradation [16–18]. Photocatalysis is recognized as a promising tool because it uses inexhaustible solar energy to treat the effluents in the wastewater. In this chapter, we have discussed the basic principle of photocatalysis and visible-light-induced photocatalytic degradation of textile dyes. Among several semiconductor photocatalysts, TiO_2 is the most preferred one owing to its high abundance, nontoxicity, cost-effectiveness, and greater oxidizing power. Modification of TiO_2 with silver nanoparticles having surface plasmon resonance characteristics is a potential candidate for enhanced solar light harvestation as well as effective charge transfer.

10.2 Basic Principle of Photocatalysis

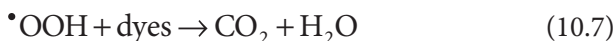
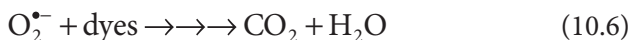
Photocatalysis has been considered as a promising technology to solve energy shortage and environment-related problems after Fujishima and Honda reported the photoelectrochemical splitting of water using a TiO_2 anode and a Pt counter electrode in 1972 [19]. In the photocatalytic processes, a flux of photons equal to or greater than the band gap energy of the semiconductor is absorbed. This excites electrons from the valence band (VB) to the conduction band (CB), leaving an equal number of holes in the VB as shown in Equation 10.1.



The photogenerated electron-hole pairs so formed separate from each other and vigorously migrate to catalytically active sites at the semiconductor surface and undergo redox reactions with the adsorbates [20]. Positive holes can oxidize OH^- or water at the surface of the semiconductor to produce hydroxyl radicals ($\cdot\text{OH}$), which possess a strong oxidizing character (Equation 10.2). These $\cdot\text{OH}$ radicals can subsequently oxidize dyes to form simpler harmless products like mineral salts, CO_2 , and H_2O as per Equation 10.3 [21].



The molecular oxygen adsorbed on the photocatalyst surface trapped the electrons present in the conduction band and is reduced to form a superoxide radical anion ($\text{O}_2^{\cdot-}$) according to Equation 10.4. $\text{O}_2^{\cdot-}$ radical anions may further react with H^+ ions to generate a hydroperoxyl radical ($\cdot\text{OOH}$) as per Equation 10.5 [22, 23]. These reactive oxygen species may follow oxidative pathways for the degradation of dyes (Equations 10.6 and 10.7) [21, 22, 24].



Through these chemical transformations, abundant solar energy can thus be effectively stored and utilized. The mechanism for semiconductor-mediated photocatalytic redox reactions is presented in Figure 10.1. However, the efficiency of a semiconductor photocatalyst largely depends on (1) the band gap of the semiconductor that allows light absorption across the solar spectrum to generate the electron–hole pairs, (2) effective separation of these charge carriers and their transport to arrive at the semiconductor surface, and (3) the availability of adequate active sites for adsorption and photocatalytic reactions. Further, to make the redox reactions thermodynamically feasible, the bottom of the CB should locate at a more negative potential than the reduction potential, and the top of the VB must have a more positive potential than the oxidation potential [25].

10.3 TiO_2 as a Versatile Photocatalyst

TiO_2 is considered as the most widely used semiconductor photocatalyst due to its high photoactivity, low cost, low toxicity, and good chemical and thermal stability [26–28]. Moreover, photoexcited TiO_2 surfaces possess super hydrophilic properties that are evident from excellent anti-fogging and self-cleaning abilities [29]. The remediation of environmental pollutants was first investigated over TiO_2 in 1977 by Frank and Bard who studied the reduction of CN^- in water [30, 31]. After this, many studies on purification of water and air through TiO_2 in the presence of solar energy have been reported [32, 33].

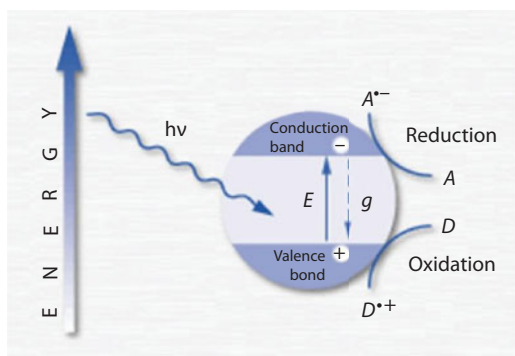


Figure 10.1 The mechanism of semiconductor-mediated photocatalytic redox reactions (where E is the excitation energy, g is the band gap, A denotes acceptor molecules, and D indicates donor molecules).

The limitation of the TiO_2 photocatalyst is its absorbance, which is 380 nm, mainly in the UV range. As solar light contains 3%–5% of UV radiation, the practical application is thus restricted. To absorb visible light (45% of solar spectrum) and near IR (about 50%), the TiO_2 -based photocatalyst need to be modified with hetero-species. The modification includes doping of both cations and anions, photosensitization, heterojunction, and combination with plasmon-based nanomaterials. Noble metals like Au, Ag, and Pt show the surface plasmon resonance phenomenon with the introduction of light. Ag exhibits surface plasmon resonance at 420 nm and, when coupled with TiO_2 , enhances the photocatalytic activity to a greater extent. Here, we have discussed the Ag-modified TiO_2 as a photocatalyst for the degradation of textile dyes.

10.4 Silver (Ag)-Modified TiO_2 (Ag- TiO_2) as Visible-Light-Induced Photocatalyst

Xin *et al.* prepared Ag- TiO_2 photocatalysts through a modified sol-gel method in the dark and studied their photocatalytic activity in degradation of rhodamine B (RhB) under visible light irradiation [34]. The degradation ratio was found to be maximum for the sample containing 5 mol% Ag. It is because the adequate amount of Ag on the surface of TiO_2 can capture the photoinduced species significantly and facilitate the transport of the photoelectrons to the surface of Ag^0 . This caused effective inhibition in the recombination of photoinduced charge carriers that leads to an enhanced photocatalytic activity. Moreover, an increase in the amount of adsorbed O_2 and surface hydroxyl groups on the surface of Ag- TiO_2 may contribute to the enhanced photocatalytic activity. Simultaneous doping and deposition of Ag introduced enough impurity bands and abundant surface states into the interfacial layer of TiO_2 , which improved the light absorption capability of the photocatalyst toward the visible region. Upon further increase in Ag content, the number of active sites for trapping the photoinduced electrons is decreased. Further, the concentration of photo-generated charge carriers is decreased due to the presence of large amounts of Ag on the surface of TiO_2 , leading to poor photocatalytic activity. A simple electrospinning process combined with silver mirror reaction was applied to synthesize Ag-coated TiO_2 nanofibers (NFs) by Guan *et al.* The Ag/ TiO_2 NFs have shown higher photocatalytic activity as compared to pristine TiO_2 NFs and degraded about 99% of the RhB solution in only 2 h under the simulated sunlight irradiation. The superior photocatalytic

performance may be ascribed to the high dispersivity of Ag NPs on individual TiO_2 nanofibers, the preferable adsorption behavior of RhB molecules on Ag/TiO_2 , the synergistic function of the well-dispersed $\text{Ag}-\text{TiO}_2$ network, and the quantum size effect of Ag/TiO_2 nanofibers [35]. Liang *et al.* demonstrated the selective photooxidation of RhB by using as-prepared TiO_2 and Ag/TiO_2 composites with high specific surface area under visible and UV irradiation [36]. RhB was photooxidized to Rh-110 (shown below) in the presence of as-prepared unannealed Ag/TiO_2 under illumination of visible light whereas complete photodegradation was observed under UV irradiation. The mechanism of photooxidation of RhB under visible irradiation is proposed in Figure 10.2.

The presence of Ag NPs in the composite helps to control the selective photooxidation of RhB under irradiation of visible and UV light. The effect of O_2^- was enhanced by the LSPR of Ag NPs under visible light, but the effect of $\cdot\text{OH}$ was improved when the Ag acted as an electron sink under UV irradiation. Controlled growth of the Ag/TiO_2 nanoheterostructures was obtained by the combination of an electrospinning technology and solvothermal route. The nanoheterostructures exhibited superior performance in visible-light-induced degradation of RhB as compared to that of the pure TiO_2 nanofiber. This excellent performance in photocatalytic activities of the Ag/TiO_2 nanoheterostructures is mainly attributed to the strong interaction between Ti and Ag species that leads to the effective separation and transportation of charged carriers. Moreover, the surface plasmon resonance of Ag nanoparticles increases the light absorption capability that extends the response of TiO_2 to visible light. The presence of Ti^{3+} in

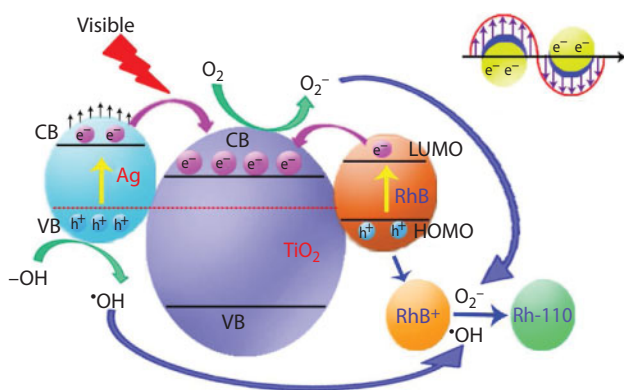
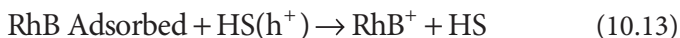
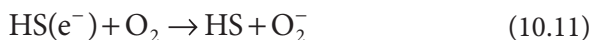


Figure 10.2 The mechanism of photooxidation of RhB under visible irradiation (reproduced from Ref. [36]).

Ag/TiO₂ also contributes to its higher photocatalytic activities. In addition, the prepared Ag/TiO₂ nanoheterostructures can be easily recycled without a decrease in the photocatalytic activity due to their particular one-dimensional nanostructures. The proposed mechanism for photodegradation of RhB is shown below [37]. Xu *et al.* fabricated a Ag/TiO₂ heterojunction photocatalyst having high surface area with uniform distribution of Ag nanoparticles by shock-induced chemical reaction of AgNO₃ and H₂TiO₃ [38]. Close interfacial contact of the heterostructure acts as a bridge for conduction electron, because of which, electron-hole pairs are separated effectively. This enhances the photocatalytic activity of the photocatalyst. Furthermore, formation of a nanojunction structure plays an important role in the surface plasmon resonance effect that enhances the visible light response. Hence, the heterojunction photocatalyst exhibited remarkably improved photocatalytic activities than P25 and shock-induced pure TiO₂ for the degradation of RhB under simulated sunlight irradiation and decomposed a maximum of 88% in 2 h. Paul *et al.* prepared Ag nanoparticle decorated anatase TiO₂ nanorods (NRs) by a solvothermal method followed by a photoreduction method. Monodispersed Ag nanoparticles (NPs) were uniformly decorated over the surfaces of TiO₂ NRs to form a Ag@TiO₂ heterostructure (HS). The defect-rich Ag@TiO₂ NR HSs with a Ag:TiO₂ weight ratio of 3:2 (TA32) significantly reduced the band gap of pure TiO₂ from 3.2 to 2.71 eV and exhibited very strong optical absorption over the entire visible region, having an absorption peak at ~520 nm due to localized surface plasmon resonance (LSPR) effect. The TA32 heterostructure has shown the highest degradation rate for decomposition of RhB under visible light irradiation. The pseudo first-order rate constant are found to be 0.033 min⁻¹ (k₁) in the first stage of degradation, which is >4 times higher, and that in the second stage of degradation was 0.083 min⁻¹ (k₂), which is ~10 times stronger than that of the bare TiO₂ NRs as well as commercial P25. The higher value of k₂ than k₁ may be attributed to ultra-fast N-de-ethylation of RhB and enhanced plasmonic effect on Ag NPs that facilitated the generation of more hot electrons for injection into the TiO₂ surface [39]. The stepwise de-ethylation of RhB under visible light irradiation could be initiated by both valence band hole and conduction band electron in the HSs as shown below [40,41]:





Dong *et al.* used hydrolysis reaction followed by thermal-induced method to fabricate one-dimensional Ag@TiO₂ anatase core-shell nanowires, which showed a high rate of photodegradation of RhB under visible light illumination at room temperature [42]. It was observed that the core-shell nanowires decomposed RhB almost completely in 15 min. The enhanced photoactivity of Ag@TiO₂ core-shell nanowires may be due to a strong localized surface plasmon resonance (LSPR) phenomenon that is induced by the photon absorption. LSPR phenomenon at the Ag@TiO₂ interface facilitates the release of electron-hole pairs. The electrons so produced diffuse into the TiO₂ shells to form O₂^{•-} radicals, and the holes that remained on Ag are used for the generation of OH[•] radicals. Both O₂^{•-} and OH[•] radicals play a crucial role in the photocatalytic degradation of organic contaminant molecules [43–46].

The Ag/Ag(I)-TiO₂ photocatalyst was successfully prepared by a facile impregnated method in combination with a calcination process by Liu *et al.* to investigate the photocatalytic degradation of methyl orange under UV and visible light irradiation separately [47]. An isolated energy level of Ag 4d was formed in the band gap of TiO₂ by Ag (I) doping. This energy level of Ag 4d extends the light absorption to the visible region in the range of 400–800 nm owing to the strong local surface plasmon resonance (LSPR) of Ag nanoparticles [47, 48], and surface metallic Ag facilitates the separation of photoinduced charged species effectively under visible light irradiation. This resulted in an enhanced visible-light-induced photocatalytic activity by Ag/Ag (I)-TiO₂ as compared to Ag (I)-TiO₂ and Ag/TiO₂. On the other hand, when UV radiation is illuminated, the presence of doping energy level of Ag (I) ions in the band gap of TiO₂ becomes the recombination center for photocarriers, as a result of which, Ag/Ag(I)-TiO₂ exhibits poor photocatalytic activity.

The Ag/TiO₂ nanotube nanocomposite heterojunction was synthesized by the uniform dispersion of hemispherical Ag nanocrystals having a diameter of about 3.8 nm over the surface of the TiO₂ nanotube (TNT). The heterojunction degraded almost 100% of RhB under visible light within 2 h.

The enhanced visible-light-induced photocatalytic activity as compared to pure TNT and P25 may be attributed to the formation of local electric field formed by the surface plasmon resonance (SPR) of Ag nanocrystals and the high adsorption capability of TNTs with large specific surface area [49].

Singh *et al.* prepared Ag-TiO₂ plasmonic nanohybrids using the CTAB-assisted facile wet chemical method and studied their photocatalytic activity toward degradation of methylene blue (MB) and methyl orange (MO) under solar light irradiation [50]. The electron scavenging action of Ag nanoparticles separated photoinduced charged species in TiO₂ efficiently and the surface plasmon resonance (SPR) absorption of Ag nanoparticles improved the solar light absorption. As a result, the nanohybrids exhibited enhanced photocatalytic activity. It was observed that on increase of Ag nanoparticle loading, the photocatalytic efficiency was increased. The mechanism of photocatalytic degradation of MB and MO is explained in Figure 10.3. About 3 to 5 nm Ag nanoparticles (NPs) were uniformly deposited on the surface of TiO₂ nanotubes (TNTs) by the photoreduction method at room temperature without any additional reducing agent to form Ag/TNTs [51]. Their photocatalytic efficiencies were evaluated by the degradation of MB and MO under exposure to sunlight (both UV and visible light). The mechanism was explained in Figure 10.4. In 150 min, Ag/TNTs decomposed about 81.2% of MB and 75.8% of MO, which are almost double in comparison to that of TNTs. The excellent photoactivity may be contributed from the effective separation of charge carriers by

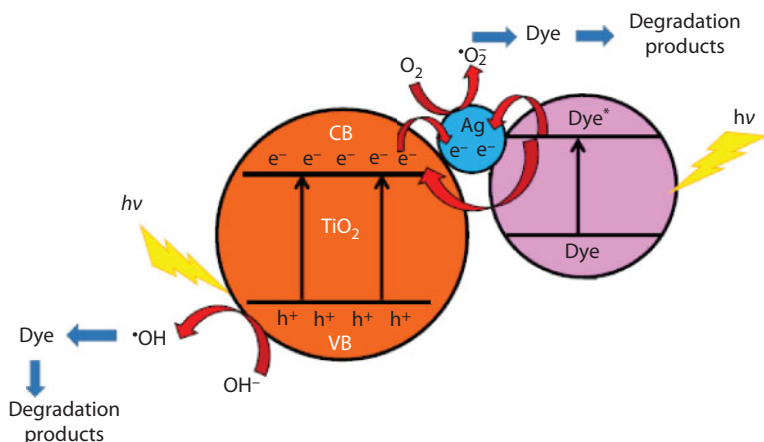


Figure 10.3 The mechanism of photocatalytic degradation of MB and MO (reproduced from Ref. [50]).

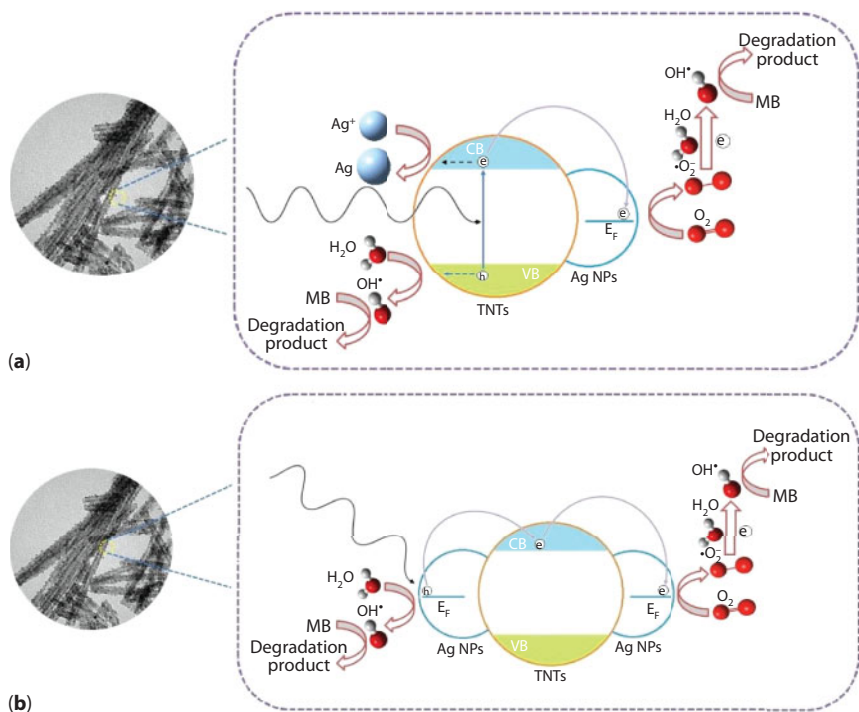


Figure 10.4 Photocatalytic mechanism of Ag/TNTs under UV light (a) and visible light (b) (reproduced from Ref. [51]).

the Ag^+ ions, which capture the photoelectrons to form Ag^0 as shown in Equation 10.15 [52].



Formation of Schottky barrier by Ag also favors the inhibition in recombination of electron–hole pairs [53]. Consequently, the synergistic effect of the oxidation states of silver significantly enhances the photocatalytic performance of the Ag/TiO₂ material [54]. Moreover, in the presence of visible light, electrons on the surface of Ag NPs resonated and became plasmonically excited to the CB of TNTs. Then, these electrons are transported to the surface of Ag NPs, where O_2 is reduced to $\bullet O_2^-$ [55]. These radicals could receive more electrons to become $OH^\bullet$. The $OH^\bullet$ free radicals are also formed when water is oxidized by the holes present in the VB of TNTs. $\bullet O_2^-$ and $OH^\bullet$ so formed oxidized MB/MO to the degradation products. Jin *et al.* synthesized a Ag@hierarchical TiO₂ core–shell nanostructure

(Ag@h-TiO₂) by a two-step hydrothermal reaction approach and investigated its photocatalytic activity toward degradation of methyl blue (MB) and methyl orange (MO) under simulated solar irradiation [56]. About 99.5% of MB and 98.2% of MO were degraded by the Ag@h-TiO₂ nanostructured photocatalyst after 90 min of irradiation. Under identical conditions, P25 decomposed 25.2% MB and 21.6% MO whereas pure TiO₂ decomposed 45.3% MB and 42.9% MO. This significant increase in photodecomposition may be attributed to the special hierarchical structure of the photocatalyst and the presence of Ag core. The hierarchical structure increases the light scattering that enabled TiO₂ to capture more photons and hence the photocatalytic activity is increased. The Ag core in the core-shell structure forms a Schottky barrier, which also contributes to the capture of photon. In addition, the photogenerated electrons of TiO₂ can be transported to the Ag core very fast and are accumulated in it. This reduces the possibility of recombination of charged species and enhances photocatalytic performance.

Sankar and his group fabricated a Ag/TiO₂ composite by the UV photochemical reduction process. They reported that Ag nanoparticles with a diameter of less than 3 nm were well distributed over the surface of TiO₂, and these particles not only extend the light absorption of TiO₂ to the visible region but also suppress the recombination of photogenerated charge carriers by trapping the electrons. Hence, the composite photocatalyst shows greater photodecomposition (about 20 times faster) of MB than the pure TiO₂ under simulated solar light irradiation [57]. Eom *et al.* demonstrated that the periodic array of Ag/TiO₂ core-shell nanowire structures enables strong localized surface plasmon resonance (LSPR), which improves the electron generation and photocatalytic activities of the TiO₂ shell. Therefore, the Ag/TiO₂ core-shell nanowire array structure provides a superior photocatalytic performance to pristine TiO₂ thin films or Ag/TiO₂ dual-layer thin-film structures toward photodegradation of MB in the UV and visible light regions [58]. Raza *et al.* synthesized a silver-decorated TiO₂ (Ag/TiO₂) nanocomposite by depositing biogenic silver nanoparticles obtained from a plant extract on the surface of TiO₂ support. Its photocatalytic activity toward degradation of MB was compared with that of Ag and TiO₂ NPs under visible light irradiation. About 90% of MB was degraded only in 40 min whereas Ag and TiO₂ NPs degraded less than 30% and 80%, respectively, in more than 100 min. The better photodegradation efficiency may be due to the effective transfer of charge from Ag/TiO₂ to the attached phytoconstituents, which suppress the recombination of photoelectrons. In addition, high specific surface area and greater number of active sites formed due to adequate dispersion and smaller spherical Ag nanoparticles

also contribute toward enhanced photodegradation. Moreover, the presence of Ag NPs extends the absorption range of TiO_2 to the visible region [59]. Li *et al.* fabricated silver-doped TiO_2 (Ag- TiO_2) nanoparticles by a miniemulsion method. It was observed that doping of Ag restricted the transformation of titania from anatase to rutile and increased the surface area as well as pore size of TiO_2 nanoparticles. In addition to this, Ag loading not only caused a red shift in the absorption edge of titania but also inhibited recombination of charge carriers by capturing the photoelectrons. This resulted in an excellent photoactivity toward degradation of MB under visible light irradiation. Ag- TiO_2 containing 0.8% Ag degraded MB solution completely in 450 min whereas only 24% degradation was noticed over pure TiO_2 under identical conditions [60]. Layered three-dimensional Ag/ TiO_2 nanocomposite architecture was prepared by using nanoimprint lithography, vertical e-beam evaporation, nanotransfer, and nanowelding [61]. Its visible-light-induced photocatalytic activity toward decomposition of MB was found to be superior to that of two-layered Ag/ TiO_2 architecture, which showed higher efficiency with respect to the Ag/ TiO_2 composite film and nanowire under identical conditions. The poor activity of the Ag/ TiO_2 composite film and nanowire may be attributed to poor absorption of visible light, whereas multiple Ag layers in the architectures produce strong SPR phenomena under visible light irradiation, because of which, higher activity is observed. Furthermore, the largest surface area that causes maximum SPR effect and broadband absorption enable three-layered Ag/ TiO_2 nanocomposite cross architecture to show highest performance. Therefore, it degraded 79.8% of MB in 150 min of irradiation, while the two-layer architecture degraded only 67.7%. He *et al.* reported that Ag nanoparticles play different roles when Ag- TiO_2 composite nanorod arrays are subjected to UV and visible light. Under UV illumination, they act as an electron acceptor to trap the photoelectrons generated from TiO_2 and thus recombination of charged species is inhibited. On the other hand, they act as an electron donor by transferring electrons to TiO_2 when excited in the presence of visible light. The composite photocatalyst exhibited higher photocatalytic performance for degradation of MB with respect to pure TiO_2 under visible light or UV light illumination. However, a higher amount of Ag loading that is greater than the optimal concentration reduced the photocatalytic activity of the photocatalyst, mainly due to the availability of limited TiO_2 surface area for adsorption of dye molecules and the increased possibility of capture of holes by Ag NPs [62]. A novel Ag/ TiO_2 nanofiber membrane was fabricated by Liu *et al.* for the solar-light-induced photodegradation of MB [63]. It was reported that the nanofiber membrane photocatalyst showed a maximum of 80.0%

photodegradation within 30 min, which was significantly high in comparison with that exhibited by the pure TiO_2 nanofiber membrane and the commercial P25 deposited membrane.

Liang *et al.* fabricated Ag-loaded TiO_2 nanotube arrays by using the anodic aluminum oxide (AAO) film and the atomic layer deposition (ALD) technique at 100°C . On increase in the cycle number of ALD, there occurs an increase in the tube thickness, which causes a red shift in the absorption of UV-visible light. The synergistic effects of surface area, wall thickness, and intensity of anatase phase resulted in the increase in photocatalytic activity of TiO_2 nanotubes. Deposition of Ag nanoparticles on TiO_2 nanotubes suppressed the recombination of electron-hole pairs, as a result of which, photodecomposition of MO is enhanced [64]. Xie *et al.* synthesized TiO_2 nanotube arrays (NTs) by the electrochemical anodization method and dispersed Ag nanoparticles with a diameter of 10–40 nm on them to form Ag/ TiO_2 NTs for the photodegradation of MO. Ag/ TiO_2 NTs exhibited higher photocatalytic activities than the pure TiO_2 NTs under both UV and visible light irradiation. Moreover, the visible light activity of these NTs is higher than that of TiO_2 NTs due to the surface plasmon resonance effect of Ag [65]. Electrospinning and the photoreduction method were applied by Zhang *et al.* to prepare Ag- TiO_2 nanofibers. The mechanism of preparation is shown in Figure 10.5. The composite photocatalyst containing 5 mol.% Ag degraded 97% of the MO solution under simulated solar irradiation for 3 h. The percentage degradation of varying Ag content composites along with pure TiO_2 nanofibers are shown in Figure 10.6. The higher photocatalytic activity of the composite over pure TiO_2 is due to Ag nanoparticles, which serve as charge-transfer sites and broaden the spectral absorption band to the visible region [66]. The dispersed Ag nanoparticles (NPs) are uniformly distributed on the surface of TiO_2 nanotube arrays (TNAs) by an electrodeposition process to form Ag-NP-decorated TNAs [67]. The uniform distribution of Ag NPs over TNAs increased the charge separation efficiency and extended the light absorption range of TNAs to the visible region. Therefore, Ag-NP-decorated TNAs exhibited an enhanced photocatalytic activity toward degradation of MO in the presence of UV-visible light. Chaker *et al.* reported that doping of Ag in mesoporous TiO_2 retains the structure and physical properties of TiO_2 . They investigated the effect of Ag loading in TiO_2 on the photocatalytic decomposition of MO under simulated solar light irradiation. The Ag-doped TiO_2 photocatalyst with 0.5% Ag exhibited the highest total organic carbon (TOC) abatement for both MO and wastewater effluent. It was further observed that the catalyst was very stable after three cycles of reuse and efficient under simulated solar light [68]. According to

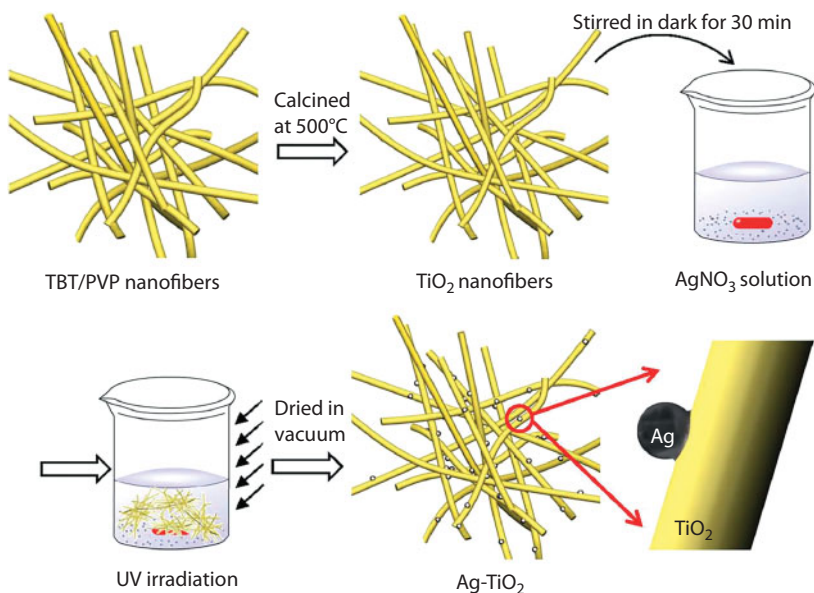


Figure 10.5 Schematic illustration of the synthesis and structure of the Ag-TiO₂ photocatalyst (reproduced from Ref. [66]).

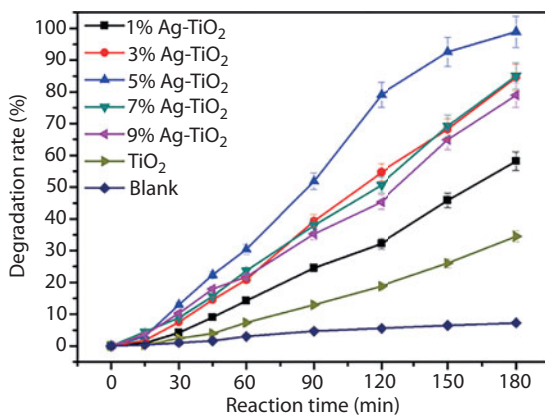


Figure 10.6 Degradation rate of MO aqueous solutions under simulated sunlight irradiation in the presence of 1% Ag-TiO₂, 3% Ag-TiO₂, 5% Ag-TiO₂, 7% Ag-TiO₂, 9% Ag-TiO₂, pristine TiO₂ nanofibers, and without catalyst for varying irradiation times; the initial concentration of the MO solution (C_0) was 20 mg L⁻¹ and the catalyst loading was 10 mg (reproduced from Ref. [66]).

Nainani *et al.*, Ag-doped TiO_2 photodegraded MO effectively by extending the absorbance to the visible region as compared to prepared TiO_2 [69]. Shah *et al.* fabricated a plasmonic catalyst, $\text{CuO}/\text{Ag}/\text{AgCl}/\text{TiO}_2$, via a reverse microemulsion synthesis route. They reported that the $\text{CuO}/\text{Ag}/\text{AgCl}/\text{TiO}_2$ photocatalyst showed about 91% degradation of methyl orange (MO) in 25 min under visible light illumination [70]. Visible light activity may be attributed to the surface plasmon resonance (SPR) properties of Ag nanoparticles, which absorb a considerable amount of energy from the visible light. Better SPR response for shifting light absorption toward longer wavelength could be due to the presence of AgCl having a high refractive index [71,72]. Moreover, AgCl is photosensitive because of its point ionic defects and electron traps [73]. In addition, it causes effective separation of charge carriers by transferring the photo electrons from the surface of Ag NPs away from the Ag/AgCl interface and holes to the surface of AgCl particles bearing Ag NPs [74]. CuO acts as a sink for photogenerated electrons, as a result of which, charge recombination is suppressed and more holes become available for enhanced photodegradation of MO.

$\text{Ag}@\text{TiO}_2$ core-shell structured nanoparticles were synthesized through one-pot synthesis followed by calcination, and their photocatalytic activity toward degradation of Acid Yellow-17 (AY-17) was investigated under solar light irradiation by Khanna *et al.* [75]. The core-shell structured nanoparticles are considered to be superior to TiO_2 or Ag-doped TiO_2 nanoparticles because of their better ability to separate photogenerated electron-hole pairs by keeping electrons in the Ag core. In addition, these decrease the band gap, resulting in effective utilization of solar energy for degradation. The optimum conditions for maximum degradation of AY-17 are as follows: pH 3, dye/catalyst ratio 1:10 (g/g), and 2 g L^{-1} of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as oxidant. Rupa *et al.* demonstrated that silver particles enrich the accumulation of conduction band electrons on the TiO_2 surface. This leads to better charge separation, which caused enhanced visible-light-induced photocatalytic activity toward degradation of Reactive Yellow-17 (RY-17) in comparison to that exhibited by bare TiO_2 . Moreover, better degradation of RY-17 may be ascribed to its enhanced adsorption on the Ag- TiO_2 surface [76]. The photocatalytic efficiency of Ag core- TiO_2 shell ($\text{Ag}@\text{TiO}_2$) structured nanoparticles under UV and visible light irradiation was compared by the degradation of Reactive Blue 220 (RB-220). $\text{Ag}@\text{TiO}_2$ exhibited a higher rate of photocatalytic degradation of RB-220 under solar light illumination, indicating that solar photocatalysis using $\text{Ag}@\text{TiO}_2$ can be an energy-efficient and cost-effective method [77].

An Ag-modified anatase TiO_2 visible light active photocatalyst with high surface area was prepared by the sol-gel process using hydrazine as a

reducing agent. The photocatalyst showed a superior performance toward degradation of Indigo carmine compared to undoped TiO_2 and commercial P25 [78].

