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The impact of nanotechnology on polyesters, polyamides and other textiles

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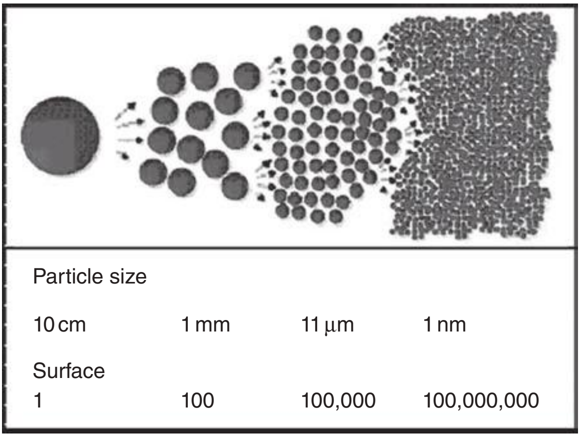
13.1 Introduction

Nanotechnology is an emerging interdisciplinary area expected to have wide ranging implications in all fields of science and technology such as material science, mechanics, electronics, optics, medicine, energy, and aerospace, plastics and textiles. Although nanotechnology is still in its infancy, it is already proving to be a useful tool in improving the performance of textiles and generating worldwide interest as is evident from 1 460 000 hits in a Google search for the words ‘nanotechnology in textiles’. Though textile technology is about 200 years old, it can provide the bridge to making nanotechnology a commercial reality, as phenomenal efforts are being made both by the industry and academicians to use nanotechnology to create radically new textiles or to enhance the conventional textiles with greater functionality [1]. It is anticipated that the market for textiles based on nanotechnology which was approximately US$13.6 billion (2007) would rise dramatically to reach US$115 billion by 2012 [2].

13.2 What is nanotechnology?

The ‘nano’ in nanotechnology stands for one billionth of a meter, i.e. 1 nm = 10^{-9} m. ‘Nano’ is the Greek word for ‘dwarf’ and approximately 10 000 times finer than a human hair. The average size of an atom is of the order of 1–2 ångstrom in radius. One nanometer comprises 10 ångstrom and hence in one nm there may be 3–5 atoms depending on the atomic radii. According to the National Nanotechnology Initiative (NNI), nanotechnology is defined as the utilization of structures with at least one nano dimension for the construction of materials, devices or systems with novel or significantly improved properties due to their nano size. In another definition of nanoscience, particles having sizes in the range of 1 to 100 nm are termed as nano particles and the application of nano-sized particles is what we call ‘nanotechnology’.



13.1 Particle size and surface at nanoscale.

It is the desire to control properties of materials on a molecular scale that gave rise to the revolutionary field of 'nanoscience and nanotechnology'. Nanotechnology not only produces small structures but is also an anticipated manufacturing technology, which can give thorough inexpensive control on the structure of matter. It is therefore called 'bottom up' technology by which bulk materials can be built precisely using tiny building blocks of nanometer size and is different from the conventional 'top down' technology, which starts from bulk materials and reduces to nanoscale dimension. The resultant materials therefore have fewer defects and superior quality.

The fundamental of nanotechnology lies in the fact that properties of materials change dramatically when their size is reduced to the nanometer range. For example, nanocrystalline copper is five times harder than ordinary copper with its micrometer sized crystalline structure. Since nanometer size grains, fibers and plates have dramatically increased surface area compared to their conventional size materials, the chemistry and physics of these nanosized materials is altered compared to conventional materials (Figure 13.1). Nano-elements thus manifest extremely fascinating and useful properties, which can be exploited for a variety of structural and non-structural applications.

13.3 Origin of nanotechnology

The concept of nanotechnology is not new as Mother Nature perfected it millions of years ago. The self-cleaning properties of lotus leaf, which are due to its carefully designed nanostructured surface and tooth and bone the natural nano biocomposites being excellent examples of nanotechnology already existing in nature.

However, the embryo of nanotechnology is believed to be the concept of ‘atomic assembly’ which was first publicly articulated in 1959 by Nobel Laureate and physicist Sir Richard Feynman, in his famous lecture titled ‘There is plenty of room at the bottom’. He stated, ‘The principles of physics so far as I can see do not speak against the possibility of maneuvering things atom by atom’. The term ‘nanotechnology’ was first coined by Norio Taniguchi at the University of Tokyo in 1974, when he defined the theoretical dimensions and tolerances in technology and also described the precision manufacturing of materials with nanometer tolerances. K. Eric Drexler, a student of MIT unknowingly appropriated the word ‘nanotechnology’ in 1986 in his famous book *Engines of Creation: The Coming Era of Nanotechnology* to describe what later became known as molecular nanotechnology (MNT). In that book, he proposed the idea of a nanoscale ‘assembler’ which would be able to build a copy of itself and of other items of arbitrary complexity. His 1991 doctoral thesis at MIT was revised and published as the book *Nanosystems Molecular Machinery Manufacturing and Computation* (1992), which received the Association of American Publishers award for Best Computer Science Book of 1992 [3].

13.4 Nanotechnology: applications in textiles

The textile industry is likely to be hugely impacted by nanotechnology, as research involving nanotechnology based finishes to improve performances or to create new functionality on textile materials has gained a big impetus/momentum across the globe. The US and Europe were the most active continents in the application of nanotechnology in the textile field in the beginning but more recently Asian countries account for nearly 50% of publications and patents registered in the European Patent Office, related to ‘Nano-textiles’ [4].

Incidently, the first commercial product based on nanotechnology was launched in the textile field, when Nano-Tex LLC, a subsidiary of US based Burlington Industries founded by Dr David Soane in 1998, launched its new cutting age technology ‘NanoCare’ for water repellent and stain resistant cotton fabrics, which sheds water like a duck’s feather. Later on, more and more textile companies began to invest in the development of nanotechnologies for textiles such as Swiss based Schoeller, Toray Inc from Japan, BASF from Germany, Ciba and Clariant to name a few.

The research in this area mainly centers around creating unique properties in everyday fabrics such as self-cleaning, water and oil repellency, stain proof, antibacterial, UV protective, antistatic, improved moisture regain and comfort in synthetic based textiles but all without compromising the original hand, breathability or durability of the fabric. It also shows promising applications in developing advanced textile materials such as nanocomposite fibers, nanofibers and other nanomaterial incorporated fibers/textiles for applications in medical, defense, aerospace and other technical textile applications such as filtration, protective clothing, etc., besides a range of smart and intelligent textiles.

These developments can be broadly classified under four major areas: i.e. nanofinishing, nanocoatings, nanofibres and nanocomposites. In this chapter, the work being done under each of these domains would be reviewed under two major headings: surface modification of textiles which includes nanofinishing and nanocoating; and fiber modifications which covers nanocomposite fibers and nanofibers. Although all the nanotechnologies discussed in this chapter are with reference to textile materials both natural and synthetic, particular references to polyester and polyamide based substrates are made, wherever applicable.

13.5 Nanotechnology based surface modification of textiles

13.5.1 Nanofinishing

Nanotechnology has opened immense possibilities in the textile finishing area resulting in innovative new finishes as well as new application techniques. Particular emphasis is on making chemical finishing more controllable and durable with significantly enhanced functionality by incorporating various nanoparticles or creating nanostructured surfaces, which led to an unprecedented level of textile performances such as stain resistant, hydrophilic, antistatic, wrinkle resistant and shrink proof abilities [5–7].

Nanofinishes are generally applied in nanoemulsion form, which enables a more thorough, even and precise application on textile surfaces. They are generally emulsified into either nanomicelles, made into nanosols or wrapped in nanocapsules that can adhere to textile substrates easily and more uniformly. Ideally nanoparticles or the molecules of these nanofinishes can be brought individually to designated sites on textile surfaces in a specific orientation and trajectory through thermodynamic, electrostatic or other approaches. Since nanoparticles have a large surface area to volume ratio and high surface energy, they have better affinity for fabrics. Therefore these finishes are more durable, effective and do not adversely affect the original handle and breathability of the fabric. A range of different textile products and finishes based on nanotechnology has already been launched in the market and these are summarized in Table 13.1. The recent developments in nanofinishing on textiles are reviewed and briefly described here.

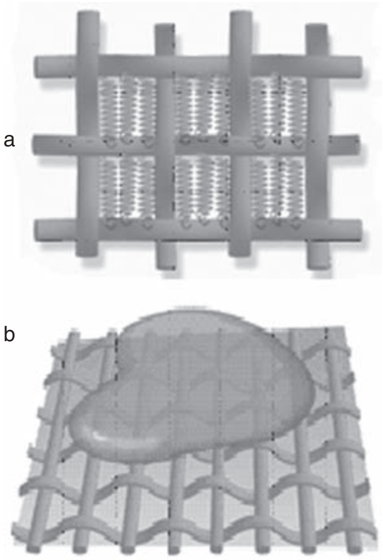
Table 13.1 Commercially available functional nanofinishes in the market

S. No.	Name of the finish	Company	Properties	References
1.	Resists Spills™	Nano-Tex	Water-repellent and stain resistant	www.nanotex.com
2.	Coolest comfort™	Nano-Tex	Impart superior wicking properties to a previously hydrophobic synthetic or resin treated cotton	www.nanotex.com
3.	NanoCare®	Nano-Tex	Helps stains to wash out easily	www.nanotex.com
4.	Zonyl®	DuPont	Water-repellent fluorinated polyurethanes as soil-release finish	www.dupont.com
5.	Zyvere®	Nanovere Technologies	Self-cleaning paint surfaces	www.nanovere.com
6.	NanoSphere®	Schoeller Textil AG	Repels water and oil drops and prevents soil particles from attaching themselves on the fabric surface	www.schoeller-textiles.com
7.	Ultra-Fresh™ Silpure	Thomson-Research Associates	Antimicrobial treatment for textiles	www.ultrafresh.com
8.	Nuva FW	Clariant	Excellent oil and water-repellent effects on textiles made from synthetic and cellulosic fibres	www.textiles.clariant.com

13.5.2 Water and oil repellent (hydrophobic) nanofinishes

A number of water and oil repellent finishing chemicals are available commercially which could be classified into wash resistant or not wash resistant on one hand and fluorocarbon containing or non-fluorocarbon based finishes on the other hand. Silicon based water proofing is also used either as such or in combination with fluorocarbon based agents. However the current market demands are for non-fluorocarbon based finishes because of growing environmental consciousness and increasingly strict legal regulations. Besides this, the durability of finish and retaining the original feel and strength of the fabric are also important criteria. Nanotechnology based novel and innovative nanofinishes seem to be closer to achieving these consumer demands.

The premier range of NanoCare® and NanoPel® nanofinishes marketed by NanoTex Inc. USA are the next generation easy care finishes based on nanotechnology. These finishes which come under the Resist Spills™ Category protect the fabric against both water and oil based liquid stains/soils [8]. Tiny whiskers aligned by proprietary 'spines' are designed to repel liquids and are attached to the fibers utilizing molecular 'hooks'. These whiskers and hooks are minute, in fact no more than 1/1000th the size of a cotton fiber. These whiskers cause the liquids or semisolids to roll off the fabric thus causing minimal staining and can be removed with simple washing (Figure 13.2). Since the attached whiskers are of nanoscale



13.2 NanoCare Technology: Tiny whiskers attached to individual cotton fibers cause the liquid to roll off.

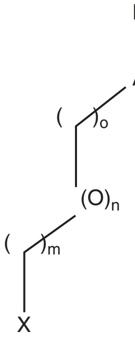
size, they do not affect the hand, breathability of fabric and can withstand 50 home launderings. The Resist Spills™ protection is applied to fabrics at mill level during finishing stage and requires no special machinery or processing conditions. The treatment can be applied either by padding or dip or dry coating. This nanofinish can be applied to natural fibers such as cotton, wool and silk as well as synthetics such as polyamides, polyesters, acrylic, etc. Leading garment-manufacturing brands such as Burlington, Galey & Lord, Dan River, Eddie Bauer and Lee have used this licensed technology for their NanoCare® range of commercial products. The large-scale production of shirts, shirting fabrics has also been licensed to several South Asian countries including India.

What are 'whiskers'?

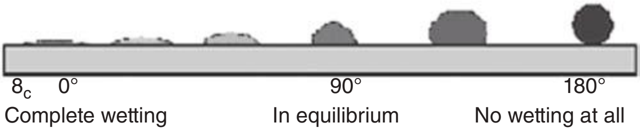
The original research demonstrated and produced by Dr David Soane forms the basis of 'NanoCare' range of finishes [7, 9–11]. The tiny whiskers '10–100 nm' in dimension are nothing but low molecular weight nanosized multifunctional molecules, which are capable of forming covalent and non-covalent bonds with cellulosic and protein fibers. These molecules are either block or graft copolymers, having multiple functional groups such as binding groups, hydrophobic groups hydrophilic and oleophilic groups. These nanosized molecules react with reactive groups such as hydroxyl, carboxyl or amino present in the surface of the fabric without blocking its pores. These tiny whiskers modify the surface properties of the treated fabric and improve water repellency, grease repellency, soil resistance and detergent free washing without affecting its strength, abrasion resistance and breathability. Due to the multiplicity of bonds and the ability of the molecules to easily diffuse into the fiber because of small nanosize, the durability of the finish is much better than the conventional fluorocarbon acrylate polymer based finish (Figure 13.3).

13.5.3 Superhydrophobic: self-cleaning nanofinishes

Many plants in nature including the lotus leaf exhibit unusual wetting characteristic of superhydrophobicity. A super hydrophobic surface is the one that can bead off water droplets completely; such surfaces exhibit water droplet advancing angles of 150 degrees or higher (Figure 13.4). In addition their contact angle hysteresis is very low (receding contact angle only a few degrees less than the advancing contact angle), producing a surface on which water droplets just roll off. A self-cleaning surface thus results since the rolling water droplets across the surface can easily pick up the dirt particles to leave behind a clean surface.



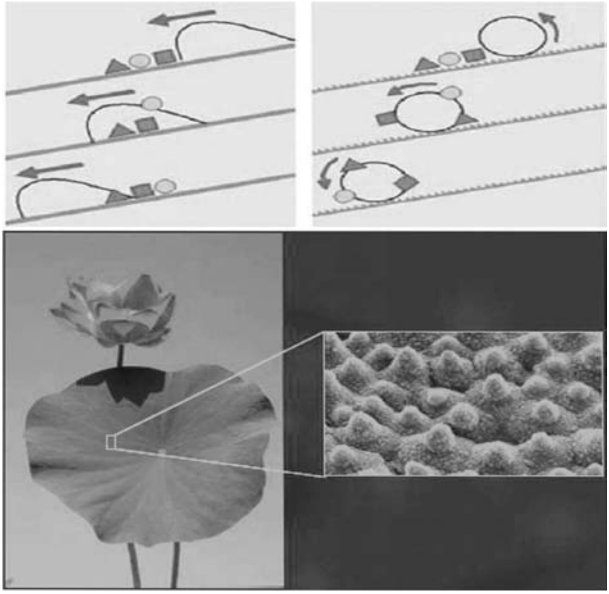
13.3 Multifunctional molecule of Dr Soane, where m, n = 0 or 1, o = 0 or 2. 'R' is a linear, branched, or cyclic hydrocarbon or fluorocarbon having C_1 to C_{30} hydrocarbon or fluorocarbon groups 'A' is $-SO_2$, $-CONH$, $-CH_2$ or CF_2. 'X' is a nucleophilic group capable of reacting with hydroxyl, amine or thiol group [7].



13.4 Contact angle and wettability (superhydrophobic surfaces have contact angle >150°).

This fascinating self-cleaning property of lotus leaf has been accomplished by nature through the use of a surface roughness in the combination with a highly hydrophobic surface. The surface topography of lotus leaf presents two different scales to the outside environment and is textured with 3–10 micron sized hills and valleys that are decorated with nanometer sized particles of a hydrophobic wax like material (Figure 13.5). The hills and valleys ensure that surface contact area available to water is very low while the hydrophobic nanoparticles prevent water into the valleys. The net result is that water cannot wet the surface and therefore forms nearly spherical water droplets, leading to superhydrophobic surfaces [12]. The increasing surface roughness due to multiplicity of microscale or nanoscale projection or cavities provides a large geometric area for a relatively small projected area. Cassie and Baxter [13] were the first to explain that water repellency of rough surfaces was due to the air enclosed between the gaps in the surface, which minimizes the substrate to water interface. Hence water does not spread and forms a droplet, which easily rolls off.

Taking the inspiration from nature there have been several approaches researched to create superhydrophobic surfaces on textiles, which mimic



13.5 Lotus leaf effect and a SEM image of its surface.

the nanostructured lotus leaf and therefore exhibit self-cleaning properties. Nano Sphere®, a lotus effect based textile finish has been developed, patented and commercialized by Schoeller Texil AG of Switzerland [14]. This water and oil repellent finish is based on a 'guest–host' system and uses a dispersion system comprised of the dispersed phase 'guest' and the dispersant 'host' components [15]. In the final finishing layer, self-organization of the 'guest' and the 'host' components leads to the 'guest' component concentrating at the upper surface of the finish layer and forming columnar structures similar to the microrough surface exerting the 'lotus effect'. The partial phase separation of the 'guest' and 'host' system results in the accumulation of the hydrophobic or oleophobic 'guest' components at the surfaces. The phase separation between the finishing layer and the surrounding air results in the dramatically enhanced water and oil repellent property of the fabric. The dispersant is an emulsion of a gel-forming component (polymeric binder) and a water and/or oil repellent components. The third component, which is the dispersed phase, is comprised of either micro sized waxes (0.1–50 micron) or hydrophobic silica particles (5–50 nm). The finish can be applied on textile material by conventional industrial application techniques such as padding, coating, spraying or foaming and can be applied to both natural, i.e. cotton, viscose, polyester/cotton blends as well as wholly synthetic polyester or polyamide textile substrates.

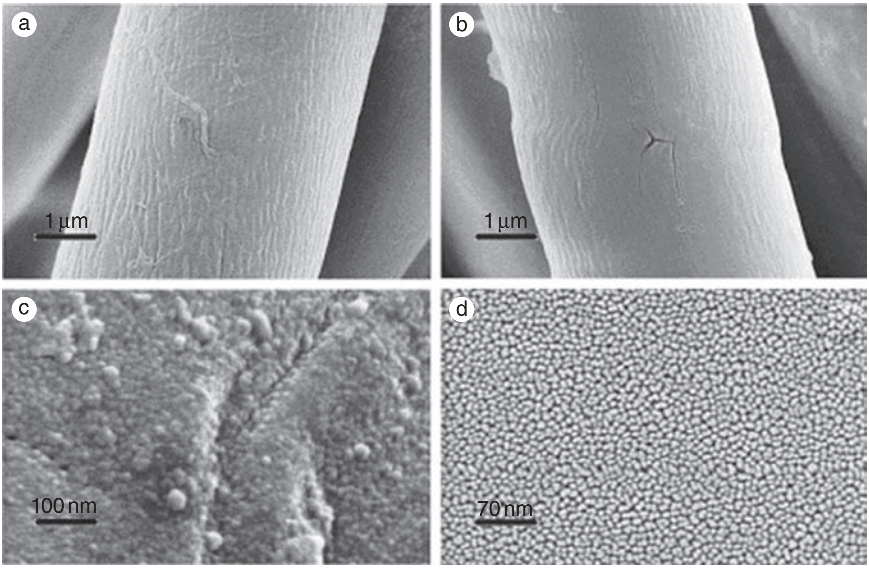
Superhydrophobic silica coating film on cotton substrates, which are transparent and durable have been reported by W. A. Daoud and coworkers of the Hong Kong Polytechnic University using low temperature sol-gel coating based on a low temperature process [16]. The coatings were produced via cohydrolysis and polycondensation of a hexa decyl trimethoxy silane (HDTMS), tetra ethoxy silicate (TEOS) and 3-glycidyloxy propyl trimethoxy silane (GPTMS) mixture. The superhydrophobic nanocomposite coating enhances the contact angle of cotton to 140°, whereas before coating cotton has 0° contact angle as it is superhydrophilic in nature. This nanocomposite coating has new applications in daily use material such as plastics or textiles and is an ecofriendly substitute for fluorocarbon based water repellant finish. There is less than 5% decrease in textile strength and tearing strength. The air permeability of the fabric remains unchanged. The washing durability of the coatings is also good which is attributed to linking ability of GPTMS that promotes a high level of adhesion at the interface.

Yu *et al.* [17] recently reported another superhydrophobic complex coating for cotton fabrics based on silica nanoparticles and perfluorinated quaternary ammonium silane coupling agent (PFSC), using a sol-gel process. Silica nanoparticles in the coating made the textile surface much rougher and PFSC, on the top layer of the surface, lowered the surface free energy. Textiles coated with this coating showed excellent water repellant property and water contact angle increased up to 145° from 133° for cotton fabrics treated with pure PFSC, without silica sol pretreatment. The silica sol and PFSC were applied to cotton fabrics by conventional pad-dry-cure process. Superhydrophobic coatings have also been reported with many other hydrophobic film-forming nanoparticle compositions such as Al_2O_3 gel, ZnO nanoparticles, aligned carbon nanotubes, $CaCO_3$ loaded hydrogel spheres and POSS nanoparticles as reported in an excellent review on nanofinishing by Gulrajani [7].

