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11.1 Background

Polymeric materials are a large and growing fraction of the fire load in homes, in commercial environments and in transportation, and are inherently flammable. In fact, in the majority of real fires, some type of plastic material is implicated, either as the primary fuel source or as one of the main contributors to the spread and severity of the fire. In addition, fires involving these materials are considerably more smoky, which is a real concern as it is now well established that smoke inhalation accounts for over 80% of all fire fatalities. Flammability, which generally refers to the propensity of a substance to ignite easily and burn rapidly with a flame, is only one indicator of fire hazard. The heat release rate (the total as well as the peak heat release rate) is the critical variable that governs the true severity and intensity of a real fire, thus dictating its destructive potential in terms of human loss and property damage.

Flame or ignition resistance is only a low level indicator of the fire safety of a material, which can be achieved with commodity plastics by adding flame-retardant chemicals. Consequently, the economic incentive to add flame retardants to commodity polymers to pass certain *prescriptive* flammability tests has focused polymer flammability research over the past few decades on the mechanisms and efficacy of flame-retardant additives, rather than on polymer flammability as an *intrinsic* material property. This trend in research, combined with the fact that flaming combustion of solids is a highly coupled, multi-phased process, and that the results of different fire tests depend on the apparatus, test conditions and sample geometry, has limited our understanding of polymer flammability.

A number of strategies, such as fuel control, fire detection, and smoke management and suppression, are continuously implemented to reduce the burden of fire. Of these, fuel control has the greatest potential to minimize fire losses. This can be achieved either by altering materials *via* fire retardants or by designing materials explicitly to minimize their adverse reac-

tion to fire. Traditionally, the rate of heat release has been considered the key parameter in fire safety engineering; nevertheless, *ignition* is also seen as the parameter that affects fire initiation, flame spread and fire growth. Remote ignition is, for example, the fastest mode of fire spread and can only be achieved by radiation heat transfer from the fire. Furthermore, flame spread can be in general described as a sequence of piloted ignitions.

11.2 Introduction

Organic polymers degrade to give volatile combustible materials when they are heated above certain critical temperatures, which in turn depend on their chemical structures. If the gaseous mixture resulting from the mixing of degradation volatiles with air is within the flammability limits, and the temperature is above the ignition temperature, then combustion begins. The combustion of a polymeric material is a highly complex process involving a series of interrelated and/or independent stages occurring in the condensed phase and the gaseous phase, and at the interfaces between the two phases (Cullis and Hirschler, 1981).

Successful strategies to reduce flammability of a polymeric material involve interrupting the complex stages of the combustion process at one or more points so as to reduce the rate and/or change the mechanism of combustion at that point. From a practical point of view, this is achieved either by the mechanical blending of a suitable flame-retardant compound with the polymer substrate (i.e. by introducing an additive) or by chemical incorporation of the retardant into the polymer molecule by simple copolymerization or by the chemical modification of the preformed polymer (i.e. using a reactive component).

Both additives and reactives can interrupt the burning cycle of a polymer in several ways: by altering the thermal decomposition mechanism of a polymer; by quenching the flame; or by reducing the heat transferred from the flame to the decomposing polymer. The flame retardant can also cause a layer of carbon to appear on the surface of the polymer undergoing combustion. This may occur through a dehydrating action of the flame retardant, generating unsaturation in the polymer. The unsaturated structures form a carbonaceous layer by cyclization and cross-linking. The higher the amount of residual char after combustion, the lower the amount of combustible material available to perpetuate the flame and therefore the greater is the degree of flame retardance of the material. Consequently, one of the ways to achieve high degrees of flame retardancy or non-combustibility of polymeric materials is to increase the amount of char production on combustion.

Successful additives include: (a) polyhalogenated hydrocarbons, which improve flame retardance by liberating halogen atoms that retard gas-phase chain oxidation reactions, (b) hydrated metal salts that decompose endothermically in a fire, thus reducing the overall heat of reaction, and which liberate water, which dilutes the flammable gases, and (c) phosphorus-based inorganic and organic additives, which promote the formation of an incombustible char, thus protecting the underlying, unburnt polymer.

It is common practice, especially from a commercial point of view, to use a combination of flame retardants for polymeric materials. In many cases, these flame-retardant mixtures can give an enhanced performance at low cost. The interaction of antimony, most commonly used as antimony oxide, with halogenated polymers or polymers containing halogenated additives, gives rise to a classic case of flame-retardant synergism (Grassie and Scott, 1985). The synergistic effects of phosphorus-nitrogen (Kannan and Kishore, 1992) and phosphorus-halogen (Gou, 1992) are also well-documented. Practical experience has led to the recognition of several combinations of flame-retardant ingredients, and these are frequently employed for flame retarding commercially important plastics.

The alternative method of flame retarding a polymer, namely by chemical modification, has several potential advantages such as: (a) that low levels of modification may suffice; (b) that the modifying groups are chemically attached and therefore less likely to be lost during subsequent service; and (c) that the modification can more readily be molecularly dispersed throughout the polymer.

11.3 Testing procedure and hazard assessments – general aspects

As a consequence of the complex nature and poor reproducibility of fire, there are many techniques for estimating the flammability characteristics of polymeric materials. The most widely used laboratory test is the limiting oxygen index (*LOI*) measurement, which is a very convenient, precise and reproducible technique (Fenimore and Martin, 1966). The *LOI* is a measure of the volume percentage of oxygen in a mixed oxygen and nitrogen gas stream that just supports candle-like combustion of a polymer sample. This value therefore enables the combustibility of a polymer to be expressed and compared with that of other materials (Table 11.1). However, the relatively high concentrations of oxygen used in making measurements of *LOI* are unrepresentative of conditions in a real fire, and generally there is a lack of correlation between the results of most small-scale and full-scale tests.

Table 11.1 Limiting oxygen indices of some polymers

Polymer	LOI
Polypropylene	18
Poly(butylene terephthalate)	20
Poly(ethylene terephthalate)	21
Nylon-6,6	24
Nylon-6	21
Cotton	16
Polyester fabric	21
Wool	24
Polyacrylonitrile	18
Polyaramid	38

Table 11.2 Some representative peak heat release rates obtained by cone calorimetry

Polymer	Peak heat release rate ^a (kW m ⁻²)
Polypropylene	1095
Poly(butylene terephthalate)	1313
Isophthalic polyester	985
Nylon-6,6	1313
Nylon-6	863
Wool	307
Acrylic fibres	346

^aMeasured under an irradiance of 40 kWm⁻²

Medium-scale experiments, based on oxygen consumption calorimetry, such as cone calorimetric measurements, are generally considered to generate parameters that are more relevant to real fire scenarios involving polymeric materials (Babrauskas, 1984). The measured parameters include time to ignition, heat release rate, total heat released, mass loss rate, effective heat of combustion, smoke specific extinction area, smoke production rate and total smoke production (Table 11.2). The central objective in carrying out oxygen consumption calorimetric measurements is to obtain parameters that represent the *true* nature of the fire hazards posed by the materials under investigation, such as heat release rates (as well as the total heat released) and production of smoke and CO (Schartel *et al.*, 2005) (Table 11.3). The measurements should be carried out on sufficiently thick samples to avoid *thermally thin* behaviour, and by using a sample holder with minimum heat losses so as to minimize the effects of the apparatus

Table 11.3 Toxic and asphyxiant gases from the combustion of polymers

Gas	Source
CO, CO ₂	All organic polymers
HCN, NO, NO ₂ , NH ₃	Wool, silk, nitrogen-containing polymers
HCl, HF, HBr	PVC, PTFE, polymers containing halogenated flame retardants
Alkanes, Alkenes	Polyolefins and other organic polymers
Benzene	Polystyrene, PVC, aromatic polyesters
Phenol, Aldehydes	Phenolic resins
Acrolein	Wood, paper
Formaldehyde	Polyacetals, formaldehyde-based resins
Formic and acetic acids	Cellulosics

employed on the values of the parameters obtained. This will ensure that the values collected through such measurements are in turn more *global* in nature (de Ris and Khan, 2000).

The burning behaviour of fabrics comprised of a given fibre type or blend is influenced by a number of factors including the nature of the ignition source and time of its impingement, the fabric orientation and point of ignition (e.g. at the edge or face of the fabric or top or bottom), the ambient temperature and relative humidity, the velocity of air, and last but not least on fabric structural variables. Generally, low fabric area density and open structures aggravate the burning rate and thus increase the hazards of burn severity as compared to heavier and multi-layered structures (Backer *et al.*, 1976). In addition, the fabric flammability is determined not only by the fibre behaviour but also by the physical geometry of the fibrous arrays in fabrics. Owing to multi-factorial dependence of the ease of ignition of textile materials, as given by the measured *LOI* values, several researchers have tried alternative techniques for measurement of the flammability of fabrics to yield values that represent the flammability as an intrinsic property of the material (Miller *et al.*, 1973; Stuetz *et al.*, 1980; Horrocks *et al.*, 1989).