10.5 Ag-Modified TiO_2 with Non-Metal Doping

The role of Ag nanoparticles loading in N-doped TiO_2 photocatalysts was studied by Gao *et al.* [79]. They reported that Ag transfers an electron from its 5s orbital to the 2p orbital of the implanted N, because of which, loss of N dopants from the oxide is restricted during the hydrothermal process, and hence, the stability of the photocatalyst is increased. Moreover, the Ag content in the N-doped TiO_2 photocatalyst enhances the photodegradation of RhB under visible light irradiation. The maximum degradation was obtained with a Ag/Ti molar ratio of 0.92 mol.%. Zhang *et al.* demonstrated that an improved visible-light-induced photoactivity was obtained for TiO_2 nanotube arrays (TNTs) by Ag loading and N doping [80]. The photocatalytic efficiency of Ag/N-TNTs was found to be 6.8 times higher than those of annealed TiO_2 nanotube arrays (A-TNTs) toward degradation of Acid Orange II (AO-II). Jiang *et al.* compared the photocatalytic performance of silver-deposited, nitrogen-doped yolk-shell mesoporous TiO_2 hollow microspheres (Ag-N- TiO_2 -YSM) with that of nitrogen-doped yolk-shell mesoporous TiO_2 microspheres (N- TiO_2 -YSM), yolk-shell mesoporous TiO_2 (TiO_2 -YSM), and P25 [81]. The photocatalytic efficiency toward degradation of RhB under visible light irradiation was decreased in the order Ag-N- TiO_2 -YSM > N- TiO_2 -YSM > TiO_2 -YSM > P25. The enhanced photodegradation capacity of Ag-N- TiO_2 -YSM may be due to the combination of the hollow yolk-shell mesoporous structure, doping of N, and loading of Ag. The mechanism of photodegradation was proposed in Figure 10.7. The hollow yolk-shell mesoporous structure possessed a large surface area that provides enough active reaction sites for improved light harvestation. This causes generation of more charge carriers required for enhanced photoactivity [82]. Further, light absorption is significantly increased by the multiple reflections of visible light within the interior cavity of yolk-shell and by the existence of C species. Increase in light absorption also causes improved photocatalytic activity [83]. Doping of N into TiO_2 creates some energy levels above the valence band of TiO_2 . As a result, band gap energy is decreased and light absorption is extended to the visible region [84].

In addition to this, N dopant acts as trapping centers for photoelectrons, thereby causing effective separation of photogenerated charged species,

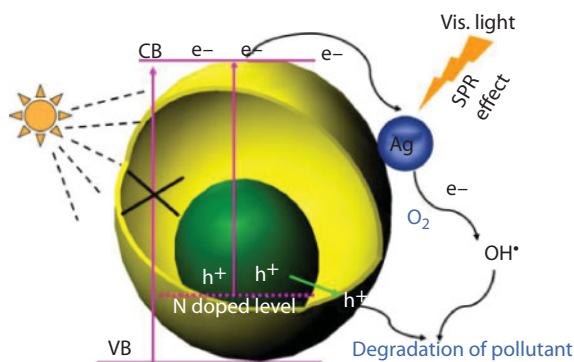


Figure 10.7 Ag-N-TiO₂-YSM showing the enhanced photocatalytic degradation of dyes under solar light (reproduced from Ref. [81]).

which leads to high photocatalytic activity [85]. The presence of Ag NPs exhibits SPR phenomenon that enables Ag-N-TiO₂-YSM to have strong and broad absorption in the visible region. Further, loading of Ag NPs generates more photo-excited carriers, and the rate of generation of such carriers can be increased by improvement of the local electromagnetic field induced by the SPR effect. These photoelectrons can also be trapped by Ag NPs located on the N-TiO₂-YSM, resulting in effective separation and an increase in the lifetime of photogenerated carriers. This rapid separation and transportation of these photogenerated carriers by Ag NPs enhances the visible-light-induced photocatalytic activity of Ag-N-TiO₂-YSM [86]. Moreover, Ag NPs possess a low-lying Fermi energy level, which serve as a reservoir of photogenerated electrons and increase the lifetime of photogenerated carriers. This also improves the photocatalytic activity of Ag-N-TiO₂-YSM [87]. However, the amount of Ag loading affects the photoactivity of the catalyst. It was reported that the photocatalytic activity of Ag-N-TiO₂-YSM increases by increasing the Ag content from 0.2% to 1.5%. A further increase in Ag loading causes a decrease in the photocatalytic activity of Ag-N-TiO₂-YSM. An excess of Ag NPs may serve as a recombination center or may cover the active sites of TiO₂ and reduce the availability of pollutant adsorption, leading to recombination charge carriers [88]. In addition, excess Ag NPs may increase the light opacity, which prevents effective light absorption by the photocatalyst. Besides this, a slight decrease in BET surface area upon the addition of Ag NPs may be responsible for the decrease of photocatalytic activity.

Xie *et al.* prepared nitrogen and carbon co-doped, silver-loaded anatase TiO₂ (Ag@NC-TiO₂) single-crystal nanosheets dominated by {001}

facets using leaves as the nitrogen and carbon source. The synthesized Ag@NC-TiO₂ nanosheets exhibited superior performance in photodegradation of RhB under visible light illumination as compared to that exhibited by NC-TiO₂, TiO₂, and P25. The higher visible light active photoactivity may be attributed to the synergistic effect between N, C, and Ag [89]. Co-doping of C and N in TiO₂ resulted in the formation of some energy levels above the valence band of TiO₂ [90, 91]. This facilitates the photocatalyst to harvest the visible region. Moreover, doping of C atom forms carbonaceous species that act as photosensitizers like organic dyes [92–95]. Thus, C atoms and RhB molecules transfer the excited electrons into the conduction band of C-N co-doped TiO₂. This electron transfer is also facilitated by the N atoms doped in TiO₂. On loading of Ag NPs onto the surface of NC-TiO₂, the photogenerated electrons are transferred to the Ag clusters, resulting in effective separation of electron–hole pairs that improves the photocatalytic activity. The photocatalytic activity evaluation of Ag-loaded N-doped TiO₂ (Ag/N-TiO₂) was carried out by Sun *et al.* for the degradation of methylene blue (MB) under visible light irradiation. The prepared photocatalyst showed 6.5 and 3 times higher performance over bare TiO₂ and N-TiO₂, respectively. This enhanced photoactivity is due to the red shift of light absorption and effective separation of photocarriers, which, in turn, are due to the synergetic interactions between TiO₂, loaded Ag, and doped N [96]. The photocatalytic efficiency of Ag and N co-doped TiO₂ nanoparticles was evaluated under batch and continuous reactors for the degradation of methylene blue (MB). The photocatalyst calcined at 400°C with 2% N and 5% Ag shows increased visible light absorption and suppressed recombination rate. The optimal conditions in the continuous photocatalytic reactor were found to be an inlet concentration of 15 mg/L and a circulating flow rate of methylene blue of 5 mL/min (Figure 10.8). The nanostructured photocatalyst retained its initial morphology and excellent photocatalytic activities after being used for 120 h [97]. Yang *et al.* reported that Ag/N-TiO₂ nanofilms exhibited improved visible-light-induced photocatalytic activity toward degradation of methylene blue (MB) due to N and Ag. In this case, N decreases the band gap of TiO₂ while Ag NPs immobilized the electrons. Further, the SPR effect of Ag nanoparticles activates photogenerated charge carriers through the transfer of plasmonic energy [98]. Uniform nanorods of N-doped TiO₂/Ag composites with 3 mm average length and 150 nm cross-section diameter were successfully fabricated by a modified sol-gel approach. The growth mechanism of rod-like Ag-N-TiO₂ was represented in Figure 10.9. The photocatalytic activity of the prepared photocatalyst was compared with that of TiO₂, N-TiO₂, and Ag-TiO₂. The rod-like Ag-N-TiO₂ showed the

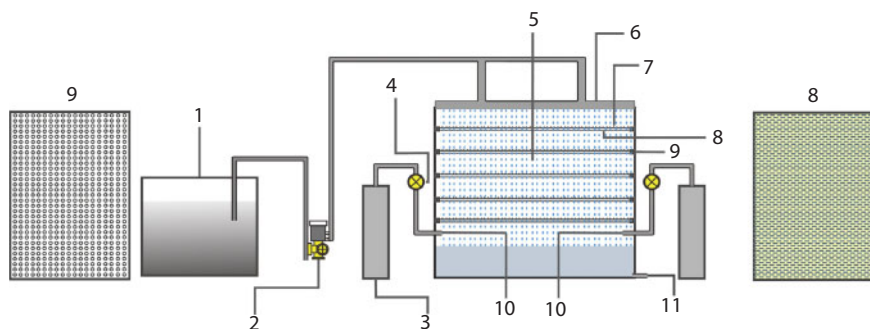


Figure 10.8 Schematic representation of continuous tank reactor: 1, Methylene blue tank; 2, advection pump; 3, O₂ cylinder; 4, gas rotameter; 5, photocatalytic reactor; 6, liquid distributor; 7, nanostructured photocatalysts; 8, glass support plate; 9, fastener; 10, O₂ inlet; 11, product outlet (reproduced from Ref. [97]).

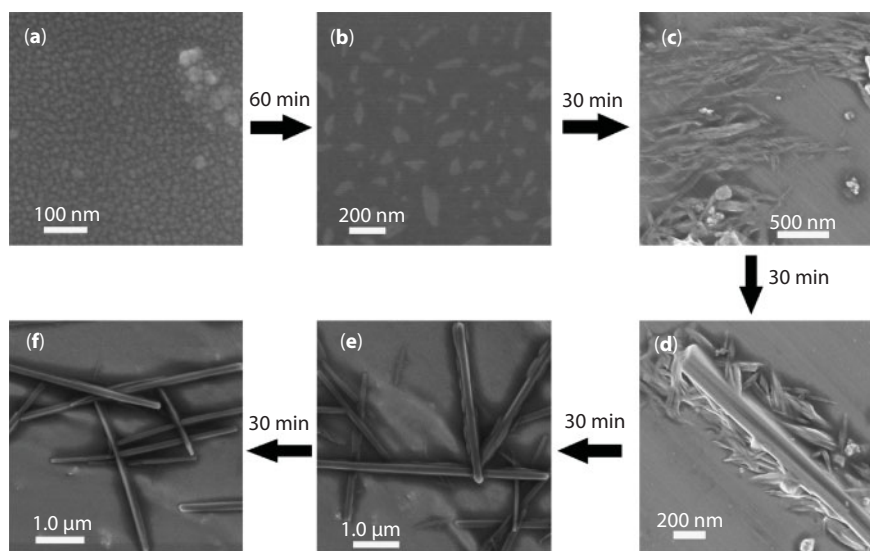


Figure 10.9 The growth mechanism of rod-like Ag-N-TiO₂ (reproduced from Ref. [99]).

highest performance toward photodecomposition of methylene blue (MB) under visible light among others and maintains high photochemical stability after five catalytic cycles, mainly due to the synergistic effect of N doping and Ag modification. In addition, the rod like morphology also plays a pivotal role in improving the stability of the rod-like Ag-N-TiO₂ photocatalyst [99]. Dhabbe *et al.* synthesized Ag-loaded N-doped TiO₂

nanocomposites through a simple combination of microwave followed by an impregnation–reduction method. The prepared nanocomposite retained pure anatase phase with an average crystallite size of 10 nm and degraded a maximum of 94.51% methyl orange (MO) within 2 h of sunlight illumination. The degradation reaction followed pseudo first-order kinetics with a highest rate constant of $2.04 \times 10^{-2} \text{ min}^{-1}$ at 1.0 g/dm^3 catalyst dose. Ag loading in N-TiO₂ increased the photodegradation efficiency by 40% due to effective suppression in the rate of electron–hole pair recombination as revealed from the fluorescence quenching of Ag-loaded N-TiO₂ composite [100].

Feilizadeh *et al.* compared the photocatalytic activity of Ag-S/PEG/TiO₂, Ag-S/TiO₂, and pure TiO₂ by studying the degradation of Acid Orange 7 (AO7) and methylene blue (MB) under low-voltage light-emitting diodes (LEDs) as the visible light source [101]. They observed that the efficiency of Ag-S/TiO₂ toward degradation of AO7 and MB was 4 and 4.8 times, respectively, greater than that of pure TiO₂. The higher photoactivity may be attributed to the incorporation of Ag and S. Ag, being an electron acceptor, traps the photoelectrons, separates the electron–hole pairs effectively, and transports the photoelectrons to the adsorbed O₂ for the generation of active species [102,103]. On the other hand, doping of sulfur could help to narrow the band gap, decreasing the crystallite size and controlling the crystallization [104,105]. Further, addition of PEG into Ag-S/TiO₂ enhances the surface area [106,107] and decreases the band gap energy [108]. Therefore, Ag-S/PEG/TiO₂ manifests 28.82% and 24.24% higher efficiency toward degradation of AO7 and MB, respectively, as compared to Ag-S/TiO₂.

10.6 Ag-TiO₂ with Other Plasmonic Metals

Zhou *et al.* compared the photocatalytic efficiency of commercial P25-TiO₂, Au/TiO₂, and Au/Ag/TiO₂ nanoparticles by studying the photodegradation of methylene blue (MB) under visible light irradiation. Only 42% of MB was degraded by P25-TiO₂, whereas degradation efficiency for Au/TiO₂ was found to be 50%. The low photocatalytic activity of P25-TiO₂ is due to its insufficient absorption of visible light, and the higher photocatalytic activity of Au/TiO₂ may be attributed to the presence of plasmonic metal Au. On the other hand, Au/Ag/TiO₂ nanoparticles degraded about 86% of MB solution under identical experimental conditions [109]. This enhanced photoactivity is due to Ag coating. Ag nanorods (NRs) displayed

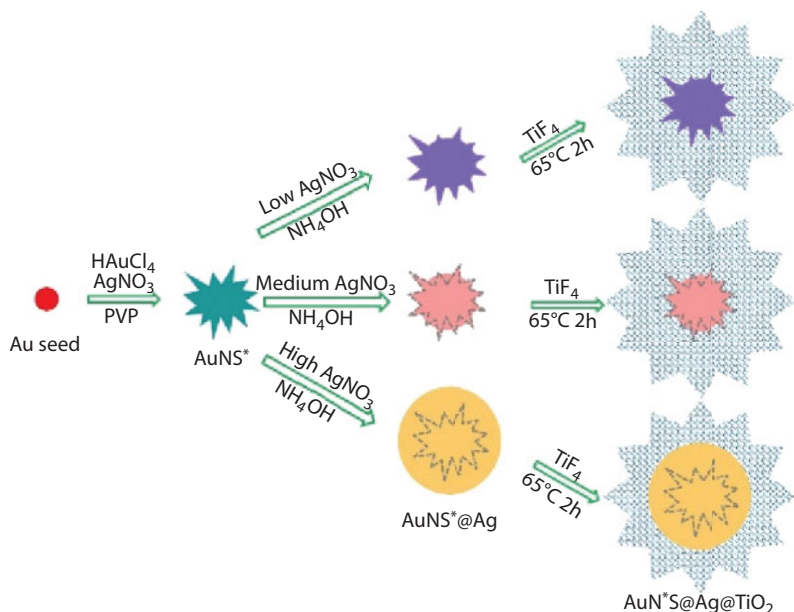


Figure 10.10 Preparation of Au@Ag@TiO₂ core-shell NPs with flower-like structure (reproduced from Ref. [112]).

higher electric field enhancements than Au NRs [110]. Also, the Fermi level of Au/Ag NRs became closer to that of TiO₂ upon Ag coating, which might also contribute to the observed enhanced photocatalytic activity [111].

Au@Ag@TiO₂ core-shell NPs with flower-like structure were prepared by a facile method as represented in Figure 10.10. The photocatalytic activity of TiO₂ toward degradation of rhodamine B (RhB) under visible light irradiation was increased by 4.7 times on incorporation of Au and Ag. The increased photoefficiency of Au@Ag@TiO₂ may be attributed to (i) the effective absorption of light by Ag-coated Au nanostars, (ii) the injection of hot electrons from the photo-excited Au@Ag core to the conduction band of the TiO₂ shell, and (iii) the spatial charge separation, as a result of which, direct recombination of the electron-hole pair is inhibited [112].

Bahadur *et al.* reported that doping of 0.02 wt.% Ag and Ni in TiO₂ leads to the refinement of particles with mesoporous size distribution and increase in specific surface area, total pore volume, average pore diameter, and higher adsorption capacities. It also enhances the optical and photocatalytic activity toward complete degradation of methylene blue (MB) within 25 min of visible and UV light irradiation [113].

10.7 Conclusion

In this chapter, the photodegradation of different textile dyes such as RhB, methyl orange, methylene blue, etc. over Ag-modified TiO_2 photocatalysts under visible light irradiation was discussed. Incorporation of Ag into TiO_2 not only enhances photocatalytic activity but also extends the light absorption range to the visible region due to surface plasmon resonance (SPR) phenomenon of Ag. The detailed mechanism of degradation was explained through chemical reactions and illustrated in figures. Upon irradiation of visible light on the surface of Ag- TiO_2 , electrons and holes are generated, which produce the active species like $\cdot\text{OH}$, $\text{O}_2^{\cdot-}$ and $\cdot\text{OOH}$ radicals. These radicals decompose the dyes into harmless products like CO_2 and H_2O . Some energy levels are formed above the valence band of TiO_2 as a result of non-metal doping (nitrogen, sulfur) into TiO_2 . This reduces the band gap of TiO_2 , because of which, a significant red shift is observed. Therefore, the combination of Ag and non-metals with TiO_2 enhances the photocatalytic activity to a greater extent. Further, the synergistic effect of a plasmonic metal (Au) along with Ag causes the injection of hot electrons from the photoexcited Au@Ag core to the conduction band of the TiO_2 shell, and hence, the visible-light-induced photocatalytic activity of the Au-Ag- TiO_2 nanocomposite is increased multifold in comparison to neat TiO_2 .

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Part 2

MECHANICAL ASPECTS

Application of Textile Materials in Composites

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Abstract

Composites are a versatile and valuable family of materials with the possibility of achieving any targeted sets of properties for various industrial sectors such as aerospace, transportation, civil construction, sports, medical, etc. A composite material is made by combining two or more materials of different physical and chemical properties to obtain a combination of properties that are superior to the individual material.

Textile materials in different forms such as sort fibers, tows, fabrics, mats, nano-fiber webs, etc. exhibit unique properties and thus have been extensively used for reinforcing purposes in composite fabrication. This chapter provides comprehensive information on properties and application of various synthetic, natural, and metallic fibers to reinforce a wide variety of materials including polymers, cement, metal, soils, and so on to improve their general performances as well as their multifunctional behaviors. Additionally, application of composites in various sectors has been discussed.

Keywords: Composites, textile reinforced composites, fiber, matrix

11.1 Introduction

Composite materials are broadly characterized as engineering materials, which are manufactured by binding two or more different materials, each of

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which performs a specific function in a composite structure. They can simply be defined as the material formed by a combination of two or more chemically and physically different components [1]. Composites are developed by emphasizing the good properties of constituents while eluding their drawbacks [2, 3]. The form and type of matrix and reinforcement vary depending on the end use requirement. For example, aluminum metal matrix composite is widely used in the field of aerospace, aircraft, and automobiles [4]. The most commonly used reinforcements in such matrices are silicon carbide (SiC) and aluminum oxide (Al_2O_3) [5], whereas ceramic matrix composites (CMCs) are extremely efficient in applications that demand high mechanical and thermal performance [6]. Polymer matrix composites (PMCs) are composed of thermoplastic (PP, polyester, etc.) or thermosetting (PEEK, PPS, etc.) polymers. They are a lightweight material and offer unique properties like corrosion resistance, high strength-to-weight ratio, high fatigue resistance, etc. They are incorporated in aerospace craft, airplanes, ship, and other weight-sensitive high-performance applications.

Textile-reinforced composite (TRC) materials are a subclass of composites that uses textile material as reinforcements. For many years, TRCs have been used as low-profile engineering materials and as a low-cost alternative (e.g., woven glass-reinforced polymer hulls for minesweepers). Although there has been continuing interest in textile reinforcement since 1970, the focus has greatly shifted since the 1980s, and with increasing dependence on composites, today, TRCs are used extensively, and because of their unique inherent properties, they have become one of the most researched materials in the modern era [6]. Unlike traditional metal reinforcements, fiber-reinforced composite properties are derived from the combination of input materials and can be varied according to application need. Properties like low density, high strength-to-weight ratio, and high modulus-to-weight ratio make TRCs superior to their metallic counterparts. In addition, fatigue strength and fatigue damage tolerance of many composite laminates are excellent. These properties have helped TRCs compete in applications, where weight is a crucial component, and they have successfully replaced metals in applications such as aerospace, automotive, etc. Another important property of TRC is the ease of engineering their properties. Just a slight change in fiber orientation can have a huge impact on reinforcement property, whereas metals are isotropic and require a high level of effort for a small improvement in their properties [7].

11.1.1 Types of Composites

Composites consist of two components: the reinforcing phase, embedded in the binder, and the matrix phase. The properties of the composite

material strongly depend on the type of reinforcement, matrix, and nature of interface between these two. Composites can be classified under different parameters. Depending on the matrix used, composites can be classified into three categories: polymer matrix composites, metal matrix composites, and ceramic matrix composites [2].

Depending on the reinforcement incorporated, the composites are separated as particulate reinforced and fiber reinforced. Composites are also characterized based on the reinforcement size: macrocomposites, microcomposites, and nanocomposites [2, 5, 7].

11.1.1.1 Classification of Composites Based on Type of Matrix

The role of the matrix in composites is very crucial. Matrices provide a continuous phase for reinforcement, by acting as a uniform stress transfer medium during loading. It also provides protection from the environment and unwanted abrasion. The matrix plays an important role in compressive loading and shear properties of the composite materials. The matrix keeps the reinforcement in its place by avoiding lateral movement, thus avoiding any chances of bucking during compressive loading [7, 8].

11.1.1.1.1 Polymer Matrix Composites

Polymer matrices are very common because of their low cost and easy processing conditions. Complex shape composites can be easily manufactured using polymer matrix composites. Polymers are macromolecules composed of many repeating units [5].

In composites application, thermosetting polymers (epoxies, vinyl esters, polyesters, etc.) and thermoplastic polymers (nylon, polyetherether-ether ketone, polysulfone, etc.) are used as a matrix component. Polymer matrices are frequently used with textile materials as reinforcement. In PMCs, fibers contribute toward high strength and modulus, whereas polymer matrices distribute the load and provide protection from weathering and corrosion.

Thermoplastic polymers like nylon become soft and melt on heating; thus, they can be repeatedly remolded or reprocessed. This ability makes their use advantageous in many applications. Thermoplastic polymer matrices, having a linear molecular chain structure, have a much higher strain-to-failure ratio compared to thermoset polymers. The failure strains range between 30% and 100% in thermoplastic while the typical range in thermosets is between 1% and 3%. This is due to the variations in the crystallinity of the structure [8].

Thermoset matrices are cross-linked polymers, forming a three-dimensional network. Once these polymers are cross-linked, they cannot be melted or reprocessed. Thus, they are shaped before going to the final curing step. Thermoset polymers have low creep and stress relaxation compared to thermoplastic polymers, and they exhibit high temperature stability and chemical resistance [2].

11.1.1.1.2 Metal Matrix Composites (MMCs)

Metal matrices are versatile engineering materials with high strength and toughness. Unlike polymer matrices, metal matrices can be used at a very high temperature and they can be plastically deformed and strengthened by using thermal and mechanical treatments. However, the fabrication temperature for metal matrix composite is quite high ($<600^{\circ}\text{C}$) [9]. Aluminum, magnesium, and titanium and their alloys are commonly used as composite matrices [10].

Due to the high temperature requirement of metal matrix composite fabrication, natural and synthetic organic fibers cannot be used with metals. For composite formation, MMCs are generally incorporated with short fibers and ceramic particulates. The major drawback of using MMC is their high density (weight) and their corrosion susceptibility, which limits their application in many fields [11–14].

11.1.1.1.3 Ceramic Matrix Composites (CMCs)

Due to their high temperature stability, good corrosion resistance, low density, and high thermal shock resistance, ceramics-based composites are used at high-temperature applications [15, 16]. The major drawback of ceramics is their low fracture toughness and poor mechanical shock resistance. Incorporation of reinforcing materials increases fracture toughness without affecting their other properties. Ceramics are commonly divided into four major groups: glass ceramics (such as lithium aluminosilicate), oxides [such as alumina and mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$)], nitrides (such as silicon nitride, Si_3N_4), and carbides (such as silicon carbide, SiC). SiC is the most preferred ceramic group because of its compatibility with both oxide and non-oxide ceramic matrices [17, 18]. Ceramic matrix composites reinforcements are used in different forms, for example, whiskers (with a length-to-diameter ratio as high as 500), platelets, particulates, and monofilament and multifilament continuous fibers [2, 5].

11.1.1.2 *Classification of Composites Based on Type of Reinforcement*

Based on reinforcement used, composites are divided into two subtypes: fiber-reinforced composites and particle-based composites. Particle-based composites are inexpensive and readily available. The effectiveness of these composites depends on the interaction of particles and matrix [2]. Based on the reinforcement mechanisms, these composites can be further classified into two categories, namely, large-particle and dispersion-strengthened composites.

Large particle composite are those composites in which the particle matrix interaction is not on atomic or molecular level but rather as a continuum mechanics. These type of particles provides the reinforcement effect by restricting the movement of matrix. Dispersion-strengthened composites are those that are manufactured using dispersed particles, that is, particles whose size ranges from 0.01 to 0.1 mm, which helps in the transfer of applied stress onto the particles.

Particle composites are compatible with all three material types—polymer, metal, and ceramics. Ceramic particles are used with metallic matrices to form Cermet, the abbreviation for the composite formed by using ceramic (Cer) and metal (Met). CerMet is formed to obtain the optimal properties of both ceramic and metal. The compatibility of these reinforcement makes them very versatile to use. For example ceramic particles reinforcements are frequently used with metals to form high performing ceramic-metal composites (CerMet). Tungsten carbide embedded with cobalt or nickel and aluminium alloy casting containing SiC particles are well known Cermet, used for cutting tools and automotive applications. Common examples of these composites include tungsten carbide or titanium carbide embedded with cobalt or nickel for making cutting tools [19], aluminum alloy casting containing SiC particles for automotive applications, etc.

Like metals, polymers are also frequently reinforced with particulates, for example, incorporation of carbon black in vulcanized rubber to enhance toughness and abrasion resistance.

Fiber-reinforced composites demonstrate much higher performance in comparison to particulate composites. Based on length of reinforcement, fiber-reinforced composites can be classified as short fiber-reinforced and continuous fiber-reinforced composites. Short fiber composites can be further classified as aligned and randomly oriented short fiber-reinforced composites. Based on the fiber orientation, continuous fiber-reinforced

composites can be classified as unidirectional, bidirectional, and multidirectional [9].

11.1.1.3 Classification of Composites Based on Size of Reinforcement

Based on the reinforcement size, composites are classified into macrocomposites, microcomposites, and nanocomposites. Macrocomposites incorporate reinforcements with a size of more 1 mm. For nanocomposites, at least one dimension of reinforcement should be less than 100 nm. Composites between macro and nano are classified as micro. Glass- and carbon-reinforced composites are common examples of microcomposites. The popularity of nanocomposites is increasing rapidly as they offer the unique advantage of high surface area, thus improving properties with comparatively less quantity of reinforcement. Nanocomposites can be further divided into zero-, one-, two-, and three-dimensional nanocomposites depending on the dimensionality of reinforcements [2].

11.1.2 Application of Composites

The versatility of composite materials as engineering materials makes them suitable in numerous applications like transportation, civil aircraft, space vehicles, military aircraft, building industry, and chemical plants. At present, composites are extensively used in engineering applications. A recent study from DuPont suggests that, by 2020, composites will form part of approximately 50% of engineering materials [20]. Composites find applications in every field, and applications vary from simple household goods to aerospace engineering parts. The low density and the tailorable nature of composites are the main reasons behind their increasing popularity [7].

Application of PMCs started with the use of composites in aeroplanes during World War II. After the war, the commercial application and research in PMCs rapidly grew, and PMCs were incorporated in various products (e.g., boat hulls). Also, during the same era, glass fiber production started at the industrial level, which further boosted the use of composites in many areas. Because of their high fatigue resistance and low density, the use of PMC in aerospace has increased substantially since then. Currently, many structural parts of military aircraft and rotor blades of helicopters are manufactured using PMCs [8]. The share of PMCs in commercial aircraft is steadily increasing. Boeing 787 has PMCs up to 50% of its total weight. PMC usage has increased in ground transport as well; currently,

bus bodies, internal structures, doors, truck cabins, and elliptical springs are among the main parts that are made entirely of PMCs. PMCs have also found their use in civil applications; other than being used in making domes, roofing, and translucent roof, they are also used in strengthening the damaged part of bridges and multistory buildings. PMC are used in gas and liquid transport pipes [5].

The abrasion resistance of MMCs is superior to that of PMCs, and they also have higher strength and higher modulus than their original metallic parts, which make them suitable in applications requiring high performance and high resistance to wear and tear such as stator vane covers, fan exit guide vanes, etc. Aerospace and automobiles are other major areas of application of MMCs [12]. Aside from high-stress applications, MMCs are also replacing metals in many other fields; for example, carbon-reinforced aluminum composite is suitable for use in electric circuit boards as they need very high thermal conductivity [14, 21].

CMCs have high temperature stability and are used in high-temperature applications. CMCs are used in aero engines, brakes, and land-based gas turbines. CMC-based automobile engines are being researched as they can offer high fuel efficiency [15]. Ceramics are hard and brittle in nature. Ceramic composites improve the fracture toughness and widen their applications and functionality. When compared with metal tools, CMC cutting tools offer high hardness and toughness at much higher machine speed. Cement-based CMCs are also used in building applications like rooftops [17].

11.2 Essential Properties of Fibers for Composite Applications

A pure polymer does not usually have the requisite mechanical strength required for various types of applications. Thus, their reinforcement with additives can considerably improve their mechanical properties. Fibers are a unique class of materials because of their anisotropy [22] and their reinforcement with polymeric matrix could bring significant enhancement in properties of composites such as lightweight, high strength-to-weight ratio, excellent weathering stabilities, and enhanced dimensional stabilities [23, 24]. Fiber-reinforced composites have been widely used in various fields, especially in aerospace, military, and automotive industries [25]. The properties of composites are a function of mechanical properties, geometry, concentration, and orientation of reinforced fibers (Figure 11.1) [26].

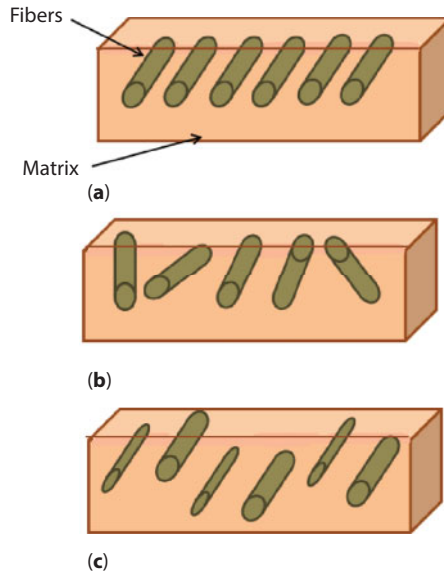


Figure 11.1 Schematic diagrams representing the effect of: (a) concentration, (b) orientation, (c) distribution and shape of fibers reinforced matrix.

11.2.1 Effect of Concentration and Geometrical Properties of Fibers

The mechanical properties of composites are directly influenced by the amount of fiber packed in the composite, and thus it is very important to keep the optimum fiber concentration. Adding too little or too high concentration of fibers can deteriorate the properties of composites [27]. Fiber volume fraction is one of the most important parameters that can be determined by the ASTM D2584 standard [28]:

$$V_f = \frac{\rho_m \cdot W_f}{(\rho_m \cdot W_f + \rho_f \cdot W_m)} \quad (11.1)$$

where, V_f is the volume fraction of fibers, ρ_m is the density of matrix, W_f is the weight of fibers, ρ_f is the density of fibers, and W_m is the weight of matrix.

The theoretical elastic properties of a composite can also be determined using the fiber volume fraction. The elastic modulus of a composite in the fiber direction of a unidirectional composite can be calculated using the following equation:

$$E = (1 - V_f)E_m + V_f E_f \quad (11.2)$$

However, when short and discontinuous fibers with random orientation are used, a “rule-of-mixtures” expression for the elastic modulus may be utilized:

$$E = KE_f V_f + E_m V_m \quad (11.3)$$

where E is the elastic modulus of the composite, V_f is the volume fraction of fibers, E_m is the elastic modulus of matrix, and E_f is the elastic modulus of fibers.

Shape, aspect ratio [length (L)/diameter (D) ratio], and fineness or titer (T ; mass per length unit) of fiber, which describe the fiber's geometry, play a vital role in determining the physical as well as mechanical properties of composites [29]. Critical fiber length (l_c), which is necessary for effective strengthening and stiffening of the composite material, is given by [30]:

$$l_c = \frac{\sigma_f^* d}{2\tau_c} \quad (11.4)$$

where l_c is the critical length, d is the fiber diameter, σ_f^* is the tensile strength, and τ_c is the fiber-matrix bond strength.