However durability against laundering and abrasion is important for textile applications. A combination of chemical and mechanical treatments can be used to create super hydrophobic nanostructures on the surface of textile materials. Mechanically roughened surfaces became an integral part of the textiles and are expected to be more durable. Mechanical treatments such as calendering, embossing, etching, schreinering, sueding, sanding or emerizing have also been used to create mechanically abraded micro roughened surfaces on textiles [7].

13.5.4 Photocatalytic self-cleaning nanofinishes

Dr John Xin and Dr Walid Daoud of the Hong Kong Polytechnic University's Nanotechnology Centre for Functional and Intelligent Textiles and



13.6 SEM images of (a) uncoated cotton fiber, (b) titania coated cotton fiber showing the morphological change in the surface structure, (c) higher magnification image of titania coated cotton fiber showing the shape and size of the titania particles, and (d) higher magnification image of a titania film coated on glass [7].

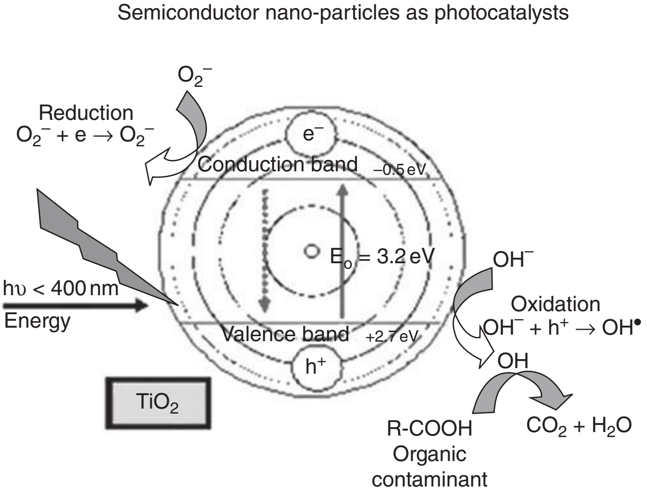
Apparel [18–20] developed a process for the sol gel coating on textile substrates at low temperature. They also claimed that photocatalytic self-cleaning properties could be imparted to the coated fabric on coating cotton with TiO_2 nanoparticles that are about 20 nm in size (Figure 13.6). The coating solution comprises a translucent sol prepared with a TiO_2 precursor (TTIP, titanium tetraisopropoxide), ethanol and acetic acid in a molar ratio of 1:100:0.5 respectively. The principal chemical reactions are summarized as follows:

$$Ti(OPr)_4 + 4\ EtOH \rightarrow Ti(OEt)_4 + 4\ Pr\ OH$$

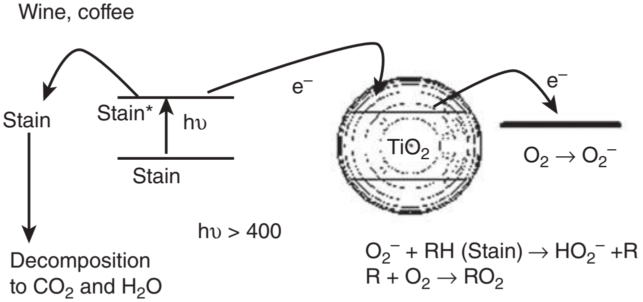
$$Ti(OPr)_4 \text{ or } Ti(OEt)_4 + H_2O \rightarrow Ti(OH)_4 + 4PrOH \text{ or } 4EtOH$$

$$Ti(OH)_4 \rightarrow TiO_2 + 2H_2O$$

The fabrics are coated with this sol using conventional pad dry cure process. The coated fabrics show discoloration of red wine and coffee stains on irradiation of samples in a Sun test solar simulator. The photocatalytic activity of semiconductor oxides such as TiO_2 is attributed to promotion of an electron from the valance band (VB) to the conduction band (CB) brought about by the absorption of a photon of ultra band gap (~3.2 eV) light whose energy (hν) > EBG. EBG is the energy difference



13.7(a) Schematic illustration of the major processes associated with TiO_2 semiconductor particle [7].



13.7(b) Suggested scheme for the discoloration of wine and coffee stains under visible light irradiation by TiO_2 photocatalyst [7].

between electrons in the VB and CB. In the presence of oxygen and/or water, superoxide ($O^{2\bullet}$) and/or hydroxyl ($OH^\bullet$) radicals are formed, which attack adsorbed organic species on the surfaces of TiO_2 and decompose them. The mechanism suggested by the investigators [21] for this discoloration is shown in (Figure 13.7a, b).

The decomposition of stain, which is an organic compound, goes through a cation intermediate (stain +) leading ultimately to the production of CO_2. The electron generated in the process is injected into TiO_2 and the conduction band starts the oxidative radical chain, leading to discoloration of the chain. The nanotitania coated fabrics maintain their antibacterial property up to 55 washes/home launderings and UV protection characteristics up to 22 washes. This has been attributed to the formation of interfacial bonding through a dehydration reaction between the cellulosic hydroxyl groups of cotton and the hydroxyl group of titania [22].

13.5.5 Hydrophilic nanofinishes

The poor moisture absorption property of synthetic fabrics such as polyester and polyamides limits its applications in the apparel sector. The new range of hydrophilic nanofinishes Cotton Touch™ and Coolest Comfort™ commercialized by NanoTex, USA makes the synthetic fabric look and feel like cotton [8].

Cotton Touch™

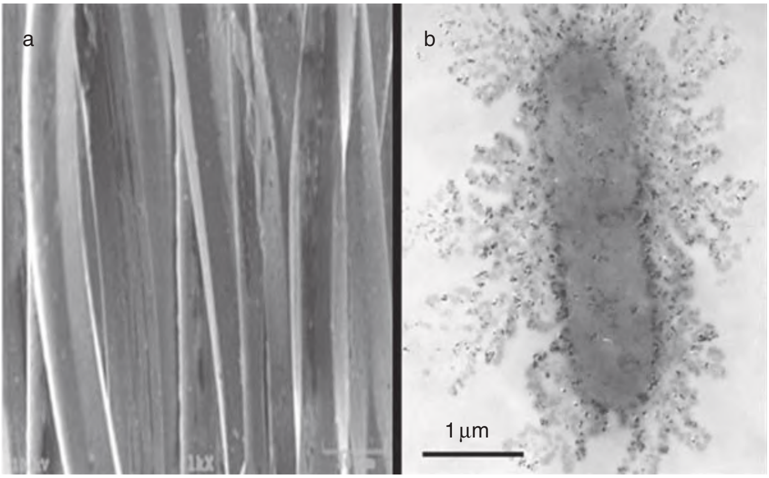
This is a naturally soft fabric enhancement designed to make synthetic fabric look and feel like cotton. It is available as Nanotouch® and gives a durable cellulose wrapping over synthetic fibers such as polyester and polyamides. Cellulosic sheath and synthetic core together form a concentric structure to bring overall solutions to the drawbacks of synthetics such as static discharge, harsh handle and glaring luster. It can also last 50 launderings and is expected to eliminate the decline in demand of synthetic microfiber and broaden the use of synthetics to new applications.

Coolest Comfort™

This fabric provides breakthrough moisture wicking to draw moisture away from the body while drying quickly. The popular product in this category is Nano Dry®. It improves the moisture absorption of polyamides and polyesters making them hydrophilic and comfortable. The main applications are in sportswear and close-to-body garments that require perspiration absorbency. The finish lasts 50 launderings.

13.5.6 Antibacterial nanofinishes

Silver (Ag) or silver ions (Ag^+) have long been known to have strong inhibitory and bactericidal effects as well as a broad spectrum of antimicrobial activities [23]. The inhibitory effects of silver ion/metal on bacteria have been attributed to the interaction of sliver ion with thiol group in bacteria as well as to the oxidative destruction of microorganisms in aqueous medium [24–25] (Figure 13.8).



13.8 Silver coated antimicrobial fibers (SEM image) and antimicrobial action of silver [25].

Even though metallic silver has antimicrobial properties, it is expected that the conversion of bulk silver to nanoparticles, i.e. 'nano Ag' will have very high specific area that may lead to high antimicrobial activity compared to bulk Ag metal. A range of antimicrobial textile finishes and products have been reported and quite a few have been commercialized, which are based on superior antimicrobial properties of silver in nanoform and are summarized in Table 13.2. Several methods have been devised to synthesize silver nanoparticles and reviewed [7]. These include chemical reduction, chemical/photo reduction in reverse micelles, or in microemulsions, radiation induced chemical reduction and mechano-chemical reaction between AgCl and Na in a ball mill. In a chemical method of producing highly concentrated stable dispersion of nano sized silver particles, silver nitrate is reduced with ascorbic acid to precipitate silver metal in acidic solution as per the following reaction [26]:

$$2Ag^+ + C_6H_8O_6 \Leftrightarrow 2Ag + C_6H_6O_6 + 2H^+$$

Silver ions and nanoparticles both have to be stabilized, as they are prone to discoloration on exposure to light. The stabilization of silver nanoparticles is achieved either by coating, encapsulation or complex formation between the loan pair of electrons on N and Ag atoms. All amines having a free lone pair of electrons can stabilize Ag ions/nanoparticles. Polyvinyl pyrrolidone (PVP) is one such example [27].

Antimicrobial yarns made from cotton, linen, silk, wool, polyester, nylon or their blends have been produced by immersing them in silver nanoparticle containing solutions. The treated yarns are yellow in color and contain 0.4–0.9% by weight of silver. The treated yarns show effective antimicrobial activity against various bacteria, fungi, etc., and the activity remains even after 100 washes with neutral soap. Nano silver particles containing antimicrobial dressings have been incorporated in wound care and have gained wide acceptance in medical industry, as a safe and effective means of controlling microbial growth in the wound, often resulting in improved healing.

13.5.7 UV protective nanofinishes

Semiconductor oxides such as TiO_2, ZnO, SiO_2 and Al_2O_3 are known to have UV blocking property [29–30]. It is also known that nanosized TiO_2 and ZnO particles are more efficient at absorbing and scattering UV radiation than the conventional size particles and thus were better able to block UV radiation as they have a much larger surface area to volume ratio and also the fact that Rayleigh Scattering due to nanoparticles is much reduced as it is inversely proportional to the fourth power of their sizes. This theory predicts that in order to scatter UV radiation between 200 and 400 nm, the optimum particle size should be between 20 and 40 nm [29]. Moreover inorganic UV blockers are advantageous as compared to organic UV absorbers, as they are less toxic and chemically stable under exposure to high temperature and radiation.

Much effort has been made on the application of UV bulking treatment to fabrics using nanotechnology [31–35]. UV blocking treatments for cotton fabric have been developed using the sol-gel method by Xin and coworkers [34]. A thin layer of TiO_2 nanoparticle is formed, on the surface of treated cotton fabric, which provides excellent UV protection, the finish is durable up to 50 home launderings. Apart from TiO_2, ZnO nanorods of 10 to 50 nm in length were also applied to cotton fabric to provide UV protection. The rods exhibited excellent UV protection [36].

13.5.8 Antistatic nanofinishes

Synthetic fibers such as nylon and polyester are prone to static charge accumulation as they absorb less water. It has been reported that nanosized TiO_2, ZnO whiskers, nanoantimony-doped tin oxide (ATO) and silane nanosol could impart antistatic properties to synthetic fibers [37–39]. ZnO and TiO_2 nanoparticles are electrically conductive materials and help dissipate the static charge in these fibers. Silane nanosol improves antistatic properties as the silane gel nanoparticles absorb moisture due to $–NH_2$ and –OH groups present. W. L. Gore and Associates GmbH have combined

Table 13.2 Commercially available nanosilver based antimicrobial products

Sl. No.	Company	Product name	Type of product	References
1.	NanoHorizons	SmartSilver™	Additive	www.nanotech-now.com
2.	ABCNanotech	SARPU	Finishing/coating solution (nanosized silver dispersed in liquor)	http://www.abcnanotech.com/
3.	AcryMed	SilvaGard®	Solution surface treatment	http://www.acrymed.com
4.	Advanced Nano Product (A N P)	Silver Nanopaste	Powder/coating solution	http://www.anapro.com/korean/default.asp
5.	JR Nanotech	SoleFreshT	Dispersion containing 0.3%w/w nanosilver	http://www.jrnanotech.com
6.	Nanocid	Silver nanoparticles	Powder/colloid	http://www.nanocid.com/index.html
7.	NanoGap	Silver nanoparticles	Powders or in organic or aqueous solutions	http://www.nanogap.es
8.	Arc Outdoors	'X-Fiber'	Fibers and fabrics with nanosilver-based antimicrobial properties	http://www.arcoutdoors.com/technology.html
9.	Shanghai Huzheng Nano Technology Co, Ltd	Nano-silver spray	Antimicrobial self-cleaning can be applied on ceramic, plate, glass and fiber	www.tradeindia/selloffer/1201107/antimicrobial-anion and infrared multifunctional paint

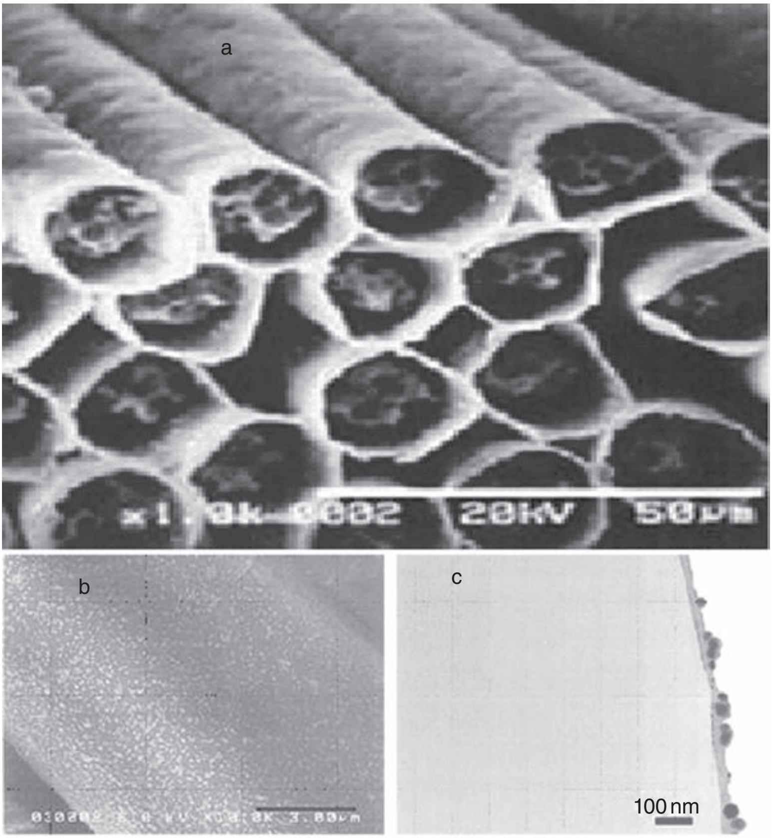
nanotechnology and PTFE (Dupont's Teflon) to develop an antistatic membrane for protective clothing. Gore-Tex® based works wear protects the wearer from electrostatic discharges [40]. Electrically conductive nanoparticles are durably anchored in the fibers of the membrane, creating an electrically conducting network that prevents the accumulation of static charge.

13.6 Nanocoatings

Nanostructured surfaces are of great interest, due to their large surface area, which might yield high functionality. Nanocoating refers to the covering of materials with a layer on the nanometer scale (10–100 nm in thickness) or covering of a nanoscale entity to form nanocomposite and structured materials. There are numerous coating procedures that are widely used including chemical vapor deposition, plasma assisted techniques, self-assembly, layer by layer coating, dip coating, sol-gel coating and electrochemical deposition mostly on planar substrates, i.e. metal, ceramic or polymer. Coating in solution is generally performed using either precursor molecules or preformed nanoparticles to form the layer. Electrostatic interaction, hydrogen bonding and covalent bondings are some of the associated forces between the coating and the material being coated. Nanocoatings on textiles have recently been explored using mainly processes such as plasma-assisted polymerization, self-assembly, sol-gel nanocoating and electrochemical deposition which will be briefly reviewed in this section.

13.6.1 Self-assembly

Toray Industries, Inc. have succeeded in developing a 'nano-scale processing technology' that allows the formation of molecular arrangement and molecular assembly necessary to bring out further advanced functionalities in textile processing [41]. This 'nano-scale processing technology' named 'NanoMATRIX' forms the functional material coating (10–30 nm) consisting of nano-scale molecular assembly on each of the monofilaments that forms the fabric (woven/knitted fabric) (Figure 13.9). NanoMATRIX is based on the concept of 'self-organization' by controlling the conditions like temperature, pressure, magnetic field, electrical field, humidity, additives, etc. It is possible to control the state of molecular arrangement and/or assembly of functional materials on each of the monofilaments in nanoscale sizes precisely by controlling the interaction and responses between the functional material to be coated and the fiber material (polymer). The application of this technology is expected to lead to the development of new functionalities as well as remarkable improvements in the existing



13.9 NanoMATRIX technology from Toray for nanocoatings on textiles through self-assembly [41].

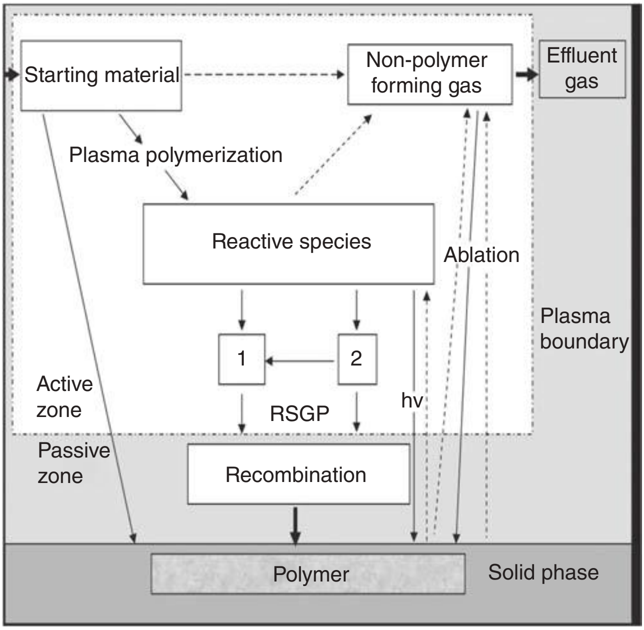
functions (quality, durability, feel, etc.) without losing the fabric's texture.

13.6.2 Plasma assisted nanocoatings

Plasma polymerization enables deposition of very thin nanostructured coatings (<100 nm) via gas phase activation and plasma substrate interactions. This dry and ecofriendly technology offers an attractive alternative to replace wet chemical process steps for surface modification (finishing) of textiles. Plasma polymerization can impart a wide range of functionalities such as water repellency, hydrophilicity, dyeability, conductivity and biocompatibility due to the nanoscaled surface modification of textiles and fibers. The advantages over conventional wet chemical processing are that it needs a very low material and low energy input, hence is environmentally friendly, it does not affect the bulk properties of textiles and fibers such as feel (touch), handle, optical properties and mechanical strength. Moreover, these plasma-assisted coatings are more durable as compared to other surface modification techniques such as wet processes, radiation or simple plasma activation because nanoscaled plasma polymer coatings get covalently attached or bonded to textile surfaces [42, 43].

What is plasma polymerization?

Plasma is considered the fourth state of matter and consists of a wide variety of active species such as electrons, ions, radicals, excited species, vacuum and ultraviolet radiation. Surface treatment of textiles is usually carried out by non-equilibrium plasmas, which are excited by the electric field. The excited electrons in the plasma have the appropriate energy to excite, dissociate and ionize atoms and molecules. Monomer gases when introduced in to the plasma reactor, enter an active zone where excitation and dissociation process are taking place to generate reactive species and then travel to a passive zone yielding recombination and stable products which get deposited on substrates, electrode or wall as thin plasma polymerized coatings (Figure 13.10). Thus plasma polymerization is a radical



13.10 Plasma polymerization via rapid step-growth polymerization (RSGP) involving an activation and a recombination zone (concept of chemical quasi-equilibria) [46].

dominated chemical vapour deposition (plasma CVD) process, thought to result in macromolecule formation i.e. mainly amorphous, and more or less cross-linked structures.

Plasma polymerization is performed using different kinds of plasma polymerizable gases (monomers) such as hydrocarbons (i.e. methane, ethylene or acetylene) or organosilicon monomers (i.e. silicone (SiH_4) or silicon tetrachloride ($SiCl_4$). There is a difference between conventional and plasma polymerization, as some gases (like methane) which can be plasma polymerized do not undergo polymerization by the conventional route. A plasma polymer typically results from a rivaling etching and deposition process depending on the plasma species present during film growth yielding a more or less cross-linked structure [44–46].

Plasma equipment

There are two types of plasma, i.e. high temperature plasma and low temperature plasma. High temperature plasma is found at atmospheric pressure in either its man made form such as plasma torch or its natural form such as lightning. Low temperature (also called low pressure) plasma techniques are mostly suitable for surface reaction, cleaning, etching and plasma polymerization [46].

Most of the earlier work on plasma processing of textiles is based on low-pressure plasmas operating between 0.1 Pa and 100 Pa, which can be activated by direct current (DC), alternative current (AC) and radio frequency or microwave (MW). However, high-pressure atmospheric plasmas, such as corona and dielectric barrier discharge (DBD), are of special interest to textile industries because of easier processibility. However, it is difficult to obtain controlled deposition conditions or uniform coating through high-pressure atmospheric plasma. This is because the plasma can be ignited only within smaller volumes, hence non-coated parts are also taking part in external interaction. Moreover, the atmospheric plasma is mostly filamentary in nature, thus leading to moving hot spots. Research is ongoing to overcome these limitations [47, 48, 49].