It should be noted here that nearly every country has its own set of standard textile fire testing methods, which are claimed to better represent the special social and technical factors peculiar to each. In addition, test methods are defined by a number of national and international bodies such as air, land and sea transport authorities, insurance organizations, and governmental departments relating to industry, defence and health, in particular. Detailed accounts of different categories of standard test methods advocated for different classes of textile materials are given in detail elsewhere (Horrocks, 2001) (Table 11.4).

Table 11.4 Selected test methods for textiles

Nature of test	Textile type	Standard	Ignition source
British standard based vertical strip method BS 5438	Curtains and drapes	BS 5867: Part 2: 1980 (1990)	Small flame
	Night wear Protective clothing (now withdrawn)	BS 5722: 1991 BS 6249: Part 1: 1982	Small flame Small flame
ISO vertical strip similar to tests 1 and 2 in BS 5438	Vertical fabrics	BS EN ISO 6940/1:1995	Small flame
Small-scale composite test for furnishing fabric/fillings	Furnishing fabrics	BS 5852: Pts 1 and 2: 1979 (retained pending changes in legislation)	Cigarette and simulated match flame (20 s ignition)
	Furnishing fabrics	BS 5852: 1990 (1998) replaces BS 5852: Pt 2 ISO 8191: Pts 1 and 2 (same as BS 5852: 1990) BS EN 1021-1: 1994 BS EN 1021-2: 1994	Small flames and wooden cribs applied to small and full scale tests Cigarette Simulated match flame (15 s ignition)
Cleansing and wetting procedures for use in flammability tests	All fabrics	BS 5651: 1989	Not applicable but used on fabrics prior to submitting for standard ignition tests
	Commercial laundering	BS EN ISO 10528: 1995	
	Domestic laundering	BS EN ISO 12138: 1997	

Table 11.4 cont'd

Nature of test	Textile type	Standard	Ignition source
Use of radiant flux	Air seat assemblies, so called 'Boeing' test	ASTM E9060 1983, uses Ohio State University heat release calorimeter	Irradiate under 35 kW m^{-2} with small flame igniter
	All fabrics/composites	NF P 92501-7, French 'M test'	Irradiate with small burner
Protective clothing	Resistance to radiant heat	BS EN 366: 1993) replaces BS 3791: 1970)	Exposure to radiant source
	Resistance to molten metal splash	BS EN 367: 1992 BS EN 373: 1993	Determine heat transfer index Molten metal
	Gloves	BS EN 407: 1994	Radiant, convective and molten metal
	Fire fighter's clothing	BS EN 469: 1995	Small flame
	General flame spread	BS EN 532: 1994 (replaces BS 5438)	Small flame
	General protection	BS EN 533: 1997 (replaces BS 6249	Small flame
	Contact heat transmission	BS EN 702: 1994	Contact temps. 100–500°C

11.3.1 Specific fire hazards associated with textile fibres

The major fire hazard associated with textile materials, in general, is shown in the high incidence of their implication in fire initiation and propagation and in the related numbers of fatal and non-fatal casualties, especially in domestic environments. Sources of relatively low intensities (such as smokers' materials) are often sufficient to bring about ignition of these materials. Furthermore, conventional textile fibres are comprised of relatively flammable fibre-forming polymers which, owing to their high specific surface area in the fibre form, significantly enhance the rate of combustion and fire proliferation. Coupled with this is the use of textile materials in vertical geometries (e.g. curtains, clothing, etc.) which encourage high burning rates when ignition is at the bottom. Textiles in upholstered furnishings and bedding are also particularly hazardous as is shown in statistics relating to the occurrence of fires in dwellings (Office of the Deputy Prime Minister, 2004). In fact, about 20% of dwelling fires are caused by textile materials (being the first material to be ignited), and about 50% of the fatalities are associated with these fires. Consequently, most flame-retardant textiles are designed to reduce their propensity to undergo ignition and flame propagation when exposed to small flame sources (e.g. burning matches) or to pilots of low intensity but of prolonged duration (e.g. burning cigarette ends). Heat-resistant textiles are not only expected to resist ignition and have reduced flame propagation rates, but also should offer a barrier to heat and flame penetration to the underlying materials or surfaces. Thus, while drapes and curtains may be rendered flame retardant, upholstered furnishing fabrics and protective clothing must be rendered sufficiently flame and heat resistant to prevent damage to underlying fillings, clothing layers or skin (Horrocks *et al.*, 2004).

11.3.2 Flame-retardant strategies for textile materials – general considerations

Textile materials may be rendered flame retardant through a variety of ways. They include: (a) post-chemical treatment of the otherwise flammable component fibres; (b) by the use of fibres that have been flame retarded during manufacture; (c) by the use of inherently flame-retardant fibrous components; (d) or by a suitable combination of the above. For example, conventional cotton and wool fabrics are flame retarded by the use of flame-retardant chemical treatments, which are often simple topical applications of flame-retardant salts (e.g. ammonium polyphosphates), coatings of retardant species (e.g. antimony trioxide/halogenated organic resin systems) or functional finishes (e.g. organophosphorus- and nitrogen-containing monomers, or polycondensates). Functional finishes are

particularly advantageous in that high levels of durability are achieved as they either polymerize within the internal fibre voids or react with functional groups in the fibre-forming polymer backbone (Horrocks, 1996).

The demands of upholstery furnishings to satisfy the aesthetic requirement of the consumer and regulatory flame-resistance standards have seen a significant rise in the use of back-coating treatments, which comprise the flame-retardant species bonded with a resin to the reverse of the fabric. Careful selection of flame retardant and resin can produce a char-generating combination which, when applied to one side (usually the back side) of a flammable textile, confers flame retardancy. This, in the case of thermoplastic fibres, offers a char-forming support, which prevents hole formation. Consequently, back coatings have been successfully applied to fabrics comprised of cotton, polyacrylic and polyester blends and mixtures of these fibres. Flame-retardant species can be antimony-bromine combinations, phosphorus-containing species or mixtures of both, often applied with a char-forming acrylic resin.

In the case of common synthetic fibres like polyesters, polyamides (nylons), polyacrylics and polypropylene, it has proved difficult to effectively flame retard owing to: (a) the fact that they do not have physical or chemical structures that are compatible with the more common functional flame retardants; (b) that during fibre production, the melt polymers are often highly reactive and they have low compatibility with many flame retardant additives; (c) that the presence of relatively high flame retardant concentrations (5–20% w/w) necessary to confer flame-retardant properties not only creates spinning fluid compatibility problems but also causes serious reductions in ultimate fibre tensile and other essential textile properties; and (d) that their thermoplasticities, coupled often with a tendency to melt, mean that shrinkage and melt dripping (often under flaming mode) are problems to be addressed in the context of secondary fire hazards posed by these materials (Horrocks *et al.*, 2005).

11.4 Polyesters

The linear, thermoplastic, polyesters are all partly crystalline polymers, soluble above their melting points (T_m) in a range of organic solvents, have glass transition temperatures (T_g) and therefore softening points that are dependent upon their precise chemical structures, and are highly flammable in their pure state with limiting oxygen indices (*LOIs*) typically of around 20. The most important polyesters from which useful fibres can be spun are the aromatic polyesters, especially poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT), owing to their relatively high crystallinities (and hence tensile strengths), T_m s and T_g s. However, of the aromatic polyesters, only PET is in wide-spread use as a commercial

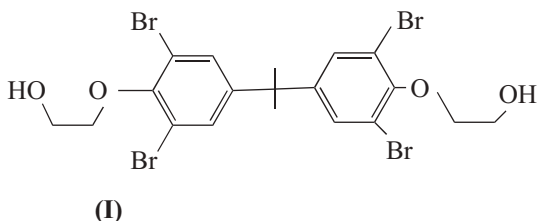
fibre, in applications as diverse as tyre cords, woven textiles and non-woven cloths.

PET, when heated to above 300°C, undergoes thermal degradation to give a variety of highly volatile products, many of which are flammable, such as acetaldehyde, methane, ethene and diethyl ether together with less volatile, but none-the-less combustible, products such as PET oligomers (linear and cyclic), terephthalic acid and ethylene glycol (Sobue and Kajiura, 1959; Kardash *et al.*, 1964). The rate-determining step is olefin elimination from glycol dibenzoate groups leading to chain scission and the production of acid and vinyl end groups (Goodings, 1961). The kinetics of this degradation have been thoroughly explored and mechanisms advanced for the production of most products, including a small amount of a carbonaceous residue (Holland and Hay, 2002). Since the pyrolysis of PET gives mainly volatile and flammable products, it would seem probable that vapour-phase flame-retardant strategies would be more effective with PET than strategies aimed solely at increasing char formation, or some other condensed-phase mechanism; however, research to date shows that, in general, mixed phase action can be engineered (Levchik and Weil, 2004).