Chen *et al.* [25] have studied the effects of mechanical and geometrical properties of fibers on composite fracture toughness based on the three-level failure analysis model. It was observed that when the fiber diameter was decreased, the failure mode was converted from fiber pullout to fiber break and also fracture toughness dropped abruptly. Thus, an optimal fiber diameter is required for the better strength of the composite. “Thinner is better” is no longer applicable for advanced nanocomposites [25]. Amuthakkannan *et al.*, on the other hand, have studied the effect of basal fiber length (4, 10, 21, and 50 mm) and fiber content (21% to 71%) on the mechanical properties of a polymer resin composite [31]. Composites with a fiber weight percentage of 68% and a length of 10 mm showed better tensile and flexural strength than other composites, whereas the impact strength of composites reinforced with 50 mm length of fibers shows the maximum impact energy absorption in all.

11.2.2 Effect of Fiber Orientation

Fiber orientation in a matrix significantly influences the properties of composites as it determines the amount of applied load transmitted by the matrix phase to fibers. It has been observed that the mechanical properties

of composites, such as strength and stiffness, are high when in the fiber direction, whereas they are weak and flexible when perpendicular to it [29]. The best mechanical properties for composites can generally be obtained when the fiber is aligned parallel to the direction of the applied load [32, 33]. However, sometimes it becomes difficult to reinforce a matrix with aligned fibers, especially in the case of natural fibers. Qi *et al.* [34] studied the effect of fiber orientation (30° , 45° , 60° , and 90° ; Figures 11.2 and 11.3)

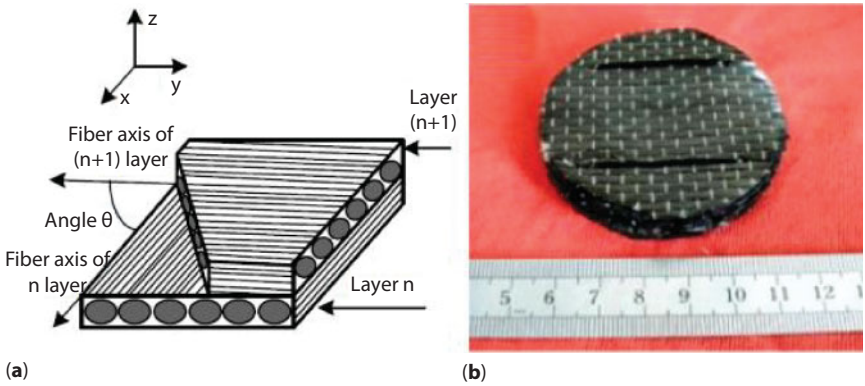


Figure 11.2 (a) Fiber orientation angle of adjacent fiber cloth layers and (b) carbon fiber preform prototype [34].

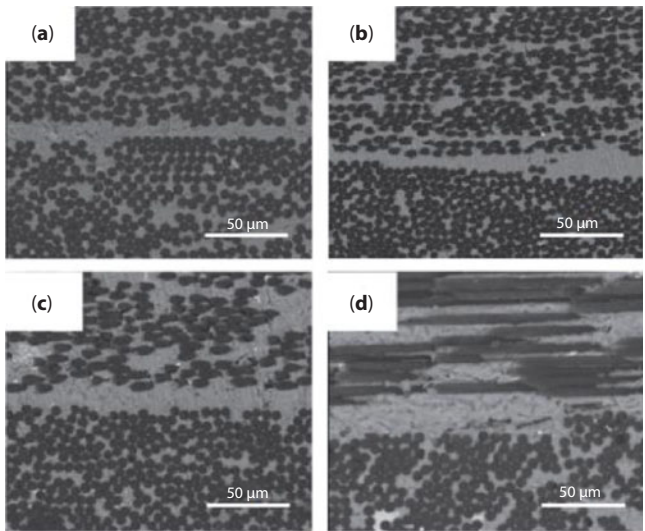


Figure 11.3 Microstructure of 2D-Cf/Al composite under different fiber orientation angles: (a) 30° , (b) 45° , (c) 60° , and (d) 90° [34].

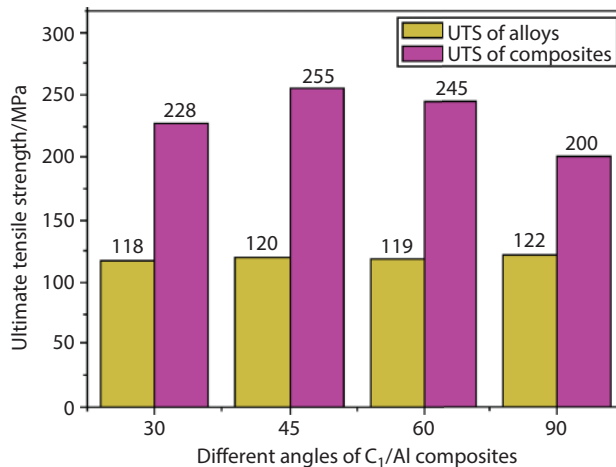


Figure 11.4 UTS comparison of the matrix and composites under different fiber orientation angles [34].

on the mechanical properties of 2D-Cf/Al composites fabricated by using liquid–solid extrusion following vacuum infiltration technique (LSEVI) [34].

It was observed that the UTS of specimen consisting of six carbon fiber layers with a fiber orientation angle of 45° showed an increased rate of 112.5% as compared to other composites, 82.2%, 105.9%, and 63.9%, with a fiber orientation of 30°, 60°, and 90°, respectively (Figure 11.4). Similarly, various other research groups such as Retnam *et al.* [35], Tarfaoui *et al.* [36], and Wazzan [37] have also determined the effect of fiber orientation on the mechanical properties of fiber-reinforced composites.

11.2.3 Effect of Mechanical and Surface Properties of Fibers

The reinforcement of matrix with high-strength fibers provides substantially enhanced mechanical properties to the polymer and makes the fiber-reinforced polymer composites suitable for a large number of diverse applications [25]. The mechanical properties of some of the natural and manmade fibers are tabulated in Table 11.1.

The better the mechanical properties of fibers, the better will be the load-bearing capacity of fiber-reinforced composites. Since stress is transferred between the matrix and fibers across the interface, good interfacial bonding is also required to achieve optimum reinforcement [40]. The surface property of fibers thus plays an important role by

Table 11.1 Mechanical properties of different fibers [38, 39].

Fiber	Density (g cm ⁻³)	Young's modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
Jute	1.44	10–30	393–773	1.5–1.8
Cotton	1.5–1.6	5.5–12.6	287–597	7.0–10.0
Coconut	1.15	4–6	131–175	15.0–40.0
Bamboo	0.6–1.1	11–17	140–230	–
Ramie	1.5–1.56	27–128	400–1000	1.2–3.8
Nylon	1.15	2–4	82.7	50.0
Carbon fiber	1.75–2.0	228	3500	1.6–2.0
Kevlar fiber	1.43	70.5–112.4	3600	2.4–3.6

favoring improved adhesion in thermally processed composites [41]. Natural fiber-reinforced composites generally show lower mechanical performance as compared to animal and mineral fiber-reinforced composites due to the limited interaction between hydrophilic fibers and hydrophobic matrices. Thus, for bonding to occur, intimate contact between fibers and matrix is essential. Various physical and chemical treatment can thus be adopted to modify the surface properties of either the fibers or the matrix to improve the interfacial strength between the two [42, 43]. Janke *et al.* discovered that the application of epoxy-based, electron-beam-compatible sizing onto surface-treated unsized IM7 carbon fibers improved the interlaminar shear strength of the composite [44], whereas Drzal *et al.* observed that the energy absorption by carbon fiber caused lower matrix shear modulus and therefore decreased the interfacial shear strength (IFSS) [45].

11.3 Textile Fibers Used for Composite Applications

Depending on end use application of the composite, the fiber, yarn, or fabric form of textile material is selected to act as reinforcement. The properties of the resulting composite are mainly influenced by the nature of reinforcement, matrix, and their interface.

Fiber-based composites occupy the largest market share in composite laminates application [1]. Although manmade fibers dominate the present

market, the use of natural fibers has been increasing. Also, alternate means of using natural fibers are being researched upon. Among natural fibers, cellulosic fibers have the highest market share in textile reinforced composite (TRC). The lignocellulosic fibers like jute and sisal are widely used in TRCs [2], whereas in synthetic fibers, nylons, high- and ultrahigh-modulus polyethylene (UHMWPE), polypropylene, and aramids (Kevlar and Nomex) are dominant. Carbon fibers are used to reinforce metals as well as polymeric structures [1].

11.3.1 Natural Fibers

Based on the source of origin, natural fibers can be classified as plant-based and animal-based. Animal- and plant-based fibers contain impurities like lignin, wax, proteins, and hemicellulose; all these impurities need to be removed from the natural fibers before they can be used as reinforcement. Pure fibers need to be extracted and separated from major impurities that are present in the natural plant or animal raw material (hemicelluloses, lignin, wax, proteins, etc. [3]). Figure 11.5 shows the classification of fibers based on their source of origin.

11.3.1.1 Vegetable Fibers

Due to the low specific weight and positive environment impact [4], interest in lignocellulosic fibers is growing rapidly and the economical production of these fibers adds benefit in their use as reinforcement. The

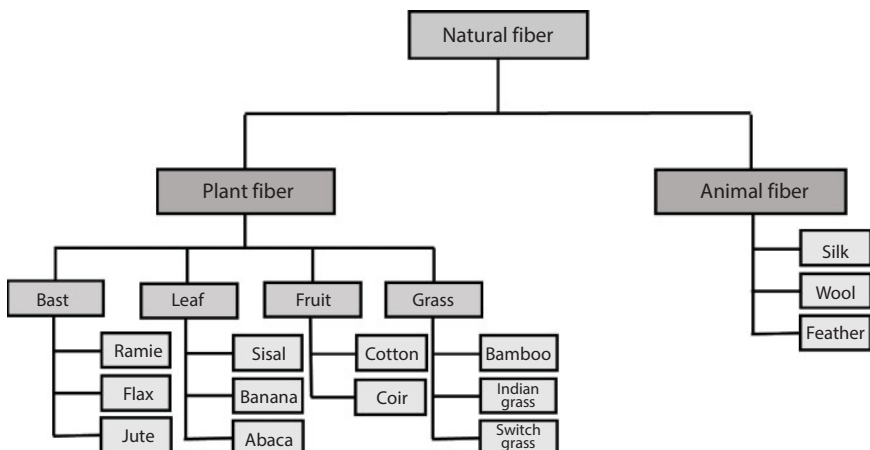


Figure 11.5 Classification of natural fibers.

hydrophilic nature of natural fibers creates a challenge in composite processing. In order to avoid the formation of a porous structure, caused by the evaporation of absorbed water, processing must be carried out with utmost care. Also, the hydrophilic group present in the fiber surface makes them incompatible with hydrophobic polymer matrices, so the natural-fiber-based composites tend to form separate phases during processing and result in poor dispersion [5].

Based on the origin, vegetable fibers are grouped into seed, leaf, bast, and fruit fibers. Bast and leaf fibers are most commonly used in composite applications. Examples of bast fibers include hemp, jute, flax, ramie, and kenaf; leaf fibers include sisal, pineapple, leaf fiber, and banana [6].

Although the origin of fiber affects the characteristic property of natural fiber to a great extent, the quality of the plant and its location, age, and precondition also affect the property considerably.

Natural fibers exhibit interfiber variation in terms of diameter, length, and mechanical properties. The properties of fibers depend on many factors such as size, maturity, and processing method used for fiber extraction. Fiber internal growth and the chemical composition of fibers affect properties such as tensile strength, density, initial modulus, and electrical resistivity. Vegetable fibers have a very complex chemical structure; generally, they are lignocellulosic, consisting of helically wound cellulose microfibrils in an amorphous matrix of lignin and hemicellulose. Cellulose content and microfibrillar angle significantly influence the mechanical properties of the fiber. Low microfibril angle and high cellulose content are desirable properties for fiber to be used as a reinforcement element in polymer composites [21].

Young's modulus of these fibers decreases with an increase in diameter. Because of the high specific modulus, close to that of glass fiber, long fibers such as flax, kenaf, and sisal were preferred over short wood fibers in the automobile sector [46, 47].

11.3.1.2 *Animal Fibers*

Animal fibers such as wool and silk have attracted a lot of research interest in the field of biocomposites. Conventionally used for clothing, these fibers have been successfully incorporated in many composites [48, 49]. Keratin is a major protein present in wool fiber, and the fiber has high surface roughness, flexibility, and high length-to-diameter ratio, and compared to cellulosic fiber, wool fiber is less hydrophilic in nature. Keratin in wool fiber is not hollow in nature, but on the other hand, feather fibers have hollow keratin resulting in lower density ($\sim 0.9 \text{ g/cm}^3$) for a given volume of fibers with low dielectric constant. These two characteristics of feather

fibers make them suitable to be used in composites for application in the electronic field [50]. A single silk filament of length ranging from 1000 to 1500 m is extruded by cocoons of silkworm; this raw filament consists of a gummy substance known as sericin, which binds fibroin filaments together. Properties of the final degummed silk filament vary with the type of breed of cocoon and the spinning parameters. For instance, when the silk fiber is directly spun from cocoon, strong fiber with high brittleness can be produced at higher spinning speeds, whereas when the fiber is spun at a lower speed, the final silk fiber shows low strength with higher extensibility. Silk filament shows poor temperature stability, and it starts to degrade at very low temperatures ($<140^{\circ}\text{C}$), but it shows good resistance against oxidation and UV rays. Also, degummed silk filaments are very susceptible to microbial attack. Silk is biocompatible in nature, which makes it suitable for applications like scaffolds, used in tissue engineering, and the silk-based biocomposites are used in the bioengineering field [51, 52].

11.3.2 Synthetic Fiber

Synthetic or manmade fibers are developed from the by-products of petrochemicals. The production of fibers is not only fast, but these fibers also offer a unique functionality to composites. Synthetic-fiber-based composites offer improved properties like resistance against corrosion and wear, improved appearance, thermal insulation, temperature-dependent behavior, and stability against weathering. Synthetic fibers such as glass, carbon, aramids, high-molecular-weight polyethylene, etc. are extensively used in development of textile reinforced composites for high-performance application. Specific properties of these fibers (such as low density, high stiffness/strength-to-weight ratio as compared to metals) make them useful in military and civilian aircraft structures.

11.3.2.1 Glass Fiber

In the composite industry, glass fibers occupy a major share of fiber-based composites. It is the most commonly used fiber for reinforcing polymer matrices. Glass fiber is a silica-based amorphous material. For modification of the properties of glass fiber, other oxides are also added. The desirable features of glass fibers for composites include lower cost, high tensile strength, high chemical resistance, and excellent insulating properties [53]. The disadvantages of glass fibers include relatively low tensile modulus and high density compared to other fibers; highly abrasive nature during handling, which results in low tensile strength; and relatively low

fatigue resistance and hardness, causing excessive wear and tear. The different types of glass fibers are E-glass, S-glass, A-glass, C-glass, and Z-glass, which are used in making composites depending on the end application [53–55]. The composition and the different properties of glass fibers are summarized in Table 11.2.

Despite having high strength, glass fiber use is limited in applications like airplane body material, bridges, etc., due to their low stiffness and rigidity.

11.3.2.2 *Aramid Fibers*

After the discovery of liquid crystalline solutions in the 1960s, aromatic polyamides with extended chains led to the creation of a new family of high-performance fibers with a combination of engineering properties. The behavior of liquid crystalline solutions and spinning of these polymers led to extensive research. The para-aramid (or p-aramid) poly(p-phenylene-terephthalamide) fibers were commercially introduced by DuPont in 1971 under the trademark “Kevlar” [56]. According to the Federal Trade Commission, the definition for aramid fiber is “A manufactured fiber in

Table 11.2 Composition and properties of different glass fibers [53].

Types of glass fiber	Composition	Properties	Tensile strength (GPa)	Tensile modulus (GPa)
A-glass	SiO ₂ , Al ₂ O ₃ , MgO, CaO, Na ₂ O, K ₂ O, Fe ₂ O ₃	Higher durability, strength, and electric resistivity	3.1	72
C-glass	SiO ₂ , Al ₂ O ₃ , CaO, MgO, B ₂ O ₃ , Na ₂ O	Higher corrosion resistance	3.4	–
E-glass	SiO ₂ , Al ₂ O ₃ , CaO, MgO, B ₂ O ₃ ,	Higher strength and electrical resistivity	3.5	87
AR-glass	SiO ₂ , Al ₂ O ₃ , CaO, Na ₂ O, MgO, ZrO ₂	Alkali resistance	2.5	80
S-glass	SiO ₂ , Al ₂ O ₃ , MgO	Highest tensile strength	1.5–3.0	72

which the fiber-forming substance is a long-chain synthetic polyamide in which at least 85% of the amide (-CO-NH-) linkages are attached directly between two aromatic rings” (Figure 11.6).

Aramids are rigid polymers and they have poor solubility in regular solvents. For spinning aramids, the polymers are dissolved in concentrated sulfuric acid. This polymer solution known as dope then extruded through the spinnerets at 100°C, and then after 1 cm air gap (results in fiber precipitation), the extruded fiber passed through cold water or through dilute sulfuric acid maintained at 4°C to remove the residual solvent [57]. As the aramid fibers are spun from the liquid crystalline polymer, the extruded fiber doesn't need any post-drawing operation. As the aramid fibers are spun from liquid crystalline polymer, the extruded fiber doesn't need any post drawing operation unlike other conventional fibers. Along with this, Aramids tend to have superior mechanical properties as a result of liquid crystal structure. Apart from having high strength and modulus, p-aramids are chemically and mechanically stable over a wide range of temperatures with high corrosion resistance [56, 58]. The potential of the p-aramid fiber as an engineering material can be realized by studying the structure–property relationships. The compressive strength of the aramid fiber is lower than other inorganic fibers. The low compressive strength of aramids can be explained by extended rigid chains, which are weakly bonded transversely. The energy absorption mechanism of aramid composites is similar to that of metals and responds to compressive stress non-catastrophically because the fiber absorbs energy in its accordion-like compressive collapse [56]. The mechanical properties of aramid fibers are influenced by their molecular orientation, molecular weight, crystallinity, skin/core structure gradients, and internal fault planes or structural defects [9]. Boeing 767 and the Airbus 320 contain about 3%–5% of composites, much of which is p-aramid or hybrids of p-aramid and carbon. Chemically inert nature and low surface energy of aramids causes poor fibre matrix interaction, hence surface of the aramid fibers needs to be modified to improve the interaction. Aramid-reinforced ballistic composites are used in military helmets, on ships for fragment protection, and for military shelters [59].

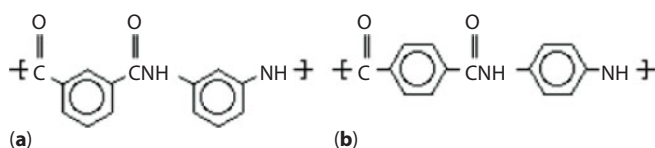


Figure 11.6 Chemical structure of (a) Nomex and (b) Kevlar [56].

11.3.2.3 Carbon Fibers

Carbon fibers refers to the category of fibers having 90% or higher carbon content by weight. Carbon fibers, known for their excellent specific strength and specific modulus, are widely used as reinforcement in composite applications [60]. Carbon fibers find their application in fields like aerospace, automotive, chemical and nuclear plants, etc., which require high strength, low density, high temperature resistance, and chemical inertness. Although cotton-based carbon filament was first prepared by Thomas Edison in 1879 for application in incandescent lamps, the commercial breakthrough came only after the 1960s when the manufacture of PAN-based carbon fiber became efficient and carbon yield increased to 50%. Currently, mesophase pitch, viscose rayon, and polyacrylonitrile (PAN) fibers are most widely used for the manufacture of carbon fibers [61].

Carbon fibers are broadly divided into three categories: general purpose, high performance, and activated carbon. General-purpose carbon fibers have an amorphous and isotopic structure. As a result, they have low strength and low modulus. High-performance carbon fibers have relatively high modulus and strength. Activated carbon fibers are categorized according to their microporous structure, which makes them superior absorption and filter agents. Commercially, carbon fibers are manufactured using pitch or PAN precursors. Isotropic pitch is used to manufacture low-cost carbon fibers. Despite having low levels of strength and modulus, they are used for enhancing conductivity and modulus in various applications. PAN-based fibers are used in manufacturing high-performance fibers. Annealing of PAN-based carbon fibers helps to increase the modulus [62].

The manufacturing process of carbon fiber includes three main steps:

- i. Thermo-oxidative stabilization in air at 180–400°C
- ii. Carbonization in inert atmosphere at 600–1500°C
- iii. Graphitization at 2000–2500°C in inert atmosphere

Precursors have a major influence on the properties of carbon fibers. PAN-based carbon fibers have a smaller crystal size and exhibit particle-like structures, whereas pitch-based fibers have a larger crystal size with sheet-like structures. The structure and crystal size influence properties like compressive strength, tensile strength, etc. [5].

11.3.2.4 Ultrahigh-Molecular-Weight Polyethylene (UHMWPE)

The ultrahigh-molecular-weight polyethylene (UHMWPE) fiber is another high-performance fiber with a high degree of crystallinity and low density.

Owing to its high strength and high impact resistance, UHMWPE shows promising results in applications like ballistic protective shield, bullet proof vests, helmets etc [62]. Polyethylene is a polymer of ethylene base $(C_2H_4)_n$. The molecular chain of UHMWPE has 200,000 repeating units of ethylene, which means 400,000 carbon units in one chain. For composite application, polyethylene is synthesized with different molecular weights like LDPE, LLDPE, HDPE, and UHMWPE. LDPE (low density polyethylene) and LLDPE (linear low density polyethylene) are polyethylenes with a molecular weight of 50,000 g/mol or less. HDPE contains linear chain polyethylene with a molecular weight of up to 200,000 g/mol. UHMWPE, in comparison, has a molecular weight of as high as 6 million g/mol [63, 64].

Owing to its high melt viscosity, UHMWPE is spun using the gel spinning technique. In this process, the polymer is dissolved in solvents like paraffin oil and the mixture is extruded through a spinneret to form a filament [5]. The extracted filament is subsequently quenched in air, and the solvent is removed before drawing and winding the final filament. Draw ratio greatly influences the strength and modulus of the filament. UHMWPE fibers have excellent strength and modulus along with a low specific weight, which make them suitable for many challenging applications. They also have excellent properties like high cut and abrasion resistance, good UV resistance, chemical inertness, impact resistance, etc. [62–64]. UHMWPE fibers do not have any active functional group on the surface, which causes difficulty during the composite preparation process. For UHMWPE composite preparation, the PE surface can be melted by applying heat, and subsequently, fibers can then be fused together by cooling the molten surface under adequate pressure. The composites produced using this process of having the same chemical material for matrix and reinforcement are known as homocomposites [65, 66].

11.3.3 Textile Preform

Textile materials are vastly utilized as composite precursors because of their technical advantages. Textile materials offer better moldability along with higher strength-to-weight ratio as compared to metals [5]. Many textile materials have been used as reinforcement in composites. Textile reinforcement can be woven, knitted, and braided [1, 2]. The classification of textile preform is shown in Figure 11.7.

11.3.3.1 Woven Fabrics

Woven fabrics are manufactured by interlacing two or more sets of yarns. Currently, woven fabrics dominate the textile reinforced composite

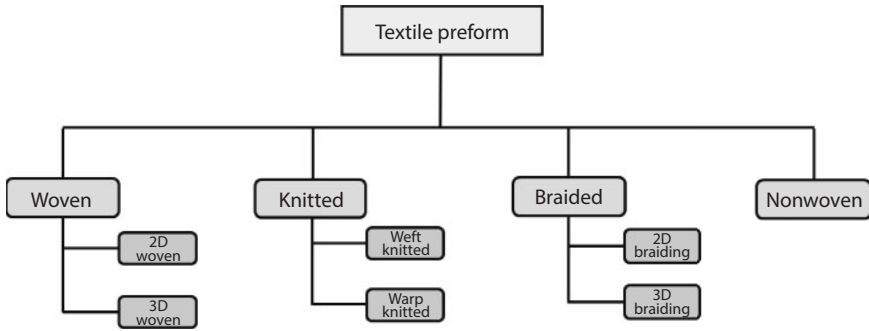


Figure 11.7 Classification of textile preform [1].

segment. The stiffness and strength behavior of woven fabric composites depend on the fabric architecture that can be varied by charring parameters like weave design, cover factor, characteristics of fibers and matrix, and factors introduced during weaving such as crimp, etc. [67, 68]. The good drapability of woven fabrics makes it easy to create composites with complex shapes and designs. Woven-reinforced composites also have better compressive strength and resistance to impact damage than nonwoven ones [69].

Woven fabrics can be produced in two dimensions or three dimensions. 2D fabrics are produced by interlacing warp and weft at 90° . Though the design of the fabric can be varied using different interlacement pattern e.g. plain, satin, twill etc. 2D fabrics are light weight and have low production cost, which makes their usage very economical. Plain, satin, and terry are common examples of 2D woven fabrics. Their low production cost and light weight make their use economical and practical.

In addition to warp and weft, 3D weaving uses an additional third z-yarn. Z-yarn runs through the thickness and acts as the binder. The z-yarn provides dimensional integrity by interconnecting the warp yarns and weft yarns through the thickness of the fabric [70]. 3D woven fabric can be produced by 3D and 2D weaving machines. Orthogonal, multilayer, and angle-interlock are the most widely used structures in 3D woven fabrics. They offer better delamination resistance and damage tolerance than the laminates with 2D woven reinforcement [71].

Woven preforms have a higher cover factor as compared to other textile preforms like knitted and braided structures for a certain thickness. However, the yarns are inevitably crimped along the whole length due to the woven nature of the fabric. With an increase in crimp, the stiffness, in-plane modulus, and tensile strength of the composite reduce

significantly [1]. When compared to unidirectional or cross-ply laminates, woven fabrics have poor conformability, reduced tensile and compressive properties, and poor resistance to in-plane shear [72].

11.3.3.2 Braided Fabrics

Braided fabrics are manufactured by intertwining or interlacing two or more sets of yarns [73]. With such design, these fabrics compete with composite preforms like filament winding and pultrusion. Braided fabrics are among the textile preforms considered for application in aircraft and aerospace. Braids are categorized based on their geometry, namely, Hercules braid, regular braid, and diamond braid (Figure 11.8). The diamond braid is formed by a single or one-over-one overlap; the regular braid has a two-over-two overlap, where one yarn overlaps two yarns; and the Hercules braid has a triple or three-over-three overlap, where each yarn goes over and then under three yarns. Another type of braid known as the triaxial braid is manufactured by three sets of yarns where the third yarn travels along the axis of the mandrel. The angle between the principal axis and braided strands is known as the braid angle. The braid angle is a crucial manufacturing parameter as the properties of the braided strand can be altered by altering the braid angle [74]. Although 2D braids have limited scope in size and thickness, their manufacture has been well developed. Biaxial and triaxial 2D braided fabrics are widely used in structural parts of many technical areas [75].

Braided structures with three-dimensional geometry have yarns running through the thickness, which helps in interlacing through the plies. There are different techniques to manufacture 3D braided structures, such as conventional maypole braiding and four-step and two-step braiding

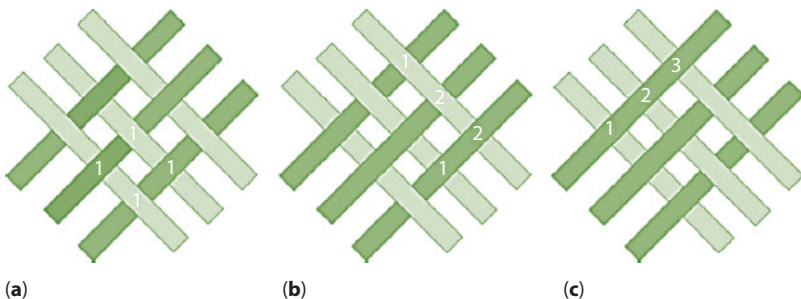


Figure 11.8 Types of braids: (a) diamond braid, (b) regular braid, and (c) Hercules braid [76].

with track and column braiding technique. With time, different braiding techniques like 3D rotary braiding and multistep braiding have been utilized to manufacture braided structures with three-dimensional geometries. The design of 3D braided structures can be engineered using these manufacturing techniques as per loading condition in the end application [74]. 3D braided fabrics have poor mechanical properties in transverse direction due to the absence of weft yarn unlike 3D woven fabrics [77]. Braided fabrics with 3D geometry with multiple axes have multiple layers that provide high delamination resistance [78].

11.3.3.3 *Knitted Fabrics*

The yarn-looped structure of a conventional knitted fabric results in obtaining some unique properties compared to other textile structures. There are two categories of knitted fabrics: weft-knitted and warp-knitted fabric. Weft-knitted fabrics are fabricated by looping with a single yarn, and these loops run in transverse direction [79]. The longitudinal row of loops is called “wale” or “warp,” and that in the transverse direction is called “course” or “weft.” In the case of warp knitting, instead of a single feeding yarn, a warp beam is used for the formation of loops. Production of knitted fabric is very economical owing to its high production rate. Due to their interlooped structure, knitted fabrics have unique properties like stretchability, which helps these structures to be easily molded into any desirable shape. Complex shapes (e.g., curved structures) can also be fabricated using advanced knitting techniques. Knitted fabric composites have good impact resistance and interfacial properties [80]. The mechanical properties of knitted composites can be easily varied using parameters like type of input yarns, knit architecture, fabric orientation, and matrix (or resin) properties.

Due to their excellent stretchability, knitted fabrics with three-dimensional geometry have enormous potential as advanced composite materials. These 3D structures can be easily manufactured using traditional knitting technologies as well as with modern complex machines. Based on structural design, 3D knitted fabrics can be divided into three types:

- i. Multiaxial or multilayer knitted
- ii. Spacer knitted fabrics
- iii. Knitted fabric with spatial geometry

The field of 3D knitted structure is little explored and a lot of research is needed to make the production and usage economical and commercial. Currently, 3D knitted fabrics are produced only in laboratories.

11.4 Surface Modification of Fibers

In the last few years, many conventional materials have been replaced by composite materials for various applications. However, the performance of fiber-reinforced composites is strongly influenced by the functionality of composite interphases. In the construction of composites, it is essential for the reinforcement to have good interaction with the matrix. To meet this condition, the surface of fiber reinforcement can be modified by various physical and chemical methods for the improvement of fiber-matrix adhesion.

11.4.1 Surface Coating

Various types of natural or manmade fibers are being used as reinforcement to improve the properties of composites. However, not all fibers can withstand high-temperature applications. Thus, it sometimes becomes necessary to develop surface coatings that can facilitate the use of these fibers for a wide variety of matrix systems. The most frequently used techniques to modify the surface of fibers include metallorganic coating, electrodeposition, CVD (chemical vapor deposition), polymer precursor coating, etc. Electroplating is used to deposit metals onto conducting substrates such as carbon fibers. A uniform coating and thickness and good penetration of fiber tow can be provided by using this process, whereas in the case of CVD, a solid film of desired composition can be produced on the substrate surface by the reaction of gaseous phase with one another and with the substrate surface. Nubian *et al.* have reported the use of the CVD technique to deposit ZrO_2 and C/ZrO_2 on mullite fibers for interfaces in mullite/aluminosilicate fiber-reinforced composites to obtain more damage-tolerant composites [81]. Goral *et al.* have demonstrated the use of the electrodeposition technique to coat the surface of steel with $\text{Ni/Al}_2\text{O}_3$. The coating of $\text{Ni/Al}_2\text{O}_3$ improved the hardness (40%) of the composite as compared to the pure metal coatings [82].

11.4.2 Plasma Surface Modification

This technique is used to tailor fiber-matrix bonding strength by modifying the chemical and physical structures of fiber surface layer. Plasma surface modification introduces the reactive groups on the surface of fibers by oxidizing it and also improves wetting by increasing surface energy. In plasma treatment, two combined effects take place, that is, fiber surface etching to remove weakly attached layers, such as oils and waxes, followed

by the formation of new functional groups. This technique is environmentally compatible and has high treatment effect without affecting the textural characteristics of the bulk materials. Modification of fiber surface by plasma to obtain composites with improved properties has also been studied by various research groups [83, 84].

11.4.3 Chemical Surface Modification

Interfacial adhesion between fiber and matrix plays an important role in improving the mechanical properties of composites. However, the hydrophilic nature of natural fibers and the hydrophobic nature of the matrix result in inherent incompatibility and poor adhesion between the fibers and the matrix [85]. Chemical treatment of reinforcing either fiber surface or matrix can thus improve compatibility between the two by changing their surface properties. The most commonly known chemical methods used for surface modification include alkaline, silane, acetylation, benzoylation, and peroxide treatment [85].

11.4.4 Mechanical Surface Treatment

Mechanical treatment of fiber for surface modification is a more environment-friendly approach as compared to other methods. The structural and surface properties of fibers can be changed by stretching and twisting the fibers, while keeping the chemical composition the same [86]. Mechanical treatment also involves the fibrillation of fiber by hydrostatic pressure. Using this technique, the fiber surface roughens and mechanical interlocking of fibers with polymer matrices improves. However, modification in this manner can reduce fiber tensile strength.

11.5 Manufacturing of Textile Composite Materials

For the commercial viability of any product, reliable manufacturing plays a vital role. As quality and cost-effectiveness are directly associated with effective manufacturing because of this, a lot of research has been carried out to improve or develop efficient methods of composite manufacturing [2]. Some commonly used techniques of composite manufacturing are compression molding, filament winding, and pultrusion, and research into these manufacturing methods dates back to the 1970s. The selection of a manufacturing technique also depends on the end use of the product; for example, resin transfer molding is extensively used for aerospace and

automotive composite manufacturing, as the technique provides flexibility and thus can create complex shapes at relatively high production speed [1]. With an increase in demand and improvement in fiber technology, manufacturing technology for textile reinforced composites is evolving at a rapid pace.