M/s EMPA, a Swiss based company specializing in this area, have developed a low-pressure plasma reactor for plasma-polymerized coatings. At low pressure (1–100 pa) the plasma zone is well defined and the mean free path lengths are high enough to allow the penetration of textile structure by energetic particles as well as by long living radicals, thus enabling textile fibers up to several fiber layers in depth to interact with external plasma media. EMPA has developed both a semi-continuous web coater (up to 63 cm in width) and a continuous fiber coater besides several batch reactors. The reactors have been typically designed for textile widths up to 120 cm but larger widths of up to 4 m are also possible. The textiles are led through plasma regions and adapted to the required process, which comprises usually a cleaning step followed by a plasma deposition step. As compared to plasma polymerization on textile fibers or web, it is easier to do it on fibers as it needs smaller reactors and the process can be more continuous. Prior to plasma polymerization, the substrate needs to be cleaned as well as activated for better adhesion with the coating [46, 48].

Plasma polymerized functional nanocoatings

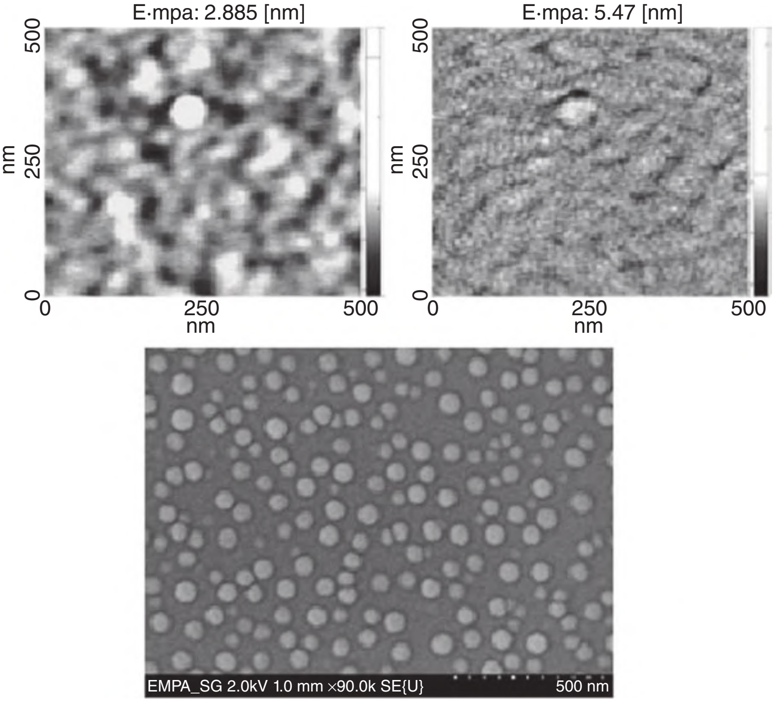
The earliest plasma treatments on textiles date back to the 1960s and focused on improving the wettability of fabrics through plasma activation. Plasma treatment in presence of non-polymerizable gases such as N_2, NH_3, O_2, H_2O, CO_2 or others generates oxygen or nitrogen-containing functional groups such as carboxyl (–COOH), amino (–NH_2), hydroxyl (–OH), or ethylene oxide (EO) units (–CH_2–CH_2–O–) on synthetic fabrics such as (PP, PET, cellulose acetate, and others) [48, 49]. The positive effects of this process are cleaning, etching, cross-linking, formation of radical sites and formation of functional groups which are not only able to enhance the binding sites in subsequent process steps of coating, dyeing, lamination and fiber reinforced composites but also to increase the surface energies of textile surfaces so as to make them more hydrophilic [41, 46, 50]. However this type of plasma activation is prone to aging due to internal reorientation effect as well as external influences. Aging can however be minimized by deposition of functional plasma polymers. Thus the internal reorientation process gets hindered by the cross-linked film network, which can be achieved by mixing hydrocarbon polymerizable gases with non-polymerizable gases, that is oxygen and nitrogen, etc. Rivaling process of etching and plasma polymerization yield highly functionalized and permanent plasma polymer coatings on textile substrates. Plasma polymerization can be performed with any kind of hydrocarbon monomer (in gaseous form), mainly acetylene, ethylene or methane are used on textile substrates. The achievable fiber properties depend on degree of cross-linking in the otherwise amorphous polymer coating deposited. The deposition of plasma polymerized coatings with well-defined penetration properties can be achieved by controlling the energy input into the active plasma zone which can be of use in controlled drug release from textile substrates. The coated surfaces also possess hydrophobic property [46].

Plasma polymerization of ethylene monomer on PET fibers was found to increase the interfacial adhesion strength between PET fibers and PE matrix in fiber reinforced composites [51]. Modification of polyester cords by low temperature plasma at atmospheric pressure in the presence of nitrogen and butadiene resulted in homogeneously coated cord surfaces. The plasma polymerized cords showed values of static and dynamic adhesion comparable to chemical treatment based on resorcinol formaldehyde latex (RFL) [52].

Plasma polymerization of organosilicon compounds is reported to impart good dielectric property, thermal stability, scratch resistance, lowered friction, flame retardant and barrier properties as well as adjusting the wetability of textiles [46, 53, 51]. Hexamethylene disiloxane [HMDSO, $(CH_3)_3Si\text{-}O\text{-}Si(CH_3)_3$] is the best common monomer, it is nontoxic and enables the deposition of siloxane coatings at low temperature. HMDSO derived plasma polymers are used for the hydrophobization of cotton, showing water contact angles up to 130° without influencing the water vapour transmission through the fabric [54]. Low-pressure plasma polymerization of unsaturated fluorohydrocarbons, i.e. C_3F_6, C_4F_8 on selected textiles has been industrially performed using a semi-continuous process to impart stain repellant properties on fabrics. Oil repellency grades of 4–5 were achievable in short treatment times (30–60 sec), which is superior to commercially available Scotch Guard finished samples. The softness, feel, color, permeability, abrasion resistance, water performance and friction coefficient properties of original fabric were unaltered by these nanoscaled ultra-thin (<100 nm) plasma coatings [55].

Multifunctional acrylic-like coatings on fibers such as polyester or polyamide have been obtained by low-pressure plasma polymerization using acrylic acid as a monomer. Acrylic coatings were found to improve their wettability, dyeability (using acid dyes) and soil resistance [56] and also improve the cell adhesion for tissue engineering [57]. The wrinkle recovery angles also improved by about 13% and no undesirable decrease in tensile strength was observed [58].

Ceramic Nanocoatings such as TiO_2, which are known for their superior hydrophilicity and photocatalytic activity, have also been obtained using plasma polymerization in presence of tetra isopropyl orthotitanate (TTIP) and oxygen as gases at low temperature (<100°C) [59]. The incorporation of nanoparticles into wet chemical coatings presents some difficulties such as agglomeration or non-uniform distribution of nanoparticles at surfaces. An in situ plasma polymerization/co-sputtering process has been used to embedded nanoparticles with homogeneous size and spatial distribution. Hegemann and coworkers [60] have recently used low pressure RF plasma discharges using acetylene mixed with ammonia to obtain interconnected nanoporous highly crosslinked coatings on textile fabrics. Co-sputtering of a silver target with Ar enabled the in situ incorporation by Ag nanoparticles within the functional plasma polymerized coating. A homogeneous distribution of Ag nanoparticles present at the coating



13.11 Nanoporous plasma C–H–N (C_2H_2/NH_3) coatings: (a) AFM topography; (b) phase contrast image; (c) silver nanoparticles deposited within C–H–N plasma coating [60].

surface was obtained and imparted antimicrobial properties to the coated substrate (Figure 13.11). A range of other functionality can be introduced onto fabrics by depositing uniform mono-dispersed nanostructured particles such as TiO_2 for catalytic and ferrous oxide for magnetic properties on the surface of fibers using this plasma polymerization technique developed by M/s EMPA.

Thus plasma polymerization can be applied to all forms of textile products such as fabrics and fibers. The characterization of the plasma polymerized nano-coatings is mainly affected by the type of precursor used, precursor flow rate, and plasma generator power applied to reactor, generator frequency and the exposure time of the substrate to plasma conditions. The up-scaling of plasma technology to industrial scale for textile applications is the major challenge faced by the researchers and technologists. Low-pressure plasma processes are still the state of the art technology, as effects produced by atmospheric plasma are comparatively weak and non-uniform. The other issues of concern are the efficiency of plasma polymerization process in terms of deposition rates and the right process speeds, so that they can be integrated with the current textile production lines. High investment cost and requirement of vacuum technology further limits the present application of this technology at an industrial scale to only niche textile products [46].

13.6.3 Sol-gel nanocoatings

The sol-gel process is a widely used technique to coat surfaces with nanoscale entities, i.e nanoparticles and finds application in a variety of areas ranging from catalysis, electronics, biomedical engineering and material science [61]. The sol-gel process involves inorganic precursors (a metal salt of an organo metallic molecule) that undergoes various reactions resulting in formation of a three dimensional molecular network. A common example is the hydrolysis and condensation reaction of metal alkoxides to form larger metal oxide molecules:

Hydrolysis

$$M(OR)_4 + H_2O \rightarrow HO\text{-}M(OR)_3 + ROH \rightarrow M(OH)_4 + 4ROH$$

Condensation

$$(OR)_3M\text{-}OH + HO\text{-}M(OR)_3 \rightarrow (OR)_3M\text{-}O\text{-}M\ (OR)_3 + H_2O$$

$$(OR)_3M\text{-}OH + RO\text{-}M(OR)_3 \rightarrow (OR)_3M\text{-}O\text{-}M\ (OR)_3 + ROH$$

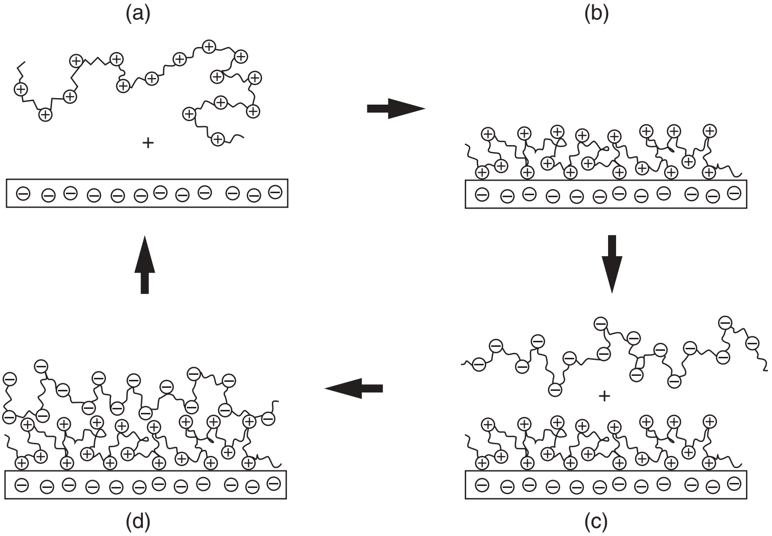
where M represents the metal and R represents alkyl group

Low temperature sol-gel based nanocoatings have been recently used to deposit layers of metal oxide nanoparticles on textile fabric surfaces to impact specific functionality, i.e. nanotitania (TiO_2) for photocatalytic activity, nanosilica (SiO_2) for superhydrophobic lotus leaf effect [7, 16, 17, 18–20] as also discussed in section 13.5.1 on ‘Nanofinishing’.

One of the major challenges in sol-gel nanocoatings is controlling the adhesion of the inorganic coatings to the substrates and also the uniformity of coating thickness. Hence reaction conditions need to be carefully monitored and controlled to allow reproducible coatings.

13.6.4 Layer-by-layer nanocoatings

Layer-by-layer (l-b-l) nanocoating technique can be utilized to fabricate thin film coatings, with molecular level control over film thickness and chemistry. A coating of this type can be applied to any surface amenable to the water based l-b-l adsorption process used to construct polyelectrolyte multi-layers including inside surfaces of the complex objects [62]. L-b-l assembly process involves sequential adsorption of oppositely charged polyelectrolytes on a solid support that results in multi-layer



13.12 Schematic of layer-by-layer nanocoatings through self-assembly [65].

coatings (or film) of nanometer thick layers (Figure 13.12). No special apparatus is required for the l-b-l process and nanocoatings can be prepared under mild physicochemical conditions. L-b-l technique has been used to create superhydrophobic surfaces which can be applicable as anti-fouling, self cleaning and water resistant coatings for micro-fluids channels and bio sensors to name a few [62, 63].

Nanocoatings on fibers or textiles is to date a relatively unexplored area with very few cited reports [64–66]. Systematic modification of the surface of lignocellulosic fibers was performed by L-b-l nanocoating process to produce negative and positively charged fibers. The fibers are coated with 20–50 nm thick polymer surface layers, which increased the interaction between the fibers during paper formation and helped to obtain stronger paper from virgin fibers [64]. Dukas and coworkers have reported antimicrobial nylon and silk fabrics by l-b-l deposition of silver nanoparticles. The heated fabrics are sequentially dipped in a solution of PDADMAC [poly (diallyl dimethyl ammonium chloride)] and silver nanoparticles, which formed a colored film of nanoparticles having strong antimicrobial activity [65].

Cotton fibers offer unique challenges to the deposition of nanolayers because of a unique cross-section as well as chemical heterogeneity of its surface. Cationic cotton surface has been coated with alternate layers of polyelectrolytes, i.e. poly (sodium 4-styrene sulphonate) and poly (allyl-amine hydrochloride) using l-b-l technique [66]. Our research group at

IIT Delhi has recently investigated this technique to deposit nanocoatings on textile surfaces using polyanion (PAH) and polycation chitosan on cotton fabric [67].

13.7 Nanocomposite coatings

A glance at the literature available shows interesting applications of polymer nanocomposites as coatings with attractive combinations of properties not achievable by neat polymeric conventional coatings. Both scientists as well as industry are actively engaged in exploring the potential applications of polymer nanocomposites as advanced coating options and some of the developments in this area are described here.

Organic-inorganic hybrid nanocomposite coatings frequently exhibit unexpected hybrid properties synergistically derived from the two chemically different components. Coatings and films based on these organic-inorganic hybrid materials are endowed with exceptional mechanical and thermal stability, allowing small thickness and making them very interesting for various applications. The organic component in the matrix offers the advantages of mechanical toughness and flexibility while the inorganic component, i.e. nanoclays or metal/metal oxide nanoparticles provides hardness, thermal stability and gas barrier properties. It has been reported that by incorporation of nanoparticles, the thin film coatings have stronger bonds and better flexibility with little cost difference. These coatings are smoother, stronger and more durable. When used on products, the results range from scratch resistant and self-cleaning surfaces to moisture absorbing clothing [68, 69]. Many companies around the world are using the properties of nanoparticles and are incorporating them within their coatings.

Novel polyurethane/MMT (clay) based nanocomposites as coatings for inflatables have been explored in an ongoing research project at the Department of Textile Technology, the Indian Institute of Technology, Delhi by Joshi *et al.* [70]. The coated fabrics showed improved gas barrier property without affecting the transparency and tear strength. Clays are believed to increase the barrier properties by creating a tortuous path that retards the progress of gas molecules, i.e. gas diffusion through the matrix resin as reported [71]. Recently Wilson Sporting Goods have introduced the Wilson Double Core Tennis Ball. The manufacturers claim that these balls retain their pressure and bounce for twice as long as conventional tennis balls [72]. The reason that these balls last twice as long is the inner core of the balls, coated with a nanocomposite coating that inhibits the permeation of air by 200% from the inside the ball. The coating was developed by InMat and utilizes aligned vermiculite platelets to impede the path of air from escaping. The platelets have an aspect ratio of 10000 to 1 and significantly increase the path/travel distance for the air. The patented coating is known as Air D-fense® and is mixed at low viscosity and hence low shear stress. The technology is being extended to the tire industry, where these coatings would inhibit the migration of oxygen inside the tire, which affects the life of the steel tire cord. This further offers the opportunity to reduce weights, improve fuel efficiency and improve pressure retention and reduce recycling and incineration costs. InMat plans to continue the development of soccer balls, footballs, bicycle tires, automobile tires and truck tires based on this technology.

Nanocomposite coatings [68] based on UV curing of clay or colloidal silica filled acrylic or epoxy resins have also been studied. The coating had improved impact resistance, tensile strength, and hydrophobicity. Clay also imparts surface roughness and makes it an efficient matting agent. Nylon 11 coatings filled with nano-sized silica and carbon black have been reported to give an improvement of 35% in scratch, 67% in wear resistance and 50% decrease in water vapor transmission rate through nano reinforced coatings compared to pure polymer coatings [73].

However, it is important to ensure that nanoparticles are incorporated into coatings for textiles or fibers without losing their superb nanoscopic properties. It is well known that due to extremely high surface area, nanoparticles take any opportunity to agglomerate so as to minimize the surface energy. The dispersion of nanoparticles in the solvent media is influenced by stirring speeds, temperature profiles and the manner and order of addition of different components. Therefore, surface engineering of nanoparticles not only aids its true dispersion at the nanolevel in the coating solution but also ideally suits the needs of specific applications, further enhancing the properties of polymer nanocomposite based coatings. The chemistry of polymer nanocomposite formulations can be optimized to achieve coatings with best performance. The synthesis of these nanoparticles in larger quantities has been attempted [74] and M/s Degussa Inc (http:// www.degussa.com) have already commercialized the process and launched a range of nanomaterials/nanoparticles for incorporating in the coatings.

13.8 Nanotechnology based fiber modifications

13.8.1 Nanocomposite fibers

Polymer nanocomposites are the advanced new class of materials with an ultrafine dispersion of nanofillers or nanoparticles in a polymeric matrix, where at least one dimension of nanofillers is smaller than about 10 nm. The nanofillers may have only one dimension in nano range – lamellar (e.g. layered silicate clays), two dimensions in nano range – fibrillar (e.g. carbon nanotubes) or all the three dimensions in nano range – spherical (e.g. metals/metal oxide nanoparticles and POSS (polyhedral oligomeric silsisquioxanes)) [75, 76].

Nano- vs microcomposite

Polymer nanocomposites have recently gained a great deal of attention because of superior properties when compared to neat polymers or conventional composites. The properties include high modulus, increased strength, improved heat resistance, decreased gas permeability and flame retardance at very low loadings of <5 wt% of nanofillers [77, 78]. In conventional composites, the mechanism of property enhancement is well understood and generally follows the rule of mixtures. On the other hand in nanocomposites, property enhancement exceeds the theoretically predicted values giving unique combination of properties synergistically derived from both the nanomaterials as well as the polymer matrix system. The volume and influence of the interfacial interactions increases exponentially with decreasing filler/reinforcement size and thus forms an additional separate phase known as interphase, which is distinct from the dispersed and continuous phases and hence influences the composite properties to a much greater extent even at low nanofiller loading (<5%). Therefore their properties are far superior to conventional composites. The interest in polymer nanocomposites further arises from the fact that they are light weight as compared to conventional composites because of the low filler loadings; they are usually transparent as scattering is minimized because of the nanoscale dimension involved and are still processable in many different ways even with nanoscale fillers embedded in the polymer matrix. The major challenges in nanocomposites are however ascertaining a high degree of dispersion of nanomaterials in the polymeric resin during nanocomposite synthesis and processing. Since the advent of nylon 6/montmorillinoite (MMT) nanocomposites developed by Toyota Motor Co. Japan [79], relentless efforts are being made globally to successfully extend this concept to almost all types of polymer matrices with a range of nanomaterials used as reinforcing entities. Polymer nanocomposites thus exploit the fascinating and useful properties of nanomaterials for a variety of structural and non-structural applications such as automotives and packaging industries, building and construction, electrical and electronics, sports and medical devices [80–82].

Polymer nanocomposites also offer tremendous potential when produced in fiber form and offer properties that leapfrog those of currently known commodity synthetic fibers. Nanocomposite fibers that contain nanoscale embedded rigid particles as reinforcements show improved high temperature mechanical property, thermal stability, useful optical, electrical, barrier or other functionality such as improved dyeability, flame retardance, antimicrobial property, etc. These novel biphasic nanocomposite fibers in which the dispersed phase is of a nanoscale dimension, will make a major impact in tire reinforcement, electro-optical devices and other applications such as medical textiles, protective clothing, etc. [83]. The work on spinning of nanocomposites started about seven years ago and several research groups across the world are exploring the synthesis, fiber processing, structure-property characterization and correlation and molecular modeling of these unique new composite fibers.