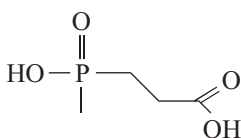
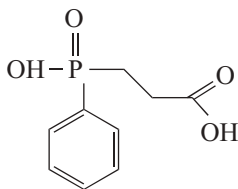
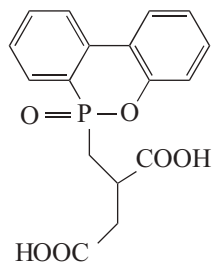
Progress in the research, development and commercial implementation of flame-retardant strategies for thermoplastic polyesters in general, irrespective of end-application, has recently been comprehensively reviewed by Levchik and Weil (2005). Thus, it is not necessary to review comprehensively this field again; rather it will suffice merely to highlight current commercial practice, significant past and recent research and development, and likely future research directions with regard specifically to the use of polyesters in fibre form.

Choice of a flame retardant for a fibre-forming polymer that is to be melt spun must take into account the possibility that the additive has the potential to interfere with the spinning process, especially if it is an insoluble particulate. Flame retardants also need to be able to withstand laundry cycles if the fibre is to be used in many textile applications. For these reasons, many established inorganic flame-retardant additives and synergists, such as metal hydroxides, antimony trioxide, ammonium and melamine phosphates, and zinc oxides and stannates, are not used in PET fibres. Even if the flame retardant is soluble in the molten polymer, it may be excluded during subsequent crystallization with the possibility of blooming and eventual loss during service. This possibility militates against the use also of many established low molecular weight halogen- and phosphorus-containing flame-retardant compounds. Thus, much research, development and commercial exploitation of flame retardants for PET fibres, especially recently, has concentrated upon the use of flame-retardant, reactive, comonomers. One early example of such a comonomer

is ethoxylated tetrabromobisphenol A (**I**), used originally by DuPont in the manufacture of its Dacron 900F[®] fibre. Such fibres, containing typically up to 6 wt% Br, have *LOIs* of around 26.



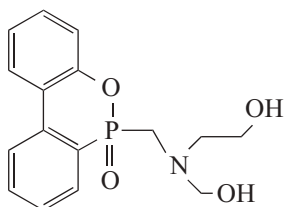
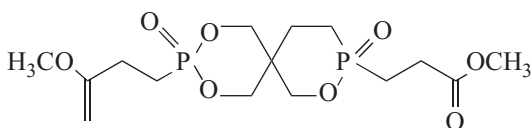
Reactive comonomers containing organo-phosphorus groups also have been developed. Thus flame retardancy has been achieved in commercial PET fibres by incorporation of 2-carboxyethyl(methyl)phosphinic acid (**II**), 2-carboxyethyl(phenyl)phosphinic acid (**III**) or their cyclic anhydrides. PETs based on the former are marketed under the trade name Trevira CS[®] (www.treviracs.com). It has been suggested that fibres containing either **II** or **III** might be further improved by the additional incorporation of aromatic dicarboxylic acid monomers to act as charring agents (Asrar *et al.*, 1999). Another commercially utilized P-containing comonomer is the 9,10-dihydro-9-oxa-10-phosphaphenanthrenyl-10-oxide (DOPO) adduct of itaconic acid (**IV**) (Endo *et al.*, 1978). Filament fibres and fabrics based on PET copolymers containing this flame-retardant comonomer are commercially available from Toyobo under the trade name, HEIM[®] (www.toyobo.co.jp) and have *LOIs* ranging up to 28.

**(II)****(III)****(IV)**

It has been reported that the effectiveness of copolymerized DOPO-type monomers can be further improved if alcoholamine derivatives of DOPO, e.g. **V**, are used rather than similar structures not containing nitrogen (Kim, 1988). Of the FR fibres based on P-containing comonomers, it has been found that those based on **IV** are the more hydrolytically stable, presumably because the P-containing group is in a side chain rather than

in the main chain (Sato *et al.*, 2000). All the phosphorus-modified PETs, however, appear to be subject to both vapour-phase and condensed-phase mechanisms of flame retardance, with the former predominating (Day *et al.*, 1981; Chang and Chang 1999).

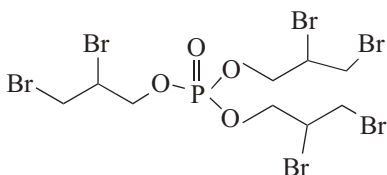
Other reactive comonomers reported to improve flame retardance in PET fibres include phosphinic acid derivatives of itaconic acid (Horie, 2002), and aliphatic and alicyclic (spiro) bisphosphonates such as **VI** (Murayama and Kashihara, 1978).

**(V)****(VI)**

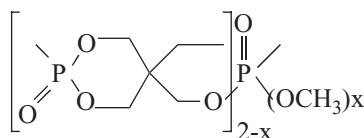
Whilst the reactive incorporation of flame retardants into polyesters may be the optimum approach to achieve effective long-term fire protection, there have been many attempts to flame retard polyester fibres using halogen and/or phosphorus containing additives. Such additives may be applied during the manufacture of the fibres or, more usually, may be applied subsequently to fabrics produced from fibres. An early commercial example of the additive approach was the use of TRIS (tris-(2,3-dibromopropyl) phosphate, **(VII)**) to flame retard PET fibre in the 1960s and 1970s. There have been several studies over the years of the mode of action of TRIS, between them giving somewhat contradictory indications. However, the emergent consensus seems to be that TRIS acts mainly in the condensed phase with the bromine helping to retain phosphorus species in the condensed phase where they catalyse various condensation reactions, leading to significant char formation (Bostic, Jr. *et al.*, 1973; Inagaki *et al.*, 1977).

Cyclic phosphonates with high phosphorus contents (**(VIII)**), manufactured by Rhodia and now marketed by Albemarle as members of their Antiblaze[®] range of flame retardants, have also been used as additives in flame-retardant PET fibres (www.albemarle.com). They are applied as aqueous solutions to the surfaces of the fibres, which are then heated to soften and swell them, allowing ingress of the additive. The process is similar to the 'thermosol' process used in the disperse dyeing of PET fibres. Mixed vapour-/condensed-phase action has been demonstrated for these types of additive (Day *et al.*, 1981). Cyclic and linear polyphosphazenes also have been suggested as flame-retardant additives for PET fibres (Masaroni and Shintarou, 1998). However, the known instability of such materials to hydrolysis would seem to rule them out for long-term use.

A further type of additive strategy employed with PET is the blending of unmodified PET fibres with flame-retarded fibres or polymer of another type. The use of PET in combination with flame-retarded cotton is well established, but use of other flame-retarded polymers is possible. For example, triphenylphosphine oxide (TPPO) used in conjunction with nylon-6 has been shown to be a good flame retardant for PET fibres. Nylon appears to work synergistically with TPPO by preventing its low temperature sublimation (Bostic and Barker, 1977).



(VII)



(VIII)

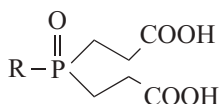
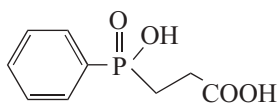
11.5 Polyamides

Owing to their aromatic structures and relatively low hydrogen atom contents, the aromatic fibre-forming polyamides, Kevlar[®] and Nomex[®] (both developed by DuPont) are naturally flame retardant with *LOIs* of around 29 and produce high char yields on burning. However, the principal aliphatic fibre-forming polyamides, nylon-6 and nylon-6,6, are less flame resistant: both have *LOIs* of around 21, depending upon formulation.

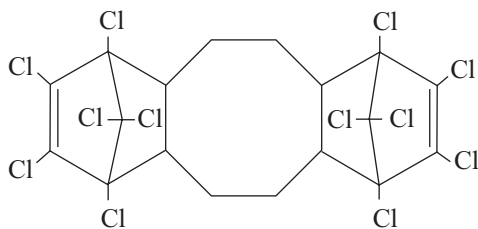
Like the linear polyesters, the nylons ‘crack’ on heating to give a variety of volatile and flammable products including, in the case of nylon-6, the monomer, caprolactam. Despite this, combustion of nylons can be relatively slow and small amounts of char may be formed, depending upon the circumstances (Levchik *et al.*, 1999; Levchik and Weil, 2000).