11.5.1 Open Mold Processes

As the name suggests, in this manufacturing method, one mold is used for composite production. The mold used can be either a male plug surface or a female cavity surface. The major matrix materials used in this process are epoxy and polyester thermosetting resins. E-glass is the most commonly used reinforcement material. Popular open mold techniques include hand lay-up, spray lay-up, pressure bag molding, and vacuum bag molding [7].

11.5.1.1 Hand Lay-Up

Hand lay-up is among the oldest techniques of composite manufacturing, and the first recorded use of this technique is for the preparation of boat hulls. The production of composite is done in an open mold by laying layers of reinforcement and resin on top of another until the required thickness is reached. The hand lay-up process includes five steps: cleaning of the mold, gel coating on the cleaned mold to easily remove the composite, laying-up of reinforcement and resin, curing, and removal of cured composites [7]. Due to its open nature, various forms of materials can be used in this method. Fiber reinforcement can be used in many forms including chopped strand mats, woven roving, woven yarns, or cloths [87].

11.5.1.2 Spray Lay-Up

Spray up is an alternative technique used for laying-up matrix and reinforcement over the mold. The process is automated and reduces the time required for the lay-up process. The method includes mixing of chopped fibers and liquid matrix resin and then spraying the mixture onto the mold surface, layer by layer, until the required thickness is achieved [7]. The same technique can also be used for gel coating of mold surface before the lay-up process. The setup consists of three parts, namely, a spray gun, a fiber chopper, and a pump. A fiber chopper is used to cut continuous roving into short fibers between lengths of 25 and 75 mm. These fibers are mixed with matrix resin in a random manner. The technique is limited to manufacturing of randomly oriented short fiber-reinforced composites [88].

11.5.1.3 Bag Molding Process

The bag molding process is used to produce highly compact and impurity-free composites. The method uses air or vacuum pressure to produce composite laminates [7]. This sophisticated method is normally used for the production of high-quality composites for aerospace applications or other demanding fields where the quality of the product is much more vital in comparison to its production cost and production rate [5]. The main goal of using the bag molding process is to obtain a compact composite laminate and to remove any volatile impurity from the resin [89]. Commercially, there are two different manufacturing techniques categorized under bag molding (Figure 11.9):

- i. Pressure bag molding (Figure 11.9a)
- ii. Vacuum bag molding (Figure 11.9b)

11.5.1.3.1 Pressure Bag Molding

A positive air pressure is used to inflate a rubber/elastomeric bag that covers the composite laminate. This forces excess resin and entrapped air out of the composite. The air pressure usually ranges between 250 and 350 kPa. Female or split mold can only be used in this method. This method is highly effective for making complex hollow structures, turbine blades, containers, etc. [7].

11.5.1.3.2 Vacuum Bag Molding

Vacuum bag molding is similar to pressure bag molding, but in this technique, vacuum pressure is used in place of positive air. Vacuum suction, up to 98 kPa, is used to remove excess air from the laminate, which, in turn,

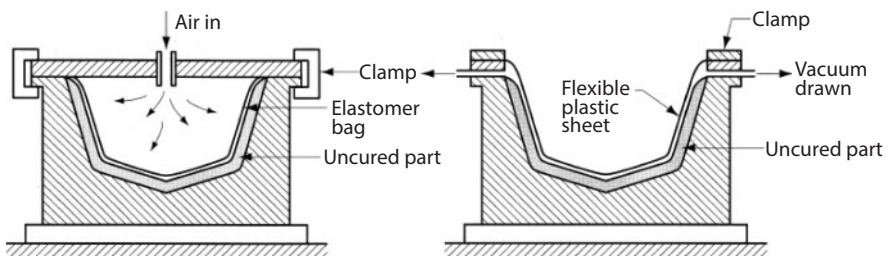


Figure 11.9 Bag molding procedures: (a) pressure bag molding and (b) vacuum bag molding [7].

improves the adhesion between layers and reduces defects in the composite laminate [7]. In vacuum bag molding, laminates produced using different methods are processed. The composites are covered by flexible and non-adhering polymer material. After completely sealing the edges, vacuum is drawn, which causes the polymer to apply pressure on the laminate. Sometimes, heating is applied in order to accelerate curing [90].

11.5.2 Closed Mold Techniques

Closed mold techniques are expansively used for the fabrication and manufacturing of three-dimensional composites. The following are among the various techniques used in closed mold processes: transfer molding, compression molding, and injection molding. These three processes are widely used for composite manufacturing.

11.5.2.1 *Transfer Molding*

In this technique, the reinforcement material is placed in the 3D mold and resin is pumped into the mold. As the mold structure can be varied easily, this makes the process ideal for producing smooth complex composites. Another major benefit of this method is that the fabric orientation can be varied according to the requirement of the composite [2].

Transfer molding fabrication methods include resin transfer molding (RTM). The resin transfer molding process is used for manufacturing near-net-shaped composites using thermoset resins with low viscosity. A high production rate can be achieved by this method of composite manufacturing. Resin transfer molding is a novel technology for the fabrication of high-performance thermoset composites. In the resin transfer molding process, the textile reinforcement is kept within a net-shaped mold, and after that, high-pressure resin is injected into the system. High-pressure resin injection helps minimize the percentage of voids within the composites, and this high-pressure injection has a drawback; that is, only low-viscosity resins can be used due to the resistance to flow [5, 7]. Thus, resins with low viscosity (i.e., thermoset resins) are used in this method. Figure 11.10 shows a pictorial representation of RTM.

In this technique of composite manufacturing, firstly the reinforcement is oriented in required direction and shape followed by laying in two-sided mold cavity. After laying the reinforcement, the molds are closed, and the resin is injected into the mold cavity until the reinforcement is fully impregnated with resin. After wetting the reinforcement, the resin is allowed to cure, and the final finished composite is removed from the mold

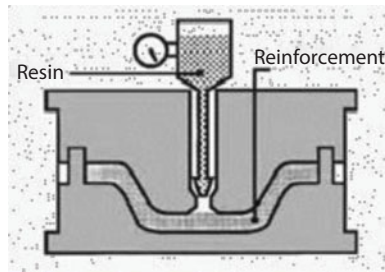


Figure 11.10 Resin transfer molding [91].

cavity. The RTM process has four components: reinforcement preforms, a two-sided mold, resin, and the resin injection pump [92].

11.5.2.1.1 Vacuum-Assisted Resin Transfer Molding (VARTM)

For economical large-scale production of composites, vacuum-assisted resin transfer molding (VARTM) has been amply used in defense and civil applications [5]. Even with low-cost tooling materials, the VARTM process is successfully used to produce high-quality composites. VARTM is a composite manufacturing process in which a polymer resin is injected into a mold containing a fiber perform in vacuum. In VARTM, a single mold is used, and the reinforcement is sealed below the vacuum bag. The vacuum in the system allows the resin to complete wetting the reinforcement without any air spaces. The curing of the resin is carried out inside the mold before the removal of the composite part. The VARTM process is cheaper than resin transfer molding (RTM), because of the use of a one-piece mold with softer material (as processes have lower injection pressure with no matching mold), which needs low machining material [7]. Hence, for cost-effective manufacturing of sandwiched composite parts like ship hulls, VARTM is preferred. The mold in VARTM is identical to that in open mold processes and can be easily redesigned for fabricating different geometries of composite parts [2]. Figure 11.11 shows the schematic diagram of a VARTM machine.

11.5.2.2 Compression Molding

In compression molding, the amount of matrix, taken as per required fiber volume fraction, is mixed with the reinforcement, followed by keeping the reinforcement in a heated mold. As the heated mold closes, the matrix fills the mold cavity. In compression molding, curing takes place while the material is under pressure and heating occurs while the mold is closed.

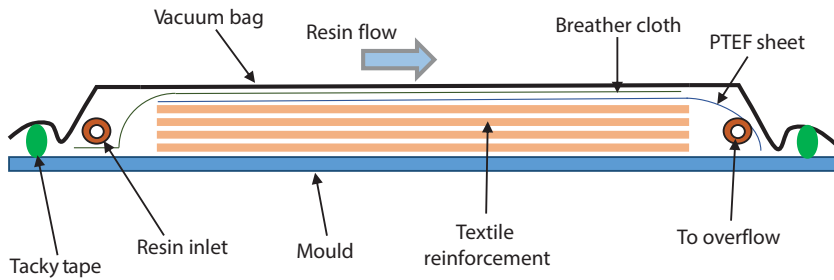


Figure 11.11 Vacuum-assisted resin transfer molding [93].

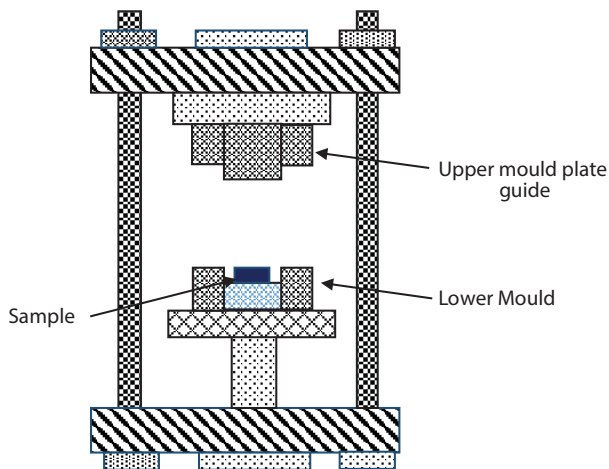


Figure 11.12 Compression molding [95].

SMC, BMC, and MC are the material systems that are processed by this molding method [7].

The CRTM process is described schematically in Figure 11.12. Injection- and compression-driven flows dominate the filling stage in compression molding. Unlike RTM, in this process, prior to the beginning of the mold filling, the mold is closed to a predetermined gap, which results in lower fiber volume fraction and, thus, in a lower resin flow resistance offered by the preform [94]. It is also possible to leave a small empty cavity on one side of the preform, further reducing flow resistance during injection. Once the required volume of resin is injected, injection gates are closed, and the mold is closed in a controlled manner. This secondary mold-closing phase drives the resin front through the preform to the vents and advances the laminate to the final part dimensions and composition. With

careful selection of processing parameters, CRTM can achieve a significant reduction in mold filling time relative to RTM [5].

11.5.2.3 Injection Molding

In this process, a thermoplastic or a thermoset system is injected under high pressure into a closed three-dimensional cavity, which is held at low or high temperature. Cooling and solidification of the thermoplastic-based system or curing of the thermosetting system takes place while the material is under high pressure [7].

Injection molding of fiber- or filler-reinforced polymer compounds is a widely used technique for fabrication of three-dimensional composite components. The major advantages of injection molding are high production and high automation level of the process. In injection molding, the filling of the mold is carried out under high pressure, resulting in short filling times (seconds). Curing takes place in the heated mold under high pressure (10–20 MPa). One example is the injection [30]. One variant of the injection molding process which have been practiced by industries includes pre-compounding of resin with short fibers and/or fillers [30], while other variant of injection molding known as SRIM, involves the injection of resin onto fabric reinforcement in a heated mold under preset pressure [5].

11.5.3 Pultrusion

Pultrusion is a continuous process used for manufacturing uniform, cross-section, long composites. Major products manufactured using pultrusion include flat sheets, solid rods, tubes, and beams. Pultrusion can also be used to produce curved surfaces and variable cross section along the length [96]. Manufacturing is done by pulling a continuous strand of roving or mats into a resin bath, containing liquefied resin and a curing agent, and later passing the resin-filled stand through a preformer before drying the composite in a preheated die. Together with resin and a curing agent, the resin bath also contains other value-adding components like colorant, UV stabilizers, etc. The amount of resin taken up is varied by changing the viscosity of the resin bath, changing the resident time, and adjusting mechanical actions. In order to increase surface smoothness, thermoplastic polyester veils can also be added to the molded product [5]. The preformers uniformly distribute the fiber bundle and squeeze out any excess resin. Final shaping, compaction, and curing take place in the die, which has a gradually tapering section along its length. The entrance section of the die is usually water cooled to prevent premature gelling, and the rest of the die is heated

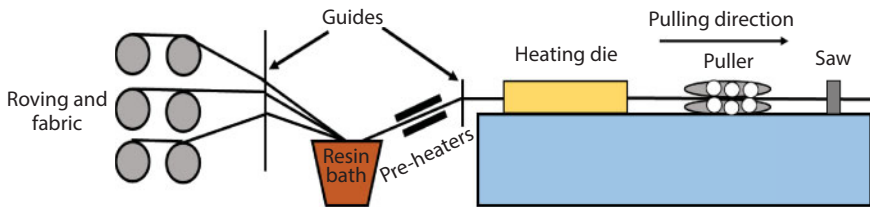


Figure 11.13 Schematic diagram of pultrusion [97].

in a controlled manner either by oil heaters or by electric heaters. Infrared heating has also been used to speed up the curing process [54]. Figure 11.13 shows the schematic diagram of the pultrusion process.

11.5.4 Filament Winding

Filament winding is used to manufacture simple as well as complex-shaped composites. In this process, continuous filaments are passed through a resin bath, and the excess resin is removed from the filament before wrapping them on a mandrel. Resin-impregnated filaments are cured on the rotation mandrel to produce axisymmetric hollow composites [98]. The process is used to manufacture automobile parts, helicopter blades, gasoline and oxygen storage tanks, etc. Similar to the pultrusion process, the resin bath contains liquid resin, a curing agent, and other value-adding components like colorant, UV stabilizers, etc. The resin taken up is controlled by controlling fiber tension, bath viscosity, and speed. After unwinding from the creel, filaments are passed through guides or a scissors bar, which maintains the tension in the filaments. Before entering the bath, filaments are banded together using thread boards or combs. The movement of filaments is controlled by guide rollers. After leaving the resin bath, excess resin is removed by squeezing the roving between wiping devices. Process parameters and winding methods are selected based on the composite strength requirement. For reinforcement, glass fibers, carbon, and Kevlar are the most commonly used fibers. Figure 11.14 shows a schematic representation of the filament winding process.

11.6 Application of Textile Composites in Various Industries

Composite materials have long been utilized in various fields including automotive, aerospace, civil infrastructure, durable goods, and defense

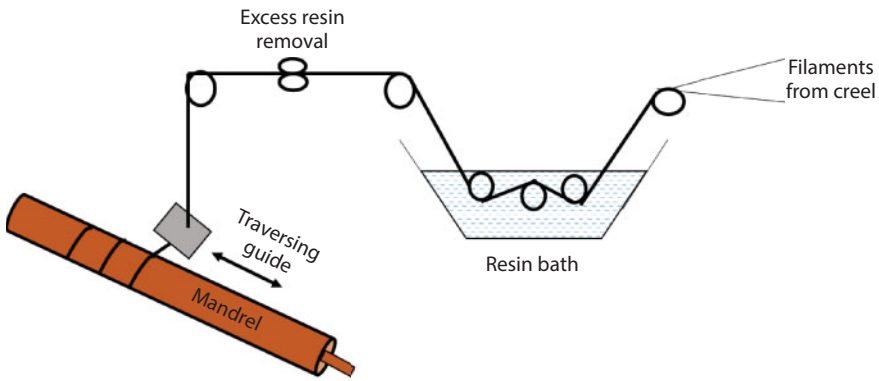


Figure 11.14 Schematic of the filament winding process [99].

Table 11.3 Composite components used in helicopters [100].

Helicopter type	Component made of composite material
MBB BK117	Main rotor blades, tail rotor blades, horizontal stabilizer, vertical stabilizer
BELL 206L	Vertical stabilizer
BELL 402	Main rotor blades
Dauphin	Main rotor blades, vertical stabilizer
McDonnell Douglas, MD	Main rotor blades, tail boom
McDonnell Douglas, MD 900	Main rotor blades, fuselage mid section, tail boom, canopy frame, internal fuselage, horizontal stabilizer, vertical stabilizer

owing to their improved properties. Listed below are some of the applications of fiber-reinforced composites.

11.6.1 Aerospace

Composites were first used in military aircraft during World War II, and since then, several types of composites have been developed and have been used in the aerospace industry. Table 11.3 shows the use of composite materials to build several parts of helicopters [100]. Owing to their various improved properties such as light weight, high strength, ability to withstand high temperatures, and thermal expansion, fiber-reinforced polymer composite materials have become popular materials for the construction

of aircraft and spacecraft. Williams *et al.* have reported the fabrication of self-healing composites consisting of carbon-fiber-reinforced epoxy with resin-filled embedded hollow glass fibers (HGF) [101]. Laminates with higher volume fractions of HGF exhibited larger degree of damage tolerance under quasi-static impact events, which is attributed to energy absorption from HGF crushing. Application of different types of fiber-reinforced composites in aerospace has also been demonstrated by various other research groups [102, 103].

11.6.2 Civil Construction

Fiber-reinforced polymer composites are marketed as the materials of the 21st century because of their superior properties such as high thermomechanical properties, excellent corrosion resistance, and high strength-to-weight ratio. In the last few decades, applications of advanced fiber-reinforced composites have been studied for soundproof and insulated buildings, highways and bridges, decking for marine and naval structures, utility poles, renewable energy harvesting, pipelines, natural composites for green buildings, and others [104–106].

11.6.3 Sports

The improved properties of composite materials render their application not only in automotive, aerospace, and other industrial fields but also in sports equipment. In order to obtain sports items with improved properties, glass fibers and carbon fibers are mainly being reinforced with

Table 11.4 Comparison of mechanical properties of wood, a composite, and a nanocomposite used to manufacture field hockey sticks [107].

Property	Wood (mulberry)	Composite (GF/epoxy)	Nanocomposite (CNT/GF/epoxy)
Density (g cm^{-3})	0.64	1.17	1.20
Flexural strength (MPa)	75	99.8	154.9
Ultimate tensile strength (MPa)	4	5.7	11.3
Young's modulus (GPa)	4.9	6.2	8.1

polymeric matrix composites. A comparison of the properties of wood, a fiber-reinforced polymeric matrix composite, and a nanocomposite is shown in Table 11.4.

11.6.4 Biomedical

In the last few years, the medical sector has gained interest in fiber-reinforced polymer composites for various applications such as components of magnetic resonance imaging scanners and C-armed X-ray couches, scanners, surgical target tools, and devices. They can also be used in prosthetics such as springs and orthotics like anterior foot, podiatric-correcting insoles, and braces. The radiolucent property of carbon-fiber-reinforced polyetheretherketone implants permits improved, artifact-free radiographic imaging compared to traditional metal implants [108]. Fiber-reinforced composite resin (FRC) prostheses also offer advantages such as good minimal invasive treatment, aesthetics, and an ability to bond to the abutment teeth [109].

11.6.5 Defense

Modern warfare across air, ground, and sea demands weight-saving, protection, and high-strength materials. Fiber-reinforced polymer composites are the best-suited materials for these purposes owing to their high strength-to-weight ratio, stiffness, toughness, and design flexibility as compared to other engineering materials. Fiber-reinforced polymer composites in defense sectors are used in military aircraft, land systems, UAVs, naval vessels, and weapons. The most common reinforcement material in marine applications is the E-glass fiber. Rohen *et al.* have demonstrated the ballistic efficiency of multilayered armor consisting of an epoxy composite reinforced with sisal fibers [110]. On the other hand, Majumdar *et al.* reported the role of ZnO nanorods on improving the mechanical and energy absorption properties of p-aramid fabrics [111].

11.7 Conclusions

Owing to their light weight and high performance, composite materials have become an integral part of engineering material. Extensive researches are being carried out to improve the performance of these composites. The properties of composites can be tailored by varying the combinations of reinforcement and matrix. Several studies have been conducted

to engineer specific types of composites by varying the type, quantity, and volume fraction of the reinforcement. Textile-based composites are being widely researched upon because of the numerous advantages they offer, when compared with other types of composite materials. Textile preforms can be made into 2D and 3D structures to support complex composite designs. Depending on the end use application, both natural and synthetic fibers are used in the composite materials. Synthetic fibers such as aramids, glass, carbon, etc. are used in challenging environment applications like high service temperature, high strength, etc. Natural fibers are used in less demanding applications and are researched for development of application-based biocomposites. Despite the recent spike in research, textile preforms can be further improved and a lot of research is yet to be carried out to improve the performance of these materials.

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Emerging Trends in Three-Dimensional Woven Preforms for Composite Reinforcements

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Abstract

Textile-reinforced composite materials with splendid mechanical properties totally unlock new horizons and possibilities in today's technical applications, leaving behind fewer opportunities for traditional engineering materials. These composite materials are composed of fibers in various architectures and resins (matrix) that together gives ideal properties with greater flexibility and cost-effective solutions for the final item. Woven fabrics acquainted with continuity and structural integrity are widely used reinforcements for fiber-reinforced composite applications. 2D weaving has the potential of producing woven fabrics on an areal basis, whereas 3D weaving can produce fabrics on a volumetric basis, which is more suitable for advanced textile composite applications. This chapter envisages the constant advancements and innovativeness in weaving technology that have made it easy to construct three-dimensional fabrics with various geometrical configurations suitable for reinforcement purposes.

Keywords: 3D weaving, preforms, composites, lightweight, structural integrity

12.1 Introduction

Engineering materials ranging from ordinary metals to advanced composites are a class of crude materials that are applied in construction or manufacturing industries in an organized way. Every material we use in our daily

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routine can probably be tailored to be used for specific cases by efficiently knowing its properties beforehand. Hence, materials have been meticulously evaluated to create a database of their properties and have been classified into four broad groups of engineering materials: metals, ceramics, polymers, and a combination of these, mainly termed “composites” [1, 2]. In today’s rapid urbanization and evident shift toward lightweight technology, composite materials are always the first choice of the construction, aerospace, and transportation industries [3, 4]. Composites are basically a combination of reinforcements that may be in the form of particulates, fibers, or fabrics with a suitable matrix that binds them together, forming a well-built interface [5–7].

Laminated composite structures, which have reinforcements in fibrous form, were the first generation of engineering materials that have penetrated the majority of highly structural sectors since the 1960s [8]. Woven fabrics made by joining two or more yarn frameworks at 90° point that displayed steadiness and noteworthy cover were also the preferred types of reinforcement especially for designing structures where the performance is essential in a particular direction [9]. 2D laminates stacked in layers exhibit better in-plane strength and stiffness properties than traditional metals and alloys, which make them potential candidates for reinforcement in textile structural composites. However, in some critical structures like aircraft and automobiles, manufacturers faced real-time problems with 2D laminates that were inferior in resisting impact damages during their service life [10, 11]. In another article, the author had identified the challenge in designing composite structures that could withstand the stresses in curved components, where the structures already in use showed poor resistance to axial compression, which leads to their eventual failure. Aside from this, they possess low through-thickness mechanical properties and also have problems in producing complex structures cost-effectively [12–15]. In the early 1980s, researchers tried another approach of improving the damage tolerance of composite structures by using highly toughened resins, but these resins turned out to be cost-ineffective, and the manufactures badly wanted an inexpensive, robust structure that could withstand the rigors of multidirectional loading with minimal damage [16]. Later studies revealed that there could be a better chance of achieving structural stability in an economical way by using three-dimensional fabric structures [17–19]. In order to improve the interlaminar properties (delamination resistance) of 2D laminates, the use of integrated three-dimensional textile preforms had begun thereafter.

3D textile structures are composed of an assembled yarn system with both in-plane and transverse yarns being integrated into the same structure

[20, 21]. Three-dimensional fabrics have been produced using various manufacturing techniques like weaving, knitting, braiding, stitching, and nonwoven manufacturing. Among the techniques, sewn and 3D weaving were found to be promising techniques to overcome the drawbacks of the stacked-reinforced composites at the early stages [22]. But in the course of time, seams turned out to be a major disadvantage in technical applications, especially when the continuity of reinforcement has to play a role. The efficiency level of reinforcement and protection with the usage of seams is definitely reduced. Furthermore, cutting and sewing create additional waste of raw materials and manual labor, adding up to the manufacturing cost [23]. Henceforth, for a better performance in technical applications where the structural integrity and continuity play an important role, the process of 3D weaving was proved to be an optimized technology for making textile preforms for reinforcement purposes. Another major advantage of weaving that actually draws the attention of textile technologists is its ability to produce a wide range of 3D composites at higher production speeds and low cost [24]. The fully integrated fabric structures are considered to be the most appropriate technique for engineering load-bearing preforms as these architectures include fiber continuity, fiber orientation, and improved fiber volume fraction, ultimately reducing the risk of splitting and delamination [25]. The quick preferences of fabrics with an outstanding thickness measurement incorporate the basic respectability of the woven structure and the fulfillment of the geometric shapes and volumes that are needed for various end-use applications. Regardless, 3D woven fabrics as composite preforms have a vital part to play in the improvement of cutting-edge material composites including medical, protection, and civil and military engineering. There have been effective endeavors in both traditional and uniquely made weaving machines to plan the construction of different 3D fabrics, mostly for the composite business.

Engineers designing 3D fabrics must be well aware of the pattern for interlacing the yarns to produce near-net-shaped preforms within the limits of the weaving principle. The selection of a particular pattern and technique for manufacturing the preforms is largely determined by the end use of the composite structure. In this chapter, 3D woven fabrics are classified based on their architectural design, and each of their structural attributes and manufacturing techniques are further explained in detail. In addition to this, an attempt is made to compile and overview the preform fabrication technologies reported and followed to date. This can provide useful information on understanding the conventional machine possibilities and necessary modifications that might be helpful for futuristic composite engineers involved in bringing various innovative structures into reality.

12.2 Three-Dimensional Fabrics

2D weaving has the potential of producing woven fabrics on an areal basis, whereas 3D weaving can produce fabrics on a volumetric basis, which is more suitable for advanced textile composite applications. In general, all textile structures have a 3D internal structure, but macroscopically, all of them are regarded as thin 2D sheets until their thickness is significantly considerable with respect to their length and width [26, 27]. There have been many definitions of 3D fabrics. Hearle defined 3D fabrics as those that have an overall 3D shape or complex internal 3D structure or both [28]. Behera *et al.* define 3D fabrics as “a single fabric system, the constituent yarns of which are supposedly disposed of in a three mutually perpendicular plane relationship” [29]. In line with this, Chen considered various configurations and geometries of the 3D woven fabrics and classified them into four different categories [30]:

- 3D solid structures (multilayer, orthogonal, and angle-interlock)
- 3D hollow structures (honeycomb, net structures, woven spacer fabrics)
- 3D shell structures (curved and dome-shaped fabrics)
- 3D nodal structures (fabric with connected segments, polar fabrics)

12.2.1 Three-Dimensional Solid Structures

As the name implies, 3D solid structures include fabric structures having defined geometrical length, width, and thickness (height) dimensions that are manufactured by properly arranging constituent yarns in a three-plane, mutually perpendicular relationship. The through-the-thickness yarns are built into the structure at varying levels and angles to obtain structures that have the desired mechanical properties and to resist delamination and impact damages. Figure 12.1 shows the line diagram of a weaving machine depicting the principle of 3D fabric structure development. There are three fundamental types of 3D solid fabrics, namely, multilayered, orthogonal, and angle-interlock structures that can be developed by adopting the traditional 2D weaving technique with multilayer warp systems.

Figure 12.1a depicts a perfect orthogonal structure in which the yarns are basically running straight in the warp, weft, and the through-the-thickness directions. This structure uses one set (non-interlacing) of warp

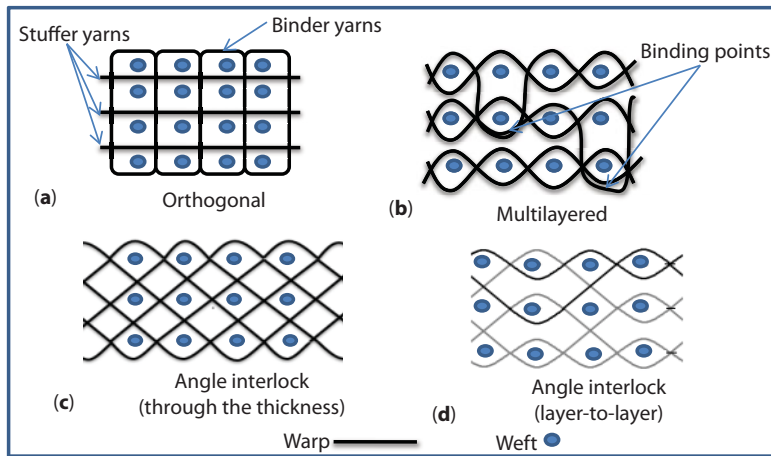


Figure 12.1 Cross-sectional view of 3D woven solid structures.

yarns reinforcing all the layers in the longitudinal direction by forming levels that are basically termed as stuffer yarns and another set of yarns in the transverse direction called weft (fillings). In addition to this, the third set of yarns running through the thickness direction (binder yarns) binds the structures altogether. It can be seen that there is no interlacement taking place between the three constituent yarn axes, which allow the reinforcement material to readily take up the load without any deviation (unlike the crimped state). In this way, fabric integration in all three directions, along with quasi-isotropic properties, is achieved directly.

Similarly, in angle-interlock structures, the warp layers are laid and interlaced in a predefined pattern so that no individual layers are identifiable. The warp yarns flow through one or more layer of weft yarns (layer to layer angle-interlock), or go through all layers of weft yarns (through-the-thickness angle-interlock), binding them together (Figure 12.1c and d). These warp yarns repetitively flow through the warp direction at an angle unlike in an orthogonal structure where the constituent yarns are laid perpendicular to each other. Further, variations in the weave architecture can be done by additionally introducing stuffer yarns within the individual levels to control and ensure the required fiber content percentage (FVF) throughout the structure.

In the case of multilayered fabrics (Figure 12.1b), the individual layers are woven from their respective warp and weft yarns, and these layers are interconnected with the aid of binding yarns. The binding warp yarns travel from one layer to the adjoining layer and back to their host layer

after the interlacements. The pattern of interlacement (binding points) of the binder warp yarns with the adjoining layers may differ according to design or structural prerequisites.

12.2.1.1 *Manufacturing Technique and Structural Attributes*

The traditional 2D weaving technique employs the interlacement of two series of yarns (warp and weft), and a slight modification in this technique to equip an additional third series of yarn can successfully be implemented to produce 3D structures. The modification would concisely be a multi-beam attachment that can hold the third series of yarns (in creating a multilayer warp) and subsequently produce for weaving, which is illustrated in Figure 12.2. This process is in full accordance with the 2D weaving principle and quite simple to modify as per the requirements, thereby making it the most preferred technique to produce most of the 3D structures [31]. There are few practically unknown techniques for producing 3D woven fabrics like dual shedding and non-interlacing (noobing) techniques [32]. The latter technique involves shedding not only in the fabric thickness direction but also in the fabric width direction, while the former technique involves a non-interlacing technique where the constituent warp yarns are positioned orthogonally throughout the weaving process and structurally integrated through binder yarns [30, 32]. These techniques though being complex with respect to machine modifications, they can equally compensate in

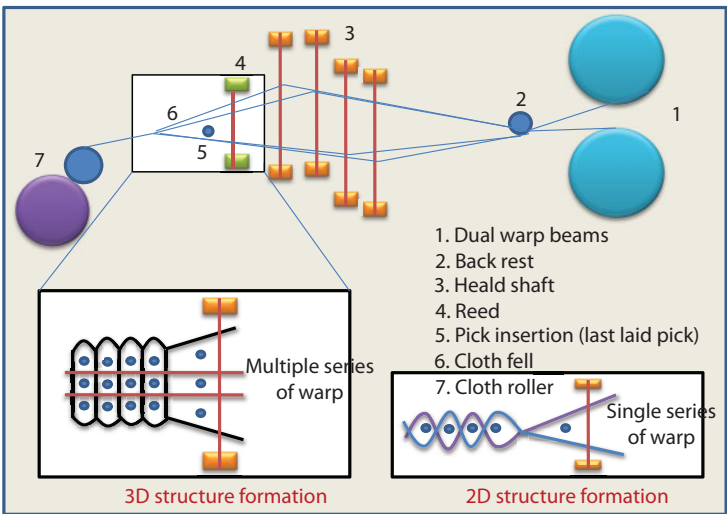


Figure 12.2 Line diagram depicting the weaving principle and fabric formation.

producing 3D solid and network like fabric preforms in any desired shape once it's set into course [33–36].

Getting into the structural attributes, Orthogonal structures have high tensile properties due to the presence of straight yarns along the load bearing directions, and their shear rigidity and flexural performances depend directly on the number of layers existing within the structures [37–39]. The structural stability of the multilayer fabrics increases with a number of layers which on angle-interlock structures, it doesn't have much significance in the warp way but positively influences the tensile and flexural properties along the weft way direction [40, 41]. Increasing the stitching frequency in the multilayer structure may allow a number of yarns to deviate away from the load-bearing direction, thereby reducing their tensile performance [42, 43]. Henceforth, composite structures reinforced with three-dimensional fabrics have been proven to be effective in improving their translaminar properties when compared to those of 2D stacked laminated structures with the introduction of reinforcing fibers in the thickness direction of the laminate.