13.8.2 Nanomaterials

All the three major types of nanofillers have been incorporated in polymeric nanocomposite fibers, viz. layered silicates (MMT), carbon nanotubes and nanofibers, metal oxide nanoparticles (TiO_2, ZnO, SiO_2, etc.) and hybrid nanostructured materials such as POSS and are briefly described below:

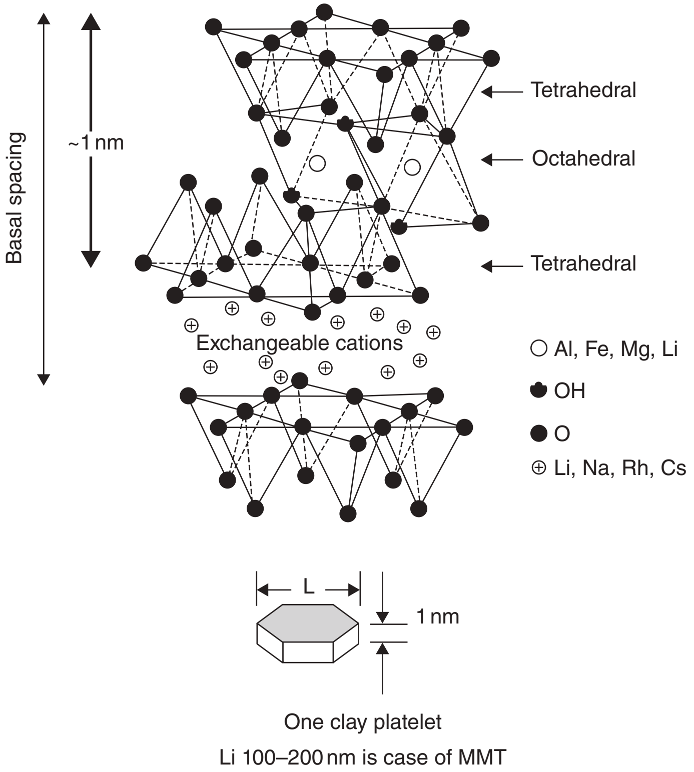
Nanoclay (layered silicates)

Layered silicates particularly Montmorillonite (MMT) clays, both natural as well as synthetic (alternatively referred to as 2:1 layered aluminosilicates, phyllosilicates, clay minerals and smectites), are the most commonly used inorganic nanoelements in polymer nanocomposite research to date [84, 85]. The chemical structure is:

Montmorillonite – $Mx(Al_4\text{-}xMgx)Si_8O_{20}(OH)_4$

M = monovalent cation; x = degree of isomorphous substitution (between 0.5 and 1.3)

Their crystal lattice consists of two-dimensional layers where a central octahedral sheet of alumina or magnesia is fused to two external silicate layers. Depending on the precise chemical composition of the clay, the sheets bear a charge on the surface and edges, this charge being balanced by counter ions, which reside in part in the interlayer spacing of the clay. Stacking of the layers by weak dipolar or Van der Waals forces lead to interlayer or galleries between the layers. The galleries are normally occupied by inorganic cations (Na^+, Ca^{++}) balancing the charge of the oxide layers. These cations are readily ion-exchanged with a wide variety of positively charged species. The number of exchangeable interlayer cations are also referred to as the cation exchange capacity (CEC). This is generally expressed as milliequivalents/100 g and ranges between 60 and 120 for relevant smectites. In layered silicates, the Van der Waals interlayer or



13.13 Structure of 2:1 layered silicates.

gallery containing charge compensating cations (M^+) separates covalently bonded oxide layers, 0.96 nm thick, formed by fusing two silica tetrahedral sheets with an edge shared octahedral sheet of either alumina or magnesia (Figure 13.13).

Pristine layered silicates usually contain hydrated Na^+ or K^+ ions. One important consequence of the charged nature of the clays is that they are generally highly hydrophilic species and therefore naturally incompatible with a wide range of polymer types. Therefore clay often must be chemically treated in order to make it organophilic. When the inorganic cations are exchanged by the organic cations, these are called organically modified layered silicates (OMLS). Generally this can be done by ion exchange reactions with cationic surfactants including primary, secondary, tertiary and quaternary alkyl ammonium or alkyl phosphonium cations. These cations in the organosilicate lower the surface energy of the inorganic host and improve wetting characteristics of the polymer matrix or in some cases initiate the polymerization of monomers to improve the strength of the interface between the inorganic and polymer matrix [86].

Table 13.3 Physical properties of carbon fiber, carbon nanofibers and carbon nanotubes

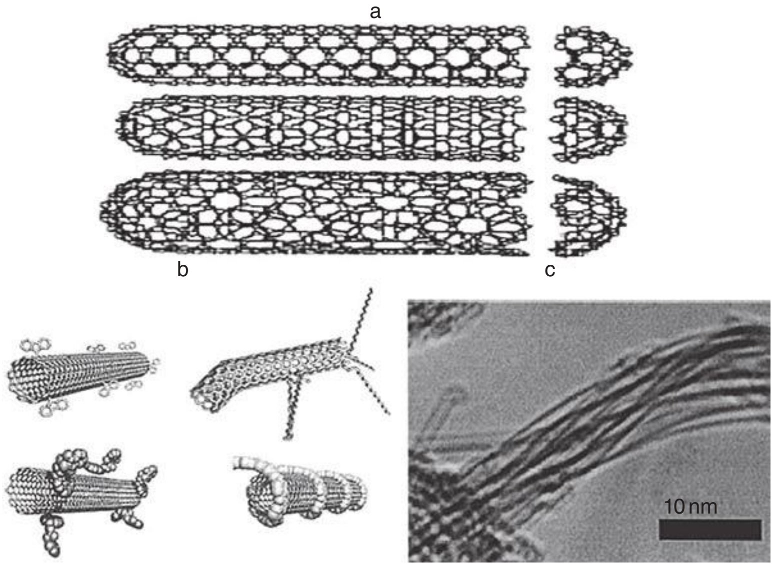
Serial no.	Properties	Carbon fibre[1]	Carbon nanofiber[2] Pyrograf I (as grown)	Carbon nanotube[3]
1	Diameter (nm)	5000	3000–20000	SWCNT(rope) ~20 SWCNT(single) ~1 MWCNT ~30–40
2	Length (nm)	–	30000–100000	1000–5000
3	Modulus (GPa)	465	400	1090–1260
4	Tensile strength (GPa)	3.92	2.7	13–52 SWCNT (rope form)
5	Strain to break (%)	0.8	1.5	SWCNT – 5 MWCNT – 12
6	Density (gm/cc)	1.88	1.80	1.3–1.5
7	Thermal conductivity ($Wm^{-1}K^{-1}$)	1400 (Max. achievable)	20	1800–3000
8	Electrical resistivity (μΩ cm)	3000 (vapor grown)[4]	1000	10^{-4} at 300 K (metallic SWCNT)

Sources

1. Donnet J., Wang T. K., Peng J. C. M. and Rebouillat S., *Carbon Fibers*, Marcel Dekker Inc., New York, 3rd Edition, 1998
2. http://www.apsci.com/home.html
3. Gogotsi Y., *Nanotubes and Nanofibers*, Taylor & Francis, Boca Raton, 2006
4. Ma, R.Z., Xu, C.L., Wei, B.Q., Liang, J., Wu, D.H. and Li, D.J. *Mater. Res. Bull.* 34 (1999), p 741

Carbon nanotubes

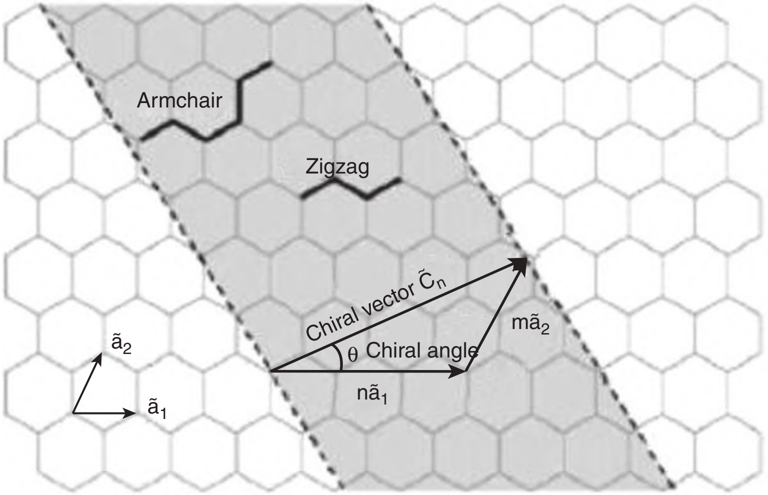
Carbon nanotubes (CNTs) were first reported by Ijima in 1991 [87]. Since their discovery, CNTs have been the focus of considerable research because of the unique and unprecedented mechanical, electrical and thermal properties they exhibit (Table 13.3).



13.14 Carbon nanotubes: (a) different types – armchair, zig-zag, chiral; (b) Functionalized carbon nanotubes: (i) covalent sidewall; (ii) defect group; (iii) non-covalent with surfactants; (iv) non-covalent with polymers; (c) Carbon nanotube in a rope form as observed under TEM [88].

Carbon nanotubes are long, slender fullerenes where the walls of the tube are hexagonal carbon (graphite structure) and often capped at each end by hemi-fullerenes. Carbon nanotubes can be visualized as a sheet of the graphite that is rolled into a tube (Figure 13.14). Unlike diamond, where a 3-D diamond cubic crystal structure is formed with each carbon (sp^3 hybridized) atom having four nearest neighbors arranged in a tetrahedron, graphite is formed as a 2-D sheet of carbon (sp^2 hybridized) atom arranged in a hexagonal array. In this case each carbon atom has three nearest neighbors [88].

Carbon nanotubes are basically of two kinds – singled-walled (SWCNT) and multi-walled (MWCNT). SWCNTs can be considered as single graphene sheet rolled up into a seamless cylinder where graphene is a monolayer of sp^2 bonded carbon atoms. MWCNTs are multilayered and simply composed of concentrically arranged single walled carbon nanotubes with a central hollow core with interlayer separation of almost 0.34 nm, an indication of the interplane spacing of graphite. A special case of MWCNTs is double walled carbon nanotubes (DWCNTs) that consist of two concentric graphite cylinders. DWCNTs are expected to exhibit higher flexural modulus than SWCNTs due to two walls and higher toughness than regular SWCNTs due to their smaller size.



13.15 Schematic diagram showing how a hexagonal sheet of graphene is rolled to form carbon nanotubes of different chirality [120].

The properties of nanotubes depend on atomic arrangement (how the sheets are rolled), the diameter and length of the tubes and the morphology of the nano-structure. The graphene sheets can be rolled up into tubes in various ways and are described by the tube chirality (or helical or wrapping), which is defined by the chiral vector (Cn) and the chiral angle (θ):

$$C_n = n_a + m_a$$

Where the integers (n, m) are the numbers of steps along the unit vectors (a_1 and a_2 of the hexagonal lattice. Using m and n, the three different types of orientation of the carbon atom around the nanotube circumference is specified as armchair, (n = m), zigzag (n = 0, m = 0) or chiral (all others) (Figure 13.15). The chirality of the carbon nanotubes has significant implications on its properties, especially on the electronic properties. All armchair SWCNTs are metallic with a band gap of 0 eV. SWCNT with $n - m = 3i$ (i being an integer ≠ 0) are semi-metallic with a band gap of few MeV, while SWCNT with $n - m \neq 3i$ are semiconductors with a band gap of 0.5–1 eV. MWCNTs contain a variety of tube chiralities, so that their properties are more complicated to predict.

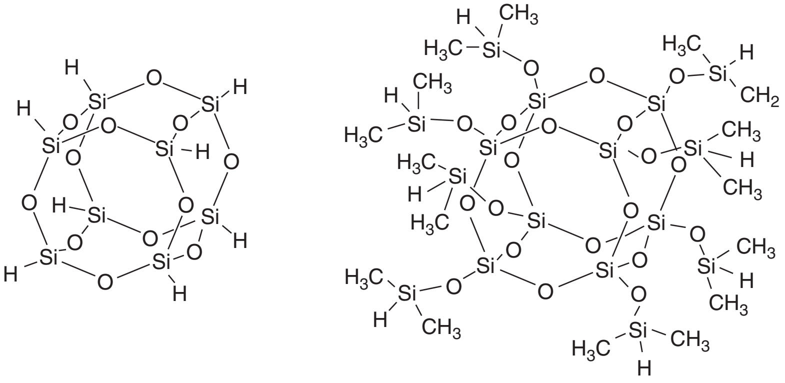
MWCNTs and SWCNTs are mainly produced by three techniques: arc discharge, laser ablation and chemical vapor deposition (CVD). The various aspects of nanotube production, purification, suspension, filling, functionalization and application as well as the fabrication and characterization of polymer nanocomposites with various types of nanotubes have been extensively reported in literature [89]. All known preparations of the carbon nanotubes give mixtures of nanotube chiralities, diameters and lengths along with different amounts and types of impurities. This CNT heterogeneity makes purifications of carbon nanotubes an essential requirement before they can be put into any application including synthesis of polymer/CNT nanocomposites.

CNTs exhibit exceptional material properties that are a consequence of their symmetric cage-like structure and exceed those of any previously existing materials. The high aspect ratio of CNTs coupled with a strong intrinsic Van der Waals force of attraction between nanotubes combine to produce ropes and bundles of CNT. SWCNTs where the attractive force is very high (0.5 eV per nm of CNT to CNT contact) are more prone to form ropes and bundles. Ropes refer to collections of SWNTs and are more uniform in diameter to form hexagonal lattices, while bundles are non-crystalline collections of SWCNTs or MWCNTs. It is for this reason that dispersion of CNTs in solvent to produce suspensions, need assistance of either sonication or surfactant addition or both combined besides mechanical stirring.

POSS

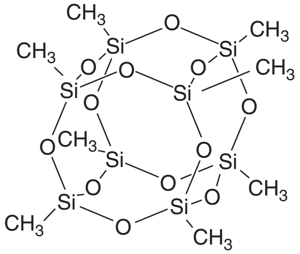
Polyhedral oligomeric silsesquioxanes (POSS) are an important class of nanostructured hybrid inorganic-organic materials and are widely regarded as one of the most promising and rapidly emerging nanocomposite materials. POSS molecules are of nanosized polyhedral or cage-type structure consisting of an inner silicon-oxygen $(SiO_{1.5})_x$ based framework with organic substituents (R) on outer corners and with a precisely defined silicon-silicon distance of 0.53 nm (Figure 13.16). The ratio of Si:O is 2:3.

The average diameter of a POSS molecule is 1.5 nm. The inorganic silicon-oxygen core is thermally and chemically robust. The organic substituents (R) are either totally hydrocarbon in nature or a range of polar structures and functional groups are also included. These organic substituents can be totally reactive or nonreactive or a combination of the two, depending on the synthetic design (Figure 13.16). According to the nature of the organic substituents, they undergo nucleophilic substitution or hydrosilylation. The density of POSS chemicals is typically in the range of 1.12 gm/ml, despite a high molar mass of about 1000 amu. The reason is most of the volume is taken up by the organic (R) groups, which lie on the outside of the cage whereas the core occupies only 5% of the overall cage volume. The physical state (solid, wax or liquid) ranges from low solubility

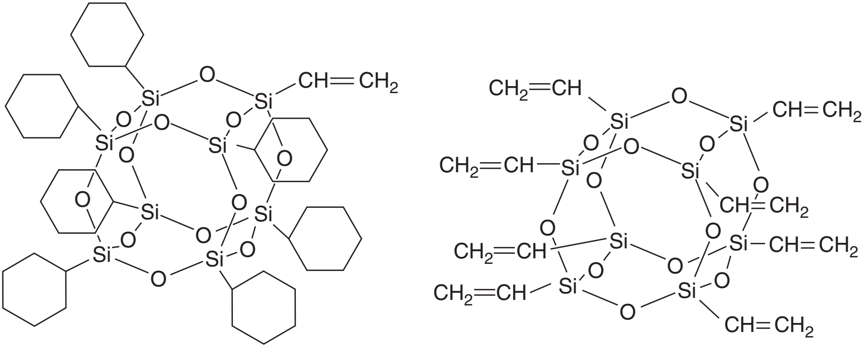


T type (T_1H_1)

Q type ($Q_nM_A{}^M$)



Nonfunctional



Monofunctional

Multifunctional

13.16 Various types of POSS structure [90].

system with T_m ~400°C to wax or grease or low temperature flowable oil depending on the nature of the organic (R) groups along with the topology of POSS cages [90].

POSS was first developed by the US Air Force for aerospace applications. POSS originally cost $5000 per pound (454 g) and took up to three years to produce. Due to simplified and redesigned process chemistry, now production cost has come down but still it is expensive. A variety of POSS monomers in form of solids or oils are now commercially available from Hybrid Plastics Company Co. (http://www.hybridplastics.com/), USA. A wide range of POSS compounds is now available that contain a combination of covalently bonded reactive functional groups that make them suitable for polymerization, surface bonding or other chemical transformations [91]. POSS moieties can thus be easily incorporated via copolymerization, grafting or blending into common plastics. POSS incorporated polymeric materials show significant improvements in use temperatures, oxidation resistance, surface hardening and enhanced mechanical properties. Reductions in flammability, heat evolution and viscosity during processing are also added advantages [92].

13.9 Polymer/clay nanocomposite fibers (PCNF)

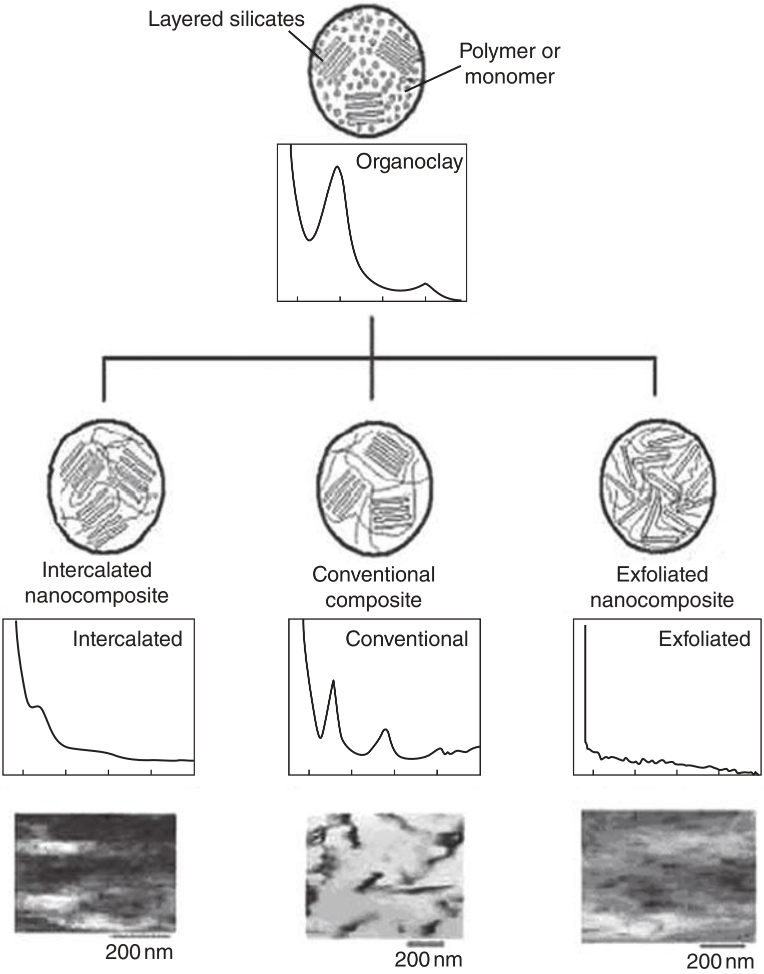
Incorporation of organoclay into a polymer matrix has been used to modify the fiber and textile performance. The main effects are in physical properties, e.g. enhanced tensile modulus and strength, reduced thermal shrinkage, controlled electrostatic behavior, high storage and reduced loss modulus under dynamic mechanical testing conditions. In addition, presence of hydrophilic clay also enhances moisture absorption (at a slow rate), dyeability, biodegradability and chemical resistance. Since clay platelets block UV irradiation PNCFs exhibit improved weatherability. Reduced flammability of PNCFs arises due to inherent nature of clay to reduce the burning rate and form char. With these improved properties, these fibers have an edge over their neat counterparts in applications of both domestic and industrial textiles [83, 93–97].

PCNFs have been mostly spun through three basic methods of fiber spinning [83]:

- Melt spinning
- Solution spinning
- Electrospinning.

The major challenges here are achieving maximum extent of intercalation and exfoliation of clays in the polymer matrix (Figure 13.17). Owing to hydrophilic character of clay, the preparation of PCNF is easiest with water-soluble polymers. The increasing nonpolarity and hydrophobic nature of polymers, makes it more difficult to disperse the hydrophilic clay in an organic matrix. The strategy used to overcome this problem is two-fold:

- Modification of clay so as to make it organophilic
- Use of compatibilizer.



13.17 Idealized polymer/clay nanocomposite structures along with their WAXD patterns and TEM images.

Organomodified clays have a quaternary ammonium ion with paraffin substituents, e.g. dimethyl di-hydrogenated tallow ammonium chloride (2M2HT) intercalated in interlayer galleries replacing the Na^+, K^+ cations making the clays organophilic and thus more dispersible in the polymer system. However, there is a tendency of quaternary ammonium ions to degrade at the higher polymer processing temperatures, i.e. 150–180°C. Attempts have been made to have groups such as 1,2-dimethyl-hexadecyl-imidazulam-MMT (IMD-MMT) and didecyl–triphenyl phosphonium-MMT (Cl2 PPH-MMT) which have higher thermal stability [98].

Nanoclay reinforced fibers have been produced from a number of polymers but only PNCFs based on polyester (PET) and polyamide (nylon 6 and nylon 66) are being reviewed in the section below.