The challenges presented in attempting to flame retard the nylons are similar to those presented with linear polyesters. That is, any additives or reactives must not substantially interfere with the melt spinning process, adversely affect crystallinity and hence physical and mechanical properties of the fibre, nor be susceptible to degradation and loss during subsequent service, including during any cleaning operations. Thus it is not surprising to discover that rather more progress has been made with flame retarding nylons for applications in plastic mouldings than for applications as fibres (Weil and Hevehik, 2004). Many of the successful strategies for flame retarding nylon thermoplastic moulding materials, such as use of metal hydrates, inorganic amine phosphates, halogenated and phosphorus-containing organics, and especially red phosphorus, are ruled out for most

applications of nylons as fibres by consideration of effects on melt spinning, fibre properties and subsequent use. As yet, it is not clear that there has been any successful commercial production of flame-retarded nylon textile fibres incorporating flame-retardant additives or reactives, although both Monsanto and Solutia have patented phosphorus-containing diacids (structures **IX** and **X**, respectively) designed to replace some of the adipic acid in the manufacture of flame-retardant nylon-6,6 for fibres (Picket and Stoddard, 1977; Asrar, 1988).

**(IX)****(X)**

However, for non-textile applications of nylon fibres, use of some well-established flame-retardant additives may be possible. Thus Dechlorane Plus[®] (Occidental Chemical Corporation) (**XI**) or some other halogenated flame retardant may be added to nylons for use in the melt spinning of carpet fibres (Stoddard *et al.*, 1975).

**(XI)**

To flame retard nylon textiles and more complex nylon fibre-based articles, there are several commercially established processes whereby treatments are applied externally in manners similar to those employed with polyesters. A well-established finish for nylon textiles is with proprietary Flamegard[®] (Bayer), thiourea-formaldehyde, resins, which are heat cured with an acid catalyst. Chemical grafting of materials to the surfaces of fibres has also been tried. For example, nylon-6 fibres have been surface grafted with poly(2-methyl-5-vinyl pyridine) and then further treated with various halogenated flame retardants to give *LOIs* of up to 31 (Efros *et al.*, 1983) and with *o*-chlorophenol to similar effect (Mukherjee *et al.*, 1981).

11.6 Conclusions and future trends

It seems unlikely that there will be any major breakthroughs with regard to new and/or improved reactive flame-retardant comonomers or conventional organic and inorganic flame-retardant additives for use in either PET or nylon fibres. The requirements to achieve satisfactory flame retardance without appreciably interfering with the spinning process, modifying the physical and mechanical properties of the fibres, or affecting long-term stability, and at economic cost, restricts options considerably.

However, since the important first barrier to ignition of a fibre (or indeed of any material) is the surface, it is sensible to ask whether or not more can be done to modify fibres or textile surfaces so as to improve flame retardance by surface modification, especially using modern vacuum or plasma deposition techniques. Some encouraging results have been reported on the plasma modification of the surfaces of polyacrylonitrile fibres so as to improve flame retardance (Akovali and Gundogan, 1990), which suggest that the technique might be more universally applicable. Already, plasma modifications of polyester fibres and fabrics have been reported aimed at modifying surface adhesion and reflectivity (Manenq *et al.*, 1999; Van Ooiju *et al.*, 1999; Lee *et al.*, 2001). Conventional vacuum coating might also be appropriate for the deposition of some types of flame-retardant surface modification to fibres and fabrics (Mikhael and Yializis, 2005).

An alternative type of flame-retardant surface treatment for fibres and fabrics is the intumescent coating, applied using conventional coatings technology. Horrocks and colleagues have achieved considerable success with this type of approach, especially for the flame retardation of cotton and wool fabrics, but the methodology is, in principle, extendable to other types of polymer-based textile (Horrocks, 1996).

Nanosopic materials are attracting increasing interest, both for surface coatings and as additives in polymers. The Nano-Tex[®] (www.nano-tex.com) surface-treatments for fabrics, based on dispersions of nanoscopic additives, and designed thus far to improve stain resistance, static build-up, and moisture dissipation in fabrics, would appear to be extendable to the deposition of nanoscopic flame-retardant formulations. The exploitation of nanoscopic particles within polymer-based fibres is also growing rapidly with the aim being mainly to improve modulus and, if possible, also tensile strength. Fibres have recently been spun successfully from polyesters containing, for example, nanoscopic organoclays (Chang *et al.*, 2004; Mun *et al.*, 2006), carbon nanotubes (Yang *et al.*, 2006) and fullerenes (Ikegame and Kono, 2006). Since the incorporation of selected nanoscopic materials into bulk polymers, along with conventional flame retardants, can significantly improve their flame retardancy, this is clearly an area that is ripe for exploitation with fibres. It is to be noted that some success with this

approach has already been reported for polypropylene fibres (Zhang *et al.*, 2004).

11.7 Sources for further information and advice

There are a variety of sources for further information and reading in the form of specialized reviews, monographs, symposia series, book chapters, and books that are entirely dedicated to the flammability characteristics, associated hazards and flame retardation strategies for synthetic polymers. Most of them pay particular attention to thermoplastic materials including fibre-forming polymers such as polyesters and polyamides. Of particular interest are the following sources of information on the subject: (a) Camino G, Le Bras M, Bourbigot S and Delobel R (1998), *Fire Retardancy of Polymers: The Use of Intumescence*, Cambridge, The Royal Society of Chemistry; (b) Nelson G L and Wilkie C A (2001), *Fire and Polymers: Materials and Solutions for Hazard Preventions*, Washington, American Chemical Society (Symposium series 797); (c) Troitzsch J (2004), *Plastics Flammability Handbook*, Cincinnati, Hanser Gardner Publications; (d) Long A C (2005), *Design and Manufacture of Textile Composites*, Cambridge, Woodhead Publishing Limited; (e) Camino G, Le Bras M, Bourbigot S and Delobel R (1998), *Fire Retardancy of Polymers: The Use of Minerals Fillers in Micro- and Nano-composites*, Cambridge, The Royal Society of Chemistry; (f) Nelson G L and Wilkie C A (2006), *Fire and Polymers: Materials and Concepts for Hazard Prevention*, Washington, American Chemical Society (Symposium series 922).

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Advances in functional finishes for polyester and polyamide-based textiles

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12.1 Introduction

12.1.1 Nylon

Nylon was the first truly synthetic fibre which at the time of its introduction in the late 1930s was supposed to have the potential to replace many of the natural fibres. It had strength, lustre, softness, recovery, resilience, good abrasion resistance, crease recovery, easy dyeability, etc. on the positive side. Eventually it did not do so, and it was primarily due to its plastic feel and shine in flat form, poor moisture regain and the propensity to develop static charge.

The initial use for the nylon filaments was hosiery, especially stockings due to its excellent recovery and shape retention properties. Most of the nylon was used in military applications especially parachutes during the World War II, which shortly followed the development of nylon. Initially an attempt was made to address the problem of durability of the apparels made from wholly natural fibres by blending nylon with cotton. However nylon could never really penetrate the woven textile segment and the introduction of superior PET/cotton blends stopped any further scope for nylon in this sector. Since then nylon has remained confined to some specific application areas which exploit its properties to the best.

12.1.2 Polyester

Polyester, which followed nylon four years later, today commands a lion's share of synthetic textile fibres. The positive attributes of polyester fibres are strength, wrinkle resistance, good wash and wear properties, durability, etc. Although it has poor moisture regain, this has been partly countered by blending it with natural/man-made fibres having higher moisture regain. In fact, polyester-cotton and polyester viscose blends today are the most important textile types after 100% cotton textiles in terms of volume generated annually worldwide.

Table 12.1 Tensile properties of nylon and polyester fibres

Property	Nylon 6,6	Nylon 6	Polyester
Tenacity (N tex ⁻¹)			
Normal	0.4–0.6	0.4–0.6	0.4–0.6
High tenacity	0.6–0.9	0.6–0.9	0.8–1.0
Breaking extension (%)			
Normal	20–30	20–40	10–20
High tenacity	15–20	15–20	5–10
Initial modulus (N tex ⁻¹)			
Normal	2.0–3.5	1.5–3.5	8–10
High tenacity	4.0	5.0	4.0
Work of rupture (mN tex ⁻¹)			
Normal	60–70	70–80	50–60
High tenacity	50–60	60–70	20–30

Table 12.2 Typical values for the yield strain and elastic recovery of various fibres

Material	Yield strain (%)	Elastic recovery % from		
		1% extension	5% extension	10% extension
Nylon	16	90	89	89
Polyester	3	98	65	51
Cotton	1	91	52	–

12.2 Properties and uses of polyester and polyamide fibre/textiles

Unlike the natural fibres the properties of synthetic fibres depend to a large extent on the morphology of the fibre, which in turn is governed by the molecular weight of polymer, extrusion and drawing conditions, and the thermal history of the fibres. Tables 12.1 and 12.2 give the general tensile and the recovery properties of nylon and polyester fibres.¹

What distinguishes the synthetic fibres from natural fibres is their high strength, durability, better chemical resistance, uniformity, crease recovery and ability to be tailored to different mechanical properties by suitable modification of fibre formation parameters.