Many researchers have worked on experimentally assessing the mechanical performances of 3D fabrics in comparison to 2D fabrics both in a raw state and in a reinforced composite state [4, 44]. Studies on mechanical behavior of 3D structures reports that the degree of crimpless yarn availability along the loading direction can be attributed to the mechanical load-bearing capacity of the 3D structures, which is in the following order for a given FVF: orthogonal < angle-interlock < multilayered structures [45]. Multilayered structures provide the highest specific strength followed by orthogonal and angle-interlock structures. The same trend is followed even with respect to an extension at the break on the application of tensile load. The ease in straightening of yarns along the loading direction as in the case of multilayered and angle-interlock structures contributes to their higher performance. The increased fabric support due to the binding effect of the binder yarns along the thickness direction positively contributes to the improvement of impact properties in 3D fabrics compared to the 2D stacking of the same thickness. With the same justification, the damage force of the 3D fabrics under a low-velocity impact test followed the sequential order of orthogonal > multilayered > angle-interlock structures [46]. Studies on the role of weave designs in mechanical performances of the structures also concluded that the number of crossover points and the availability of straight yarns offer excellent structural association under the mechanical loads [47].

Solid structures with different structural designs can be produced by proper modification of these basic weave architectures either by varying the

number of layers or by varying the interlinking of through-the-thickness yarns with weft yarn layers at any required levels or by varying the types of constituent raw materials and thereby providing an added advantage of producing complex near-net-shaped structures [48]. In general, the make-shift in the weave architecture of 3D fabrics can enhance the in-plane rigidity, impact resistance, Damage tolerance, fraction thickness, dimensional stability and subtle conformability of the preforms. 3D solid fabrics can certainly be a good choice of reinforcement material when the composite structures with larger thickness are to be developed.

12.2.2 Three-Dimensional Hollow Structures

As the name says, hollow structures refer to the structures with hollow cavities of various geometrical shapes along their cross-sectional direction. They can be classified on the basis of their structural forms:

- 3D hollow structures with flat/even surfaces
- 3D hollow structures with uneven surfaces
 - a. Single-base layers, for example, stiffened panels
 - b. Multiple layers, for example, honeycomb structures

All these structures can be manufactured using the conventional weaving technique with slight or no modifications from the regular weaving process. Figure 12.3 illustrates some of the basic structures that belong to the abovementioned classification, and a detailed description of the structures and their production technique is presented.

12.2.2.1 3D Hollow Fabrics with Flat/Even Surfaces

These structures consist of two outer flat surfaces separated by a hollow core cavity of various geometrical profiles. Primarily, the structure consists of three layers, of which two layers form outer flat surfaces and the third layer forms the connecting layer between them. The length of the outer fabrics would be equivalent to the length of the structure, whereas the length of the connecting layers depends on the thickness (distance between two outer layers) and the core configuration of the structure. The idea of developing such structures was coined in the view of finding an alternate solution in developing integrated composite sandwich structures [49, 50].

A sandwich structure (Figure 12.4a) is a special form of laminated composite conceptualized by two thin, high-strength face sheets designed to carry flexural loads bonded to a thick, lightweight core designed to carry

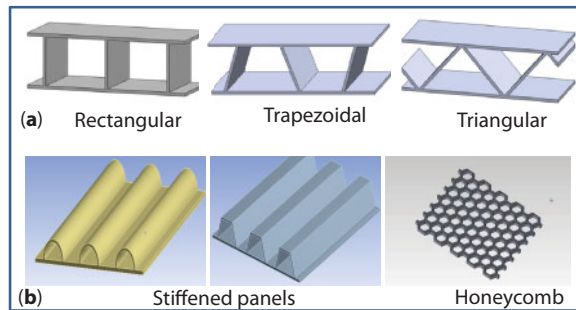


Figure 12.3 3D hollow structures of (a) even/flat outer surfaces and (b) uneven surfaces.

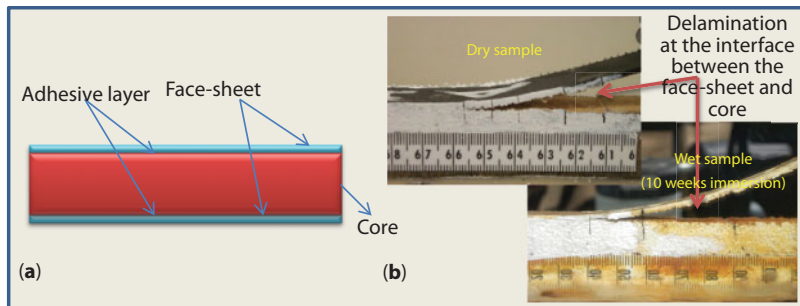


Figure 12.4 (a) A typical sandwich structure model and (b) the most probable failure mode (image modified and reproduced from Ref. [58]).

shear loads [51, 52]. The use of composite sandwich structures in transportation and constructional engineering applications is encouraged as these structures offer exceptional stiffness-to-weight ratios leading to the overall reduction in structural weight and fuel utilization [53]. Sandwich structures must be designed to fulfill the essential structural criteria of withstanding all sorts of mechanical stresses induced during their service life.

Many authors have reviewed and described that the failure behavior of the conventional sandwich composites primarily depends on damage mechanisms such as matrix cracking, fiber bridging in the skins, shear cracks in the core, and interfacial debonding at the skin–core interaction [54–56]. Catastrophic failure of a sandwich beam appears to be the result of initiation/propagation and interaction of these failure modes, as influenced by the type of loading, constituent material properties, and geometrical dimensions [57]. The traditional 3D sandwich composites were only

used in structural parts of non-load-bearing, but not in structural parts of load-bearing. This was because the face sheet and core of the 3D sandwich composites were bonded by glue, which consequently caused delamination (Figure 12.4b) and damage under mechanical loads. In order to meet the abovementioned criteria and overcome the problems of delamination, sandwich structures must be produced from woven integrated structures that include localized reinforcements (between the face sheet and core) [58, 59].

Spacer fabrics are one class of 3D structures with hollow spaces having two distinct fabric surfaces along with the variability of connecting spacer yarns and thicknesses that can offer some of the most innovative solutions of today [60]. The use of three-dimensional spacer fabrics in sandwich structures provides an opportunity to strengthen the skin-to-core bond while preserving the physical integrity of the core. They have a high stiffness-to-weight ratio and very high delamination resistance compared to the 2D laminated structure of the same thickness.

Initially, woven spacer fabrics were developed with pile yarn connections maintaining a hollow space between the two face sheets (Figure 12.5a). However, such structures pose serious problems in maintaining their structural stability during composite processing along with the difficult even resin distribution throughout the structure. In addition to this, the pile threads undergo angle distortion, which would be severe in the case of thicker fabrics, and have limited capacity to withstand high pressure and shear stress [61]. The eventual discovery reveals that the woven cross-links (Figure 12.5b), in comparison with pile yarn connections, can yield significantly higher strength against tensile, compressive, and especially bending forces [50, 60]. Formation of 3D shapes in spacer fabrics can be carried out during the weaving stage itself, thereby reducing labor cost for composite making in future steps compared to any assembly technology.

12.2.2.2 *Production Technique of Woven Spacer Fabrics*

Figure 12.6 demonstrates the production principle of spacer fabrics with woven cross-links. For the manufacture of woven 3D spacer fabrics, a minimum of two warp systems is necessary. Weaving starts with base fabrics of plain weave that are preferably not connected to each other. When the necessary length of the spacer fabric is reached, the warp yarns of the outer fabric layers are separated into two groups. Between them, one group continues to weave the wall section of the fabric while the other group continues to float without any interlacement with weft yarns. In order to achieve

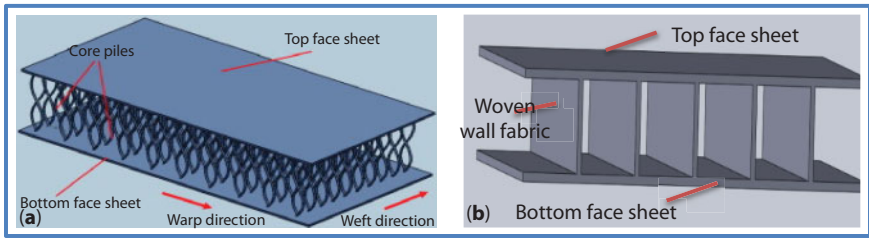


Figure 12.5 Woven spacer fabric integrally woven with (a) vertical pile yarn and (b) vertical woven fabric between the outer fabric layers (image modified and reproduced from Ref. [60]).

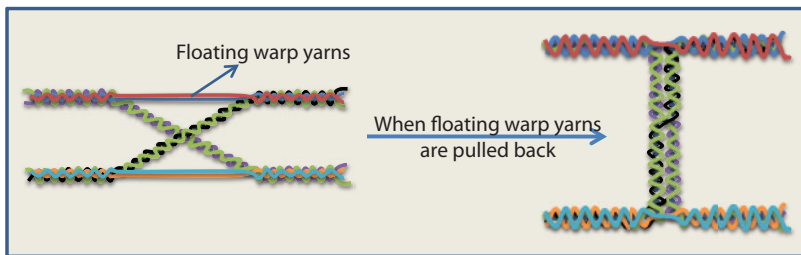


Figure 12.6 Principle of rectangular spacer structure formation.

continuity in the reinforcement yarns between the outer base fabrics, the wall fabrics traverse each other halfway through the cross-link length, after which the wall fabric continues to weave the remaining half-length of the wall fabric. The floating yarns and the wall fabrics are conjoined again as a single layer after a couple of interlacing weft yarns. At this stage, the warp pull-back mechanism is used where the floating yarns of the base fabric will be pulled back into the beam. At the last weft's beat-up of the wall fabric, the reed pushes the formed wall fabric section together as a pleat between the outer layers. This leaves the fabric structure with a double-layered cross-link linking two woven outer base fabric layers.

To increase the strength of the woven fabrics (at the outer fabric layers and cross-link), the weft density can be increased to meet the requirements. Thus, a modified weaving technique, in combination with the warp pull-back mechanism, allows the inserted woven cross-link to differ in spacing or dimensions and produce different profiles of the spacer fabrics [61–62]. Further, “X,” “II,” and “V” profiles are other possible spacer profiles that can be manufactured with the same weaving principle.

12.2.2.3 *Three-Dimensional Hollow Structures with Uneven Surfaces*

These structures may have a single base layer with geometrical hollow cavities formed on one side/either of the sides or multiple layers with cavities constructed in each layer forming a network. The former structures were introduced in developing composite panels with integrated stiffener sections, and the latter corresponds to honeycomb structures that are all defined by the geometrical dimension of the hollow profiles (Figure 12.3).

12.2.2.4 *Integrated Stiffened Preforms*

Metallic stiffener assemblies are manufactured separately and mechanically fastened or welded together. Such structures in composites are made by stacking 2D laminates in required shape and resin impregnated during composite making process [63–67]. Well in such stacked structures, the lack reinforcement in the through-thickness direction increases the risk of delamination at the joints which would be the main cause for most of the failures, to begin with. Usage of mechanical fasteners to prevent delamination would generate structural inhomogeneity and stress-concentrated regions that would favor the untimed failure process. To overcome the problems of delamination, 3D woven preforms with better structural integrity can be a right option [68]. 3D weaving leads the way to designing near-net-shaped preforms that can offer structural integrity and ease of handling during composite manufacturing by reducing the number of individual parts and improving the assembly technique. Various researchers have worked on delivering a systematic procedure to weave stiffener structures, the generalized principle of which is explained below [49, 65, 69, 70].

12.2.2.5 *Production Technique of Stiffener Fabrics*

The design for producing integrated stiffener fabrics has two phases, which are described below. In the first phase, the top and bottom layers are woven together up to a predetermined length. The predetermined length would be equal to the distance between the two stiffeners. Upon reaching the required length, only the top layer would continue weaving, while the bottom layer warp yarns continue to float up to a length that is equivalent to the height of the stiffeners. In this phase, the warp yarns of the bottom layer that were left floating are pulled back using a warp pull-back mechanism. Few picks will be woven after reaching the required stiffener length

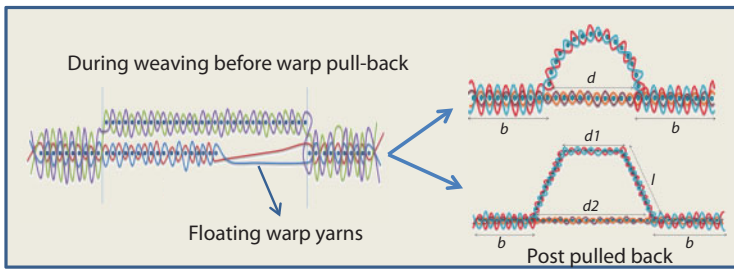


Figure 12.7 Phases of stiffener fabric formation (image modified and reproduced from Ref. [69]).

to facilitate the pull-back action, so that weft yarns of the stiffener section won't slip away while weaving the next repeat section.

The production of this fabric would require two beams, where one beam would be for base layer production and the other would be for stiffener structure formation. By varying the fabric length and the stages at which the pull-back mechanism is used, stiffener structures with various geometrical profiles can be produced; Figure 12.7 shows the production of one such example.

12.2.2.6 Honeycomb Structures

The creation of honeycomb fabrics is realized through a multilayer weaving technique where each fabric layer interconnects with adjacent layers at regular intervals to a given length. This forms a network in the overall structure, and when opened in the thickness direction, 3D structures with hexagon-shaped cells are created. The constituent fabric layers are woven in the pattern of 1/1 plain weave because of its simplicity, firmness, and structural integrity. Layer to layer can be interconnected in three different ways; by weaving the two adjacent layers as a single layer fabric (bonded wall) with double warp density or by stitching (layer interchange) or by following the pattern of orthogonal weave structures in weaving the connecting region. The hollow cavities of the cells run along the structures in the weft direction, as it is the easiest way to produce from the weaving process.

12.2.2.7 Principle of Structure Formation

In general, a honeycomb consists of an array of hexagonal cells made from the combination of four free walls and two bonded walls. Both walls are

structurally single-layered fabric except that the number of warp yarns involved especially in bonded walls is twice that in the free wall. The basic construction parameters that define the cell in a honeycomb structure are opening angle, thickness, and length of the constituent walls. In compliance with the weaving principle, the honeycomb structure is woven flat during the weaving stage and opens up according to the pre-decided opening angle at the consolidation stage post weaving [30, 71, 72].

Figure 12.8 shows a repeat unit of the honeycomb structure in which two hexagonal celluloids are connected to each other. To understand the weave architecture in a better way, the repeat unit can be divided into four regions, regions a, b, c, and d, in which regions a and c represent the separation between the fabric layers, region b denotes the adjacent layers joining together at an alternate interval that actually becomes an integral part of the adjacent celluloid, and region d illustrates the joining of the adjacent layers, but this time, the layers are different from the previous ones. Regions b and d represent bonded walls and regions a and c represent free walls.

Honeycomb structures are generally denoted in the form:

$$xL(y+z)P$$

where x refers to a number of layers involved in making the hollow structure, y refers to the bonded wall length, and z refers to free wall length, measured in a number of picks. L and P are the notation of layers and picks, respectively. For example, an 8L5P honeycomb fabric denotes that the structure engages eight fabric layers, whose free wall and bonded wall are weaved with five constituent picks.

After specifying the honeycomb structure with desired parameters, weave design and lifting plan are created accordingly. The creation of weave design can be done manually on a graph paper, which requires skilled

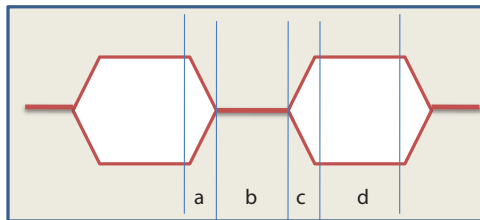


Figure 12.8 Repeat unit of a honeycomb structure depicting the four regions attributed to structural development.

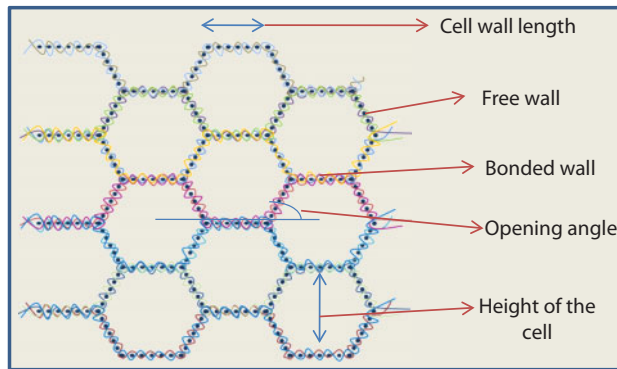


Figure 12.9 Cross-sectional weave architecture of a honeycomb structure.

hands, and the process seems quite cumbersome. The procedure can also be performed quickly using weave design software, for example, Hollow CAD [73]. To begin with the weave design development, let us consider a honeycomb structure with four fabric layers and a pattern of interlacement between warp and weft as illustrated in Figure 12.9. Two sets of warp yarn each responsible for weaving the top and bottom layers interlace with the weft yarns positioned according to the architecture.

A detailed investigation on the mechanical and energy absorbent properties of the honeycomb structures reveals that they can effectively be used as a core material for sandwich panels to retaliate against compression and impact design loads [74–76]. Composites involving honeycomb structures as reinforcements can have relatively high strength-to-weight ratios, which would be more relevant in designing today’s lightweight structural materials.

12.2.3 Three-Dimensional Domed Fabrics

Initially, cutting and sewing of 2D woven fabrics were the method opted to produce dome-shaped structures. But during their service life, seams (stitching) could not keep up to the mark in terms of reinforcement strength and protection [77]. The cut and sew method fully destroys the continuity of fibers within the structure, making it essential to entirely rely on seam strength to improve performance efficiency [78]. In addition to this, cutting and sewing technique requires an entire process line involving sophisticated machines coupled with unavoidable wastage of raw material and workforce which adds up to the overhead cost [79].

To overcome the disadvantages of the cut and sew method, formation of curvature shapes in fabrics is introduced through the following techniques:

1. Combination of weaves (patchy design)
2. Molding process
3. Weaving with differential take-up
4. Weaving of corner-fitting plies

12.2.3.1 *Combination of Weaves*

The most economical dome-forming technique is through the combination of weaves having long and short float lengths [80, 81]. In certain fabrics with identical warp and weft densities, the weave with more interlacements per repeat unit tends to occupy a larger area while that with fewer interlacements causes the fabric to constrict dimensionally. The same principle was used to develop the dome-structured fabrics. A combination of plain, 2/2 twill, and 5-end satin was used in different parts across the width of the fabric, creating a patchy design. One such pattern of weave combination to produce the domed structure is demonstrated in Figure 12.10. For example, the plain weave with the most interlacements and the firmest one are introduced in the middle section of the fabric, which is surrounded by 2/2 twill weave (in the middle section) followed by the 5-end satin at the periphery (with the longest average float length among the three). The plain weave at the middle section has the tendency to occupy a greater

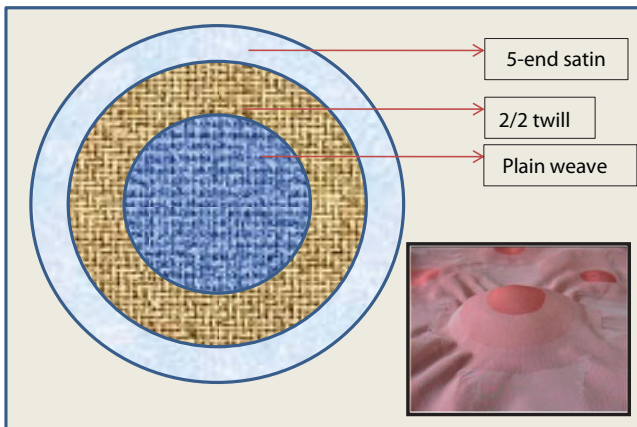


Figure 12.10 Development of dome structure in fabrics through combination of weaves (image modified and reproduced from Ref. [30]).

portion of the area and thus projects out of the fabric plane while the 5-end satin weave has the inverse tendency to squeeze, thereby enhancing the shell formation propensity. The extent of the plain weave fabric section projecting outward away from the fabric plane eventually forms the dome [30, 82]. This weaving technique requires individual control of warp yarns during dome formation which would be possible when the warp yarns are supplied from a creel packages rather than warp beams.

This method of dome formation is a quick and easy way to produce relatively small dome effects on the fabric. Perhaps, the technique was moderately successful due to its practical difficulty in producing larger dome effects since it merely depends on the permutation of different weaves. Moreover, a combination of weaves is a design prerequisite that requires a precise insight into weave architecture and lifting plan, which is essentially a skillful process.

12.2.3.2 Molding Process

A two-dimensionally woven fabric to some extent can be converted into dome- or shell-type structures through the mechanical aid of pre-decided molds and thereafter consolidated and resin-impregnated to obtain composite structures [83]. The extensibility of the yarns in the fabric structure and the allowance of shear would be the main deciding parameters to define the formability of the fabrics into curved shapes [84–85]. Figure 12.11 shows the molding process of a typical 2D fabric into a

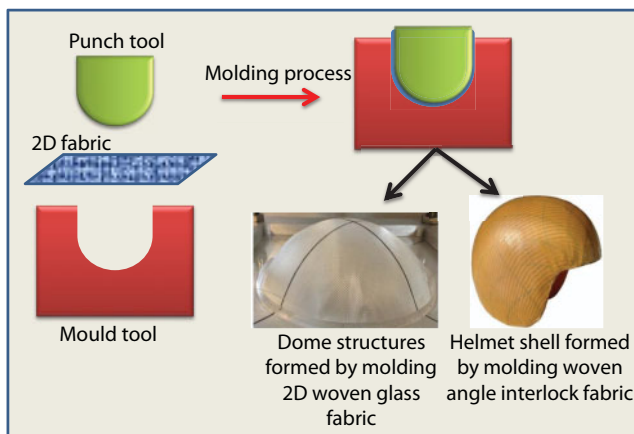


Figure 12.11 Molding process flow to develop a curved dome structure from 2D fabric preforms (image modified and reproduced from Refs. [30, 90]).

hemispherical 3D curved structure. Various curvatures can be tried out straightforwardly by pre-deciding the shape of the punch tool and the mold.

In the due course of performance, the manufacturers were reported back from the consumers with certain pros and cons associated with this method. The pressure applied to the fabric during the molding process would leave the reinforcement with inevitable additional strains as well as changes in the orientation of fiber layers and yarns [86]. The change in fiber orientation not only deviates the reinforcement material away from the load-bearing directions but also leads to shear deformation, sliding of fibers, undesired yarn extensions, and local wrinkles in the fabric [87, 88]. These problems altogether would cause a serious drop in the performance efficiency of the structure during its service life. Nevertheless, the interyarn friction at the crossover points along with the limitation of space within the fabric structure pretty much limits the moldability of the fabric. The moldability of the fabric into dome-shaped curvatures can be improved elegantly by using elastic yarns. But the same elastic yarns make the formation of sharp corner fittings more complicated. In general, pre-analyses of the shear resistance property of different fabric structures would effectively facilitate the designing process of 3D shell structures for various aesthetic and technical applications.

12.2.3.3 *Weaving with a Differential Take-up System*

Weaving is a balanced process, which signifies that the ratio of input (warp let-off) to output (fabric take-up) of the weaving loom is constant [30]. Weft densities would be the deciding factor for optimizing the rate of weaving; that is, the higher the take-up pace, the lesser is the weft density in the fabric, and vice versa. Any disturbance in the balance, whether in the let-off or take-up mechanism, would lead to discontinuation of the regular weaving process. However, this can be deliberately performed to get hold of some fancy effects on the 2D fabric structure, and dome construction would certainly be one of them. To facilitate this purpose, the first and foremost prerequisite would be to divide the width of the warp sheet into several sections and balance the weaving process (let-off and take-up) individually. This would be achievable if the weaving machine is equipped with creel (or section-wise through multiple warp beams) to supply the input yarn material and some sort of customized take-up mechanism to collect the woven fabric at different rates across these sections.

In accordance with this principle, Busgen [89] patented a personalized take-up mechanism in which the conventional one-piece take-up roller was replaced by the combination of discs that could be electronically controlled

to execute individual take-up movement. To put this into action, the warp yarns supplied to the weaving area were divided into five different sections and the take-up movement of each section was controlled by its respective discs mounted on the roller as shown in Figure 12.12. The sections weaving the dome area were taken forward at a higher rate while the sections weaving the base fabric were taken forward at a comparatively lower rate by means of the discrete take-up roller. This results in the excessive length of the fabric projecting outward, taking up a domed shape once the fabric is removed from the loom. To facilitate the differential take-up mechanism, the let-off must also be equally equipped with the feasibility to control the warp yarns individually. Warp yarns can be delivered either from the creel or through multiple warp beams (each beam carrying warp yarns with respect to their sections), whichever is ideal based on the available infrastructure. It is obvious that the weft density at the dome area would be less in comparison to the base area, and some additional weft yarns can be added to normalize the material density throughout the fabric.

Since the discrete take-up roller turns out to be an integral part of the weaving machine, it would probably disturb the weaving of normal fabrics, leading to economic constraints. To provide a convenient solution to this production inconvenience, Chen *et al.* [82] developed an easy-to-use

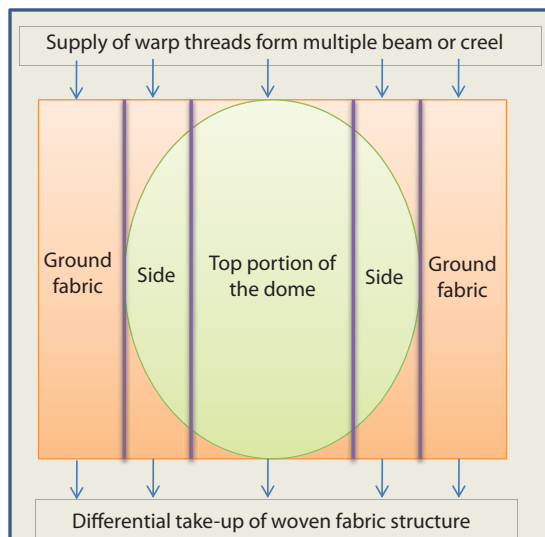


Figure 12.12 Fabric width divided into sections with their respective take-up arrangement depicting the overview of the differential take-up system (image modified and reproduced from Ref. [89]).

add-on device consisting of a profiled take-up roller system that can be easily attached in continuation to the regular take-up arrangement of the loom. The device consists of a roller, a profile chain engaged to the roller, and a frame holding them both as shown in Figure 12.13. The profile can be chosen based on any required shape, and the profile chain roller is designed to ensure uniform linear movement without stretching or slackening the fabric until it reaches the cloth roller. Dome formation is attributed to the synchronization of uneven take-up and let-off across the width of the fabric. It is obvious that the design lengthens the fabric path but the removal of add-on devices recommences the original setup of the loom, which would be ready for weaving normal fabrics. The device is economical and can effectively assist in the production of differently shaped dome fabrics either from single-layer, multilayer, or angle-interlock fabrics.

12.2.3.4 Weaving of Corner-Fitting Plies

The defective tolerance level for most aircraft and automobile spare parts is very stringent. Although the forming technique using mold is fast and more efficient in producing semicircular curvature parts, it suffers from a design limitation—it is ineffective in maintaining the dimensional stability of the preform while molding it toward sharp-edged structures. For

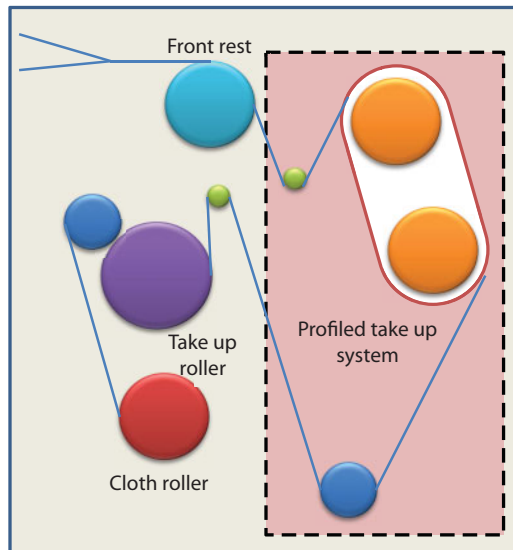


Figure 12.13 Add-on device used in continuation to the regular take-up mechanism (image modified and reproduced from Ref. [82]).

instance, the strong shear effects manifested in the form of large wrinkles and yarn slippages are observed at the sharp corners while forming a square or tetrahedral structure from single-layer textile reinforcement [87]. Furthermore, the outcome would be more prominent when multiple stacking or multilayered reinforcements (3D solid woven structures) are considered for molding, thus leading to variation in fiber volume fraction and local permeability of the fabric preforms. Therefore, alternative methods for producing textile structures devoid of such problems are most welcome. Wang *et al.* came up with a technique called surface 3D weaving to produce complex structures, further describing its potentiality to interweave sharp corners without the need of a 2D product or any forming techniques.

The manufacture of corner-fitting plies is explained in three consecutive steps, and the phases of fabric formation are shown in Figure 12.14. The first step is concerned with beaming and picking of warp yarns along the “X” direction. Second, the yarns along the “Y” direction are interlaced with those along the “X” direction to weave a two-dimensional planar fabric that would actually form the upper surface of the square box structure. In the third step, upon completion of weaving the upper surface fabric up to a predetermined dimension, the free ends of the “X” and “Y” yarns are altogether turned by 90° and continued weaving along the “Z” direction,

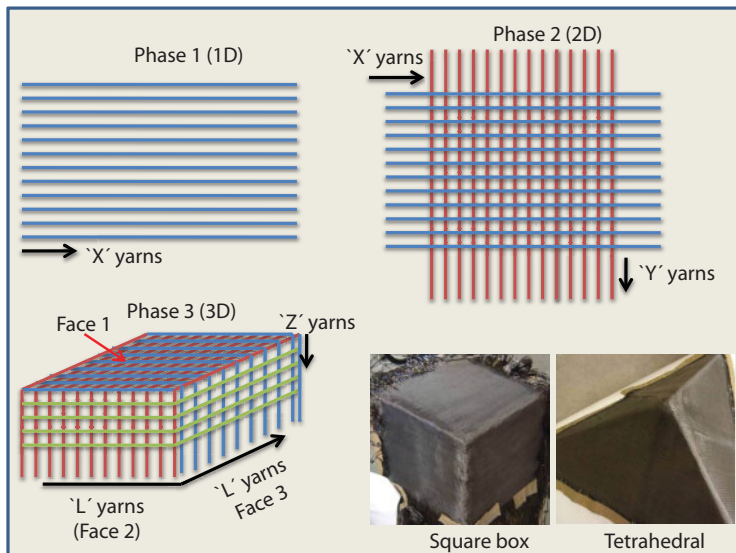


Figure 12.14 Phases of corner-fitting plies formation (image modified and reproduced from Ref. [90]).

forming the lateral faces of the box structure. The weft insertion, in this case, would follow the rectangular path, unlike the regular rectilinear path.

Figure 12.14 (inset) illustrates a corner-fitting square box and tetrahedral preform structure woven from the above-explained principle. The authors could observe the complete absence of wrinkles and the constituent yarns were perfectly in control at the sharp edges, maintaining the continuity and homogeneous local permeability between the adjacent faces of the developed structure [90]. Compared to the traditional molding technique, surface 3D weaving can be reliable in producing structures with complex geometries (specifically with sharp edges) in a single route. On the other hand, the technique is totally skill based, lengthy, and difficult to put into practice for bulk production.

12.2.4 3D Nodal Structures

Figure 12.15 shows a typical single-layer woven tube structure constructed by the interweaving of upper and lower fabric surfaces. It is obvious that the fabric is woven flat with bound selvage at the weaving stage, and when taken off the weaving machine, the structure is apparently pulled into a cylindrical profile. The thickness of the structure can be augmented by replacing the single layer with a multilayer or angle-interlock weave structure. Further, the segmentation of the woven tubes into two or more offspring segments would lead to the truss-like assembly of structures. In structural engineering, a truss is a structural assembly that consists of two or more members (strut) organized and connected to a node in such a manner that the assemblages as a whole preform like a single object. They are also called nodal structures in view of the fact that the individual elements are connected to the mainstream through a node. Currently, the production of truss

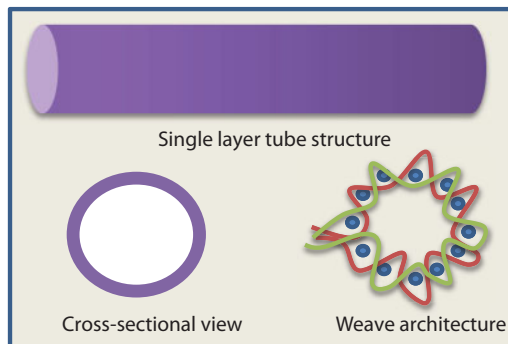


Figure 12.15 Line diagram of a single-layer cylindrical tube structure.

structure assemblies requires various technologies to connect the individual struts collectively within the desired truss configuration. Many researchers have worked on modifying the weave architecture through the concept of 3D weaving to develop woven nodal structures that would become more attractive in the composite world [91, 92]. Woven nodal structures basically refer to woven tubes that are coupled to a node according to the desired strut-strut configuration. The capability of 3D weaving to create the nodal structures in required shape would be a reliable technique to fabricate integrated structural components with repeatability and provision to quick style change to newer configurations devoid of any added necessity of laying-up or assembly procedure.

To produce a nodal structure of any required configuration, it is important to understand the intersections of the yarns along the warp, weft and through-thickness direction to finalize the weave architecture. Various textile modeling software packages are developed till date to facilitate the development of 2D planar truss configurations, thereby easing the process of multilayer weave generation and associated weave segmentation, which leads to the development of 3D nodal structures. For instance, WeaveStudio CAD/CAM software was developed based on the Pierce derivative model considering lenticular yarn cross-sections for an explanatory geometric modeling and 2D/3D weave generation also providing an insight visualization of various weave architectures [93]. Software tools with geometrical modeling and predictive capabilities that ensures precise visualization, production and validation of the structures are advanced in today's technical world. WeaveEngineer is another package designed specifically for hollow fabrics (similar to nodal structures) that allows weave generation alongside geometrical predictive and mechanical modeling.