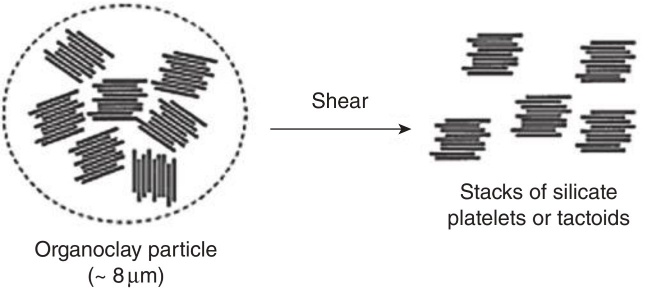
13.9.1 Polyamide/clay nanocomposite fibers

Polyamide-6 (PA 6)/clay nanocomposites have been widely investigated due to their much superior tensile strength and modulus, improved heat resistance (heat distortion temperature increases from 65°C to 120°C) as well as excellent gas and water barrier properties [99–100] over their neat PA6 counterparts. However, specific studies on spinning and characterization of polyamide/clay nanocomposite fibers have been relatively few and are reviewed here [101–112].

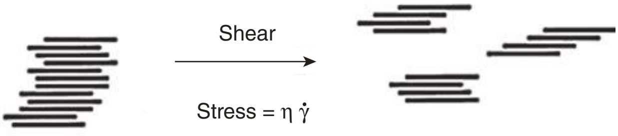
Nylon 6 (PA 6)/clay nanocomposite fibers (PAMC) are generally produced using the melt-spinning route, where nylon 6 chips are compounded with MMT nanoclays during the melt extrusion process using mostly twin-screw configuration. Attempts have also been made to spin fibers of PA 6/clay by in-situ polymerization technique using double screw reactive extrusion [103]. The molecular weight and weight distribution measured for the polymerized PAMC fibers measured by GPC showed a tendency to first increase and then decrease with increasing screw speed. It succeeded in inserting a covalent linkage between OH-groups of organomodified silicate and the amino groups on PA 6.

The compounding of MMT clays into polymeric matrix is usually done on a single or double screw extruder, where the dispersive forces, i.e. shearing action inside the barrel, is responsible for breaking the minor components domain, i.e. clay particle to desired size and get homogeneously distributed in the matrix (Figure 13.18). It is reported that extensional flow mixer generates better dispersion and distribution mixing and is claimed to be orders of magnitude more efficient than shear mixing [83]. Hence the extensional flow mixer has been designed as an inexpensive mixer to be attached to either single or twin-screw extruder.

PA 6/clay nanocomposite fibers have also been produced using a high-speed melt spinning process at take-up velocities of 1–5 km/min. The clay used in all these researches is the most widely used organomodified MMT clay at the 2–5-wt% loading. Careful control of drawing conditions such as drawing temperature and ratio and subsequent annealing step are important to get the desired properties and has been investigated by several researchers [102, 104, 106, 110, 117]. The effect of clay on the fiber structure development and resultant properties has been reported by several researchers [101, 103–104] but more in detail by Giza *et al.* [110, 111] from Tokyo Institute of Technology, Japan.



(a)



Shearing of platelet stacks leads to smaller tactoids

(b)

Platelets peel apart by combined diffusion/shear process

(c)

13.18 Mechanism of exfoliation of clays: (a) organoclay particle break up; (b) clay tactoid break up; (c) platelet exfoliation.

PA 6 generally crystallizes in two crystalline forms, α form, which is monoclinic, and metastable γ form, which is pseudohexagonal. The α form generally grows by slow cooling from the melt or develops on annealing or drawing. The γ form is obtained by fast cooling from the melt notably in fibers spun at moderate spinning rates. The nanoclays in PA 6/clay nanocomposite fibres are reported to behave as γ-nucleating agents in both injection molded samples as well as oriented spun fibers [112]. However, these rapidly turn into alpha crystal form upon drawing. Matrix shearing in between the MMT platelets during drawing imparts better packing and cohesion to hydrogen bonded planes and thus improves their thermal stability as compared to those of neat PA 6 fibers [112]. PA 6/clay composite fibers also showed higher crystallinity in the case of whole take up range (1–5 km/min) as compared to neat PA 6 fibers (1–7 km/min) although the clay content does not affect the crystallinity values when produced using high speed spinning much. The PA 6/clay fibres when spun at such high speeds show better orientation of crystalline entities and also higher birefringence values, but only in the low take up region (up to 3 km/min). The orientation induced crystallization led to direct formation of α form crystals in the spin line, which started at 2 km/min for PA 6/clay fiber and at 4 km/min for neat PA 6 fiber as revealed by WAXD studies. The PA 6/clay nanocomposite fibers showed superior Young's modulus at all take up velocities but tenacity was higher only in low temperature velocity region where crystallization in the spin line of neat PA 6 did not occur yet [110, 111]. Thus nylon 6/clay nanocomposite fibers show reduced crystallinity and lower molecular orientation, which explains the observation of no significant improvements in tenacity in most of the studies. However, stiffness of intercrystalline regions and role of rigid clay particles in stress transmission behavior explains the superior modulus in PA 6/clay nanocomposite fibers.

Apart from improved mechanical properties the presence of clay in PA 6/clay fibers also affects its dyeing ability. The DSC studies show that presence of clay in PA 6 induces γ crystalline form, increases the crystallization temperature and decrease the melting point. A higher amorphous content observed improves the accessibility for disperse dyes. Thus PA 6/clay yarn dyes itself faster with disperse dyes than an unfilled PA 6 yarn while it gives opposite effect with acid and metal complex dyes. In both cases, nanoclay fixes on the amino sites and thus prevents fixation of acid or metal complex dyes [103]. The incorporation of clay in PA 6 fibers also leads to improved fire resistance and lowered flammability properties, thus offering a new promising route for flame retardant textiles with permanent effect and at low cost [108, 109].

13.9.2 Polyester/clay based nanocomposite fibers

There are significant opportunities for enhancing the properties of polyester fibers by incorporation of inorganic layered silicate nanoclays (MMT), as revealed by a number of research studies and patents reported in the literature [113–119]. Poly (ethylene terephthalate), PET/MMT clay nanocomposites are generally prepared by in situ interlayer polymerization [113–115] and then melt spun to produce monofilaments with varying draw ratios. The nanocomposite is prepared by mixing ethylene glycol, dimethyl terephthalate in the presence of organically modified silicate (0.5–15%), 0.001–1.0% additives and/or 0.001–1.0% catalyst (oxide acetate of Sb, Ge, Ti or Sn) and then polymerizing it [114]. The organic modifiers used for MMT clays are mostly phosphonium cationic salt [94, 113], which make the organomodified clays thermally stable and thus able to withstand the high temperatures involved during PET polymerization. The clay is generally well dispersed in the PET matrix as observed under scanning (SEM) and transmission electron microscopes (TEM), but some clays were agglomerated at a size level in the range 10–20 nm [116]. The interlayer distance of MMT dispersed in the nanocomposite fiber was further enhanced because of the strong shear stresses during melt spinning [117].

The structure and properties of the PET/clay nanocomposite fibers have been studied as a function of organoclay content and the draw ratio (DR) given. The PET/clay hybrid nanocomposite fibers generally show improved thermal stability and mechanical properties as compared to their neat counterparts [116] even at low organoclay contents (<5 wt.%). The composite fibers also exhibit improved dimensional stability, higher modulus and low shrinkage. The tensile properties generally increase with increasing clay content up to DR = 1. However the values decrease with increasing draw ratio (DR 1–6) and also higher clay content beyond a critical concentration [94, 118]. DSC and WAXD test results show that incorporation of clay generally accelerates the crystallization of PET but the crystallinity and orientation of drawn fibers is generally lower than that of drawn neat PET fibers [95]. The strong interaction between MMT and PET restricted the motion of PET chains, which developed a special continuous network structure and inhibits thermal shrinkage of PET and also improves other thermo-mechanical properties of PET fibers.

The PET/clay nanocomposite fibers with improved properties have the potential of finding application in tire cords to reinforce the rubber [96, 119]. High strength, heat resistance, heat resistant adhesion and low heat emission properties are required for tire and tire cords. Polyester tire cords are more attractive for this use but have some weaknesses. PET/clay nanocomposite fibers can overcome some of the weaknesses of the neat PET fibers and thus enhance the stability, uniformity and ride comfort. The incorporation of clay in polyester fiber also improves its dyeability with disperse dyes and making deep dyeable polyester a possibility [114].

13.10 Carbon nanotube (CNT) based nanocomposite fibers

Nanocomposites based on polymers dispersed with carbon nanotubes and nanofibers are beginning to receive substantial attention today because the carbon nanotubes offer immense potential to impart unique mechanical, electrical and thermal properties to polymeric fibers both polyester and polyamides [120]. Carbon nanotubes are characterized by high flexibility, low mass density and large aspect ratio, i.e. 300–1000. Some nanotubes are stronger than steel, lighter than aluminum and more conductive than copper. The theoretical and experimental results on single wall carbon nanotubes (SWNTs) show extremely high tensile modulus (640 GPa to

1 TPa), tensile strength (150–180 GPa) and failure strains too, of the order of 5 to 20%. SWNTs also possess very high electrical and thermal conductivity (theoretically >6000 $W/m^{-1}k^{-1}$). Depending on their structural parameters, SWNTs can be metallic or semi-conducting [120]. The first nanocomposites based on CNTs were reported by Ajayan *et al.* in 1994 [121, 122]. The major challenges in polymer/CNT nanocomposites are as follows.

The 'less than ideal' and inconsistent nature of CNTs: all known methods of CNT production, give a mixture of CNTs with different chiralities, diameters and lengths, along with varying amount of impurities and structural defects within the sample or that from different batches. Hence, it is very difficult to obtain reproducible results [120]. Dispersion of CNTs in a polymer matrix is also very crucial to achieving the predicted properties. Due to Van der Waals interaction, SWNTs typically form bundles of 30 nm in diameter containing several hundred tubes within a bundle. These tubes are also highly entangled and the degree of entanglement depends on their length. Various physical and chemical approaches have been tried to disperse them, which include sonication, choosing the correct dispersion medium and use of surfactants to aid in dispersion [123]. Another great challenge is the efficient translation of CNT properties into the polymer matrix, which means ensuring a good interfacial interaction between the two; CNTs being inert, are not easily dispersed and will not interact with most of polymer matrix systems.

The approaches used are to functionalize the CNTs by oxidation, end cap functionalization with long aliphatic amines and sidewall functionalization using fluorination, alkylation, etc. [124]. Polymer grafting to create functional groups on CNTs has also been reported, which improves their dispersion as well as the interfacial interaction [125]. Non-covalent functionalization is achieved by adsorbing different polymers onto SWNT to improve dispersion. The SWNT solubilization by 'polymer wrapping' is also an alternative method for tuning the interfacial properties of nanotubes [126] (Figure 13.14).

Carbon nanotube orientation preferentially along the fiber axis plays a very critical role in imparting high tensile properties in CNT based polymeric nanocomposite fibers. SWNTs with a density of 1.3 g/cm^3 have the potential of producing a high performance fiber with at least twice the specific tensile strength and specific tensile modulus of the presently known state-of-the-art PAN based carbon fiber [120, 123, 127] even at very low loading. However, large scale economic synthesis of CNTs and the ability to synthesize CNTs of uniform diameter and chirality will be critical to the commercial success of this new advanced class of materials for both molded parts, films as well as fiber forms. The CNT based polyester and polyamide nanocomposite fibers will be reviewed in this section.

13.10.1 Polyester/CNT based nanocomposite fibers

Oriented polymer systems such as fibers provide a unique opportunity to align the CNTs in one particular direction during the process of melt spinning and the subsequent drawing step. However one of the obstacles to widespread use of application of the nanotubes is the inability to orient them in one particular direction. Jose and coworkers at University of Alabama at Birmingham [128], focused on aligning carbon nanotubes in Vectra (a thermotropic liquid crystalline polymer) as well as polypropylene matrix during melt spinning into fibers. CNTs in two different weight percentages (0.5% and 1.0%) were used. Correlation of CNT alignment along the fiber axis and dispersion in the polymer matrix was studied using TEM (Transmission Electron Microscopy). Significant improvement in mechanical properties, i.e. tensile strength and modulus and a substantial increase in onset of decomposition temperature indicated both a good dispersion as well as a highly aligned CNT system.

Inherent hierarchical structure was observed in the form of fibrils that develop in vapor grown carbon nanofibers (VGCF) dispersed in a liquid crystal polymer matrix by Rohatgi *et al.* [129]. The tensile properties were sensitive to the diameter of extruded filament, the amount of VGCF added and other parameters related to the extrusion process. There is a noticeable increase in mechanical properties of composite filaments with decreasing filament diameter irrespective of VGCF content.

13.10.2 Polyamide/CNT nanocomposite fibers

There are several reports on nylon/CNT nanocomposites, where CNTs (single or multiwalled) or CNFs (carbon nanofibers) are infused into the polymer through liquid route using sonication or dry route followed by melt mixing in a single or twin screw extruder [130]. Alignment of CNTs and CNFs in the compositions was enforced during extrusion or subsequent stretching process. However, fullest potential of CNT reinforcement has not been harnessed in polyamide/CNT nanocomposite fibers, primarily because of lack of alignment or failure to develop strong interfacial bonding between CNTs and polymer.

Mahfug and co-workers [131] report a method to fabricate nylon 6/CNT reinforcement, where the MWNT reinforcement at low loading (<1 wt%) leads to 50% increase in tensile strength which is almost twice that of unreinforced nylon and never reported elsewhere in the literature. The spectacular enhancement of mechanical properties is attributed to the successful alignment of CNTs and the high interfacial shear strength developed during the fabrication process. The methodology described by them is different from that generally reported and involves special distributive mixing of CNTs using a specially designed die and a prolonged thermal stabilization process prior to melt extrusion. These polyamide/CNT nanocomposite fibers have a great potential for use as multifunctional textile materials in several technical and advanced composite applications [132].

13.11 Nanoparticle based nanocomposite fibers

Preparation of PA 6/nano titanium dioxide (TiO_2) composites and their spinnability has been reported by Zhu *et al.* [133] of Dong Hua University, Shanghai, China. The nanoscaled TiO_2 particles were surface treated with coupling agents prior to mixing with molten PA6. The composite fibers showed improved mechanical properties as compared to pure PA 6 fibers and composite fibers with unmodified TiO_2.

PET/SiO_2 nanocomposites were synthesized using in situ polymerization and melt spun into fibers. The fibers PET/SiO_2 nanocomposite [134, 135] fibers showed a greater degree of weight loss as compared to pure PET fibers when they were hydrolyzed using alkali treatment. Superfine structures such as cracks, craters and cavities introduced due to this facilitated deep dyeing of PET/SiO_2 nanocomposite fibers. PET/silica as spun nanocomposite fibers show improved tenacity, modulus and lower heat shrinkage [136]. The silica nanoparticles get well dispersed in PET in the range 10 nm with narrow distribution. On the other hand, PET/TiO_2 nanocomposite fibers have been prepared by in situ polycondensation and melt spinning [137]. Nanotitania were first treated with a coupling agent to introduce functional groups on surface of titania particles and thus aid in dispersion of nanoparticles homogeneously. The UV protection property of these fibers was much enhanced ($UPF > 50$) because of high refractive index and absorption of UV light by the rutile form of nanotitania incorporated. However, these fibers had slightly reduced tensile strength and elongation at break. PET nanocomposite fibers have been reported with a range of other nanoparticles also, i.e. TiO_2, SiO_2, ZnO and $CaCO_3$. The nanoparticles are treated with low surface tension additive before mixing with PET [138].

POSS based nanofillers have been incorporated in PET and polyamide fibers/filaments and show improved thermomechanical properties and better retention of modulus at higher temperatures [139]. These fibers can find application in automotive tire reinforcement [140, 141]. However, the extent of reinforcement was found to be variable in the case of PET systems, which can be either due to low interaction between PET and POSS causing processing problems related to some water generation or chemical transformation of the POSS particles themselves [141].

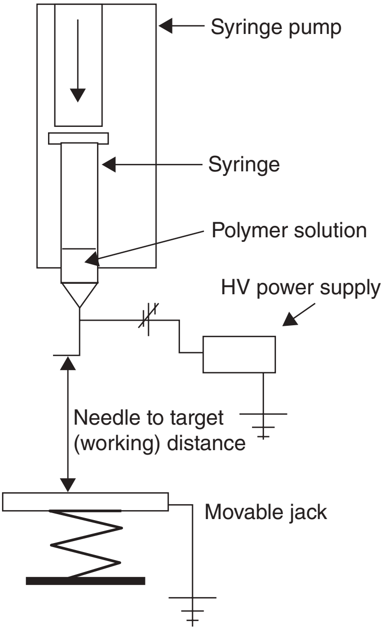
13.12 Nanofibers

Recently, there has been an increased interest in producing nanofibers that are submicron size in diameter. Typically conventional melt blown ultrafine fiber diameter ranges from 2000 to 5000 nm, whereas polymeric nanofibres ranges from 50 to 500 nm. Nanofibers are characterized by an extraordinarily high surface area per unit mass (for instance nanofibers with 100 nm in diameter have a specific surface of 1000 m^2/g) high porosity and lightweight. These unique properties of nanofibres make them potential candidates for a wide range of applications such as filtration, barrier fabrics, protective clothing, wipes and biomedical applications such as scaffolds for tissue engineering [142].

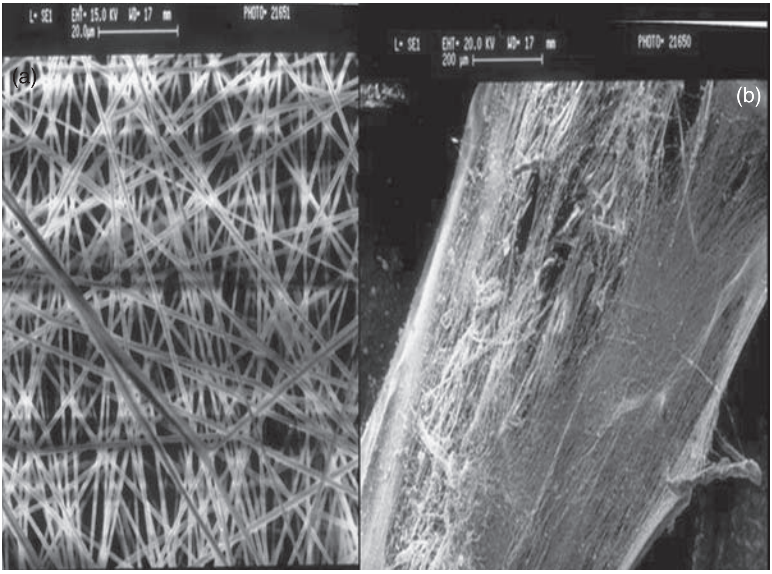
13.12.1 Electrospinning

The manufacturing technique most commonly associated with polymeric nanofibers is electrospinning, which is fundamentally different from conventional fiber production techniques, and is based on electrostatic forces. The idea dates back at least 60 years, but recent interest has been renewed by the pioneering work done by Dr Darryl Renekar at the University of Akron [143], who demonstrated electrospinning for a wide variety of polymer solutions including rigid rod polymers. The basic theory of the nano-fiber spinning process and the parameters affecting the process, thermal and mechanical properties of electrospun nanofibers has been much reviewed [144–147].

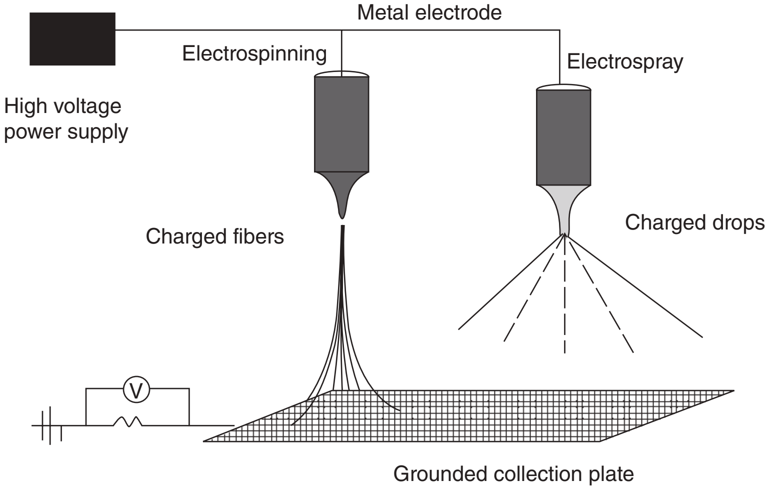
Electrospinning is a process that produces continuous polymeric nanofibres (diameter in the submicron range) through an action of an external electric field imposed on a polymer solution or melt. In this technique, a polymer is dissolved in a solvent (polymer melts can also be used) and placed in a glass capillary, which is sealed at one end and a small opening in a necked down portion at other end. A high voltage potential (730 kV) is then applied between the polymer solution and a collector near end of the capillary tube (Figure 13.19). When a voltage is applied to the polymer solution, the electric force results which cause a jet of polymer solution flowing from a droplet tip to be drawn toward a grounded collector. After the jet flows away from droplet in a nearly straight line, it bends and whips into a complex path and other changes in shapes occur, during which electrical forces stretch and thin it at very large ratios (about 100 000) in a short distance and in less than one second. After the solvent evaporates, solidified nanofibers are left, mostly in nonwoven web form on the collector. This nanofiber deposition cannot be seen by the naked eye and is generally viewed under the scanning electron microscope (SEM) (Figure 13.20).