To a large extent the application areas for any fibrous material are determined by its mechanical properties. A look at Tables 12.1 and 12.2 makes it obvious that the yield and recovery behaviour of polyester and cotton are similar. Polyester also has a much higher initial modulus than polyam-

ide and similar to that of cotton. Hence in a polyester-cotton blended yarn, the contribution of the two components to the overall strength is better as the stress–strain curves of cotton and polyester are similar. However, due to the lower initial modulus of polyamide fibres, the contribution of the polyamide component to the overall strength in a cotton-polyamide blend is poor. This has resulted in huge popularity and success of polyester-cotton blends. Polyamide, on the other hand has excellent recovery properties which make it ideal material for knitted garments where better fit and shape retention are more important. However, polyamide is a versatile fibre that can be used in a wide range of applications: fashion garments, functional sports and leisurewear, ladies' hosiery, lingerie, sewing thread, carpets, upholstery² and even technical applications such as balloons and parachutes, sails, climbers' ropes and automotive fabrics. It is also increasingly being used in blends with natural fibres and other man made fibres.

Polyamide fibres are available in a wide range of linear density and cross-sections: ultra-fine microfibres of less than 1.0 dtex for lightweight articles such as hosiery and lingerie to coarse fibres of up to 2100 dtex for robust articles such as suitcases, rucksacks and shoes. Round, trilobal and dumb-bell shaped cross-sections are most common. Number of filaments in the yarn varies enormously and it is this that determines the properties of the end product.

12.3 Imparting functionality through finishing/coating/laminating

Although synthetic fibres like polyester and polyamide have many positive attributes, their inherently low moisture regains and high strength result in problems of static generation, easy soiling and pilling. Part of these problems can be overcome by blending these fibres with natural fibres. However, in applications where synthetic fibre component is very high (or 100%), these problems remain. Additionally, there are greater functional demands from these fibres. On one hand, the ever more demanding customer requirements require the traditional apparel garments to be antistatic, antimicrobial, easy to clean, stain proof, etc. On the other hand the increasing use of these fibres for technical applications demands functionalities like water-repellency, water-proof breathability, gas barrier, flame-proofness, UV protection to name a few from textiles made from these fibres.

There are basically four approaches to impart functionality to the textiles made from polyester and polyamide textiles:

- By incorporating a suitable additive in the melt or dope of the fibre polymer to produce intrinsically functional filaments (e.g., Trevira, the intrinsically flame retardant polyester fibre)

- Applying a suitable chemical/mechanical finish to the textile
- Applying a coating of a functional chemical formulation on the textile substrate
- Laminating the textile with a preformed film or layer (an adhesive would be needed to bond the film/layer with the textile).

It must be noted here that coating and lamination approach to impart functionality would alter many of the desired properties of an apparel textile like flexibility, breathability, drape, etc. and hence may not be suitable for such applications. Discussions on imparting functionality at melt or dope stage is beyond the scope of this topic and hence only the remaining three approaches would be discussed.

12.3.1 Antistatic

One of the problems generally faced while using wholly or predominantly synthetic textiles is their tendency to generate static electricity. In most cases the generation of static charge is a minor irritant leading to small problems like clinging of garments, mild shocks, increased soiling, but in rare cases can lead to fire, explosion and damage to electronic components. The problem of static generation becomes acute with synthetic fibres in low humidity conditions. The static generation can be reduced by increasing the humidity of the workplace, incorporating the antistatic agents³ in the polymer melt or dope before fibre spinning, blending of conductive fibres with synthetic fibres or application of an antistatic finish after the manufacture of the fabric. A detailed discussion on the causes and solution of static generation problem can be found elsewhere.³

The static generation may manifest itself in problems at two distinct stages. There may be problems related with the production of textiles, i.e.,

1. repulsion of fibres from each other in charged slivers
2. lapping of fibres around rollers
3. ballooning of yarns
4. electrostatic attraction between fabrics and lint/soil.

Then there may be problems related to the use of the textiles, like generation of static on walking over a carpet, etc. Majority of the chemical finishes used as the antistatic agents for synthetic fibres today are the variants of the finishes which have been in the market since the 1970s. Traditionally the antistatic finishes for polyamides have been based on ammonium salts, quaternary ethoxylated amines and quaternary fatty amide amines.

The static problem on polyester can be reduced to some extent by sodium hydroxide treatment (weight reduction). The effectiveness of the treatment

can be increased by finishing it with a reactive polyethylene glycol of mol. wt 1000 which is durable up to 30 launderings.⁴ Silane nanosol has been successfully prepared⁵ with an organic precursor to improve the anti-static property of polyester fabrics. The experimental results show that the anti-static property of treated PET fabrics was enhanced considerably by sol treatment, while there were no negative effects on the whiteness, strength and handle of the treated fabrics. Static charge usually builds up in synthetic fibres such as nylon and polyester because they absorb little water. Cellulosic fibres have higher moisture content to carry away static charges, so that no static charge will accumulate. As synthetic fibres have poor anti-static properties, research work concerning the improvement of the anti-static properties of textiles by using nanotechnology has been undertaken. It was determined that nano-sized titanium dioxide,⁶ zinc oxide whiskers, nano antimony-doped tin oxide⁷ (ATO) and silane nanosol⁵ could impart anti-static properties to synthetic fibres. TiO₂, ZnO and ATO provide anti-static effects because they are electrically conductive materials. Such materials help to effectively dissipate the static charge which is accumulated on the fabric. On the other hand, silane nanosol improves anti-static properties, as the silane gel particles on fibre absorb water and moisture in the air by amino and hydroxyl groups. Nanotechnology has also been applied in manufacturing an anti-static garment. W. L. Gore and Associates GmbH used nanotechnology and polytetrafluoroethylene (PTFE, Dupont's Teflon®) to develop an anti-static membrane for protective clothing. Gore-Tex® I Workwear protects the wearer from electrostatic discharges. Electrically conductive nano-particles are durably anchored in the fibrils of the Gore-Tex® I membrane of Teflon, creating an electrically conductive network that prevents the formation of isolated chargeable areas and voltage peaks commonly found in conventional anti-static materials. This method can overcome the limitation of conventional methods, which is that the anti-static agent is easily washed off after a few laundry cycles.⁸

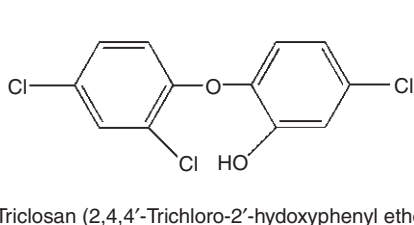
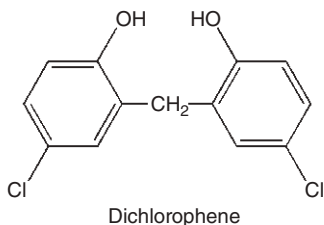
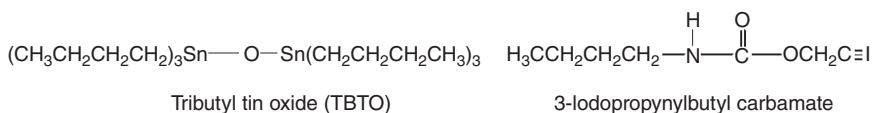
12.3.2 Antimicrobial

There are two distinct roles the antimicrobial finishes have to play: firstly the prevention of the growth of disease causing microorganisms on textiles which may not cause biodeterioration of textiles but can cause malodour, stains and cross-infections. Second, the protection of the textile itself from attack by the mildew, mould and rot producing microorganisms. The synthetic fibres especially polyester and nylon are generally not attacked by microorganisms; hence the discussion on antimicrobial finishes in this section will be confined to the finishes which deal with disease and odour causing microorganisms.

An ideal antimicrobial for textiles would have to fulfil the following basic requirements. It should provide safety in the form of low toxicity to the consumer, e.g. it would not cause allergy or irritation to the skin. Its application would not adversely affect textile properties or appearance. It should be compatible with common textile processing and the resulting antimicrobial efficacy has to be durable against repeated laundering. Today such finishes are coming under increasingly heavy pressure from regulatory bodies to conform to strict environmental and safety norms.⁹

There was a spurt in the use of antimicrobial finishes for textiles during World War II. A large number of compounds belonging to many classes like inorganic salts, organometallic compounds, phenols, thiophenols, antibiotics, formaldehyde derivatives, amines, etc. were tried and processes developed to make textiles resistant to microbes.¹⁰ Today many of these compounds have been banned or phased out due to their high toxicity and potential to cause environmental damage. Examples of such compounds are copper naphthenate, copper 8-quinolate and many organo mercury compounds.¹¹ The antimicrobial finish may act by one of three mechanisms; controlled release (chemical or physical), regeneration and barrier layer. The application of the finish itself may be by insolubilization on textile fibre, chemical modification of the fibre by covalent bond formation, coating on the textile fibre surface or microencapsulation.