The basic steps in one of the methods used to construct a nodal structure are listed below [94–96]:

1. Translation of 3D to 2D strut geometries
2. Development of single-layer or multilayer weave architectures on 2D graph template
3. Formulating node/nodal boundaries and inner segmentation
4. Varying the number, dimensions, and angular orientation of the child struts

12.2.4.1 Translation of 3D to 2D Strut Geometries

A node can be defined by its parameters like strut length, strut wall thickness, strut diameter throughout the length and at the point of intersection,

strut angle orientation, and strut–strut proximity. All these nodal specifications together establish the 3D geometrical boundaries, and furthermore, the resulting geometry is flattened theoretically to conclude the approximated 2D dimensions (Figure 12.16). The overall thickness of the 3D-to-2D converted structure is equivalent to the summation of upper and lower walls, whereby the thickness of each wall is equated to the integration of its constituent layers. The number of layers in each wall can be varied as per the required dimension of the truss assembly, but the layers must be symmetrically distributed within the top and bottom wall to ensure a balanced wall construction.

12.2.4.2 Development of Weave Architectures on a 2D Graph Template

The foremost step in the translation of weave geometries involves sketching an actual nodal schema on a 2D graphical template. The figure shows a typical “T”-shaped nodal geometry applied on a 2D graphical template along with its idealized overall boundary thickness. The positioning of the nodal structure on a graphical template along a 2D plane is done by a series of coordinates that identifies the number of layers and accounts its constituent warp and weft yarns within the weaving length, width, and thickness

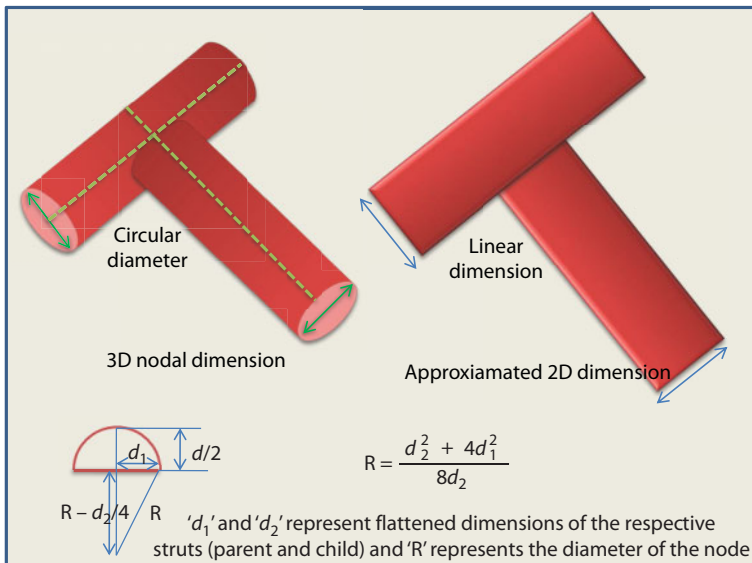


Figure 12.16 Structural attributes of T-nodal structures in three dimensions and approximately converted two dimensions.

dimension. The scaling of the graphical template is set in accordance with the linear densities and thickness of the constituent yarn material selected. Nevertheless, certain weaver's parameters like fabric sett within the level and between the levels, fabric sett at the nodes, and jacquard harness configuration (shedding system in the loom) must be considered along with the pre-mentioned nodal specifications to facilitate the easy opening of the structure from 2D to 3D after the loom state.

12.2.4.3 *Formulating Node/Nodal Boundaries and Inner Segmentation*

A simple "T"-shaped nodal structure consists of a parent strut and one child strut connected together, creating a node and node segmentation within the adjoining area. Knowing the flattened dimension of the parent (strut 1) and the child (strut 2) struts enables the calculation of the circumference of the nodal region, which is the point of interaction. From Figure 12.17,

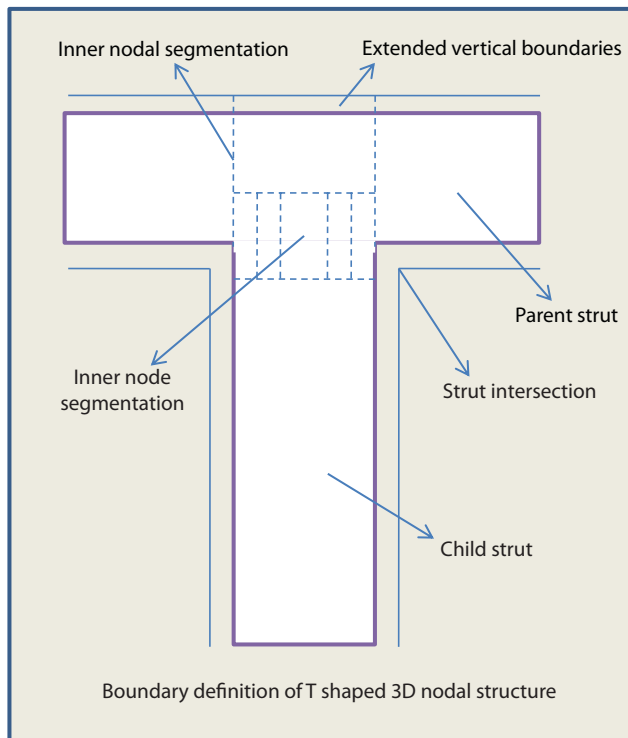


Figure 12.17 Nodal boundaries and node segmentation of a T-nodal structure.

the boundaries behind the node are the extension of the outer edges of the child struts and the boundaries below the node line form the horizontal strut wall, both maintaining the continuity (elongation) between the inner node areas of the parent strut and the adjoining child strut. The same style of interlacements is allocated at the node area to form the extension of vertical boundaries of the child strut from the main strut. The junction of the parent and the child truss must be constructed in segments with different weave combinations. The use of minimal number of weave combinations would result in non-formable 2D-to-3D fabric that would hinder the opening of the strut circumference. Augmenting the number of segmentation within the inner and outer nodal area can easily eliminate the distortion within the seam and extended vertical boundaries. A combination of weaves allocated to each of these segmentations would successfully enable the right composition of constituent levels so that it can transform from 2D to 3D nodal structures ultimately. In addition, the selection of each style of weave design is attributed toward achieving increased vertical interlacements within the thickness direction of the boundary wall.

12.2.4.4 *Varying the Number, Dimensions and Angle Orientation of the Child Struts*

Within the production feasibility of the 3D nodal woven structures, various strut-to-strut configurations are achievable within a 2D plane alongside the provision to alter the nodal's parameters. The contact area where one strut interacts with another forms a node that basically requires an optimized consideration along the three principal axes of a weave architecture. In addition to the continuity of the node formation along with boundary definitions and segmentation, multiple strut-strut interactions can also be accommodated through a series of elementary nodal configurations. These elementary nodals further define the future nodal derivatives on the basis of the strut dimension, strut orientation, and strut proximity.

Strut-to-strut angle variations can be obtained by just adjusting the upper and lower curved boundaries (dimension of the segments) according to the required angle with no alterations to the inner segmentations and the weave architecture used within the nodal segments (Figure 12.18). The positioning of the warp and weft interlacement is coordinated and the compounded wall thickness is estimated by the individual layer thickness being summed up to the required number of levels.

With the flexibility of this technique, the preforms are structurally integrated without any additional process of lay-up alongside the preservation

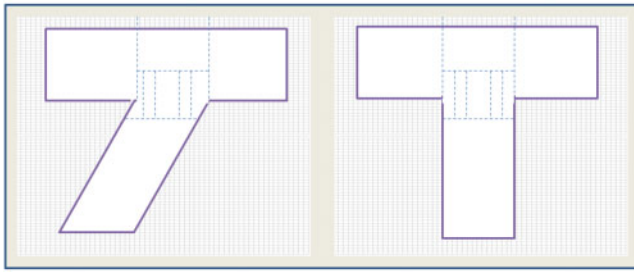


Figure 12.18 Strut-to-strut angle variation on a graphical template.

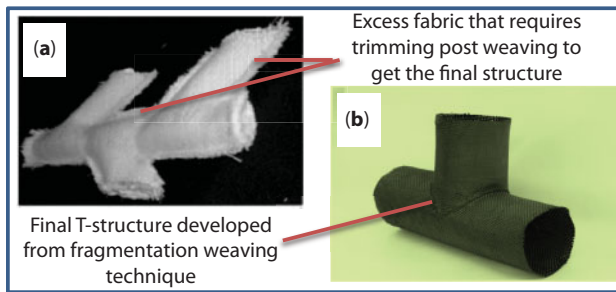


Figure 12.19 3D nodal structures developed from full-width 2D planar weaving and fragmental weaving (image modified and reproduced from Refs. [30, 97]).

of all the geometrical aspects of the nodal structures. Figure 12.19a shows an example of an integrated nodal structure that depicts the combination of varying the number of struts, angle, and orientation. All these structures can be developed on a loom with single or multiple widths with exact replication.

However, the overall fabric necessitates a post-weaving step to trim the excess fabric apart from the nodal structure. Unfortunately, this would result in material loss, and more importantly, the continuity in the reinforcement between the components is hindered. To fulfill the growing requirements of the nodal structures, Fazeli [97] systematically developed a concept of nodal structure formation based on fragmentation and individual development of sub-elements through suitable modifications (with respect to flattening and weaving as multilayers, which are later on pulled to realize the final tubular structure) on a narrow weaving machine, and Figure 12.19b shows “T” profiled nodal structures developed from this technique.

12.3 Challenges and Future Directions

Composite structures have already proven their advantages over weight savings and potentiality to replace conventional engineering materials. The utilization of textiles in the structural development of composites has been reported since the 1900s. There is no doubt in the fact that the selection of preform type and its respective manufacturing technique is highly dedicated to the design of the required structural component. In order to avoid the delamination prone failures, development of preforms with better structural integration will be an everlasting challenge for the preform engineers. On the other hand, despite the fact that the initial investments in composites are high, manufacturers still prefer them in structural application merely to reduce in-service operational and maintenance cost. Most of the research efforts in today's composite world is focused on reducing initial cost as well as in-service cost. In search of economically attractive solutions, efforts have resulted in discovering several innovative techniques suitable for the industrial sector. Apart from the scientific development in the manufacturing technology, quantitative efforts on process design, tooling, quality standards, etc., must be equally emphasized to reduce the initial cost and increase the application potential of composite structures in various technical and constructional markets.

Furthermore, during research and development, each and every sample in a group cannot be involved in the testing procedure to predict their characteristic properties. Obtaining a perfect combination of resin, fiber, and their respective contents in a composite is improbable. Advances in structural modeling and process-based analysis are necessary to virtually predict their behavior and justify their service life. Validation of such simulation tools on a research scale and further associating them to the manufacturing process can improve the confidence in understanding the challenge of developing an ideal product. Besides, development of textile preforms and their conversion to composites are labor-intensive, involving manual work in almost every phase, increasing the risk for errors and defects. In working towards quality improvement and wastage reduction, implementing of process automation that can provide quick adaptability to the current process line can be taken up as a new challenge.

A steady increase in composite use for structural applications has been observed recently, but thermo-set resin-based composites experience difficulties in recycling and remolding. The majority of defective composites and discarded structural components after repair end up as landfill waste, which is roughly estimated to be around 30%. Many technologically oriented

companies use high-quality and eco-friendly fibrous reinforcements (e.g., recycled carbon fiber, natural fibers) that can influence the growing quantity of advanced composite waste. Alongside waste categorization and reliable source generation of waste materials for recycling, quantitative research to demonstrate the feasibility of such materials is also necessary.

12.4 Summary and Outlook

When textiles are preferred for composite applications other than wearable purposes, when textiles are preferred for composite applications, their properties like axial rigidity, formability and structural stability under design loads becomes the major prerequisites. Being the lightest among the preforms, 3D hollow structures are an excellent choice for energy absorption as they can endure impact loads. 3D dome structures can be used in developing integrated curvature fabrics suitable specifically for designing female body armors. 3D nodal structures are used in designing integrated truss structures of various configurations, such as in industrial hosing and vehicle and machine component engineering, and they are currently also used in developing textile vascular prostheses for medical applications. Undoubtedly, the properties of each structure differ from the way it is being constructed, and each method of 3D weaving is qualified to produce fabrics for a specific application.

Today, the inspiration for presenting 3D textiles in composites is not only to expand the out-of-plane properties but also to decrease the work expense during assembly and to integrate more functionality into the component. Exploring preforming technology with infinite perspectives to solve specific engineering problems is an art, and this chapter briefly reviews all the categories of the 3D woven fabrics and the possibilities in solving the problems for which these fabrics are intended for. The field of 3D weaving and 3D textiles is quite broad; it doesn't begin and end with this chapter alone. Readers can pursue their deep interest in 3D weaving by referring to various research works reported and published to date.

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Evolution of Soft Body Armor

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Abstract

The origin of body armor dates back to the history of mankind. With the accelerating developments in firearm technology, new materials and designs are being exploited extensively to accomplish the new-age requirements of configuring lightweight and flexible body armor with adequate energy-absorbing capacity. The present chapter encompasses the fundamental concepts and findings relevant to the ballistic response of textile materials essentially required to be borne in mind while designing soft ballistic materials, as well as the journey of evolution of soft body armor starting from nylon flak jackets to present-day shear thickening fluid impregnated fabric armor woven from high-performance yarns. Besides, a detailed discussion about the advancements in soft armor technology in the form of hybrid panel armor system, 3D fabric technology, multiphase STF systems, etc., has also been presented.

Keywords: Impact energy absorption, high-performance fibers, textile structural parameters, shear thickening fluid, rheological parameters

13.1 Introduction

A body armor protects the human body from potential injuries caused by speeding projectiles or sharp weapon attacks during battlefield confrontations or in other dangerous situations like criminal conflicts, angry mob, etc. It is the most vital element of protective gear used by soldiers in combat and by police officers during law enforcement operations. A modern

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body armor falls into two categories, namely, soft body armor and hard body armor. A soft body armor is primarily composed of multiple layers of high-performance woven fabrics (weighing below 4.5 kg) and can suffice to perform against low-level firearm threats up to the NIJ IIIA level. On the other hand, a hard body armor is composed of metallic or ceramic plates and is meant to arrest projectiles fired beyond the NIJ IIIA level. For the brave hearts fronting the heavily equipped enemy, a soft body armor is conjoined with a hard one to ensure sufficient protection.

While developing body armor intended for protection from a ballistic impact, it has always been desired to use light yet strong materials such that enhanced performance is obtained at reduced weight. The invention of synthetic fibers geared up the evolution of light-weighting soft body armor. The trend started with the M-1951 model, a body armor system consisting of a flexible pad to cover the upper chest and shoulders, made out of basket-weave fabric of nylon, and Doron plates to cover the lower chest [1]. However, it was actually the advent of high-performance fibers like p-aramids in the 1960s and ultrahigh-molecular-weight polyethylene (UHMWPE) in the late 1970s that ushered a new era of soft body armor materials. These high-performance fibers possess high modulus and breaking strength and are hence capable of absorbing the impact energy of high-velocity projectiles. However, a large number of fabric layers (20–50), woven from yarns of such high-performance fibers, are required to manufacture a conventional soft body armor. Thus, the material assembly becomes heavy, bulky, and inflexible, interfering with the dexterity and comfort of a soldier. Often, the troops are reluctant to don them due to their heavy weight and rigidity, that too with uncertainty about protection. This poses a challenge to the fiber and textile researchers across the globe to develop lightweight, flexible, and comfortable armor panels, with enhanced impact resistance absorption that is sufficient enough to compete with the latest firearm technology [2].

A significant improvement in the performance of soft body armor has been attained with the help of a unique class of fluids called “shear thickening fluid” (STF), as reported by various research groups around the world [3–6]. It is a non-Newtonian fluid that shows a drastic rise in viscosity beyond a critical shear rate. STF has gained tremendous attention in the field of soft body armor for its ability to enhance stab, puncture, and ballistic resistance of high-performance fabrics without compromising their weight and flexibility. Further advancements in its properties are being sought through the development of multi-phase STFs. Besides, extensive efforts are also being directed toward improvement in fabric structure and optimization of panel configuration so as to achieve maximum ballistic

protection. This chapter reviews the significant findings and accomplishments so far in the development of soft body armor technology directed toward enhancement of ballistic energy absorption with simultaneous reduction in weight and thickness of the armor.

13.2 Constituents of Soft Body Armor

Soft body armor panels span over multiple dimensions of length owing to their structural hierarchy from polymer to fiber/filament to yarn to fabric to panel assembly. The possibility of variations in their architecture at all aforementioned sublevels makes the ballistic impact onto such materials a complex multiscale problem. Flexible woven fabrics, which are the most preferred choice for developing soft body armor, are inherently anisotropic in nature and exhibit a series of phenomena during a projectile–armor interaction [7]. In addition to this, when certain surface chemical treatments are performed to further enhance the ballistic performance of these fabrics, the projectile–armor interactions become even more complicated. A thorough understanding of the fundamental mechanisms of energy absorption, occurring at all scales of length of the armor panel during a ballistic impact, has been gradually built up over many years through experimental, analytical, and numerical techniques, which are presented in this section.

13.2.1 Response of a Woven Fabric to Ballistic Impact

The mechanisms involved in a woven fabric armor panel subjected to a ballistic impact depend on a combination of many synchronous factors. The energy lost by the projectile/bullet is absorbed by the fabric panel through various damage and energy-absorbing mechanisms, namely, yarn pull-out (comprising of yarn de-crimping and yarn translation), fiber plastic deformation, and fiber fracture [8–11]. These phenomena are further dependent on fiber type, yarn linear density, fabric sett, fabric weave, dimensions of fabric sample, number of fabric plies and their arrangement, etc. [11–14]. Therefore, it is impossible to single out any one factor as the controlling parameter of this process. For example, if the ballistic performance had depended solely on yarn toughness, then nylon would have been a better option against Kevlar. However, it is undoubtedly not true, as stated by Prosser *et al.* [15]. This calls for an explicit listing of all the involved parameters before investigating the role of an individual parameter. The fiber properties, yarn and fabric geometry, the pattern in which multiple

fabric layers are stacked in the panel, as well as the surface chemical modifications made to the fabrics together determine the structural response.

To precisely engineer a fabric for ballistic resistance, the first requirement is a profound understanding of the mechanisms of impact energy absorption at three levels: fiber, single ply of fabric, and multiple plies of fabric. It includes the generation and propagation of shock waves within the fibers of the yarns, in the fabric plane, as well as between fabric planes. Besides, the effect of fiber, yarn and fabric properties, and the contribution of surface chemical treatments also need to be understood thoroughly.

13.2.1.1 Propagation of Longitudinal and Transverse Waves

To begin at the fiber level, Smith *et al.* [16] proposed a 1D analytical model, according to which a ballistic impact generates two stress wave fronts: longitudinal wave and transverse wave (Figure 13.1), for the dissipation of energy. The longitudinal wave travels outward from the point of impact along the yarn axis at a constant velocity, causing stretching in the yarn and generating an in-plane movement. The velocity of this wave can be expressed as:

$$c = \sqrt{\frac{E}{\rho}} \quad (13.1)$$

where c is the longitudinal wave velocity (m/s), E is the Young's modulus of fiber at high strain rate (Pa), and ρ is the yarn bulk density (g/m^3).

Simultaneously, the projectile tends to deflect the yarn vertically by pushing it forward, thereby causing an out-of-plane motion of the fabric. In other words, as the transverse wave propagates outward from the point of impact, the yarns at the periphery tend to flow toward it [17].

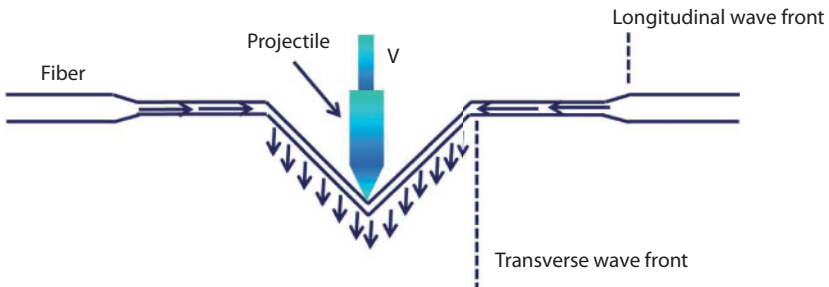


Figure 13.1 Wave propagation in a transversely impacted fiber [17].

The velocity of this transverse wave changes every time it interacts with a reflected wave, and can be expressed as:

$$u = c \sqrt{\frac{\epsilon}{1 + \epsilon}} \quad (13.2)$$

where u is the transverse velocity (m/s) and ϵ is the strain in yarn.

Both these waves sweep across the fabric and transfer the projectile energy to fabric strain energy and kinetic energy—the two principal energy absorption modes that may be expressed as follows [18]:

$$E_s = A t \epsilon^2 \sqrt{\frac{E^3}{\rho}} \quad (13.3)$$

$$E_k = A t \epsilon^2 \sqrt{\frac{E^3}{\rho}} \left(3 - 2 \sqrt{\frac{\epsilon}{1 + \epsilon}} \right) \quad (13.4)$$

where E_s is yarn strain energy, E_k is yarn kinetic energy, A is yarn cross section, and t is time after impact.

This stored energy continues to increase until the projectile is arrested or the fabric is penetrated. Yet another mode of energy absorption is friction, that is, the energy dissipated by friction between warp and weft yarns, between the projectile and fabric, and between adjacent fabric layers. Although their contribution to total energy absorption is very minimal, these frictional effects significantly influence the strain energy and the kinetic energy [19]. Numerous studies have been carried out to explore the significance of frictional coefficient of yarn during an event of ballistic impact [20–23].

The kinetic energy carried by the stress waves generated at the point of impact is dissipated through fiber deformation and interfiber friction when they slip or slide against each other. Fabric failure via yarn or fiber rupture (fiber deformation and fracture) also contributes considerably to impact energy absorption. It occurs when the strain in yarn or fiber exceeds their failure strain [24]. The mode of yarn/fiber rupture and the energy absorbed due to it are based on the inherent properties of the fiber. For example, it has been observed that p-aramids fail by fibrillation, whereas UHMWPE fibers fail due to shear or melt damage [25]. Another fabric failure mode having significant contribution in energy absorption is yarn pull-out, which is further dependent on inter-yarn friction [26–28].

Kirkwood and his colleagues [29, 30] developed a semi-empirical model to quantify the energy dissipated via yarn pull-out, considering yarn de-crimping and yarn translation as the two main mechanisms for energy dissipation. Several other researchers have investigated the role of fiber type, fabric structure, and testing parameters in determining the yarn pull-out behavior of high-performance fabrics [31–34].

Since fabric layers have a limited energy absorption capacity, it is necessary to develop different panel designs to stop a projectile whose kinetic energy exceeds the energy absorption limit of the armor. The undissipated energy is absorbed by each succeeding fabric layer until the projectile is eventually stopped from penetrating the armor panel completely [35, 36]. The absorbed energy of a projectile is propagated longitudinally on the fabric plane and the part of energy that cannot be absorbed causes trauma at a certain depth in vertical direction to the fabric plane, which might be fatal [37]. Both these phenomena are dependent on fiber and yarn properties and fabric construction. Considering the lack of quantitative understanding of energy absorption and the exact mechanisms involved in various target systems due to the complexity involved in projectile–armor interaction, investigations have been made for the same via both empirical and analytical approaches [37–43]. Apart from this, continuous efforts to establish numerical models for the prediction of ballistic performance of soft armor materials have also been made over the years [7, 22, 44–46].

13.2.2 Factors Influencing Fabric Ballistic Performance

A fabric armor panel is a system of subsystems spanning a multiscale of nanometres (polymer chains) to centimetres (multilayered panel), involving an interplay of numerous mechanisms. This being a broad concept, it is required to understand the failure mechanism from the perspective of fiber, to yarn, to single-ply fabric, to multiple-ply fabric systems and some 3D fabrics, and finally extend to STF-impregnated fabrics.

13.2.2.1 Fiber Properties

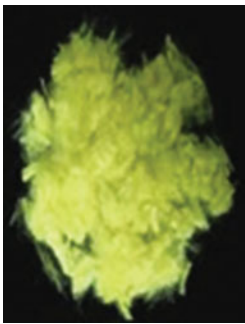
The speed of propagation of shock/stress wave formed on the fabric plane during ballistic impact depends on the energy absorption and propagation ability of fabric layers and, subsequently, on the fibers they are constituted of. It is evident from Equation 13.1 that the higher the Young's modulus of elasticity of the fiber and the lower the density of the fiber, the faster will the stress wave propagate through the yarns, as well as transmit quickly

to the adjacent yarns in the fabric through the crossover points. Thus, a higher number of yarns will be involved in the energy absorption process, consequently increasing the energy dissipation [47]. The performance attributes (strength, stiffness, toughness, environmental and chemical resistances, melting temperature, etc.) desired from a fiber for being used as ballistic-resistant materials are determined by the molecular structure of the polymer it is made of.

Innovations in manufacturing technology during the 20th century led to the discovery of high-performance synthetic fibers like nylon, fiberglass, p-aramids (Kevlar, Twaron, Technora, Nomex), and ultrahigh-molecular-weight polyethylene (Spectra, Dyneema) possessing high strength-to-weight ratio, which is the most essential property of a ballistic-protective material. Table 13.1 presents a list of popular high-performance fibers with relevant properties. Due to their unique molecular structure, aramid fibers exhibit outstanding high performance over old synthetic fibers, fulfilling the design requirements of a lightweight, flexible, and covert body armor. UHMWPE is a thermoplastic fiber composed of extremely long polymer chains that allow the material to transfer the load effectively. It has the lowest density among all the high-performance fibers and also retains higher specific strength and lower moisture absorption in comparison with aramids, thereby gaining ground as the most eligible candidate for the production of soft armor. McDaniel *et al.* [41] attempted to understand the effect of fiber meso/nanostructure on the mechanical response of Kevlar and Dyneema fibers and concluded that the latter is, in general, more compliant than the former due to weaker interfibrillar interactions. However, the inter-yarn friction in UHMWPE fabric is very minimal and is disadvantageous for ballistic applications. To overcome this, Chu *et al.* [49] proposed plasma-enhanced chemical vapor deposition (PCVD) as an effective technique for enhancing the friction between UHMWPE yarns, without causing any adverse effect on the mechanical properties of the fabric.

Moving on, PBO (polyphenylene benzobisoxazole) satisfies the physical requirements for ballistic applications, but its properties have been found to degrade on exposure to moisture owing to loosening of fiber morphology [50]. It also shows poor tensile retention properties in comparison to Kevlar, on being exposed to sunlight. Another high-performance fiber in the league, M5 or polyhydroquinone-imidazopyridine (PIPD) invented by the Dutch chemical firm AkzoNobel in the late 1990s, is a promising contender due to its superior mechanical properties to its forerunners. It is commercially unavailable as of now, and is still in the research and development stage [51].

Table 13.1 Typical properties of high-performance fibers [48].

Fiber class	Images	Specific fiber type	Density (g/cm ³)	Elastic modulus (GPa)	Tensile strength (GPa)	Strain to failure (%)
Glass		S-glass	2.48	90	4.4	5.7
Para-aramid		Technora	1.45	70	3	4.4
		Twaron	1.44	121	3.1	2.0
		Kevlar 29	1.44	70	2.96	4.2
		Kevlar 129	1.44	96	3.39	3.5
		Kevlar 49	1.44	113	2.96	2.6
		Kevlar KM2	1.44	70	3.3	4.0

UHMWPE		Spectra 900	0.97	73	2.4	2.8
		Spectra 1000	0.97	103	2.83	2.8
		Spectra 2000	0.97	124	3.84	3.0
		Dyneema	0.97	87	2.6	3.5
PBO		Zylon HM	1.56	270	5.8	2.5
PIPD		M5	1.70	271	3.9	1.4

13.2.2.2 Yarn Structure

The influence of yarn structure on the impact resistance performance mainly depends on the utilization efficiency of individual fibers. Cunniff [52] reported that the efficiency decreases while going from fiber to yarn, subsequently from yarn to fabric, and ultimately from single fabric to multilayer fabric assembly. This may be attributed to the fact that all fibers share different loads individually when they come in contact with a projectile, and thus, these fibers tend to break successively, rather than breaking together. Finer yarns, being capable of providing uniform load sharing due to higher fiber-to-fiber cohesion, are hence preferred over coarse yarns [53]. Moreover, yarns to be used for impact-resistant applications should have very low twist (maximum 7°) so as to achieve maximum strength and minimum yarn slippage. Twist angle higher than this adversely affects the tensile properties of yarn [54], as well as causes yarn slippage, making it more likely for the projectile to penetrate the space created between the yarns [55].

13.2.2.3 Yarn Friction

Another important parameter affecting the ballistic properties of a woven fabric is inter-yarn friction. Slippage between the yarns becomes difficult with the increase in frictional force between them. When a projectile penetrates a fabric woven with yarns having high coefficient of friction, it breaks the yarns and then tries to pass through the fabric. However, if the inter-yarn friction is low, the projectile pushes the primary yarns sideways (or away from the point of impact) and opens a way for itself, known as “wedge-through.” This causes less absorption of impact energy by the destroyed first layer, after which the projectile passes through successive fabric layers [37]. As illustrated in Figure 13.2, high inter-yarn friction causes less sliding away of yarns and offers more resistance to projectile, hence prolonging the time for penetration of projectile in that fabric layer.

Inter-yarn friction also controls the energy required to pull out a yarn from the fabric structure, which is also a significant source of energy dissipation during the failure mode of fabric [29, 30]. Duan *et al.* [56] concluded that the inter-yarn friction helps in maintaining the structural integrity of the fabric and hence allows more yarns in the periphery of the impact zone to participate in stress distribution. Both yarn strain energy and yarn kinetic energy are high for higher inter-yarn friction, thereby contributing indirectly to fabric energy absorption. Wang *et al.* [20] also reported that

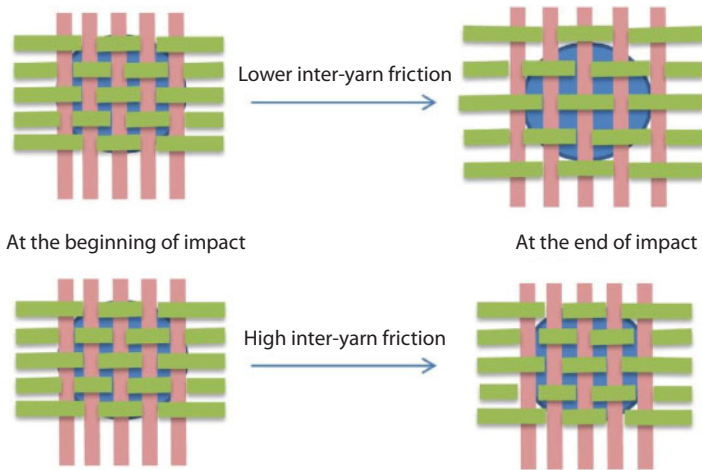


Figure 13.2 The sliding of primary yarns as a response to impact [23].

the fabrics with high inter-yarn friction take a longer time to reach their fracture strength.

Bazhenov [57] treated the yarn surface with colloidal silica to increase the inter-yarn friction and observed an improvement in the ballistic performance of fabrics woven from these yarns. Briscoe and Motamedi [58] showed that a moderate increase in inter-yarn friction, brought by oiling the fabrics at different levels, caused a significant change in ballistic performance by increasing the energy-propagating ability of the fabrics. The same was verified using a numerical model, where an increase in inter-yarn coefficient from 0 to 0.1 doubled the ballistic limit of the fabric [59]. However, further increase yielded little difference in the ballistic limit. Zhou [55] investigated the effect of inter-yarn friction on the fabric energy absorption and observed that the energy absorption for inter-yarn coefficient of friction $\mu = 0.4$ was almost 1 J higher than that for $\mu = 0$. Further increase in the value of μ led to a decrease in fabric energy absorption. This is similar to the finding of Zeng *et al.* [59], although the value of μ at which the highest ballistic performance was calculated in that study was 0.1. The deterioration of ballistic performance at very high coefficient of friction may be attributed to restrained yarn mobility and de-crimping, causing local stress concentration and, ultimately, early damage of primary yarns.

In another numerical investigation into the effect of inter-yarn friction on ballistic response of fabrics, Chu *et al.* [23] calculated the contribution of energy absorbed by the primary and secondary yarns to the total energy absorption by the fabric at varying levels of inter-yarn friction, the results

of which are depicted in Figure 13.3. They observed that with an increase in coefficient of static friction (CSF) and coefficient of kinetic friction (CKF), the secondary yarns dissipate more energy up to an optimum level that is determined by fiber type. However, primary yarns exhibit an opposite behavior. It was also noted that the proportion of energy absorbed by the secondary yarns is always greater than that of primary yarns. Also, at higher levels of inter-yarn friction, the diversion of stress wave propagation from primary to secondary yarns is accelerated. Thus, the overall energy absorption by the fabric increases with an increase in inter-yarn friction, below the optimum level of CSF and CKF, beyond which the stress diversion at points of interlacements (or crossovers) is not affected.