13.19 Schematic diagram of electrospinning set-up [153].



13.20 SEM images of (a) electrospun nanofibrous web, (b) cotton yarn coated with nanofibrous web.



13.21 Electrospraying and electrospinning set-up [147].

The electrospinning process can be considered as a variation of the electrospraying process. In the electrospraying process, the surface of a hemispherical liquid drop suspended in equilibrium at the end of the capillary will be distorted into a conical shape in the presence of an electrostatic field. A balancing of the responsive forces resulting from the induced charge distribution on the surface of the drop with the surface tension of the liquid causes this distortion. Once a critical voltage (Vc) is exceeded, a stable jet of liquid is ejected from the cone tip. The jet breaks into droplets as a result of surface tension in the case of low viscosity liquids. For high viscosity liquids the jet does not break up, but travels to the grounded target. The first case is known as electrospraying and is used in industries to obtain aerosols and when applied to polymer solution and melts (second case) it generates polymer nanofibres through the electrospinning route (Figure 13.21) [147]. The morphological studies indicate that electrospinning process does partially orient the molecules in fibers, although to date all nanofibers produced are without any control over forces during orientation and crystallization.

Most of the literature on electrospinning has explored a variety of polymer/solvent systems from which fibers can be produced. Only a few studies have addressed the processing/property relationships in electrospun fibers. The structure and property of electrospun nanofibers are predominantly determined by the synergistic effect of solution parameters and electrostatic forces. Processing parameters considered are solution concentration and viscosity effects, spinning atmosphere effects, accelerating voltage effects and tip to target distance [146, 147]. Solution viscosity has been found to influence fiber diameter, initiating droplet size and jet trajectory. Increasing solution viscosity has been associated with the production of large fiber diameters. Spinning atmosphere has been associated with the jet splaying phenomenon also reported by Renekar *et al.* [148]. Other processing variables, such as acceleration voltage, electrospinning current and tip to target distance have also been investigated and linked to fiber morphology and defect structures [149].

13.12.2 Nanofiber morphology: effect of process parameters

Voltage dependence [147]

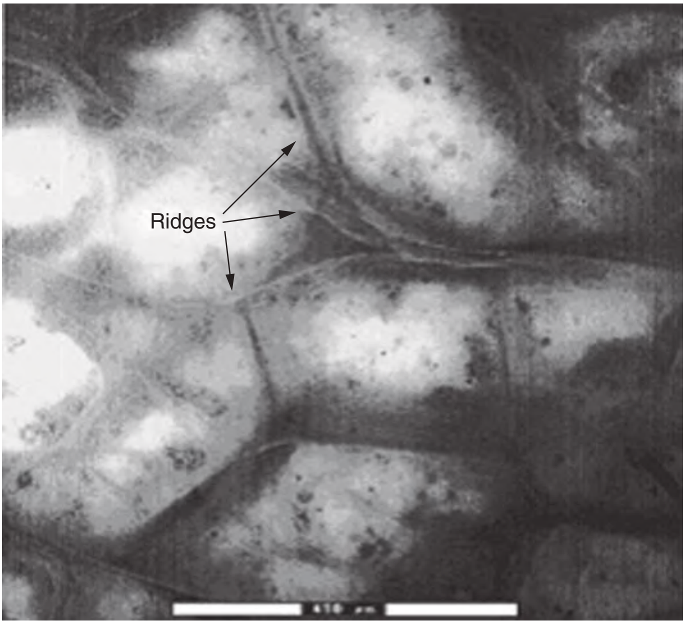
As the accelerating voltage is increased, electrospinning current generally increases step wise, which reflects in increase in mass flow rate from the capillary tip to the grounded target, when all other variables such as surface tension and charge density are kept constant. This is generally related to changes in originating droplet shape, which is related to bead defects in electrospun fibers. At low voltages, the electrospun fibers have a cylindrical geometry and distinct decrease in bead defects. As voltage increases, the density of bead defects significantly increases.

Concentration dependence [147]

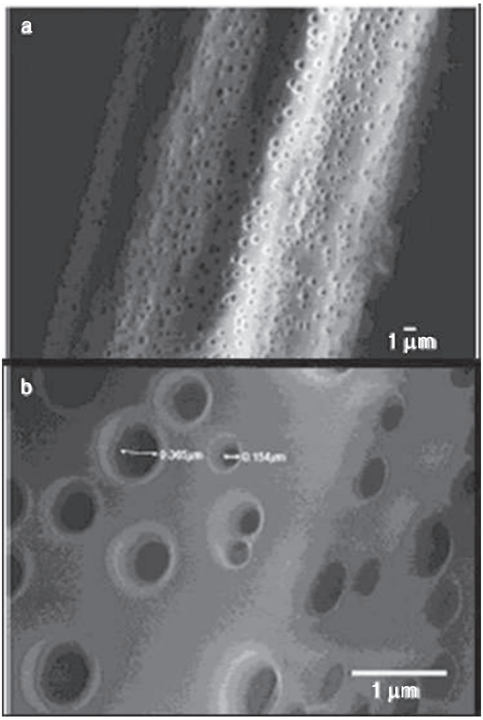
Solution surface tension and viscosity also play an important role in determining the range of concentrations from which continuous fibers can be obtained in electrospinning. At low viscosities ($\eta < 1$ poise), surface tension has dominant influence on fiber morphology and below a certain concentration drops will form instead of fibers. At high concentration ($\eta > 20$ poise), processing is inhibited by the inability to control and maintain the flow of a polymer solution to the tip of the needle by the cohesive nature of high viscosity solutions. Although the range of concentrations that produce fibers will obviously vary depending on the polymer/solvent system used, the forces of viscosity and surface tension will determine the upper and lower boundaries of the processing window, other variables being constant.

Buer and co-workers [146] further investigated the various electrospinning equipment design parameters such as controlled feed rate of polymer solution using a syringe pump, choice of capillary material, extraneous currents and varying collecter geometries (static, moving screen or plate) and construction material, etc. on the quality of nanofibers produced. Electrospinning is thus a fast and simple process of producing a wide range of nanofibers. The collected webs of nanofibers usually contain fiber with varying diameters from 50 nm to 2 μm. Sometimes the main fiber breaks up into many smaller filaments, a process called ‘splaying’, which happens because of electrostatic instabilities under certain conditions. As compared to melt blown nanofibers, electrospun fibers have a much narrower diameter distribution.

The path of electrospinning jet being a combination of bending, looping and spiraling generally leads to nanofibers in mostly a nonwoven web form with no preferred orientation. There have been attempts to produce electrospun ultrafine fibers in an aligned fashion by the use of a cylinder surface moving linearly. The fibers are taken up tightly in a circumferential manner resulting in a fair alignment. The other route is to dampen the jet and control the deposition of electrospun fibers on a target. A series of charged rings acts as an electrostatic lens and changes the shape of the electric field. Modification in collector designs such as moving planar surface [150] or a cylinder with a rotating high speed [151] and a collector with a gap [152] are other approaches to collect nanofibers in an aligned form. An interesting and unique observation has been reported by Beck Tan and coworkers [147], where they observed that electrostatic effects also influence the macroscale morphology of electrospun textiles and may result in the formation of heterogeneous or 3D structures. They also observed that residual charge left on electrospun fibers affects the way they organize themselves on nonwoven textile substrate. 3D honeycomb structures were observed by them under a microscope when using dilute solutions onto a wire screen (Figure 13.22). Rabolt and coworkers [153]



13.22 3D structure of a nonwoven fiber mat electrospun from a 7-wt% solution of PEO in water onto a cloth substrate [147].



13.23 FESEM image of porous polystyrene (PS) electrospun fibers [153].

have created a highly micro- and nanostructured ‘porous’ morphology in electrospun nanofibre (Figure 13.23), thus increasing their range of application significantly. The pores vary from densely packed, well-formed nanopores to large flat pores. The increased surface area of electrospun fibres was due to highly volatile solvents used.

Other techniques to produce nanofibers

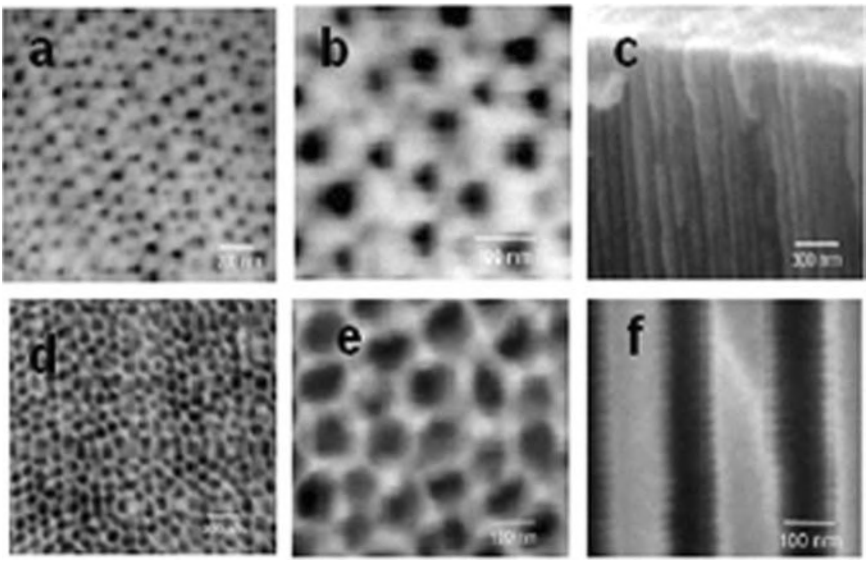
Although electrospinning has been most widely reported in producing nanofibers, the low production rates of this process are a major limitation in upscaling this technique, and thus make it mostly a laboratory curiosity. However, attempts have been made to speed up the process using multiple syringes [154] as well as using needleless spinning. The production rate of nanofibers through electrospinning is generally measured in grams per hour.

Nanofibre Inc. Aberdeen, North Carolina, USA, have developed a unique process of producing nanofibers through melt blowing using a molecular die [155]. The fibers produced are a mixture of both micron and sub-micron sized fibers. But it is a relatively inexpensive technique and can produce nanofibers in large quantities at a cost of $10 per kg. Although it is a relatively inexpensive technique and can produce nanofibers in large quantities at a cost of US$10 per kg, the broad range of fiber diameters produced is a concern. If perfected this technique can certainly take nanofiber production to a commercial future because of higher production rates as compared to electrospinning.

The other technique is that based on making bicomponent fibers that split or dissolve. The most researched is the production of islands in the sea fiber using a standard spin/draw process. The production rate is 5 kg/h at a take up speed of 2500 m per minute. Both PET and PA 6 nanofibers of diameters approx (300 nm) can be produced using EVOH as sea polymer, and the ratio being 50/50. Unlike electrospinning and melt blown technique, the nanofibers produced are in a narrow range and the projected cost is 1 to $5 per kg. Another possible approach is the use of bicomponent fiber spinning to manufacture nanofibres by the splitting process. The number of segments needs to be greater than 16 and use a water-soluble polymer in a small ratio along with PET and PA 6 [156].

Toray Industries Inc. [157] have developed a new technology for producing multifilament nanofibers comprising monofilaments whose diameter is in nanorange. The technology is versatile not only in its ability to be applied to commodity polymers such as nylon or polyester, but also in that nanofibers can be manufactured using existing production equipment. They have succeeded in producing for the first time nylon nanofibres having uniform diameter in nanorange through optimization of rheological properties of polymers themselves. Since nylon nanofibers are of multifilament continuous structure, they can be easily fabricated into a wide array of products while the orientation and shape of the nanofibers can be easily controlled, enabling their application to be extended into various fields. The nylon nanofibers produced have about 1000 times larger surface area than conventional fibers, thus adsorption and adhesion properties and novel functions attributable to fiber surface are also more pronounced and promise a variety of applications as advanced materials. The moisture absorption of these nylon nanofibers is about two to three times higher than conventional nylon, which is comparable to cotton.

In another ongoing NTC project at Georgia Tech, USA [158], a unique method of producing nylon and polyester nanofibers using ‘extrusion polymerization’ through mesoporous silica and aluminum channels as nanoreactors is being investigated (Figure 13.24). Unlike electrospun nanofibers, which are neither strong nor stiff, the polymer molecules in these fibers are not oriented. The nanofibers produced using this new technique will possesses high mechanical properties as they have a high degree of crystallinity from extended chain crystals formed inside the nanochannels.



13.24 (a, b, c) Alumina nanochannels as prepared (pore size ~40 nm), (d, e, f) pore formation and widening (pore size ~100 nm), (e, f) longitudinal structure of nanochannels for alumina [158].

Thus, new researches in producing nanofibers in a continuous and aligned mono- or multi-filament form with more uniform diameter and narrow range have a potential to bring nanofibers in the market place, at a reasonable price and acceptable production rates. Nanofibers have been produced mostly through electrospinning from a wide range of polymeric materials [159] but other techniques as described above [160] also show a lot of promise in the future success of nanofibers.

Polymer nanocomposite based nanofibers

Recently, electrospinning has also been extended to making nanofibers from polymer nanocomposites, incorporating nanoclays, CNTs and other nanoparticles and adding a new dimension to nanofibers. Fong *et al.* [161] were the first to report electrospun nanofibers (~100 nm) based on nylon 6/exfoliated MMT clay using hexafluoro-iso-propanol (HFIP) as the solvent. The resulting nanofibers had highly aligned MMT layers (normal to fiber axis) and nylon 6 crystallites (layer normal/parallel to fiber axis). Other polyamide 6,6 or polyamide nanocomposite electrospun fibers have also been reported based on MMT clay [162, 163, 164] as well as CNT as nanofiller [165]. Polyester/CNT composite nanofibers have been produced through electrospinning at varying CNT content [166]. These composite fibers can be further used to manufacture fabrics, antistatic materials, electromagnetic shielding materials, high performance separation medium, reinforcing materials, electrical and thermal conductivity materials, wave absorbing materials, etc.

Fibers and nanofibers of PA 6/MMT clay nanocomposites (diameter between 100 to 500 nm) can be collected as nonwoven fabrics or as aligned yarns. The electrospinning process resulted in highly aligned MMT layers (layer normally perpendicular to the fiber axis) and nylon 6 crystallites (layer normal, parallel to fiber axis) [165, 167]. The PA 6/clay nanofiber web deposited on a nonwoven substrate as a continuous coating increased the contact angle and time required for water penetration relative to uncoated substrate [164].

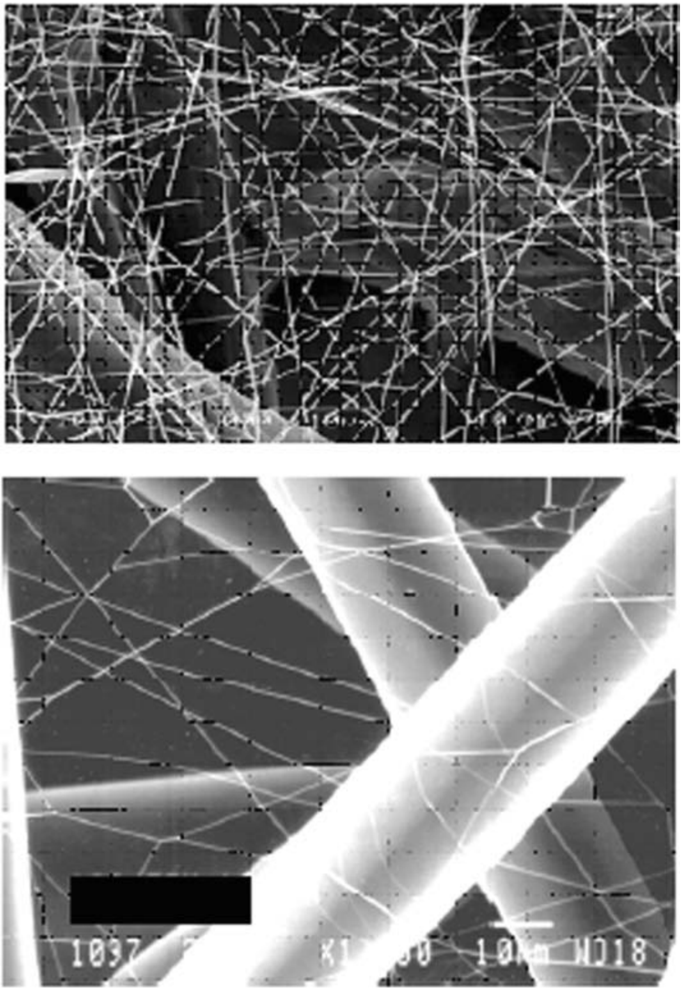
Functionalized nanofibers for advanced applications

Functionalized nanofibers can be defined as nanofibers with specific additives for imparting special functionalities and capabilities to nanofibers thus widening the scope of their applications. The materials that have been added are metal/metal oxides at a nanorange, biological materials such as enzymes, drugs, CNTs (single as well as multiwalled) as well as nanoclays [168]. These value added nanofibers can be used effectively for several high-end applications in filtration, chemical protective clothing, biomaterials, drug delivery and tissue engineering. These polymeric nanofibers can also find applications in chemical and process industries such as catalysts, physical and chemical adsorption processes, etc. and are excellently reviewed by Ramkumar *et al.* [169].

Donaldson Company Inc. USA is one of the pioneers in this field and has commercialized the production of nanofiber webs from electrospinning for a broad range of filtration applications [170]. Nanofibers provide dramatic increases in filtration efficiency at relatively small decreases in permeability (Figure 13.25). Nanofiber filter media can contain airborne contamination in the personal cabin of mining workers. However, the production process and quality control of electrospinning nanofiber webs present special challenges. The parameters which have to be carefully monitored are polymer and solvent selection, electrical field control, solvent evaporation and management and nanofiber web formation and characterization. Quality control of nanofiber web also requires novel techniques based on real time measurement about web consistency.

13.13 Future trends

Nanotechnology has emerged as the ‘key’ technology, which has revitalized material science and led to the development and evolution of a new range of improved materials including polymers and textiles. This overview on



13.25 Ultraweb – nanofiber filter media from Donaldson [170].

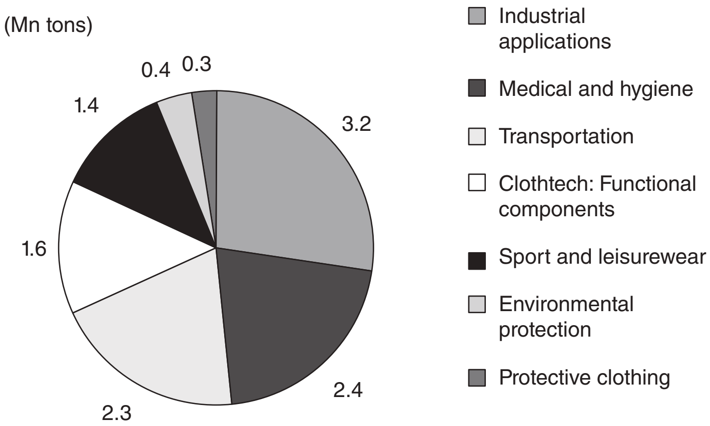
the impact of nanotechnology on textiles with a particular reference to polyester and polyamides indicates a clear shift to nanomaterials as a new tool to improve properties and gain multifunctionalities. Organized nanostructures as exhibited by either fibers, nanocoatings, nanofinishing, nanofibers and nanocomposites seem to have the potential to revolutionize the textile industry with new functionality such as self-cleaning surfaces, conducting textiles, antimicrobial properties, controlled hydrophilicity or hydrophobicity, protection against fire, UV radiation, etc. without affecting the bulk properties of fibers and fabrics.

However there are many challenges in the development of these products, which need to be intensively researched so that the wide range of applications envisaged can become a commercial reality. An excellent dispersion and stabilization of the nanoparticles in the polymer matrix is crucial to achieving the desired nano effects. The tendency to agglomerate due to an extremely high surface area is the major problem facing the effective incorporation of nanoadditives in coatings/finishing as well as in nanocomposite preparation. Surface engineering of nanoparticles and combining them with functional surface-active polymers can bring the nanoparticles onto fibers/textiles without losing their superb, nanoscopic properties. More and more companies have specialized in making stable dispersions of ZnO, Ag, SiO_2, etc. through the surface engineering of nanoparticles.

Nanocomposite fibers based on clay show a lot of promise with their improved properties such as stiffness, strength, heat deflection temperature, weatherability, moisture and dye absorption, reduced shrinkage, flammability, etc, over their neat counterparts. These enhancements are achieved with a small increase in density and cost. The most popularly used nanofillers are the natural layered silicate clays, i.e. MMT although synthetic clays with well-controlled and reproducible geometry and composition also need to be further explored. Incorporation of only a few percent of carbon nanotubes (CNTs) can significantly alter not only the mechanical properties but also enhance electrical and thermal conductivity of fibers. However dispersion and exfoliation of carbon nanotubes continue to be a challenge. Large-scale economic synthesis of CNTs particularly MWCNTs and SWCNTs with controlled diameter and chirality will largely determine the future commercial viability of these products. Nanofibers characterized by high surface area offer promising applications as efficient filters, scaffolds for tissue engineering, vehicles for controlled delivery of medicines and pesticides and more recently for biosensor applications. However, faster production of nanofibers with controlled diameter, uniformity and aligned morphology will play a crucial role in their future commercial success.

To conclude: nanotechnology definitely has the potential to bring revolution in the field of textiles. Estimated production of different nanotechnology based technical textiles by the year 2010 is illustrated in Figure 13.26. There is however a word of caution and the issues of concern are:

(a) Large scale production of nanoparticles and their cost
(b) Impact of uncontrolled release of nanoparticles in the environment and their effect on human health and ecology widely covered under the domain ‘nanotoxicology’
(c) Practical philosophy and ethics on the widespread use of nanotechnology based products.