Some of the old products which still find use are tributyl tin, dichlorophene, 3-iodopropynyl butyl carbamate, benzimidazol, derivatives of salicylanilides and alkylolamide salts of undecylenic acid. The structures of two antimicrobial agents are given in Figure 12.1. A popular and widely used agent is 2,4,4'-trichloro-2'-hydroxyl diphenyl ether or triclosan. It is used in mouthwashes, toothpastes, liquid hand soaps, deodorant products and also in textiles. Tinosan AM 100 and Tinosan AM 110 are antimicrobial finishing agents based on Triclosan produced by Ciba Specialty



12.1 Molecular structures of two antimicrobial agents.

Chemical Ltd Germany. These products are designed to impart durable antimicrobial efficacy to fabric made by polyester, polyamide fibres and blends of such fibres with cotton and wool. The active antimicrobial agent in these products acts like disperse dye and can diffuse into the fibre with a very high exhaustion rate. During use, the antimicrobial active agent can migrate to the surfaces of the treated textiles at a slow yet sustained rate providing excellent and durable antimicrobial efficacy.¹²

Durable and regenerable antibacterial textiles were prepared by Sun and coworkers¹³ by continuous grafting of cyclic amine monomer 3-allyl-5,5-dimethyl hydantoin (ADMH). The textiles selected were nylon, polyester, acrylic, polypropylene and natural fibres. After the grafting process, the treated textiles were exposed to dilute chlorine solutions which convert hydantoin structures to N-halamines, which act as powerful, durable and regenerable antibacterial agents against bacteria *E. coli*.

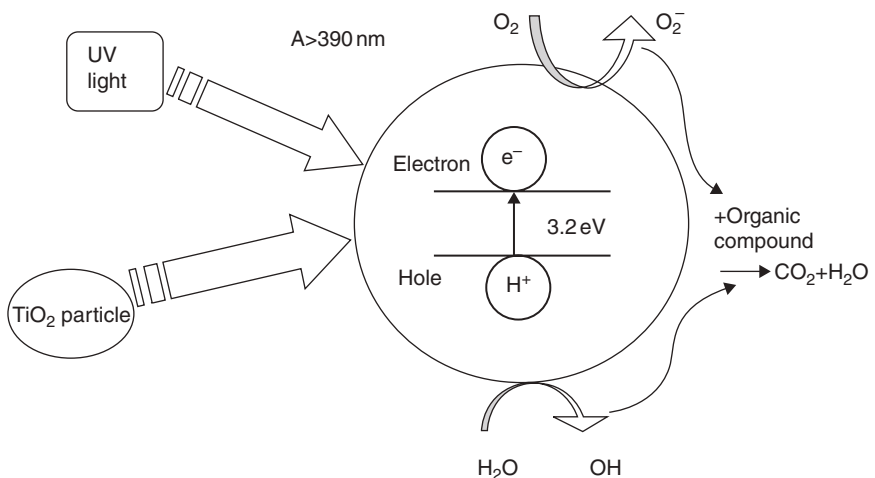
In a novel process¹⁴ light activated antibacterial nylon textiles were prepared by Bozja by grafting on proporphyrin IX and zinc proporphyrin IX. The fibres were active against *S. aureus* after exposure to 10000 lux and against *E. coli* after exposure to 60000 lux. No activity was shown in absence of light.

A simple way of creating antibacterial nylon fibres has been reported by Sun *et al.*¹⁵ The carboxylic end groups in nylon were utilized for interaction with cationic quaternary ammonium salts in alkaline conditions. The role of pH, time and temperature and the structure of cationic salt were critical in determining the effectiveness of the process. Use of optimized conditions produced wash fast antibacterial textiles. Using similar strategy, Kim *et al.* produced antimicrobial nylon 6,6 textiles by treating it with Berberine,¹⁶ a natural cationic colorant.

Recently cyclodextrins have been finding increasing use in textile finishing due to their ability to form inclusion complexes (ICs) with certain compounds (host) and the property to release the host at a controlled rate. This approach was used by Gawish *et al.*¹⁷ They grafted glycidyl methacrylate (GMA) onto nylon 6 and then reacted β -cyclodextrin (CD) or monochlorotriazine β -cyclodextrin with GMA. The CD cavity was used for the formation of inclusion complexes with some biocidal guests including p-hydroxy benzoic acid, AgNO₃-ethanol amine mixture, iodine, N,N-dimethyl tolunamide (DETA), citronella, jasmine and sweet basil. The ICs thus formed act by controlled release of biocide and are active over long periods of time.

For imparting anti-bacterial properties, nano-sized silver,¹⁸ titanium dioxide and zinc oxide¹⁹ are also used. Metallic ions and metallic compounds display a certain degree of sterilizing effect. It is considered that part of the oxygen in the air or water is turned into active oxygen by means of catalysis with the metallic ion, thereby dissolving the organic substance

to create a sterilizing effect. With the use of nano-sized particles, the number of particles per unit area is increased, and thus anti-bacterial effects can be maximized. Nano-silver particles have an extremely large relative surface area, thus increasing their contact with bacteria or fungi, and vastly improving their bactericidal and fungicidal effectiveness. Nano-silver is very reactive with proteins. When contacting bacteria and fungus, it will adversely affect cellular metabolism and inhibit cell growth. It also suppresses respiration, the basal metabolism of the electron transfer system, and the transport of the substrate into the microbial cell membrane. Furthermore, it inhibits the multiplication and growth of those bacteria and fungi which cause infection, odour, itchiness and sores. Hence, nano-silver particles are widely applied to socks in order to prohibit the growth of bacteria. In addition, nano-silver can be applied to a range of other health-care products such as dressings for burns, scald, skin donor and recipient sites.²⁰ Titanium dioxide is a photocatalyst; once it is illuminated by light with energy higher than its band gaps, the electrons in TiO_2 will jump from the valence band to the conduction band, and the electron (e^-) and electric hole (H^+) pairs will form on the surface of the photocatalyst. The negative electrons and oxygen will combine into O_2^- ; the positive electric holes and water will generate hydroxyl radicals. Since both are unstable chemical substances, when the organic compound falls on the surface of the photocatalyst it will combine with O_2^- and OH^- respectively, and turn into carbon dioxide (CO_2) and water (H_2O). This cascade reaction is called 'oxidation-reduction', and the mechanism is shown in Figure 12.2. Through the reaction, the photocatalyst is able to decompose common organic matters in the air such as odour molecules, bacteria and viruses. Several



12.2 Photocatalysis mechanism of titanium dioxide.

papers have discussed the use of the photocatalytic property of TiO_2 in the field of textiles.¹⁰ It was determined that a fabric treated with nano- TiO_2 could provide effective protection against bacteria and the discoloration of stains, due to the photocatalytic activity of nano- TiO_2 . On the other hand, zinc oxide is also a photocatalyst, and the photocatalysis mechanism is similar to that of titanium dioxide; only the band gap (ZnO : 3.37eV, TiO_2 : 3.2 eV) is different from titanium dioxide. Nano- ZnO provides effective photocatalytic properties once it is illuminated by light, and hence it is employed to impart anti-bacterial properties to textiles.²¹

12.3.3 Soil release/stain proof

Soiling of textiles is a natural process as it increases the entropy of the soil-textile system. The process of soiling may occur mainly by one of three ways, i.e., a direct contact between a textile and soil, a soiled surface coming in contact with a non-soiled one and by electrostatic attraction of airborne soils onto the electrostatically charged textile surfaces.²² Soil may be of many types: 1. water soluble; 2. particulate; 3. bleachable; 4. oily or greasy (hydrophobic); 5. proteinaceous; and 6. mixed or composite.²³

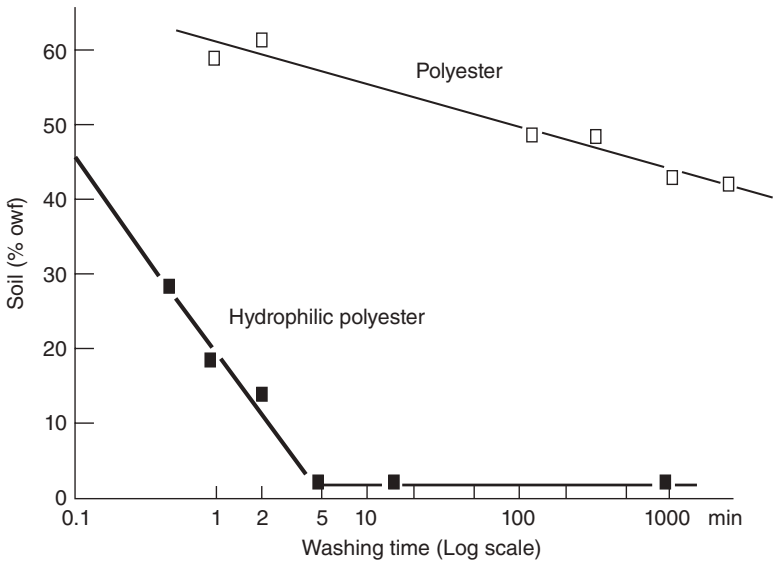
The adsorption of the soil generally occurs by Vander der Waals forces, which operate only over very short distances. It is the oily or greasy soil that is the most difficult to remove from hydrophobic textile fabrics like polyester, acrylic and nylon due to the difficulty in the wetting of soil-fibre interface. It has been shown that the removal of oily soil involves three stages:

1. An induction period during which wetting of the soil-fibre interface takes place
2. Release of the soil from the textile surface by roll up mechanism and
3. The final stage during which little soil removal takes place.