13.2.2.4 Fabric Structure

It is a well-established fact that woven fabric structures possess superior impact-resistant properties than nonwovens and knitted structures [13, 60]. As stated earlier in the previous sections, the flexible network of warp and weft contributes to energy absorption via several mechanisms like deformation and rupture of primary yarns, deformation of secondary yarns, friction between yarns, friction between yarns and projectile,

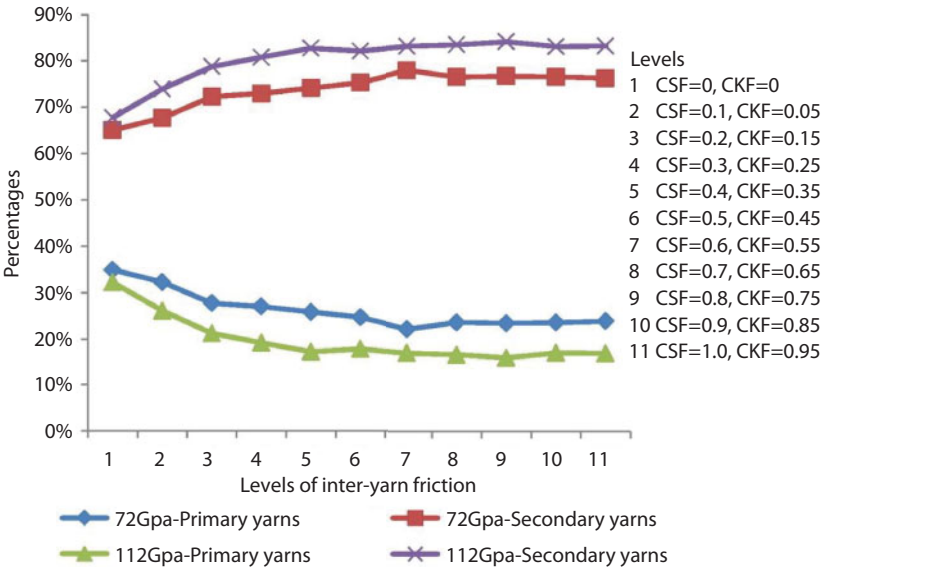


Figure 13.3 The proportion of energy dissipated by secondary yarns and primary yarns [23].

and formation of a dome [61]. It has been reported that square fabrics, that is, those possessing the same thread density and yarn linear density in warp and weft directions, exhibit better ballistic impact performance than unbalanced patterns for a constant fabric areal density [52, 62]. Yarn crimp, which is the waviness in yarn path generated due to interlacement of warp and weft during weaving, also has a significant role to play. When a projectile strikes a fabric, straightening of crimped yarns takes place in the initial stage of fabric deformation. This de-crimping of yarns reduces the modulus of the fabric during the first stage of tensile stretching [63]. Thus, projectile faces little resistance and negligible amount of energy absorption occurs. In other words, the fabric does not start providing protection until the yarns finish de-crimping and thereafter begin to stretch. As reported by Tan [64], this leads to excessive blunt trauma to the human body. Low level of yarn crimp leads to an increase in the fabric tensile modulus, and is hence preferable.

Woven fabrics are known to possess different crimp in warp and weft directions (Figure 13.4) owing to the dynamics of their manufacturing process. The weft yarns are stretched to break before the warp yarns because of lower crimp in the former. As a solution to this asymmetric deformation, Chitrangad [65] suggested preparing a hybrid fabric with balanced crimp degree by using yarns with higher tenacity or greater elongation rate in weft direction. This is expected to prolong the deformation of weft until the warp reach their failure point, thus improving the impact resistance performance of the fabric. However, new-generation fabrics are preferred to be woven with the same yarn type and thread density in warp and weft directions, so that equal warp and weft crimp produces equal deformation in both directions during a ballistic impact. This type of fabric construction leads to higher level of energy absorption [66].

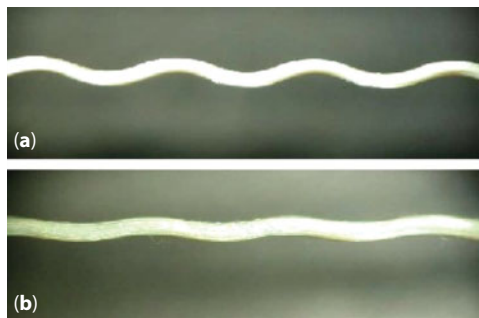


Figure 13.4 Microscopic view of level of crimp in (a) warp and (b) weft of a woven fabric [64].

For fabrics with the same level of yarn crimp, low yarn linear density and high fabric tightness are desirable to achieve enhancement in ballistic performance [67]. When a fabric is woven with high cover factor, the dissipation of strain energy is increased as more yarns tend to fall in the primary yarns zone (in direct engagement with the projectile). Also, a higher number of points of interlacements lead to the transmission of stress to a larger fabric area by involving a higher number of secondary yarns. The yarn pull-out force has also been reported to increase concomitantly with an increase in the fabric sett [33]. It has been reported that for ballistic applications, the cover factor should be between 0.6 and 0.95 [65]. In the case of cover factors greater than 0.9, yarn properties degrade at the time of weaving, whereas, for cover factors below 0.65, fabrics tend to be too loose. Loosely woven fabrics are prone to exhibit a wedge through effect, similar to what happens at a low level of inter-yarn friction, as discussed already in Section 13.2.2.3.

The cover factor of a woven fabric is further dependent on its weave pattern. Zhou [55] compared the specific energy absorption for UHMWPE fabrics of different weaves, namely, plain, 2/1 twill, 3/1 twill, and 7-end satin, via FE modeling and found plain weave to exhibit the best ballistic protection. It may be inferred from here that fabrics with longer floats, like satin weave, have less number of points of interlacements between warp and weft yarns. This restricts the transmission of energy from the primary yarns to the secondary ones, consequently leading to poor impact resistance performance. This superiority of plain weave over other weave patterns determined numerically has also been validated experimentally by other researchers as well [66, 68, 69].

It has been suggested by Roylance *et al.* [70] that a fabric capable of distributing the energy more equitably in all directions could give better ballistic performance. Triaxial fabrics, consisting of three sets of parallel threads intersecting at 60° , were considered to be one of the possible approaches to achieve that. Hearle *et al.* [71] compared the ballistic performance of biaxial and triaxial fabrics by determining the number of layers required to stop a bullet. They concluded that a triaxial fabric exhibits better performance due to the hexagon-shaped dome formed upon impact, in comparison to the pyramid-shaped dome formed in the case of a biaxial fabric (Figure 13.5), leading to more even spreading of energy around the impact zone. El Messiry and Eltahan *et al.* [72] found triaxially woven fabrics to perform better against stab resistance in comparison to plain woven and knitted fabrics owing to the superior structural integrity and mechanical properties of triaxial fabrics [73].

Moving further, unidirectional (UD) technology, wherein cross-plyed filaments are combined with an elastomeric matrix into a laminated system

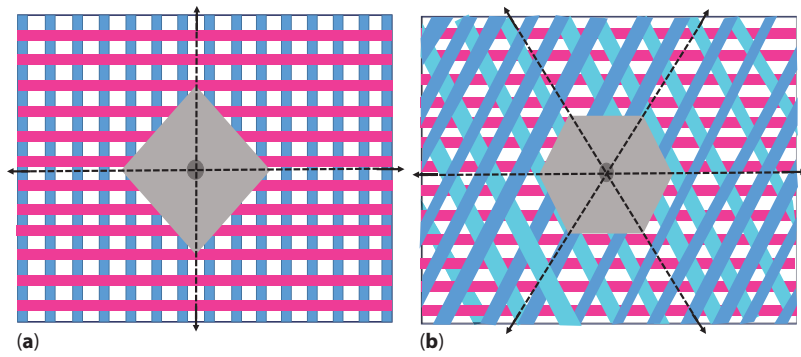


Figure 13.5 Two-dimensional representation of shapes of dome formed in (a) biaxial and (b) triaxial fabrics upon impact.

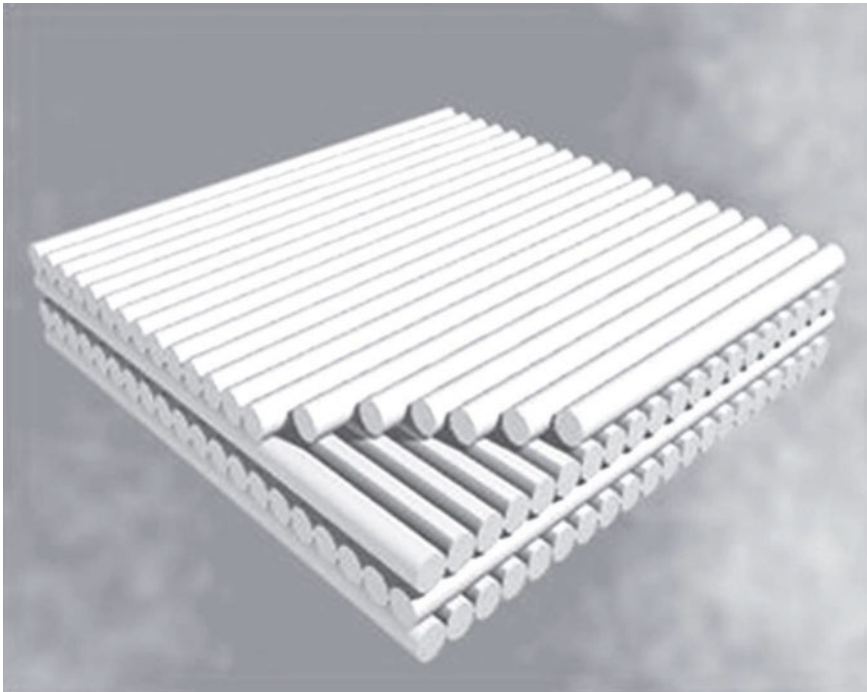


Figure 13.6 Schematic view of arrangement of cross-plyed filaments in a UD fabric/laminate [13].

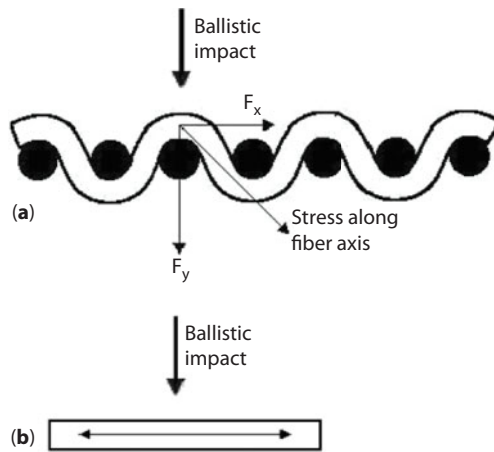


Figure 13.7 Impact load distribution in (a) woven fabric and (b) UD fabric [75].

(Figure 13.6), also provides a structure with equitable distribution of energy in all directions. Unlike woven fabrics, a unidirectional fabric is crimp-less, and the yarn profile is straight. Consequently, it does not exhibit the initial de-crimping phenomenon and thus the high modulus of the fiber is retained. The fibers react quicker due to laminate stiffness coupled with fiber stiffness and also spread energy to a greater extent. Also, due to the absence of crimp, a significant amount of impact stress is propagated on the fabric plane itself, as depicted in Figure 13.7. On the contrary, a woven structure is more compliant and leads to deeper blunt trauma because of prolonged fiber stretching and the propagation of impact stress in vertical direction also, other than in-plane [74]. The performance of unidirectional and cross-ply laminates has been compared with that of woven structures by numerous researchers [13, 75, 76], concluding superior performance of the former for the same areal density.

13.2.2.5 *Number of Layers*

It is well understood that a single layer of a high-performance woven fabric cannot suffice to make an efficient armor panel against a ballistic impact. Hence, multiple numbers of fabric layers are stacked one upon another and stitched to make a soft armor panel for real-life application. Numerous studies have been performed to investigate the performance of such multiply assemblies. It has been reported by Cunniff [52] that a spaced panel system exhibits better ballistic performance, as its impact energy absorption is exactly equal to the sum of the energy absorption of individual plies.

On the contrary, in a layered panel system (without space), the total energy absorbed by the panel is lesser than the sum of the energy absorbed by all the fabric layers in it. It was observed that less impact energy is absorbed in the layered systems of Kevlar, Spectra, and nylon armor panels in comparison to the spaced single-layer system. The deterioration in performance was believed to be a result of constrained transverse deflection of the front layer by the rear layers. It was thus concluded that the interference between layers prevents the stacked layers from achieving their maximum individual energy absorption capacities. The superiority of a spaced armor system over a layered system has also been reported by Lim *et al.* [77]. They also stated that at impact velocities below the ballistic limit of a single-ply, no benefit can be availed by additional plies. Novotny *et al.* [78] applied FE analysis to prove that the effect of layer spacing varies with the number of layers in a panel. The ballistic performance is considered to be insensitive to layer spacing up to 10 plies. However, for number of plies ranging from 20 to 50, the effect of layer spacing becomes prominent with the increase in the thickness of the panel.

Apart from all these parameters (discussed in Sections 13.2.2.1 to 13.2.2.5) that are intrinsic to the armor architecture, several other external parameters/factors related to testing techniques also affect the ballistic performance of the fabrics significantly. An extensive amount of work has been published for investigating the effect of such parameters: projectile parameters like projectile geometry, projectile impact velocity, impact angle, etc. [79–81]; sample mounting parameters such as sample dimensions, boundary conditions, pre-tensioning, etc., to name a few [82–85]. The conclusions derived from these studies should be borne in mind during the evaluation of the armor panels for ballistic resistance.

13.2.3 Significant Properties of STF

STF is a dense colloidal dispersion comprising of solid particles (silica, calcium carbonate, silicon carbide, etc.) in a dispersion liquid (water, polyethylene glycol, ethylene glycol, silicone oil, etc.). This special type of fluid exhibits non-Newtonian flow behavior, that is, with increase in shear rate or shear stress, it shows an abrupt increase in its viscosity [3]. Several researchers [86–94] have postulated various mechanisms of particle–media interaction in an STF system against increasing shear rate.

The pioneer theory explaining the physics behind shear thickening is the *order–disorder mechanism* proposed by Hoffman [86]. According to it, the particles in the suspension remain in an ordered form below a critical level of shear rate. However, beyond that level, the drag forces between the

particles increase, resulting in disruption of the ordered arrangement. This order-to-disorder transition causes abrupt increase in the viscosity of the STF system. This behavior has been established by both light scattering and shear rheology analysis [87]. However, there is a limitation associated with this theory, that is, for shear thickening (ST) to be possible, all the particles should primarily be well arranged in an ordered fashion at low shear rate and then start to disorder on increasing the shear rate. On the other hand, other elaborate studies [4, 5] suggest that ST can also occur without this order–disorder transition. Out of the numerous proposed theories, *hydroclustering mechanism* [3, 90] may be regarded as a convincing and acceptable approach for elucidation of the ST mechanism. According to it, the particles are in a state of continuous Brownian motion at equilibrium condition and hence remain at random positions, with persistent particle-to-particle repulsive forces. However, as an external shear force is applied on an STF-system, the particles align themselves along that shear force, thereby approaching toward an ordered structure and lowering its viscosity. On further increasing the shear rate, hydrodynamic lubrication forces arise among the particles and begin to dominate over the repulsive forces at a certain (critical) shear rate, causing clustering of particles. This disordered or jammed condition of particles alters the viscosity profile of the dispersion system, establishing the initiation of shear thickening with an abrupt increase in viscosity (Figure 13.8). This mechanism has been further supported by different high-end characterizing techniques, such as neutron scattering, shear rheology, and rheo-optical tests [91]. Recently, a new theory, *contact network rheology*, has been postulated for describing the mechanism behind ST phenomena [92–94]. According to this theory, ST is strong and stable when the interparticle contacts do not get to relax in the imposed shear time. It is to be noted here that the hydroclustering mechanism is applicable in case of low shear stress only. Melrose *et al.*

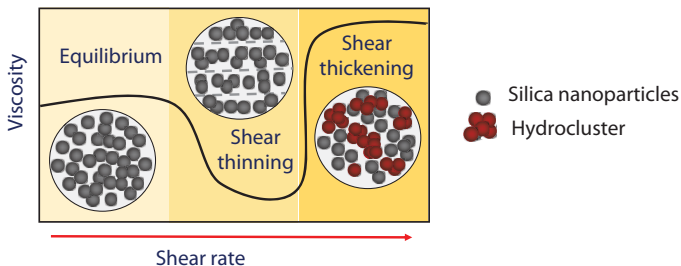


Figure 13.8 Basic hydrocluster mechanism of shear thickening fluid.

[95, 96] pointed that merely hydrodynamic effect can generate only mild thickening. To justify the strong shear thickening arising at high stress transmission, contact interactions need to be considered. In case of large-scale shear force, highly concentrated particles come in contact with each other and take longer time to relax than the applied shear time. As a result, they form stable contact network-based structures that increase the viscosity of the system. By means of numerical simulation based on contact theory, Pednekar *et al.* [97] established that not only the hydrodynamic lubrication forces but also the interparticle attractive forces responsible for keeping the particles in contact should be incorporated while simulating the ST phenomena. Moreover, the suspension concentration also plays a significant role as the possibility of interparticle contact is higher in a higher solid fraction system [98].

Generally, two rheological parameters of an STF are evaluated: peak or maximum viscosity and critical shear rate or onset of ST transition. Nowadays, some new parameters are also analyzed for the better understanding of the behavior of an STF. *Thickening ratio*, defined as the ratio of maximum viscosity beyond the thickening point to the viscosity at critical shear rate, helps determine the intensity of the thickening of the system. Besides this, *thickening period*, which is the difference between critical shear rate and the peak viscosity shear rate, also provides useful information [99]. Many researchers [100, 101] have also investigated the rheological performance of STFs in oscillatory mode for analyzing the interaction between different constituents of the system in terms of change in the storage and loss modulus with respect to angular frequency. Apart from this, large amplitude oscillatory shear rheology (LAOS) is another modern technique that is used for the investigation of the viscoelastic property of an STF system [102].

The performance of an STF can be determined on the basis of the aforementioned rheological parameters, which are further affected by several factors. Hasanzadeh *et al.* [103] have categorized these factors in three zones: particle parameters, dispersion media parameters, and the flow field/environment, as depicted in Figure 13.9. This section presents a thorough review of the parameter–property relationships governing the performance of an STF.

13.2.3.1 Particle Volume Fraction

Particle volume fraction may be defined as the fraction of solid particles in total volume of the colloidal dispersion, and is known to significantly

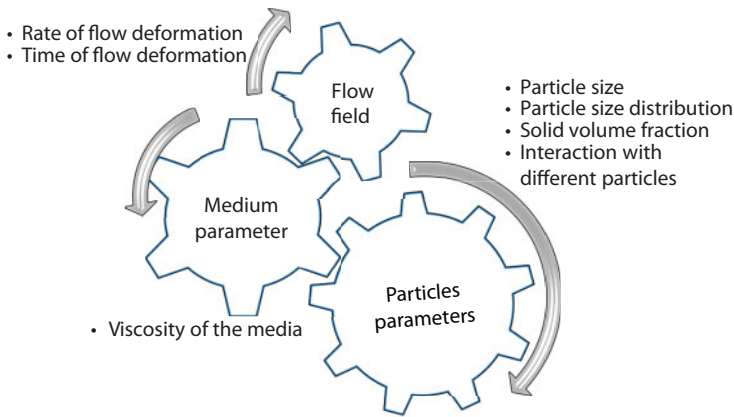


Figure 13.9 Parameters affecting the rheological performance of STF.

influence the ST phenomena. A threshold amount of volume fraction is necessary for triggering ST phenomena in the colloidal dispersion. Barnes [104] suggested that the minimum solid volume fraction required for the onset of thickening behavior is 0.5. In case of higher particle volume fraction, the movement of particles is hindered, resulting in higher peak viscosity of the STF. Additionally, as the particle volume fraction increases, the critical shear rate is shifted to lower magnitude. This may be explained by the hydroclustering theory, according to which the hydrodynamic lubrication force is inversely proportional to the interparticle distance [3]. A higher solid volume fraction implies higher number of particles and hence small interparticle distance, which further increases the hydrodynamic forces in the system, creating a favorable condition for the formation of hydroclusters. Thus, it may be interpreted from here that very minimal shear force is needed to overcome the particle–particle repulsion force in a high solid volume fraction system, thereby decreasing its critical shear rate. The contact networking theory also supports the same [93], as highly concentrated particles form a distinct contacted microstructure network that facilitates stress transfer within the system.

13.2.3.2 Particle Aspect Ratio

The aspect ratio of a particle, that is, the ratio between its length and breadth, is often exploited for tuning the properties of an STF. Particles with high aspect ratio are prone to show higher viscosity since they have

a higher tendency for interlocked jamming due to their long length. Also, the hydrodynamic stress is proportional to the cube of the dimensions of a hydrocluster [90]. As the clusters formed by linear (rod-like) particles are greater in dimensions than the ones formed by the spherical particles, the former will constitute a more efficient STF system. Wetzel [105] reported that it is possible to achieve prominent ST behavior even for lower solid volume fraction, with the help of high-aspect-ratio particles. They observed that high-aspect-ratio (7:1) CaCO_3 -based STF exhibited highest peak viscosity only at 0.35 solid volume fraction, whereas the lower-aspect-ratio (4:1) CaCO_3 -based STF was found to achieve that at 0.45 solid volume fraction. High-aspect-ratio rod-like particles can reach and entangle more particles within the system, facilitating the formation of strong hydroclusters [43]. Figure 13.10 summarizes the dependency of the rheological performance of an STF on the particle aspect ratio [104].

13.2.3.3 Particle Size

Particle size is another important factor affecting the rheological performance of an STF. Barnes [104] stated that the critical shear rate of shear thickening is inversely related to the square of particle radius. This may be linked with the Brownian repulsive forces existing between the particles. Owing to their large surface area, small-diameter particles exhibit stronger repulsive forces, necessitating the need for even more shear force to overpower them. As a consequence of this, the critical shear rate shifts to higher

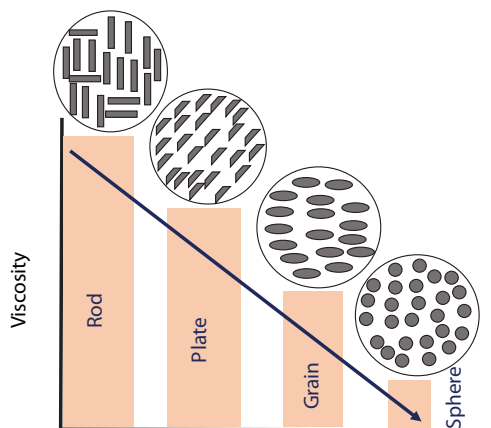


Figure 13.10 Effect of particle aspect ratio on viscosity.

values. On the other hand, larger-diameter particles exhibit less repulsive force, which can be overcome by less shear force, and hence low values of critical shear rate can attain that characteristic abrupt rise in viscosity required for ST behavior. Maranzano *et al.* [106] performed a theoretical analysis based on simplified two-particle force balance of the interparticle repulsive forces and the hydrodynamic compressive forces and established a similar relationship between critical shear rate and particle size.

13.2.3.4 Particle Size Distribution

Barnes [104] reported that wider particle size distribution led to the shifting of critical shear rate to higher magnitude. In this case, two clay particles of different sizes: 9 μm (A) and 0.7 μm (B), were added in different blend proportions such that the solid volume fraction of the suspension was maintained at 0.44. From the viscosity versus shear rate profile of the three blend compositions (0:100, 50:50, 85:15), as depicted in Figure 13.11, it may be concluded that only 100% B particles showed shear thickening phenomena at lower critical shear rate zone. In other words, blending of coarser particles in the suspension did not enhance the shear thickening phenomena and was rather detrimental. D'Haene and Mewis [107] studied the rheological behavior of concentrated colloidal dispersions composed of bimodal distributed particles and noted that replacing some large particles by smaller ones (at constant total solid volume fraction) resulted in a drastic decrease in the peak viscosity.

13.2.3.5 Particle-Particle Interactions

It has already been mentioned that particle-particle interactions play a major role in shear thickening phenomena [108]. Particles may remain in neutral condition or repel each other due to steric hindrance or an entropic effect. The deflocculated particles were found to exhibit shear thickening phenomena at higher shear rate whereas the flocculated ones showed shear thinning [104], as depicted in Figure 13.12.

13.2.3.6 Particle Hardness

On the basis of new contact network theory, particle hardness also influences the rheological performance of STF significantly. Kalman *et al.* [109] selected two types of particles: hard silica particles and relatively softer polymethyl methacrylate (PMMA) particles to investigate the effect

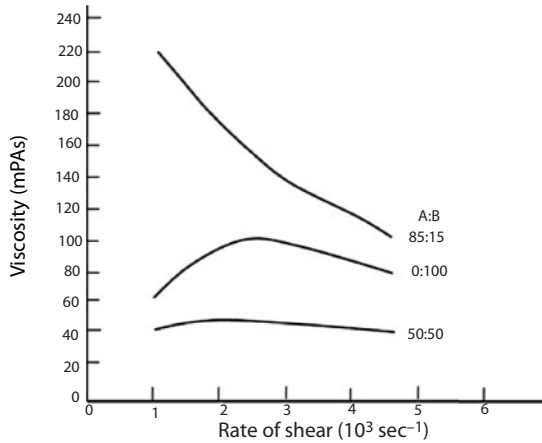


Figure 13.11 Effect of particle size distribution on shear thickening properties [104].

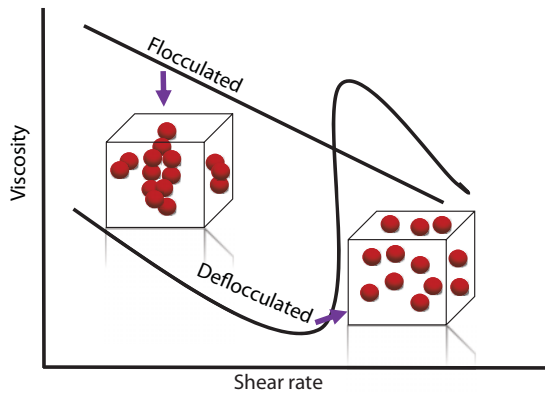


Figure 13.12 Schematic representation of interparticle interactions on STF performance.

of particle hardness on shear thickening phenomena. At higher shear rate, harder particles were found to perform better due to their superior mechanical properties. In the light of network rheology theory, microstructures are formed due to mechanical contacts between the particles at high shear rates. In case of softer particles, high shear stress generated at high shear rates causes deformation of the particles, ultimately affecting the stability of the hydroclusters such that the viscosity of the system is decreased. Recently, Jiang *et al.* [110] confirmed the same by tuning the

hardness of poly(styrene-acrylic acid) (PS-AA) nano-spheres dispersed in ethylene glycol, by changing the percentage of cross-linking between PS-AA nanospheres. A very small amount of cross-linker (0.3%) was able to alter the peak viscosity of the STF up to 385 Pa·s, as against 158 Pa·s of the non-cross-linked particle-based STF. Petel *et al.* [111] also worked in the same direction and concluded the same.

13.2.3.7 Particle Roughness

The particle-to-particle interactions are predominant in determining the properties of an STF, and are in turn affected by various factors, particle roughness being one of them. Feng *et al.* [112] conducted a comparative rheological study between smooth monodispersed spherical silica and rough fumed silica. The surface roughness was generated via a flame pyrolysis process, wherein amorphous silica fused into branched, chain-like, three-dimensional secondary particles, which further agglomerated into rough particles. It was seen that the fumed silica-based STF exhibited a prominent thickening at lower solid content. This could be attributed to stronger hydrocluster formation due to more contact points on its aggregated fractal structure, which also results in obstruction of dispersion media, and hence higher viscosity. Additionally, fumed silica-based STF exhibited low critical shear rate and higher peak viscosity owing to its higher effective solid volume fraction. Liu *et al.* [113] synthesized core shell silica-dopamine structures and established that the shear thickening effect of the STF prepared from them was much better than that of regular silica-PEG STF. They also speculated that the thick shell structure creates a rougher surface on particles, which increases the particle-to-particle frictional coefficient, thus increasing interparticle attraction forces, and subsequently creating favorable hydrocluster formation conditions.

13.2.3.8 Particle Modifications

The contact network rheology mainly focuses on the frictional contact between the particles, which is tailored by their surface properties. The modification of particles for enhanced performance of STF is in the limelight nowadays. Yu *et al.* [114] modified silica nanoparticles with ethylene glycol and noticed a decrease in the maximum viscosity, along with an increase in the critical shear rate. It was also found that the maximum solid content of the STF increased after surface modification, which could be attributed to the formation of three-dimensional aggregates between EG

and PEG through hydrogen bonding. This led to a decrease in the probability of flocculation of particles, which further resulted in accommodating higher particles in the STF. Hwang *et al.* [115] synthesized silica coated multiwalled carbon nanotubes and observed that even minute (3%) addition of this Si-MWNT in 65% pure silica-based STF brings a decrease in the critical shear rate. Simultaneously, the viscosity of the system increased considerably due to increased total solid content in the STF system. Joselin *et al.*, Li *et al.*, and Talreja *et al.* [116–118] carried out functionalization of silica particles with various silane agents, so as to achieve enhanced interaction between silica and PEG molecules in the STF prepared from them. Yang *et al.* [119] conducted an extensive study to analyze the role of surface chemistry of silica particles on the rheological performance of STF on the basis of contact network theory. Different kinds of silica nanoparticles were synthesized with different functional groups such as Si–O–Si bond, –OH, benzyl, alkyl, –NH₂, and oligoethyleneglycol methacrylate (OEGMA) polymer brushes and were found to exhibit either continuous or discontinuous shear thickening (CST or DST) based on the type of change in interparticle interaction (hydrogen bond interaction, van der Waals interaction, and π – π stacking effect) brought by that particular modification. This could be attributed to the change in critical solid fraction (ϕ_c), a major factor governing transition from CST to DST, as a result of surface modification. It was also concluded that the onset of shear stress is negatively correlated with the repulsive forces between the particles. Liu *et al.* [120] used PVP K30 as a rheology modifier and observed that modified SiO₂@PVP STF showed a dramatic enhancement in viscosity in comparison to the physically mixed SiO₂ and PVP-based STF. This may be due to enhanced interparticle interaction because of retention of chemically modified PVP molecules on the surface of particles, which was minimal in the case of physical mixing where a large number of PVP molecules remained in the dispersion media only.

13.2.3.9 Liquid Medium

Apart from the variables associated with silica particles, the properties of the dispersion media also affect the rheological performance of the STF system to a remarkable extent. The preliminary studies [105, 121] in this context were focused around exploring the significance of molecular weight of dispersion media using PEG-200, PEG-400, and PEG-600. It was thus established that longer molecules have a higher tendency to form entanglements between their free chains. Consequently, the Brownian

motion or the movement of the adjacent fluid layers with respect to each other is restricted, leading to interruption in the equilibrium state of the STF system, thereby increasing its viscosity and decreasing its critical shear rate [121]. Shenoy *et al.* [122] explained that an increase in the molecular weight of the media decreases the critical shear stress of the system, because of adsorption of the polymer chains on the surface of silica particles. Moriana *et al.* [123] investigated the difference between fumed silica-based STFs made from different carrier fluids (PPG-400 and PEG-400) and observed lowering of critical shear rate in the former one. They stated that owing to the smaller degree of polymerization of PPG, the solvation layer formed around the particles is affected such that the interparticle distance reduces, subsequently reducing the particle–particle repulsion forces that require less external shear force for the initiation of shear thickening. It was also suggested that the presence of a methyl branch on the molecular chain of PPG makes it rigid (to flow), because of which the interchain distance increases, consequently reducing the probability of chain entanglement and creating a favorable environment for the rearrangement of the microstructures under shear flow.

13.2.3.10 *Effect of Temperature*

It is well understood that temperature is one of the most important variables governing the viscosity of any fluid system. The general decrement observed in viscosity upon increase in temperature occurs due to the breaking of hydrogen bonds between particles and liquid media.

High temperature actually retards the initiation of shear thickening by increasing the Brownian motion between all the constituents of the STF [124]. It is also reported that high temperature causes an extension of the thickening period and reduction in the thickening ratio [125]. At high temperature, the interparticle repulsive forces become dominant due to an increase in the Brownian motion of the particles. Therefore, more shear force is needed to overcome it for stimulating the formation of hydrocluster with actuation of hydrodynamic force. As a result, the critical shear rate of the system increases. Besides, the solvation layers (Figure 13.13) over the particle surface are depleted with the increase in temperature, which further disrupts the thickening behavior of the system due to increased interparticle distance, as well as due to insufficient hydrodynamic force being exerted by the particles with disturbed hydrodynamic diameter [126]. Moreover, at higher temperature, the intrinsic viscosity of the media decreases due to opening up of chain entanglements of the carrier/

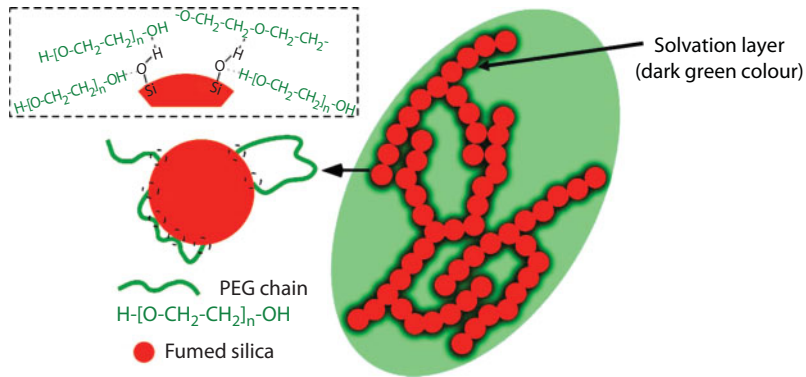


Figure 13.13 Schematic view of hydrocluster formed by the interaction between fumed silica and solvation layer of liquid PEG media [126].

dispersion fluid. Hence, the dominant interparticle repulsive forces in less viscous carrier fluid delay the formation of hydroclusters at high shear rate. On the basis of contact rheology theory, as the interparticle distance increases, contact network formation becomes difficult, causing deviation in the ST phenomena.