13.26 Estimated production of nanotechnology based textile products in 2010 (www.unitex.be).

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Part III

Applications of fibrous polyesters and polyamides

14

Polyester and polyamide fibres – apparel applications

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14.1 Introduction

Fibres are the building blocks of textile materials and there is a strong correlation between the fibre properties and properties of resultant textile products. The major end use application of textile fibres is its use in apparel fabrics. For thousands of years, cotton, wool and silk have been the most common and popular natural fibres for apparels. Invention of synthetic fibres especially polyamide and polyester and fibre engineering can produce, modify and tailor fibres in ways far beyond the performance limits of fibres drawn from silkworm cocoon, grown in the fields, or spun from the fleece of animals.

Polyamide refers to family of polymers called linear polyamides made from petroleum. The generic name polyamide fibre has the same meaning as nylon fibre, but nylon fibre is used principally in countries that derive their fibre technology directly or indirectly from the USA, and polyamide in countries that derive their technology from Germany. These two generic names continued to retain identical meanings when they were jointly redefined by ISO in 1977 as 'having in the chain recurring amide groups at least 85% of which are attached to aliphatic or cyclo-aliphatic groups'. This change was made in order to exclude the new aromatic polyamide (aramid) fibres such as Nomex and Kevlar that had very different properties and end uses. There are two common methods of making polyamide for fibre applications. In 1931, American chemist Wallace Carothers was working on research carried out in the laboratories of DuPont Company where he focused on the miracle fibre 'polyamide 6,6'. In this approach, molecules with an acid (COOH) group on each end are reacted with molecules containing amine (NH_2) groups on each end. The resulting polyamide is named on the basis of the number of carbon atoms separating the two acid groups and the two amines. Thus polyamide 6,6 which is widely used for fibres is made from adipic acid and hexamethylene diamine. Polyamide 6 and polyamide 6,6 have different performance characteristics and

14.1 Different molecular structure of polyamide 6 and polyamide 6,6.

polyamide 6,6 has highly dense structure whereas polyamide 6 is an open molecular structure as shown in Fig. 14.1.

In another approach, a compound containing an amine at one end and an acid at the other is polymerized to form a chain with repeating units of $(–NH–[CH_2]n–CO–)_x$. If n = 5, the polyamide is referred to as POLYAMIDE 6. In both cases the polyamide is melt spun and drawn after cooling to give the desired properties for each intended use. By 1938, Paul Schlack of I. G. Farben Company in Germany, polymerized caprolactam and created polyamide 6. It was the first synthetic fibre to go into full scale production and the only one to do so prior to World War II. Today, polyamide is used worldwide second only to cotton and polyester.

Polyester is a polymer, which is produced from coal, air, water and petroleum products. Among the earliest commercial polyesters were the alkyd resins or glyptals, based typically upon reaction of glycerol and phthalic anhydride to form a highly branched and ultimately cross-linked polymer and used in paints.[1] When Dr Carothers was carrying out his fundamental research on methods for making long chain molecules such as those which constitute polymers and resins, he discovered not only the polyamides as used for manufacture of nylon fibres but also polymer known as polyester from diols and dicarboxylic acids that were not fibre forming. The discovery of terylene and its manufacturing was pioneered in Britain. Actually it was first made by J. R. Whinfield while he was working with J. J. Dickson in the research laboratories of The Calico Printers' Association Ltd in Manchester in 1941. High melting fibre forming polyester was synthesized from ethylene glycol and terephthalic acid.[2,3] It was first commercially produced in 1952 by the DuPont Company in the United States. DuPont initially named the fibre as fibre V but then coined it as Dacron in 1951. Polyester fibres have outstanding characteristics like wrinkle resistance and springing back into its crisp smooth shape, stretch and shrinkage resistance, strong and soft hand, excellent pleat retention and easy care properties. It is next to cotton in worldwide use.

Polyester fibre has good easy care properties and polyamide fibres have better elastic properties. These yarns are then either woven or knitted to develop fabrics. There is a strong relationship between textile materials and its quality. Major works in improving the properties, use of various forms and modification of fibres through texturing and spinning processes as well as blending have contributed to the wide expansion of these fibres.

Then quality of textile materials is manifested in different ways such as aesthetic appeal, feel or hand, etc. It is basically judged by how a textile material feels when touched or handled. Judging of fabrics is done both by subjective and objective methods.[4]

Thanks to the superior performance of fabrics made from polyester and polyamides, these fibres have now reached a stage that they can outperform 'the natural fibres' and can be engineered according to the market needs.

14.2 Properties of polyesters and polyamides and their suitability for apparel applications

Today's apparel fabric maximizes enjoyment and comfort in indoors as well as outdoors and in any kind of weather. Waterproof, windproof and breathable through different finishing processes are just a few of many properties in demand. Some of the important characteristics of polyamide and polyester fabrics are given in Table 14.1.

The polyamide yarns of 3.3 tex are used for hosiery and 4–22 tex for apparel. The texturing process is used to stimulate the properties of natural staple yarns of increased bulk with benefits of thermal insulation, cover, softness and fullness and moisture transport.

Stretch properties can be imparted to polyamide fibres using textured nylon in combination with elastane yarns. Certain desired properties can be built into polyester and polyamide fibres during production. External form and constitution of fibres confer on the fibre certain properties which

Table 14.1 Characteristics of polyamides and polyesters for apparel application[5,6]

Polyamide	Polyester
Lightweight and very strong	Strong, stretchable
Stretchable and drapes well	Resistant to crease and shrink
Durable	Durable
Easy to clean, as dirt does not cling, dries quickly	Easily washed
Resistant to abrasion and chemicals	Resistant to abrasion and chemicals Resistant to mildew
Low in moisture absorbency	Does not absorb moisture making it hot and clammy when worn in hot temperatures
Filament yarns provide smooth, soft, long-lasting fabrics	Not damaged by sunlight or weather
Spun yarns lend fabrics light weight and warmth	Dries quickly. It is crisp and resilient when wet or dry

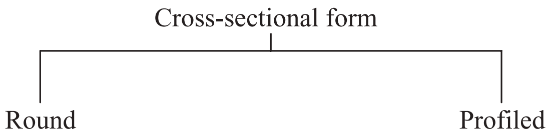
are advantageous for certain end products. The following modifications are also employed in order to achieve the various properties of the final product:

- fibre cross-section and surface filament size reduction (microfibre, superdrawing, alkalization)
- fibre blends
- bicomponent fibres
- bulk/texture (texturing and high bulk yarns)
- twisting, intermingling mixed yarns (hetero yarns, mixtures)

The fibre manufacturing process, in combination with further processing and finishing, results in a definite fibre structure regarding molecular structure and order, from which arise the fibre properties and finally the fibre capability in use. In this way, the final properties of the finished product are determined in terms of fibre properties.

Cross-section and filament surface form strongly influence the properties of the final product. In the case of melt-spun staple and yarn, the producer can determine the cross-section and surface form, as well as decide on whether to produce solid or hollow filaments, whereas these are partly determined by the strong influence of spinning conditions in the case of solution-spun yarns. Once chosen, the filament cross-sectional shape and form determine many yarn properties, which, in turn, determine the optical, tactile, physiological and technological properties of the final article. There are further opportunities to modify the cross-section and surface shape of fibre or fabric during further processing (e.g. texturizing, alkalization) in order to change the properties of the final product, but these are less effective than a modification introduced in the production stage.

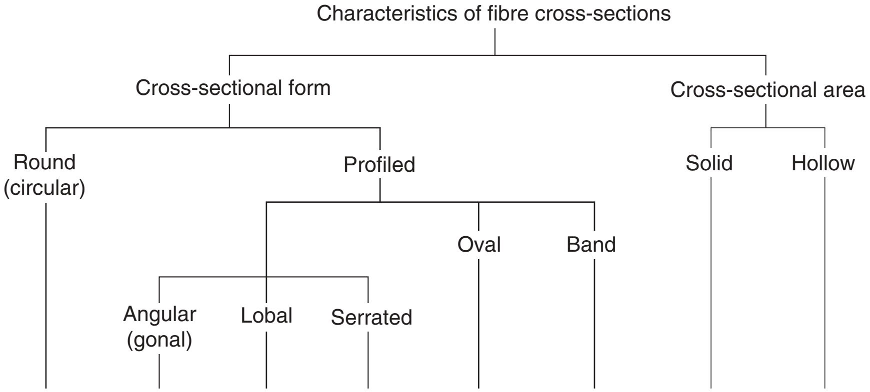
Different polyester and polyamide fibre cross-sections and surface characteristics are shown in Figs. 14.2 and 14.3.[7]



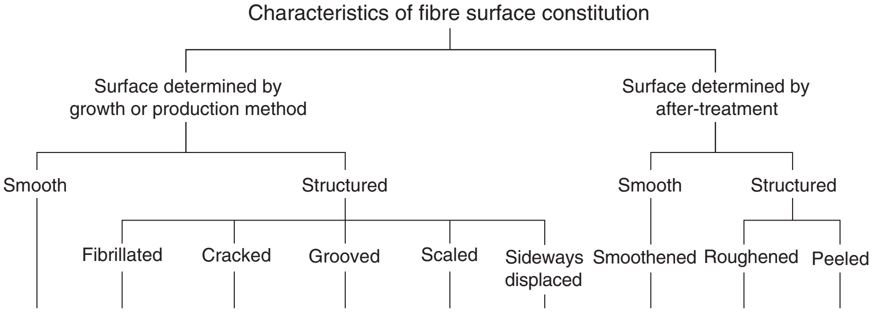
Profiled encompasses the 2-lobed, 3-lobed (trilobal), rectangular (round, 4-lobed), star shaped (*n*-lobed).

14.3 Different fibre types for apparel purpose

Polyamides and polyesters have large number of types for different application but even then only some important types are widely used (Table 14.2).



14.2 Different fibre cross-sections.[7]



14.3 PET and polyamide fibre surface characteristics.

The polyester and polyamide filaments and fibres of different aesthetic and functional properties are made by choosing polymer spin condition and draw conditions. In the case of polyamides mostly polyamide 6 and polyamide 6,6 are used and this comprises over 90% of commercial polyamide fibre production. The preferred polyesters are PET, PPT and PBT. Some important trade names and producers of polyamide 6, polyamide 6,6 and polyester are given in Table 14.3.

Three important characteristics of apparel fabrics for certain end uses are[9]

- Flame retardant – fabrics usually have a coating or film lamination against flame which provides a high level of protection and heat retardancy.
- Wet weather – water-repellent finished fabric provides normal comfort in the foulest weather due to their breathable and windproof characteristics. At the same time the fabric provides thermal insulation by

Table 14.2 Types of polyesters and polyamides[8]

Polyesters	Polyamides
Poly(ethylene terephthalate) [PET]	Poly(caprolactam) [polyamide 6]
Poly(propylene terephthalate) [PPT]	poly(Hexamethylene adipamide) [polyamide 6,6]
Poly(butylene terephthalate) [PBT]	
Poly(ethylene naphthalate) [PEN]	Poly(undecalactam) [polyamide 11]
Poly(propylene naphthalate) [PPN]	
Poly(butylene naphthalate) [PBN]	
Poly(butylene succinate) [PBS]	Poly(lauryllactam) [polyamide 12]
Poly(ethylene adipate) [PEA]	Poly(hexamethylene dodecanediamide) [polyamide 6,12]
Poly(butylene adipate) [PBA]	
Poly(lactic acid) [PLA]	Poly(hexamethylene sebacamide) [polyamide 6,10]
Poly(3-hydroxybutyrate) [PHB]	
Poly(cyclohexane dimethanol terephthalate) [PCT]	

Table 14.3 Trade names and producers

Fibre	Trade names	Producer
Polyamide 6,6	Antron, Cantrece, Cordura	DuPont
	Ultron, Wear-Dated	Monsanto
Polyamide 6	Anso, Capolan, Captive, Hydrofill	Allied
	Natural Touch, Zefran, Zefsport	BASF Fibres
	Zeftron, Shareen	Courtaulds
Polyester	Hollofil, Reemay, Sontara	DuPont
	Angelette, ESP, Ceylon, comfort fibre	Celanese
	Lambda, Serene, Superba, Wondercrepe	BASF
	Crepesoft, Golden Glow, Golden Touch	
	Natural Touch, Silky Touch, Ultra Touch	

holding insulating air layers in the garment, maintaining warmth in the cold weather.

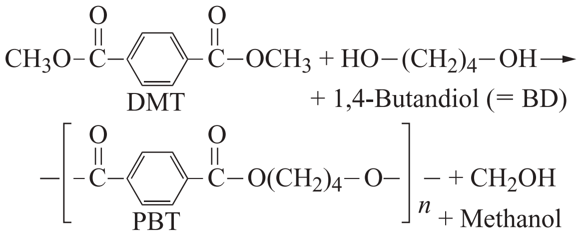
- Anti-static – this is to protect from static charge in the environments and anti-static fabric is durable along with being serviceable. It withstands regular cleaning abreast of retaining effective functional performance.

14.3.1 HM–HT cotton type polyester staple fibres

PET staple fibres can be blended with many natural and man-made fibres, and for this purpose have to match in linear densities and in the initial modulus. The HM–HT-cotton type (high modulus, high tenacity) shows similar properties as fine cotton. The HM cotton type is meant for blending with cotton. The viscose type is suited for blending with rayon and/or viscose staple. In spite of the different course of tenacity and elongation for more than 10%, the wool type and the anti-pilling wool type are particularly well suited for blending with wool. These PET staple fibres (high modulus high tenacity cotton type) with 1–2.5 dtex per fibre are gaining importance because of their ideal blending properties with cotton.

14.3.2 Polybutylene terephthalate (PBT)

Since its introduction around 1968, the production now increases annually about 10–15%, with increased 1,4 butandiol (butylene glycol). Butandiol (BD) is primarily obtained from acetylene and formaldehyde. New processes start with ethylene via promoethanol or with propylene via allylacetate and the oxo process. Polycondensation follows the scheme or analogue starting with TPA and with water as a byproduct. During the polycondensation butandiol is also regained.



Yarns have a low moisture regain (about 0.4%) and very good crimp stability – important for BCF (bulked continuous filament) yarns. Considering the sales value of the byproducts, PBT yarn cost is already lower than PA-6 yarn cost. Another application is the combination with PET in bicomponent yarns to achieve crimp or dye effects.

Fibre forms also influence the textile process and the product scheme which finally segregate the apparel sections according to fibre form (Table 14.4).

There are various forms of polyamide and polyester fibre depending on the application areas:[9]

Table 14.4 Typical process/product scheme

Product	Staple fibre and tow	Textile yarns, flat and textured		
Spinning	Conventional spinning speed (LOY)	Increased spinning speed (POY)	High spinning speed (HOY)	Very high spinning speed (FOY)
Drawing texturizing	Large drawframes and crimpers	For flat yarns; as per LOY or drawtexturized	Spin draw wind or drawtexturized	Direct use or texturized
End use, application	→Apparel fabrics →Outerwear →Lining →Underwear	• Apparel fabrics – Outerwear fabrics – Linings • All weather clothing • Underwear		

- Polyamide tow fibre
- Polyamide staple fibre – if staple fibre has to be processed into yarn on the cotton system then the tow is cut to fibres of 40 mm or less. Staple fibres for knitwear in which polyamide blended with wool are cut to staple length in the range 60–150 mm.
- Polyamide and polyester filament – polyamide flat filament yarn having 15–400 denier is applicable to clothing, industrial and knitted fabrics and POY is used for texturizing purpose. Different drawtextured polyamide and polyester filament yarns having high count micro-multifilament yarns of 50 to 600 denier are used for high grade clothing and decoration fabrics like ladies' wear, pants and jacket fabrics, stocking and casual fabrics. Semi-drawn and fully drawn polyester, polyamide and polyamide/polyester conjugate air textured filament yarns having 160–1000 denier are commercially used for sports wear, beach shorts and top coats as they provide a hairy feeling as natural cotton with characteristics of light weight, high wear resistance and easy to clean features. Some commercial blend proportions of polyester and cotton for wide variety of shirts, trousers and vests are described in Table 14.5. Various finishes to improve the appearance and function of shirts are used.

14.4 Blends of polyamide and polyester

Blending is one important process which provides the desirable attributes for apparel as single fibre cannot provide all desirable fabric properties.

Table 14.5 Polyester/cotton blend proportion for different types of apparel[10]

Type of apparel	Fabric	Blend	Finish & care
Casual shirt	106.3 g/m^2, Dobby weave	60% cotton/ 40% polyester	Light soil wash
Performance polyester Industrial work shirt	134.6 g/m^2, Poplin	100% spun polyester	Superior colour retention Soft hand Wickable finish No-pill finish Pre-cure durable press, soil release and wickable finish
Women's work motion blouse	127.5 g/m^2, Stretch poplin Memory stretch fabric for flexibility	75% polyester/ 25% cotton	Pre-cure durable press w/soil release and wickable finish Industrial wash
Industrial work shirt	120.48 g/m^2, Poplin	65% polyester/ 35% cotton	Pre-cure durable press w/soil release and wickable finish Industrial wash
Geometric micro-check work shirt	110.5 g/m^2, Poplin	65% polyester/ 35% cotton	Pre-cure durable press w/soil release and wickable finish Industrial wash
Western style uniform shirt	113.39 g/m^2, Chambray	65% polyester/ 35% cotton	Pre-cure durable press Industrial wash
Performance knitted shirt	155.9 g/m^2, Pique knit	50% polyester/ 50% cotton	Soil release, wickable finish Industrial wash
Formerly work pants	240.97 g/m^2, No-iron twill	65% polyester/ 35% cotton	Soil release Home wash
Insulated vest	255.14 g/m^2, Blended duck	65% polyester/ 35% cotton	Industrial wash

Blending helps use the positive attributes of both synthetic fibre like wear and easy care properties with better feel and high moisture absorbency property of natural fibres. Different natural and manmade fibres are blended in different combinations to produce a wide variety of yarns.

Polyester fibre can be suitably blended with cotton and viscose because of the complementary nature of the properties. The blend of polyester with viscose/cotton results in reduction of most of the negative features of polyester like poor moisture absorption, poor static dissipation, poor moisture vapour transmission, poor feel, warm, crisp hand, lower comfort, non-biodegradable, while negative features of viscose/cotton such as poor crease retention, poor wrinkle recovery, poor tenacity, lower abrasion resistance, higher staining tendency, difficulty of washing, lower colour fastness are overcome by the presence of polyester in the blend.

In general, the main motives behind blending are:

- Combination of merits of different fibres
- Reduction of cost by use of cheaper fibre with higher cost fibre in a blend
- Opportunity to produce colour effects.

Polyester and polyamide fibres which have a number of positive attributes when strength, elasticity and durability are considered, have a number of negative attributes as far as handle and comfort related properties are concerned. Comfort attributes of fibres like cotton and viscose can be combined with hard wearing and heat settable attributes of synthetic fibres to produce fabrics with the right balance of properties. Desirable or undesirable attributes of fibres can be affected by the actual textile construction. Yarn and fabric parameters, together with finishing treatments and garment design can considerably change the comfort level produced by a garment.

Synthetic-, chemical- and natural fibres each have their own specific properties, none of which alone may satisfy the requirement of a specific end use. In such cases, it can be advantageous to combine the properties of two or three fibre types in order to obtain an optimum for the end use in question or to enhance a particular product characteristic.

In principle, the following methods can be used to mix or blend fibres or yarns:

- Combining different staple fibres or staple fibre with natural fibre in flock or at carding
- Combining filament yarns and/or staple yarns by means of plying, twisting or entangling
- Combining yarns during fabric manufacture.

The following fibre combinations have proved themselves successful in terms of processability and optimization of product properties:

Table 14.6 Typical apparel fibre blend ratios[12]

Blend component	Blend ratios (%)	Application examples
PET/cotton	50/50, 65/35, (67/33)	Underclothing, shirts, blouses, nightwear clothing, poplin coats
PET/cellulose	70/30	Work- and sportswear
PET/linen	65/35, 80/20	Leisurewear, clothing
PET/silk	70/30,75/25,80/20,85/15	
PET/wool	55/45, 70/30	Suits, trousers, costumes, dresses, coats, jerseys, pullovers, uniforms
PET/PAC	50/50,60/40,65/35,70/30	Leisurewear, clothing, women's slacks, pullover, jerseys
Wool/PA	75/15, 80/20, 85/15	Uniforms, socks, handknitting yarns
PET/PAC/wool PET/PAC/cellulose PET/PAC/others	55/15/30, 30/40/30	Jersey, clothing, pullovers
Staple combinations of high shrinkage PET	30 . . . 40% high shrinkage component	Trousers, clothing, jacket

(a) chemical or synthetic fibres with natural fibres – polyamide with wool, polyester with wool, cotton, flax
(b) chemical or synthetic fibre with one another
(c) polyamide 6 with viscose, acetate, polyvinyl chloride, polyamide 6,6, polyester or electrically conductive fibres (containing carbon or metal for antistatic protection) – polyester with cotton, polyacrylonitrile, elastane (spandex) or viscose

The above list is not complete in itself, furthermore, new fibre mixtures are constantly being devised for reasons of fashion and technological advances. Typical apparel fibre blend ratios are detailed in Table 14.6.