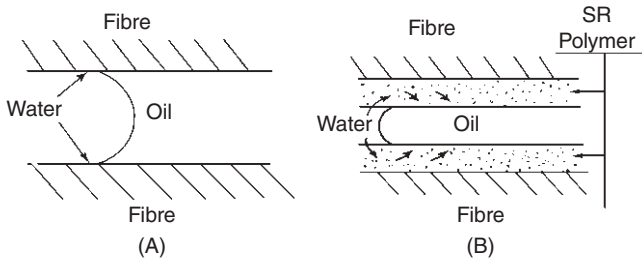
The rate of soil removal is governed by the length of the induction period which may be short or very long, as wetting of hydrophobic soil-hydrophobic textile system may be slow (Figure 12.3).

The rate and extent of soil removal can be increased by application of an essentially hydrophilic soil release finish on the hydrophobic fibre. This soil release finish facilitates the faster hydration of the fibre surface. The water can diffuse through the soil release film under the oily soil and hasten its removal (Figure 12.4).

To increase the durability of such a soil release finish on a hydrophobic fibre, it must be amphiphilic in nature. The oleophilic part can be anchored on the fibre while the hydrophilic portion is oriented outward. The soil release finish may be classified based on the nature of hydrophilic component of the finish, i.e., carboxylic, hydroxyl or oxyethylene groups. The



12.3 Effect of an acrylic soil release polymer on removal of degraded motor oil from polyester fabric: (□) untreated polyester, (■) polyester with an acrylic soil release polymer.²²



12.4 Diffusion of water into the interface of oily soil on a hydrophobic fabric:²² (A) no soil release agent; (B) soil release polymer.

mechanism and basic chemistry of the soil release finishes have been very well covered by Palinthorpe³ and Kissa.²²

Non-polymer treatments

The soil release property of the polyester fabric can also be increased by making the fibre surface hydrophilic by alkaline hydrolysis. Treatment of polyester fabric with 10% NaOH causes formation of -OH and -COOH

groups on fabric surface leading to excellent soil release properties comparable to those obtained with conventional soil release finishes but more durable.²⁴

Plasma treatment

Plasma irradiation of nylon and polyester fabric surface is another effective way of improving the surface hydrophilicity. This approach is increasingly being explored for surface modification of textile fabrics. Plasma treatment can be carried out in mainly two ways. In presence of a suitable precursor, a thin polymeric film can be deposited on the fabric surface. The properties of the treated textiles are governed by the chemical nature and the thickness of the deposited film. In absence of any precursor, surface functionalization (by oxidation or hydrolysis) or increase in surface roughness may occur. Remarkable increase in the wettability of polyester and polyamide fabrics was observed^{25–26} on exposure to low temperature plasma. While Okten and Seventekin²⁵ reported improvement in soil resistance of the treated fabrics, Kartick *et al.*²⁶ report formation of nanosized vertical and horizontal channels on polyester and nylon fabric surfaces. They surmise that these channels may contribute towards increased hydrophilicity of the textiles. Cireli *et al.*²⁷ used acrylic acid as the precursor and the reported significant improvement in the wettability of polyester and nylon fabric probably due to the deposition of a hydrophilic polymeric film on the treated fabrics. However Stefecka *et al.*²⁸ observed formation of –COOH groups on polyester monofilaments on exposure to atmospheric nitrogen plasma but did not find any evidence of any surface roughness.

12.3.4 Water repellent

A detailed account of the principles and the chemistry of water repellency and water proofing is given by Holme²⁹ and Kissa.³⁰ Conventionally the approach to water repellency has been the application of a coating of relatively hydrophobic materials like insoluble metal salts of soaps, waxes, organometallic complexes, silicone compounds and lately fluorochemical compounds on the textile substrate. These finishes are usually applied by conventional method of pad-dry-cure. To be effective, the fabric construction needs to close and the finish must be able to coat all the fibres and fill the interstitial gaps between the yarns.

Today, the textile finishes are moving from simple water repellent finishes to ultrahydrophobic/superhydrophobic finishes which are characterized by contact angles in excess of 150°. These are discussed in detail in [Chapter 13](#).

Table 12.3 Heat energy produced by various activities and corresponding perspiration rates

Activity	Work rate (Watts)	Perspiration rate (gram per day)
Sleeping	60	2280
Sitting	100	3800
Gentle walking	200	7600
Active walking	300	11500
With light pack	400	15200
With heavy pack	500	19000
Mountain walking with heavy pack	600–800	22800–30400
Maximum work rate	1000–1200	38000–45600

12.3.5 Waterproof/breathable

Waterproof/breathable fabrics are defined as fabrics that will withstand over 1000 mm of water (9.8 kPa) pressure without leaking, whilst allowing water vapour to pass through. In applications like rainwear, outdoor sports clothing, small tents, climbing and mountaineering, etc. Water vapour breathability becomes an important functional requirement. Such textiles are created by coating or laminating some waterproof/breathable material onto a textile substrate.

The current account of waterproof breathable textiles will outline the basics only. For the detailed accounts of the same, the reader is directed elsewhere.^{31–32} The requirement of this particular functionality in waterproof fabrics is needed as the human body produces heat and perspiration at varying rates at almost all times as a result of metabolism. The rate of heat and moisture generation depends on the intensity of the physical activity undertaken. Table 12.3³¹ gives the heat and perspiration produced by the average human body.

According to Table 12.3, human body produces heat and perspiration even when there is apparently no physical activity (sleep). It is important to maintain the body core temperature to feel comfortable. If a person becomes wet in very cold weather, then the core temperature of the body may go down dangerously, resulting in a condition known as hypothermia. On the other hand if the body heat and perspiration are not allowed to escape at a rate sufficient to maintain the body core temperature, then core temperature of the body may rise dangerously, resulting in a condition called hyperthermia. In normal cases, these can cause discomfort, but in extreme cases can lead to injury, incapacitation or even death. Hence for all the apparel applications, which have been given waterproof treatments, breathability becomes a necessary functionality. There

are essentially four ways in which the textiles can be made waterproof/breathable:

- densely woven fabrics
- membranes
- coatings and
- biomimetics.

Densely woven fabrics

These were first developed during World War II. Very densely woven cotton fabrics were prepared by keeping the fibres as parallel to the yarn direction as possible. In contact with water, the fibres swell to block all pores to prevent the penetration of the fabric by water. The products based on such an approach are still commercially important, Ventile being one of the brand names.

Membranes

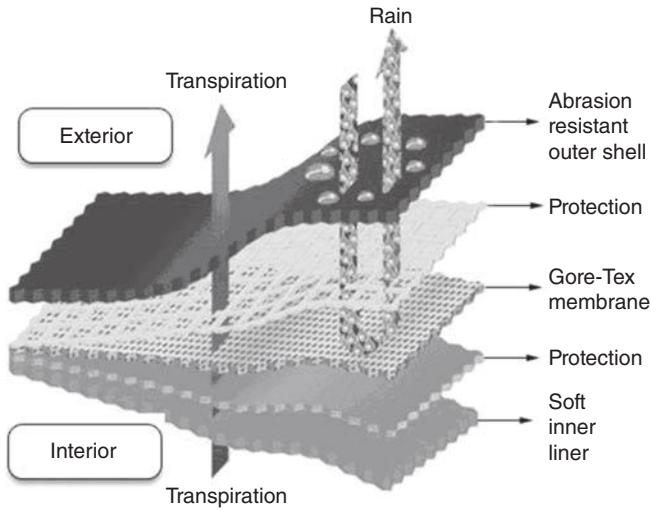
These are very thin ($\sim 10 \mu\text{m}$) polymeric films having a very high resistance to water penetration. These are of two types.