13.2.4 Interaction of Fabric and STF

Having discussed the individual responses of fabric structure and the STF system to impact or high shear force, it is now important to have an insight into the ballistic response of an STF-impregnated fabric. It is to be noted here that the fabric layers of a soft body armor are treated with STF in such a manner that the nanosized particles of silica oxide, along with its carrier fluid (usually PEG-200), are incorporated deep into the interstices of the fabric structure. In other words, the STF system resides all over, on the surface of filaments in the multifilament yarns. As discussed in Section 13.2.3, on application of high shear force, an STF system shows a drastic increase in its viscosity, changing its state from liquid to solid due to the formation of hydroclusters. It is this characteristic feature of STF that is exploited in impact energy absorption applications. Upon ballistic impact, the STF particles residing on the surface of yarns experience a shear force due to the relative movement of yarns with respect to each other. This shear force is sufficient enough to cause hydroclustering, as shown in Figure 13.14. Besides, the STF acts like a bonding material and causes the entire fabric to participate in energy dissipation, rather than only the impact zone.

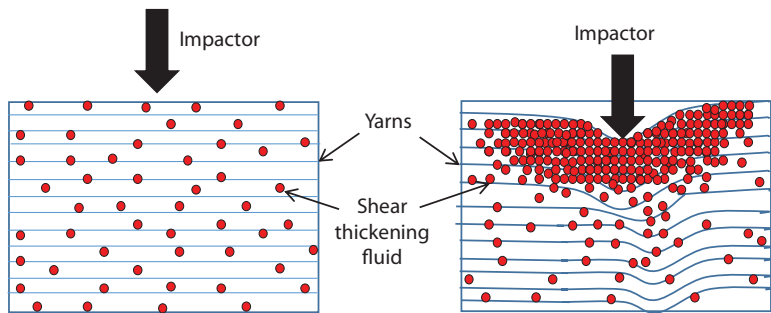


Figure 13.14 Schematic representation of STF–fabric interaction before and after impact.

According to Srivastava *et al.* [10], STF impregnation contributes to impact energy absorption by a fabric in three ways:

- a. Energy dissipation due to STF
- b. Increased yarn-to-yarn friction
- c. Better coupling and load transfer between fibers and yarns

Besides the experimental confirmation of enhancement of impact resistance with the application of STF, numerical investigation of the same has also been performed. Park *et al.* [127] explored the ballistic response of STF-treated Kevlar fabric in LS-DYNA assuming the coefficient of friction value of silica nanoparticles instead of the coefficient of friction of Kevlar as used in neat fabric, and confirmed that STF impregnation has a positive effect. Lee *et al.* [128] implemented a computational model using the experimental data of yarn pull-out tests in order to characterize the frictional response of an STF-impregnated high-tenacity fabric. Similar numerical analysis have been reported by Mirrahimi *et al.* [129], Lu *et al.* [130], and Khodadadi *et al.* [46] as well.

13.3 Performance Evaluation of Materials

When a person wearing a body armor is hit by a projectile, there are two possibilities: penetration of the projectile, which is often fatal, and non-penetration injury to internal organs caused by the deformation of armor, generally termed as blunt trauma. Thus, it is extremely essential to evaluate any material fabricated to be used in ballistic applications, for its response to an impact. Since the projectile–armor interaction is a complex dynamic

phenomenon, several approaches are used, individually or in combination, to gauge the efficacy of an armor panel against a ballistic impact:

- a. Analytical approach
- b. Semi-empirical and empirical approach
- c. Numerical approach
- d. Experimental approach

13.3.1 Analytical Approach

This method relies on general continuum mechanics equations and laws, like the conservation of energy and momentum. A set of different parameters involved during the impact process are utilized to formulate the governing equations for the prediction of failure mechanism. The drawback of this approach lies in the complexity that arrives with increasing number of variables. Several research groups have worked in this respect [16, 38–40, 43, 61, 131, 132] and have obtained satisfactory success, yet there is a lot of scope to further improve these models.

13.3.2 Semi-Empirical and Empirical Approach

Empirical studies involve examining the fabric response and obtaining constitutive relationships and failure criterion based on the analysis of data obtained through experimental work. Techniques like curve fitting, non-linear regression analysis of experimental data, and statistical distributions are put into use. The method is effective only for a small set of variables. Besides, its accuracy is also dependent on the accuracy of the experimental data obtained [42, 133, 134].

13.3.3 Numerical Approach

This approach is based on techniques like finite element and finite difference methods. With the advent of supercomputing, commercial finite element packages, like ABAQUS, DYNA3D, and LSDYNA for conducting analysis or simulation, are becoming popular owing to their low cost, against the conventional expensive and destructive experiments. Finite element packages also allow using user-defined material models instead of standard material models, and hence provide a means to test newer theories based on numerical solutions. Moreover, FE codes have been proven to be capable of handling the complex projectile–fabric interactions, inter-yarn friction, and woven fabric deformation and failure [22, 135, 136].

Most of the available literature focuses on experimental and theoretical analysis of a single fabric layer. However, the real complexity arrives when the number of fabric plies increase (as in an armor panel), since new energy dissipation mechanisms, as well as increased interactions between different plies of the fabric and between the target and projectile, have to be taken into account. Some studies to simulate the ballistic impact on armor manufactured out of multiple identical layers of fabric also have been conducted [78, 137]. Very limited numerical investigation has been done for ballistic impact on hybrid armor panels composed of fabric layers woven from different fibers [138, 139], or with fabric layers stacked at different angles to warp axis [140]. Attempts have also been made for the numerical analysis of the ballistic impact behavior of 3D orthogonal interlock [21] and angle interlock woven fabrics [141].

13.3.4 Experimental Approach

To validate the aforementioned theoretical concepts, it is required to obtain experimental data for parameters like amount of impact energy absorbed, yarn pull-out force, residual velocity of the projectile, etc., which is possible via practical experiments only. Experimental analysis gives a hands-on experience to investigate the individual and combined effect of various parameters on the ballistic response of developed armor materials, and might as well reveal some new mechanisms of energy absorption and failure. The conventional techniques used by several researchers for the performance evaluation of a ballistic impact-resistant material include determination of V_{50} and residual velocity, back face signature or blunt trauma assessment, high-speed photography, dynamic impact test, yarn pull-out test, etc. [10, 26, 37, 62].

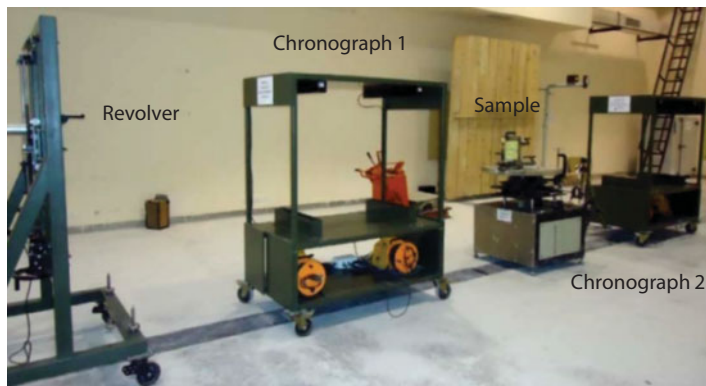
Before understanding the details of these methods, it is important to note that the judgment of the efficacy of the materials tested by these methods is based on the criteria laid down by some established standards, of which the National Institute of Justice (NIJ), U.S.A. 0101.06 (2005) is the most popular. As explained in Table 13.2, body armor has been categorized on the basis of different parameters of the projectile. A soft body armor should be capable of providing protection against threats up to level III A [142]. The methods of performance evaluation via experimental techniques are explained hereafter.

13.3.4.1 Ballistic Energy Absorption Assessment

For ballistic evaluation of an armor material, the test assembly is composed of a weapon mounted on a stand, a material clamping setup, and

Table 13.2 The NIJ Standard 0101.06 performance test summary [142].

Armour type	Test bullet	Bullet weight (g)	Reference velocity (m/s)	BFS depth (max mm)	Bullet	Weapon
IIA	9 mm FMJ RN	8.0	373 ± 9.1	44		
	.40 S&W FMJ	11.7	352 ± 9.1	44		
II	9 mm FMJ RN	8.0	398 ± 9.1	44		
	.357 MAG JSP	10.2	436 ± 9.1	44		
IIIA	.357 SIG FMJ	8.1	448 ± 9.1	44		
	.44 MAG SJHP	15.6	436 ± 9.1	44		
III	7.62 mm FMJ	9.6	847 ± 9.1	44		
IV	.30 CALIBER M2AP	10.8	878 ± 9.1	44		

**Figure 13.15** Experimental setup for ballistic evaluation [143].

two chronographs (for projectile velocity measurement), arranged as depicted in Figure 13.15. Here, the projectile or bullet passes through the first chronograph before striking the fabric surface, and thereafter through the second chronograph, placed just behind the fabric sample. In the cases where the projectile perforates through the test material, the impact energy absorbed may be considered as the kinetic energy lost by the projectile,

and is calculated using its strike and residual velocities as represented by Equation 13.5:

$$\Delta E = \frac{1}{2} m (v_i^2 - v_r^2) \quad (13.5)$$

where ΔE is the projectile energy loss, m is the mass of the projectile, v_i is the initial/strike velocity, and v_r is the residual velocity of the projectile.

13.3.5 Ballistic Limit or V_{50} Test

V_{50} is defined as the average of an equal number of maximum partial penetration velocities and the minimum complete penetration velocities that occur within a definite velocity speed. In other words, it is the incident impact velocity at which there is 50% probability of partial penetration and 50% probability of non-perforation [144]. The test setup required for this test is the same as that used in residual velocity assessment (Figure 13.15). A minimum of two each, partial and complete penetration velocities are essential to determine the V_{50} . Generally, 4 or 6 or 10 rounds are fired [145].

13.3.6 Back Face Signature or Blunt Trauma Assessment

This test is conducted for non-perforating conditions so as to estimate the extent of deformation on the rear face of the panel. The significance of this assessment lies in the fact that the blunt trauma caused by this panel deformation might prove to be dangerous for internal organs, if its dimensions exceed the limits mentioned in the established standards (NIJ standard = 44 mm). Here, the test material is backed with a resilient material (usually oil based clay) simulating the human body. Upon impact, a pit representative of blunt trauma is formed in the clay-backing in the transverse direction of the panel, as demonstrated schematically in Figure 13.16. The depth and diameter of the pit should be measured after each test. Besides blunt trauma assessment, the information obtained from this test also helps in the determination of the number of layers of fabrics required to stop a projectile of known mass and velocity.

13.3.7 Yarn Pull-Out Test

The significance of inter-yarn friction in governing the ballistic response of a fabric material has been elaborated in Section 13.2.2.3. Yarn pull-out test allows the estimation of the level of inter-yarn friction in a woven fabric

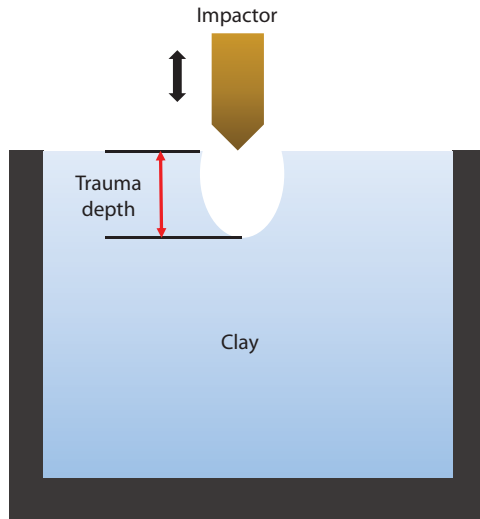


Figure 13.16 Schematic arrangement for back face signature assessment.

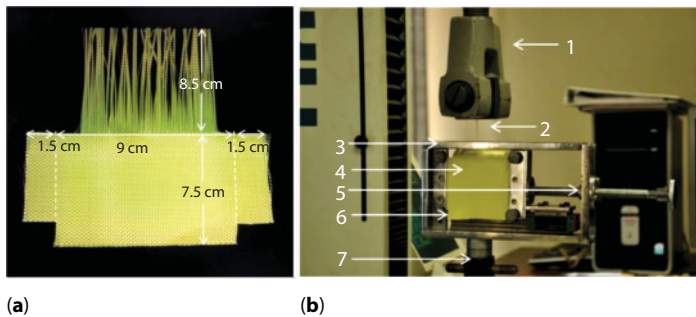


Figure 13.17 (a) Sample dimension of yarn pull-out test; (b) yarn pull-out experimental setup: 1, movable jaw; 2, yarn to be pulled; 3, frame; 4, fabric sample; 5, adjustable screw; 6, fastener (to fix fabric); 7, clamp holder [33].

sample. In this procedure, one/some yarns at the center of the fabric are gripped by the upper jaw of the tensile testing instrument, and the lower part of the fabric is clamped at its edges by a specially fabricated jaw. Such an arrangement facilitates pulling of the yarn(s) by the upper jaw without distorting the fabric sample. Majumdar *et al.* [33] have described both the sample preparation technique and the experimental setup by a photographic view (Figure 13.17). The yarns are pulled at a set traverse rate, and the force required to pull them out of the fabric is measured. This information is useful in comparing the level of inter-yarn friction between different

fabric samples, such that higher yarn pull-out force corresponds to higher inter-yarn friction.

13.4 Advancements in Soft Body Armor Technology

From the use of nylon flak jackets to UHMWPE fabrics for making soft body armor, researchers have never stopped seeking for the better. As of today, there are still many issues that need to be addressed in bringing advancements in the soft body armor technology. It is required to obtain maximum possible reduction in the mass and thickness of the armor panel by reducing the number of fabric layers used. This is being tried to achieve through the production of *hybrid panels*, as well as by seeking further enhancement in the rheological performance of STF through *multi-phase STF systems*. It is also required to improve the structural integrity of the multi-ply panel system, without compromising its flexibility. This may be accomplished by using *three-dimensional (3D) fabrics*. This section will present a review on the work done in these areas.

13.4.1 Hybrid Armor Panels

Body armor is traditionally manufactured by stacking numerous woven fabric layers having a resultant weight of 4 to 5 kg [146]. Several studies have been conducted on the multilayered panels composed of identical fabric layers to be used as ballistic resistant materials [52, 147–149]. However, it has been reported by many [40, 78, 150], that the projectile velocity slows down progressively while perforating the successive fabric layers in a panel. This indicates that the impact from the projectile, as well as the response to it, varies between the fabric layers within a panel. It has also been reported that the total energy absorbed by a panel is lesser than the sum of energy absorbed by all the fabric layers in it [78]. Moreover, with the increase in the number of layers, the growth rate of strain energy absorption in the successive fabric layer decreases [151]. Karahan [75] claimed that in the case of the non-perforating projectile, a significant amount of the total energy absorption in an armor panel is absorbed by the front layers, whereas the reverse happens in the case of a perforating projectile. The same was proven with the help of FE analysis by Joo and Kang [152, 153]. All these findings confirm that the ballistic response by each layer in the panel is different and varies with its position. Thus, using the same material for all layers in a panel is obviously not the most rational solution to achieve maximum ballistic resistance and reduction in

panel weight. Hence, judiciously arranging multiple fabric plies of different characteristics is key to ensuring the best use of their corresponding properties and thus enables the ballistic panel to absorb maximum impact energy [154].

To engineer a hybrid armor panel, the ballistic responses of each layer in a panel need to be understood thoroughly. It is believed that the fabrics near the impact face are prone to be sheared to failure, whereas those near the back face tend to undergo tensile failure [11, 155]. Therefore, using shear-damage-resistant materials near the impact face and tensile-damage-resistant materials near the back face should be advantageous. This has been validated both experimentally and numerically by Chen *et al.* [43]. Zhou [55] reported that UHMWPE woven fabric is more resistant to shear failure, and UD fabric gives higher resistance to tensile failure. Based on this fact, he further investigated the ballistic performance of the hybrid panels designed by mixing the two materials in various sequences, and confirmed that placing UD material in rear layers and UHMWPE woven fabrics in the front layer led to superior ballistic performance compared to the panels designed in the opposite sequence. This improvement also allows reduction in the weight of the armor because of usage of less material. In another study by Wilusz [156], hybrid panels created using both UD fabrics and woven fabrics showed better performance over single-phase aramid filament layer-up panels, on the basis of back face signature assessment. Cunniff [52] suggested that the fabrics near the rear face may impede the transverse deflection of the fabrics on the front face and hence proposed placing low-modulus materials on the front face and high-modulus fabrics as subsequent plies. Porwal and Phoenix [132, 157, 158] attempted to develop theoretical and computational models to understand the effects of stacking sequence on the V_{50} velocity of flexible hybrid armor systems. Several other attempts to model the ballistic-resistant efficiency of individual layers in armor panels have been made so as to further understand the energy absorption and failure modes of the panels [40, 159, 160].

Yet another interesting pattern of fabric stacking to improve the ballistic performance of an armor panel involves playing with ply orientation. Wang *et al.* [140, 150] have reported that the ply orientations significantly affect the ballistic performance of a multi-ply armor panel. Plain woven fabric panels were stacked in different patterns with respect to their laying angle, so as to construct quasi-isotropic panels as depicted in Figure 13.18. Considerable improvement in the amount of energy absorbed by quasi-isotropic panels with angled plies, in comparison to their conventional aligned (or orthotropic) counterparts, was observed in ballistic testing. The panel $[0/22.5/45/67.5]_2$, with the highest level of quasi-isotropy, showed

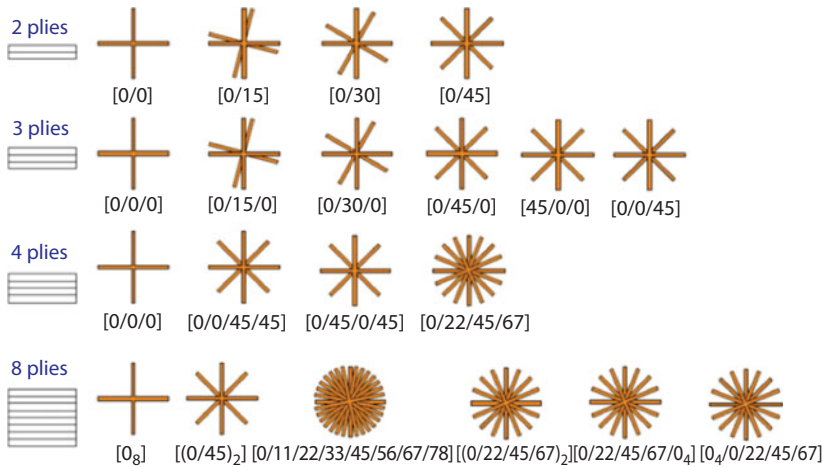


Figure 13.18 Schematic representation of quasi-tropic arrangement of fabric panels with different numbers of plies [150].

maximum ballistic resistance. Moreover, the difference in the stacking sequence of the angled plies also caused a difference in the impact energy absorption. Thus, it may be inferred that for a large number of plies, an optimized stacking sequence can bring significant improvement in the ballistic performance at a substantial lower weight than an aligned panel made with the same number of layers [13, 161].

13.4.2 3D Fabrics

Conventionally, two-dimensional (2D) plain woven or UD fabrics are considered to be the most favorable materials for manufacturing both soft armor panels and hard composite panels. Both exhibit considerably good mechanical properties and can be produced at low cost.

Nevertheless, there are certain drawbacks associated with them like poor layer-to-layer stress transfer, poor interlaminar shear strength, and poor structural integrity of the panel assembly upon ballistic impact, as well as the requirement of a large number of layers to be stitched together and subsequent creation of weak spots at stitching points, among others [13, 162]. As a solution to these problems, 3D orthogonal and interlock fabrics have come up as new promising materials for designing soft armor panels, attributed to their numerous advantages over 2D and UD fabrics [163, 164]. They exhibit higher strength, higher through-the-thickness, and interlaminar properties owing to their integrated structure,

and do not require extra stitching processes [165, 166]. A 3D woven fabric is composed of three systems of mutually perpendicular yarns, against two systems in conventional 2D woven fabrics. The stuffer warp yarns and weft yarns are interconnected by binder warp yarns that move in the Z or vertical direction. Figure 13.19 gives a schematic representation of three types of 3D structures: orthogonal, angle interlock, and warp interlock, so as to have an insight into the kind of interlacement between different systems of yarns in a 3D weave.

The stuffer warp yarns remain straight and contribute to the tensile strength in that direction to their maximum potential [168]. The binding warp yarns interlace between layers in the Z direction and contribute to the strength in the thickness direction by imparting the structure an inherent capability to dissipate the impact energy over a larger area, while maintaining the structural integrity [169]. David *et al.* [8] explained that the 3D architecture causes the impact load to be resolved in three directions (longitudinal, transverse, and vertical) rather than just two, hence enhancing the energy absorption capacity.

Composites made using 3D woven fabrics have been found to outperform 2D laminates [170]. Bandaru *et al.* [171] compared the mechanical response of 2D plain woven and 3D angle interlock fabrics for low-velocity impact, with an intention to predict their performance on being transformed into composite laminates. Plenty of literature is available for the application of 3D woven fabrics as substrates for composites to be used as hard body armor [13, 14, 172–174]. However, relatively less amount of work on using 3D woven fabrics as soft armor material has been done as

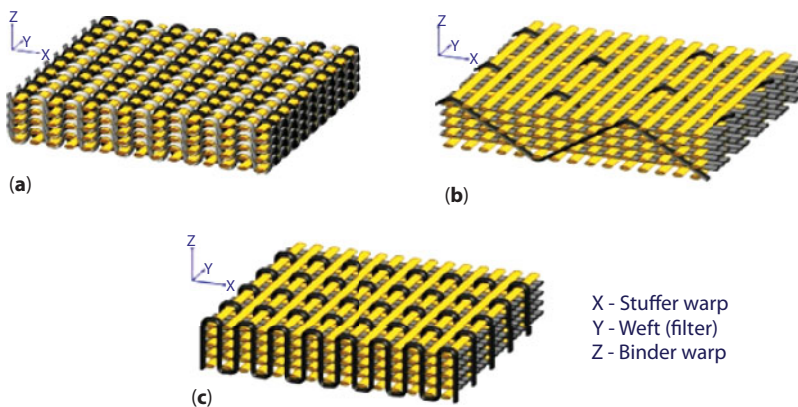


Figure 13.19 3D weave patterns: (a) orthogonal, (b) angle interlock, and (c) warp interlock [167].

yet. Shi *et al.* [175] stated that the non-crimp feature of both warp and weft in the orthogonal structure imparts highest energy absorption among all 3D structures.

With the increasing number of women in the military services, there has been an increasing demand for well-fit female armor. The conventional techniques used for designing female body armor are based on cut-and-sew, fabric folding, and stretch-molding of 2D high-performance fabrics and have several drawbacks associated with them. Chen *et al.* [176] have proposed angle interlock fabrics for making seamless front female body armor panels, owing to their good formability and moldability, and have also validated the same [141].

Moving further, a major accomplishment in this arena has been made by Majumdar *et al.* [143] by optimizing the structure of 3D woven orthogonal fabrics, and their subsequent reinforcement with shear thickening fluid for the development of soft armor material complying with the NIJ IIIA threat level. Fabric panels composed of neat and STF-impregnated 3D fabrics having a stuffer-to-binder ratio of 3:1 or 4:1, along with Kevlar XP sheets, were found to stop all the bullets fired at a velocity of 430 m/s, with depth of back face signature within 31 to 39 mm (less than the NIJ standard of 44 mm).

13.4.3 Multiphase STF Systems

A multiphase STF system refers to a single-phase STF in combination with different types of additives, namely, ceramic particles, metal nanoparticles, nanotubes, nanowires, etc., and is known to exhibit superior properties over its virgin/unmodified counterpart [100, 101, 177–185]. It has recently been reported to find extensive application in the development of soft body armor owing to its potential to remarkably increase its impact energy absorption capacity [177, 180]. This section will focus on both rheological and ballistic performance of multiphase STFs.

The pioneers in this arena were Wagner and Wetzel [177] who reinforced STF via blending with short and inert filler fibers, and observed changes in properties like *load transfer* and *tensile strength* of the STF. As already discussed in Section 13.2.3.2, particles with higher aspect ratio have a greater tendency to form hydroclusters owing to the presence of more contact points. Thus, addition of fibrous entities in an STF system is expected to promote hydrosclustering, as depicted in Figure 13.20. Wagner and Wetzel also claimed that addition of different high-performance fibers, chopped to a length of less than 1 cm, improves the stress transfer of prepared STF

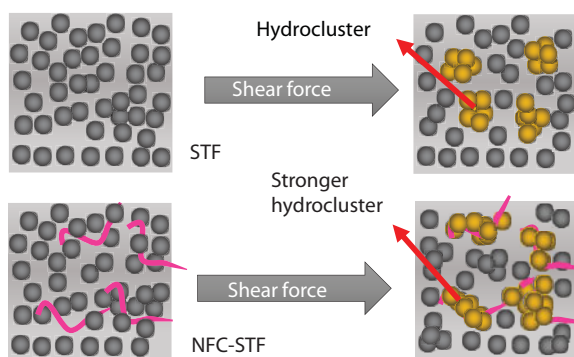


Figure 13.20 Scheme of STF mechanism in the presence of nano-fibrillated cellulose.

upon impact, due to high modulus and stiffness of the additional fibers. As a result, these STFs are anticipated to have significant performance in ballistics-, puncture-, and shock-resistant materials.

Ghosh *et al.* [178] took a step further in this direction and analyzed the influence of surface $-OH$ groups of cellulose nanofiber (CNF) fillers on the rheology of silica-based STFs in both steady and dynamic states. They reported that upon addition of a miniscule amount of CNF (0.2%) in STF, the peak viscosity increased from 36.8 Pa·s to 139.0 Pa·s. Also, the critical shear rate of the system shifted to a lower level, owing to higher interaction between CNF and silica particles. CNFs with high aspect ratio form entangled microstructures with a large number of hydroxyl groups ($-OH$) present on the surface of CNF. These $-OH$ groups take part in the formation of hydrogen bonds in the system. Thus, CNFs interact more with silica particles and among themselves, leading to decrease in distance between particles and the entangled network of nanofibers, which subsequently opposes the flow behavior and causes shear thickening at lower shear rate, and with higher peak viscosity.

In many studies [179, 180], addition of halloysite nanotubes (HNTs), naturally occurring aluminosilicate nanotubes, to STF has also been explored extensively. Passey [179] investigated the performance of HNT-reinforced silica-based STFs and observed an unexpected diminution in the ST behavior that was attributed to the strong hydrogen bonding of micro-sized HNTs and fumed silica being unaffected by other external forces like Brownian forces, stochastic forces, etc. On application of shear force, the hydrodynamic forces dominate over other forces, following which the nanotubes align themselves along the flow in an organized fashion. Further

increase in shear force triggers the formation of hydroclusters, whose extension is, however, hindered by the HNTs, consequently vanishing the thickening performance of the STF. On the contrary, Laha *et al.* [180] have reported that the introduction of HNTs to STF reduces the critical shear rate and increases the peak viscosity to a considerable extent. In order to understand the contribution of HNTs toward enhancement of ST mechanism, a hypothetical analysis was also performed to calculate the distance to be travelled by silica nanoparticles for hydrocluster formation in both single-phase and multiphase STF systems, that was found to be shorter in the latter case. This study was not limited to just rheological analysis, but also involved investigation of impact resistance performance of Kevlar fabrics impregnated with these STFs, wherein 40%–50% increment in impact energy absorption was observed in the case of fabrics treated with the HNT-Si STF system.

A similar study was carried out by Hasanzadeh *et al.* [100, 101] by preparing STFs using multiwalled nanotubes (MWNTs) in varying concentrations: 0.4%, 0.8%, and 1.2% of silica. Steady-state and dynamic-state rheological analysis of these STFs revealed that little amount of MWNT disrupted the ST phenomena, by retarding the initiation of thickening and further showing a lower thickening ratio. This unusual behavior of multiphase STFs has been explained on the basis of difference in the strength of hydrogen bonding among silica, PEG, and MWNTs. The bonding between MWNT and PEG is stronger than that between MWNT and silica; thus, more shear force is required to overcome it so as to initiate the formation of hydroclusters, thus increasing the shear rate. Further, the puncture resistance performance of HMPP fabrics treated with these STFs demonstrated considerable increase in peak load and energy absorption, in the case of single-phase STF. However, for multiphase MWNT-loaded STFs, relatively less improvement was observed due to the adverse effect on ST behavior as already noted in rheological analysis.

Very recently, Tan *et al.* [181] reported a significant increase in the viscosity of silica-based STFs after addition of SiC nanowires up to an optimum concentration, beyond which an unstable chain of nanoparticles is created. The dynamic response of pure and SiC-reinforced STFs was also analyzed by the split Hopkinson pressure bar (SHPB) mechanism, which revealed that a limiting value of flow stress always comes into play in a traditional nanoparticle-based STF system at high strain rates due to the dominance of lubrication forces. This may be overcome by the addition of SiC nanowires that hinder the flow of nanoparticles (Figure 13.21), thereby increasing the shear stress significantly, indicating the usability of multiphase STFs for applications involving large dynamic loading [182].

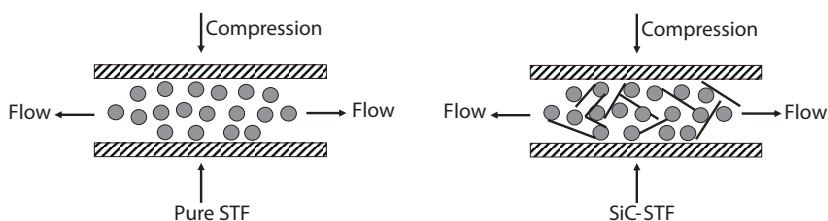


Figure 13.21 Schematic representation of STF with and without SiC nanowires.

Other than the long additive molecules discussed as yet, some studies have also been carried out with different oxide and carbide particles. Huang *et al.* [183] observed considerable enhancement in the ST behavior of multiphase STF systems prepared with varying concentrations of graphene oxide (GO) nanoparticles from 0% to 0.3% of net 15% solid volume fraction. The sheet-like structure of the GO particles has a larger hydrodynamic diameter than granular silica, which causes a significant congestion effect that advances the formation of hydroclusters, implying a lower critical shear rate. Besides, the interaction between GO and silica particles is very strong, and the agglomeration of silica on the surface of GO particles leads to a discontinuity in hydroclustering, thereby decreasing the peak viscosity of the multiphase STFs. Balali *et al.* [184] reported that the glass fabric composites prepared using nano-clay-reinforced silica-based STFs offered superior quasi-static puncture resistance than neat glass fabrics, as well as composites prepared using single-phase STF.

Gürgen *et al.* [185] conducted a comparative analysis of three different additives, namely, boron carbide, silicon carbide, and aluminum oxide, in silica-based STFs. They concluded that the ST phenomenon is rather disturbed by the ceramic additives and is largely dependent on their concentration and particle size. Excess quantity of these micro-sized additives lowers the optimum or critical concentration of the elementary silica particles as well as hampers the continuity of the hydrocluster structures, thus adversely affecting the ST behavior. However, the deviation from ST behavior is less in the case of finer additives owing to less disruption of hydrocluster networks than by the coarser ones. Gürgen and his co-researchers [186] also carried out an extensive study on silicon-carbide-particle-based STFs and further extended their study to evaluate the penetration resistance performance of Twaron fabrics impregnated with them [5]. Despite the inferior rheological properties of multiphase STF over single-phase STF, the fabrics treated with them exhibited superior impact energy absorptivity. This may

be attributed to enhanced inter-yarn friction, additive–fabric interaction, and additive–impactor interaction.

As evident from the various studies discussed in this section, the effect of additives is case-specific, and hence generalization of the same is not possible. However, the science behind their behavior may easily be associated with several established theories. A rigorous analysis of the effect of additives in determining the rheological performance of multiphase STF is required to acquire a comprehensive understanding.

A novel research regarding protecting STF from moisture and simultaneously strengthening its ST behavior by employing shear-stiffening gel (STG) has been reported by He *et al.* [187]. An STG is a class of viscoelastic material that exhibits enhancement in its inherent dynamic mechanical properties like storage modulus, elastic modulus, and yield stress on the application of dynamic shear loading and high strain rate compressive forces [188–190]. Increase in strain rate causes state transition in STG from viscous liquid to rubbery to glassy, involving absorption of impact energy [191]. STG/Kevlar/STF composites were prepared and evaluated using yarn pull-out test, modified split Hopkinson pressure bar test, rod penetration test, and knife cutting test. The results confirmed the positive contribution of STG doping toward enhancement of impact resistance performance.

13.5 Conclusion

Enormous efforts have been made by researchers around the world to produce lightweight, flexible, and comfortable soft body armor with high energy-absorbing capacity. Numerous studies related to new concepts and designs of ballistic protection have been conducted to meet the new demands of achieving enhanced impact resistance at minimal volume and mass. Other than the development of more efficient fibers, several alternative schemes like unidirectional laminates, 3D fabrics, hybrid panels, multiphase STF system, etc. have also been investigated. However, due to the diversity and complexity of myriad associated factors, optimization of an armor panel configuration is a great challenge, especially via experimental methods. The biggest hitch is that these factors do not work in synergy and their contribution is further a function of several other parameters, necessarily not following linear trends. Therefore, the research should be focused on numerical simulation of a panel structure so as to encompass the effect of maximum parameters involved in determining its impact resistance performance.

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