Polyester blends well with other fibres. It blends with wool, acetate, or rayon to improve the durability of the fabric and even to make it easy washable, if the percentage of polyester is high. It adds the quality of wrinkle resistance to the fabric and eliminates crushing of napped fabrics, and reduces fading. The fabric aggravates pilling problems after being blended with wool.

Polyamide blends well and blended fabrics have good dimensional stability, elastic recovery, shape retention, and abrasion resistance properties. Polyamide is very resilient, hence after blending it helps in eliminating the crushing of napped fabrics such as velvet.

14.5 Apparel applications of polyamide and polyester fabric

The application of polyamide expanded from the initial hosiery market to other apparels by exploiting easy care properties.[13] In many textile applications, flat yarns with relatively coarse filaments were used in tightly woven or knitted fabrics. These fabrics had a limp and rather plastic handle, poor ability to wick moisture away from the body, and a strong tendency to build up static charges, leading to clinging and sparking. The fabrics were frequently shiny. In the 1970s the newly developed polyester/cotton blends offered superior comfort in many apparel applications and polyamide was displaced from these end-uses.

For apparels, producers engineer their products to meet the needs of particular uses – filaments have become finer and non-circular in cross-section, also textured yarns are used. These products, together with changes in fashion, led in the late 1990s to a revival of interest in polyamide for outerwear. The brand names like Tactel, Antron and Tactesse for particular applications are used.[15]

14.5.1 Polyamide fabric

1. Polyamide is widely used in women's hosiery and lingerie due to its high elongation and excellent elastic recovery quality. It is also used as sportswear, jackets, pants, skirts, raincoats, ski and snow apparel, windbreakers and children's-wear.
2. Apparel: Blouses, dresses, foundation garments, hosiery, lingerie, underwear, raincoats, ski apparel, windbreakers, swimwear, and cycle wear.

14.5.2 Polyester fabric

1. Polyester clothing has a good stability and strength and is resistant to stretching and shrinkage. It is not damaged by sunlight or weather. It is widely used as dresses, blouses, jackets, separates, sportswear, suits, shirts, pants, rainwear, lingerie and children's-wear.
2. Polyester fabric is manufactured in many weights and it is used as fibrefill in pillows and upholstery. In upholstery, polyester is generally blended with wool to eliminate crushing and reduce fading.

14.6 Comparison of polyesters and polyamides

Polyester and polyamide fibres both have attained their peak position in textile world and polyester is predicted to be dominating in the fibre race

Table 14.7 Comparison of polyester and polyamide properties[11,6]

Properties	Polyester	Polyamide
Initial modulus	600–1200 gftex^{-1}	200–300 gftex^{-1}
Degree of elasticity	90–98 at 2% elongation 70–90 at 10% elongation	95–100 at 2% and 10% elongation
Moisture regain	0.4% at 65% RH	2.8–5.0%
Breaking elongation	12–55%	16–65%
Tenacity	25–54 gftex^{-1}	32–65 gftex^{-1}
Thermal conductivity	0.141 W/m K	0.243 W/m K

in coming years also. There are certain properties which separate the two fibres from most of the others and help to distinguish the area of application of polyester and polyamide fibres (Table 14.7).

14.7 Pivotal fibre modification

In recent years, polyester and polyamide variants such as stretch, microfibre, recycled, antimicrobial are increasingly used in addition to these fibres with traditional attributes.

Various innovative achievements through modification of technique or product have made it possible to confer the comfort and coolness of cotton, the soft warmth of wool and glamour and rustle of silk to polyester fibre.[16] Cotton-like effects can be given to fine polyester staple of 1 denier or less with microporous surface. This improves moisture absorption. Micro-crimped polyester filaments with irregular cross-section have improved comfort and aesthetics. Wool-like effect can be imparted by dyeing cationic-dyeable polyesters to deep shades. Polyester textured yarns have wool-like characteristics since they have better thermal insulation and more moisture retention. The hollow polyester fibres have good thermal insulation. Thus there are multiple effects that are given to nylon and polyester.[14] Some of the important modifications of polyester and polyamide fibres are discussed below.

14.7.1 Modification at polymer stage

ICI claims the preparation of improved linear polyester having better affinity for basic dyes by carrying out the polycondensation process in the presence of diphenyl sulphonic acids or their salts. ICI have also suggested a method of preparation of polyester of improved moisture regain by the addition of 5–10% by weight of sodium sulphate, of particle size less than 3 microns, to a slurry in ethylene glycol during polymerization.

Lee *et al.*[18] grafted acrylic acid by exposing impregnated drawn crystalline polyester fibres to gamma radiation in the nitrogen atmosphere and found that the resulting fibre has good absorption and tensile properties and affinity for basic dyes. Hebeish *et al.*[17] have reported the properties of polyester/cotton blended fabric grafting with 2-methyl 5-vinyl pyridine using benzoyl peroxide as initiator. Fabric properties such as moisture regain, tensile strength and elongation at break have been found to increase with an increasing degree of drafting whereas crease recovery angle and electrical resistivity show a decreasing trend. It shows that certain desirable properties are adversely affected by attempts for making polyester hydrophilic. Blending turns out to be one of the important ways for imparting hydrophilic properties to the polyester apparels. And cotton/PET blends have been widely used in apparel applications because of improved comfort properties.

DuPont offers several stretch polyester derivatives based on its 3GT technology. The first 3GT product is named Sorona. Three carbon glycol is used to make these new fibres, unlike regular polyester which is made with two carbon glycol, hence the name 3GT. DuPont has developed a bio-source process that uses a fermentable sugar as a feed stock. It ferments sugar using a biocatalyst that converts the sugar into 1,3 propanediol (3G) which is purified to fibre grade. Properties of Sorona are:[18]

- Stretch and recovery are better than polyamide and regular polyester. Thus fabrics retain their shape and have enough stretch with recovery for comfortable movement
- Sorona, like polyamide, has lower modulus and is much softer
- It is easy to dye with same dyestuff as polyester without carrier.

Toray Industries, Inc. has developed a unique polyamide fabric Miramatte that realizes the softness and feel of polyamide and also features a high-quality plumage-like touch (‘Fine Feather Feeling’), with a refreshingly comfortable dry feel, and optimum drape. At the same time, Miramatte has excellent anti-ultraviolet and anti-transparent properties, and gives full play to its characteristics even if thin textile is used. The product is thus ideally suited to production of lightweight clothing.[19]

Regarding the polyamide fibre to be used in Miramatte, Toray has increased the inorganic particles, which are effective for anti-ultraviolet and anti-transparent properties in the polyamide polymer, by approximately three times which is as much as the maximum density achieved with existing mass production. In addition, the particles are distributed uniformly not only in the fibre but also on its surface. It can be perfectly designed to develop cross-section variations and fine denier because of the uniform distribution of the inorganic particles at the stage of polymerization. In view of the consistent popularity of polyamide materials for sports and casual wear in the fashion industry, Toray as the top producer of polyamide fibre in Japan has been carrying out research and development on new polyamide materials. The company plans to continue developing new polyamide products with features like:

- High-quality plumage-like touch
- Comfortable dry feel
- Optimum drape
- Refreshing feel
- Soft and matt colour tones with luxury feel
- Anti-ultraviolet property (UV covering ratio: more than 90%)
- Remarkable anti-transparent property
- Thin and lightweight clothing.

T 400 is polyester-based DuPont fibre developed with 3GT technology but it contains other components that produce low-to-moderate wovens, or true elastic stretch and recovery. It has stretch recovery, resistance to chemicals and abrasions are better than textured polyester and polyamide. It targets more 100% man made and blended fabric for ready-to-wear, typically with 20–30% Type 400 content.[20]

Nylstar inherited Elite stretch polyester from Schneer. Elite is modified polyester with permanent stretch properties and 98% recovery. The beauty of Elite is the ease with which it can bring staple spun yarns. The newest version of elite is a microfibre, which can be used for activewear.

14.7.2 Modification at spinning stage

Modification of polyester fibre – Ultra fine fibres

An ultra fine fibre is conventionally defined as a fibre of less than 0.7 denier. These fibres are often known as microfibres. An ultra fine fibre could be extruded by reducing the polymer output at the spinneret and drawing by a large drawing ratio.

Toray put the suede like new material Ecsaine on the market. Only ultra-fine polyester fibre can reproduce deer suede from the microscopic as well as macroscopic structural point of view. Ecsaine is made of homogeneous ultra-fine polyester fibres of less than 0.1 den and provides an epoch making appearance and hand as a clothing material. The pedal shaped conjugate fibre by DuPont was probably the first example of a potential ultra-fine filament.

As bending and torsional stiffness is inversely proportional to diameter, ultra-fine fibres are extremely flexible. The following characteristics can be shown:

- A softness, flexibility and smoothness
- A fine textile structure
- Formation of micro-pockets in fabrics
- A high filament density per textile surface
- Characteristic interfacial properties
- A small radius of curvature (resulting lustre and characteristics colour)
- A large aspect ratio (the ratio of length to diameter)
- A quick stress relief
- Low resistance against bending
- Fine edge.

The island in sea technology provides the industrial way of suede type artificial leather, silk like fabrics. The technology is further extended to spin the multi-component conjugate fibre, and a suede type artificial leather of high dyeability was developed with three component conjugate extrusion where the component (polyester and polyamide) ultra-fine fibres have sheath and core structure.[21]

Water absorbent polyester fibres have recently been commercialized in Japan. Kilatt by Kanebo is a hollow fibre having a narrow slit through which water enters into the inner space and exits. Another water absorbent hollow fibre, Welkey, is made by Teijin.

14.7.3 Developments in blends

Polyester and polyamide conductive fibre

Apparel applications of conducting fibre are mainly in electrostatic discharge (ESD 10^{-9} S/cm) applications in work-wear, dust-free garments. Typical bi-component fibres containing carbon black or white metal reach the requirement also in mixed fibre materials. However the conductive polymer materials reach 10–100 S/cm conductivity, and can be used in electromagnetic impulse (EMI 10^{-3} S/cm) protection. Belltron commercial products have introduced carbon-black based sandwich structures having electric resistance 10^8 to 10^{10} Ω/cm and 10^6–10^8 Ω/cm in 2.5 g/d tenacity polyester and polyamide fibre respectively.[15] The comparable values for white metal powder construction were 10^8–10^{10} Ω/cm for both co-centric and side-by-side polyamide based bi-components 3 g/d tenacity fibre. The spinnability of the polymer melt has been shown to be a very complex challenge even for the homogeneous thermoplastic.

Dacron Plus is softer polyester with better drape. Dacron Duracotton, primarily for apparel, offers improved compatibility with cotton to create more durable fabrics that still have the look and hand of cotton but is enhanced by Dacron. DAK America's Delcron brand, carried over from the Akra side of the business, is offering a new moisture management product called Delcron Hydrotec with superior wicking properties and improved finished fabric costs. Delcron Colorbrite is a cationic dyeable fibre that achieves more brilliant colorations than typical polyester. Delcron high trek is a blend of almost equal parts of wool, acrylic and hollow polyester, created to be washable for garments as school uniforms and outdoor jackets.[22]

KoSa recently introduced polyester yarns that are dyeable at lower temperatures than regular polyester, offering excellent printing and dyeing effects when blended with other heat-sensitive fibres such as spandex, wool and acetate. It is a single polyester yarn engineered with cotton like hand and appearance that also stretches. It is atmospherically dyeable and can be combined with other yarns for circular and seamless knitting, making it suitable for use in sports and thermal wear, intimate apparel, T-shirts and loungewear.

Far infrared filament yarn

This is a healthy care fibre with the property of heat and temperature maintenance and health protection. The yarn will be made from the polymer which is mixed with far infrared elements, so the far infrared filament yarn can emit electromagnetic wave of 4–14 μm. The wave can permeate into the deepest skin and hypodermic tissue and enable the water molecules inside the body to resonate. The water molecules violently vibrate and generate heat efficacy and then make the hypodermic deep temperature rise and capillaries expand. And it enables the water molecules of the cellular surface to be activated and speed the move of the calcium ion and therefore improve blood circulation and strengthen metabolism so that it vitalizes the tissue, quickens nutrition absorption and expels harmful substances in order for the body to acquire health and vitality. Its features:

- Vitalizing the skin with warmth-maintaining effects
- Prevention of chronic disease
- Increasing the immune system and health protection function
- Improving blood circulation and strengthening metabolism.

Related end uses

1. Suitable for applying to the fabric for metabolism improvement and warmth keeping
2. Functional underwear
3. Anti-varicosity hosiery
4. Exercise protector
5. Light and cold protective fabric and lining.

Anti-microbial filament yarn

Anti-microbial fibre is a fibre containing the inorganic anti-bacterial zeolite. The antibacterial zeolite is a multi-hole ceramic with silver. When the bacteria touch the ceramic, the silver ion and the enzyme in the bacteria cells will have a chemical action. It will restrain the activity of the bacteria and prevent the bacteria from procreating. Then it destroys the bacteria and achieves the effect of anti-bacteria and odour prevention. Related end uses are underwear, sweat shirts, hosiery, lining, cold protecting coats and gloves.

Polyamide filament trilobal bright

A trilobal cross-section makes good effect of light reflection and is used to produce clothing fabrics with high brightness, lustre and softness.

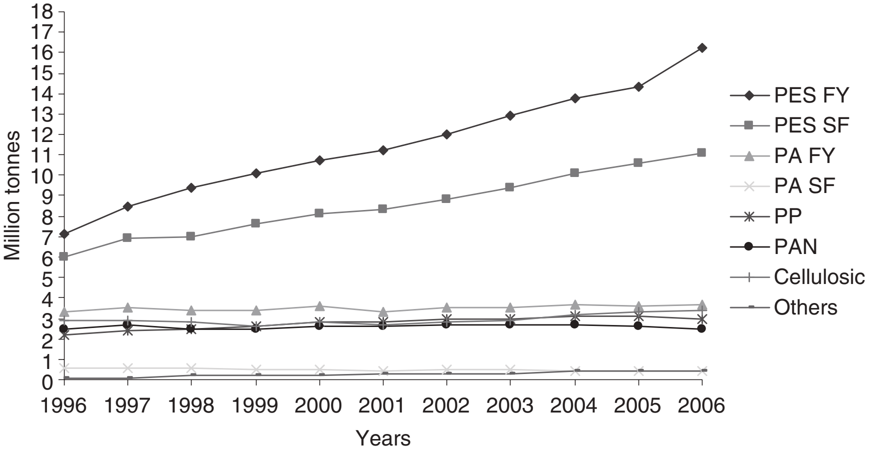
Polyamide/polyester conjugate micro-filament[23]

Polyamide and polyester conjugates are usually made of 25% polyamide and 75% polyester. The yarn self splits in sanding when dyeing and finishing. So there is no need of caustic reduction, or only need of light weight reduction. This saves process cost, avoids waste water pollution and dyeing failure. The conjugate filaments have soft touch, lightness, graceful shine, and adequate bulkiness and are used to make high density fabrics with excellent wet penetration and ventilation properties, silk-like fabrics and artificial leathers. Excellent water absorption bath towel robe can be made from polyamide/polyester conjugate filaments.

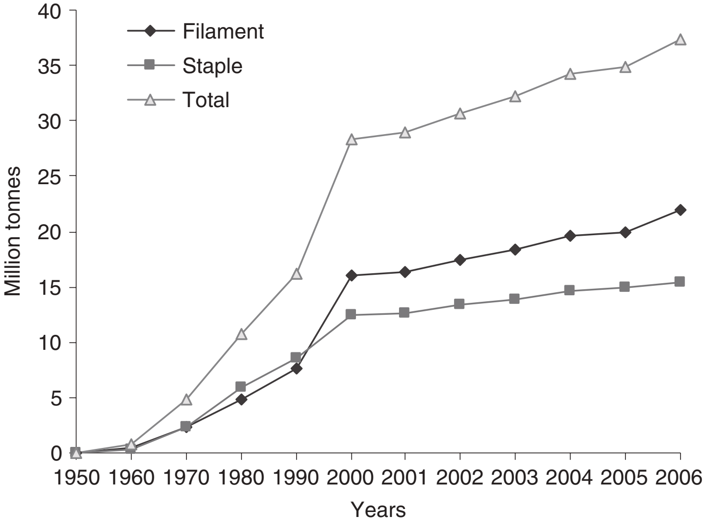
14.8 Current market potentials

The development of man-made fibres in the last 40 years has been very great compared to natural fibres. Figure 14.4 illustrates the trend of man-made fibre growth in the past 10 years. The synthetic fibre segment produced a 3.2% higher output, mainly stimulated by 6.5% surging output of polyester filament yarns. The global polyester industry achieved a growth rate of 4.4% at 27.4 million tonnes. Much of the growth was driven by strong expansion of filament yarn that rose 6.5% to 16.3 million tonnes whereas the staple fibres showed slow growth of 1.6% to 11.1 million tonnes.

Asia accounts for 88% of the volume produced. Although several Asian countries suffered from reduced output volumes, this region has the ability to lift production by 6.4% to 24 million tonnes. Greater Europe and America ended the year with reduced production by 5.2% and 10.2% respectively.



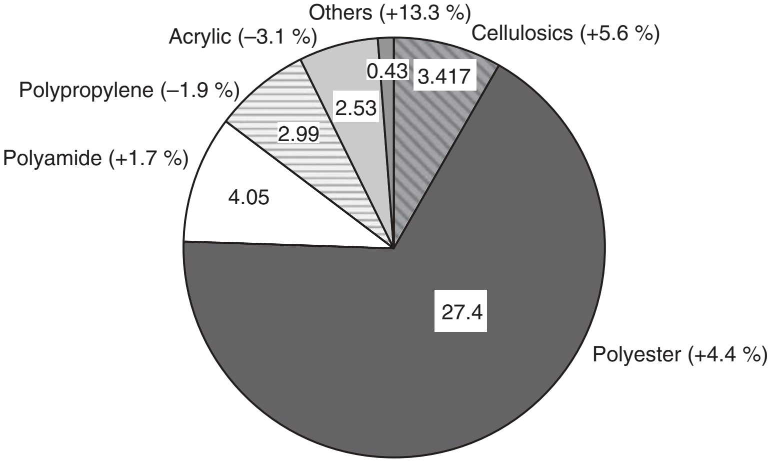
14.4 Comparison of polyester and polyamide production with other fibres.



14.5 Production of synthetic fibres.

Filament fibre production has overtaken the staple fibre production in last 10 years (Fig. 14.5). Staple fibre business involves big players like PR China and India which produced an additional supply of 450 thousand tonnes and lower production rate in countries like Greater Europe, US, Taiwan and Brazil.

Polyamide fibres showed 1.7% increased output in 2006 by achieving 4.05 million tonnes (Fig. 14.6). The steadily increased caprolactam and



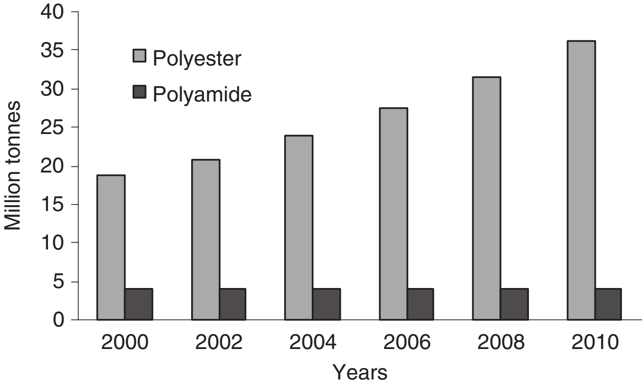
14.6 Production of man made fibres in million tonnes and percentage increase shown in brackets during 2006 over the production in 2005.

polymer prices, depressed housing market in the US and substitution to other lower priced fibres slumped the staple fibre production by 8.0% to 376 thousand tonnes.[22] The total filament market recovered by 2.8% to 3.7 million tonnes. Stagnant market conditions in Greater Europe and 4% decline in America was facing a 8.6% increase in Asian production. PR China expanded production by 21.5% to 825 thousand tonnes and Taiwan witnessed a 3% increase in filament output. Meanwhile, the contribution from Korean polyamide industry declined 6.5%.

14.9 Future prospects

According to the United Nations, world population will reach 6.82 billion people by 2010. A world population of 6.57 billion corresponds to an average per capita consumption of 10.5 kg and the increased response of South East Asia in exports. The total man-made fibre production is estimated to be 48.4 million tonnes in 2010.

In 1990 world polyester production was 8.58 million tonnes and polyamide production was 3.88 million tonnes. By 2006, polyester production had tripled to 27.307 million tonnes and polyamide reached 4.115 million tonnes. And this increase forever changed the world map of fibre production. Long the preserve of Europe and the United States, fibres now are produced worldwide, with recent emphasis, particularly China, Taiwan, South Korea and most recently, India. China's share of the polyester filament production grew from 15.7% in 1990 to 62.8% in 2006.



14.7 History and projected volumes in 2010 of polyester and polyamide.[24]

It appears there will be a competition between India and China in polyester fibre manufacturing. Some big Indian textile and apparel companies have acquired world recognized brands for their polyester products. Figure 14.7 details the recent history of the major participants of polyester and polyamide and projects the volume by 2010.

Polyamide, the granddaddy of man made fibres, seems to be losing its share to polyester, overwhelmed by sheer volume if not performance. Many woven industrial and apparel fabrics seem to favour polyester. Polyamide's dyeability is an advantage, but not sufficiently so to overcome the supply and variants available in polyester.

14.10 Acknowledgement

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