Microporous membranes

These membranes are typically made from PTFE (poly tetra fluoroethylene), PVDF (poly vinylidene fluoride) or hydrophobic PU (polyurethane) and have a large number of micropores ($1.4 \text{ billion}/\text{cm}^2$). The pore size is $2\text{--}3 \mu\text{m}$ which is too small to allow water droplets ($100 \mu\text{m}$) to pass through but large enough for the water vapour to transmit through. Additionally the hydrophobic nature of the polymer enhances the waterproof effect, although the same may cause the problem of adhesion with the base fabric. One of the most widely known products used in waterproof breathable industry is Gore-Tex® membrane, based on expanded PTFE. [Figure 12.5](#) shows the SEM of a Gore-Tex membrane and its mechanism.

Hydrophilic membranes

These are solid monolithic films without any pores. These are prepared from chemically modified polyester or polyurethane. The transmission of the water vapour takes place by diffusion through the membrane. The polyester or polyurethane is modified to incorporate up to 40% polyethylene oxide or polyether groups. These groups form the amorphous part of the membranes and provide the required hydrophilicity for the diffusion of the water vapour.



12.5 Schematic diagram of a composite Gore-Tex fabric for outdoor clothing.³³

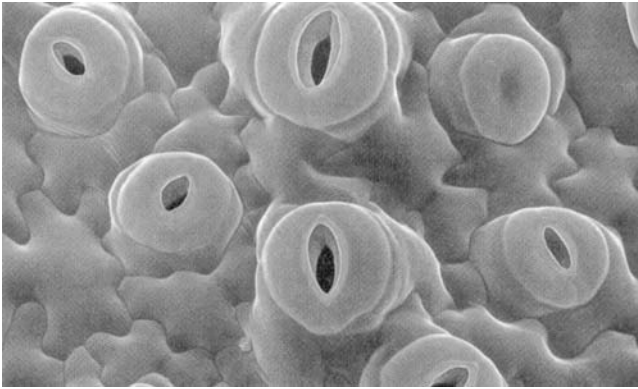
SympaTex® brand of fabrics is an example of waterproof/breathable fabrics based on copolymer of polyester and polyether. Recently the engineering plastics division of DSM, Sittard/Netherlands has introduced Arnitel polymer. This co-poly-ether-ester based polymer can be made into monolithic films for waterproof/breathable textile applications.³⁴ Another waterproof/breathable fabric based on similar mechanism is the eVENT brand of fabrics.

Coatings

Coatings are also layers of polymeric materials which are much thicker than the membranes. These are also microporous and hydrophilic in nature. The basic chemical nature and the mechanism governing the passage of water vapour in coatings are essentially similar to those of the membranes. However, the rate of moisture transmission decreases sharply with increase in the thickness of the coating.

Biomimetics

Biomimetics mimic the biological structures and mechanisms in man-made products. For example, the mechanism of a leaf stomata, which opens when plant needs to transpire more water vapour and closes (Figure 12.6) when it needs to reduce it, has been the inspiration for some products.³¹



12.6 Electron micrograph showing leaf stomata.³⁵

Akzo Nobel has developed one such product called Stomatex®.³⁶ Stomatex is generally made from thermo-insulating closed-cell foam materials such as Neoprene. It uses a pattern of dome-shaped vapour chambers, each with a tiny pore in the centre. While resting, excess body heat and perspiration rise into the dome-shaped chambers and exit through the tiny pores at a controlled rate. The chambers flex and stretch with each movement of the body, causing excess heat and perspiration to be pumped out of the small pores. This unique action of the vapour chambers increases and decreases with the user's level of physical activity.

There are other fabric constructions which do not use membranes, coatings or laminates but can keep the wearer dry by directing the water as well as moisture away from the body. Hence these fabrics have a directional effect as far as the transport of water in liquid and vapour forms is concerned. These can also be called breathable. Nikwax Directional Textiles as used by Páramo Directional Clothing Systems and Feather and Fur Technology supplied by FurTech are some examples of such directional fabrics. Links to the brand products of other waterproof/breathable textiles can be found on the internet.³⁷

In a breakthrough development, a smart temperature controllable water vapour permeable polyurethane (PU) film has been developed. The film can control its water vapour permeability (WVP) with temperature change by itself. This was achieved by optimizing the hard to soft segment ratio, PEG content and isocyanate index of the PU polymer. It was found that smart PU film is obtained at MDI/PEG/PBA/1,4-BD ratio of 3:0.6:0.4:2. The polymer has a T_g of ~24°C and the WVP starts to increase above 18°C, which is close to the T_g of the PU polymer.³⁷

12.3.6 Hydrophilic finishes

Textile fibres with inherently low moisture regain like polyester, nylon, acrylic, polypropylene, etc. can cause problems of static charge accumulation, soil pickup/poor soil release and poor wettability. In many applications improved wettability or moisture absorption is important. There have been attempts to render these fibres hydrophilic to improve their moisture absorption capacity. Many of the soil release finishes are in a sense hydrophilic finishes as they rely on the improved hydrophilic character of the fibre to release hydrophobic oily and greasy soils.

One approach in this direction is to create polar and ionic groups on the surface of the fibres by hydrolysis and plasma treatment. This approach has already been discussed. The other approach is to apply hydrophilic polymers onto the fibre surface and create some kind of bonding between the finish and the fibre to obtain a reasonable degree of finish durability.

In one such approach Roos *et al.*³⁹ used cationic starch, cationic cellulose derivatives and hydrophobically modified cationic cellulose for modification of polyester fabric. The main reason for the adsorption of the cationic polymer on PET surface was slightly negatively charged surface of polyester. Application of the cationic polymers resulted in significant improvement in the wetting behaviour of polyester fabric.

Recently there has been a tendency to apply natural hydrophilic proteins to improve the hydrophilicity of synthetic fibres. Silk sericin, a byproduct of silk degumming process, has received special attention lately in this regard. In one such attempt,⁴⁰ polyester swollen with benzyl alcohol, was grafted with N-vinyl formamide by electron beam irradiation technique. The grafting degree on polyester could be controlled by the swelling degree and by monomer concentration. This was followed by hydrolysis with H_2SO_4 and sericin was fixed with a cross linking agent, ethylene glycol diglycidyl ether. The grafted fabric showed good wettability and antistatic property. The increase in wettability was due to incorporation of amide groups on the surface of the PET, which was expected also to have antibacterial effect.

Kongdee *et al.*⁴¹ used supercritical carbon dioxide to impregnate sericin into polyester. They found no impregnation of PET with sericin if polyester surface is not modified as there is no interaction between hydrophilic sericin and hydrophobic polyester. However, if the PET surface is modified with alkali to generate $-OH$ and $-COOH$ groups on fibre surface, sericin is bound to the polyester fibre surface rendering it hydrophilic.

12.3.7 UV protective finish

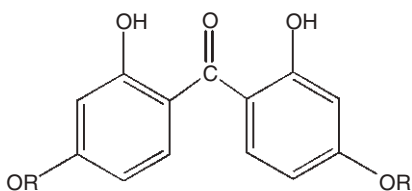
Sunlight is an essential source of all life on earth. Although the solar spectrum may extend from below 200 nm to above 3000 nm at sea level, it is

the lower wavelength portion (200–400 nm), which is important. This is essentially the high-energy portion and generally known as Ultra Violet radiation (UVR). Whereas the visible region of the solar spectrum is essential for most life sustaining processes on earth, it is the UVR that can cause some undesirable effects due to its high energy.⁴²

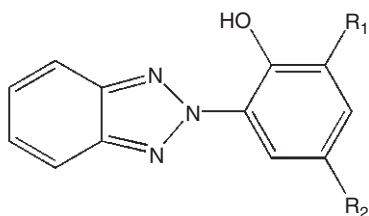
Almost all the radiation of wavelength below 290 nm is filtered out by the ozone layer in earth's atmosphere. The UV part of the solar radiation (290–400 nm) is beneficial to human beings in small doses; however, large doses, especially in the short UVB range (280–315 nm), may cause sunburns, skin cancer, photokeratitis, photodermatitis, etc.^{43–44} In addition to its deleterious effects on human beings, it also deteriorates the material properties of apparel, upholstery, draperies, carpets, furniture, paints, electronic parts, building construction materials – wood, plastic panels, etc. and other articles of outdoor use and limits their durability and life span.

With the alarming increase in the rate of ozone layer depletion in the earth's atmosphere, the risks involved due to prolonged exposure to solar UV radiation are increasing day by day. Hence it becomes imperative to protect the human skin and other materials from harmful effects of solar UV radiation. There are various approaches to tackle this problem. For protection of human skin, use of sunscreen lotions and other cosmetics is quite common. The experts have recommended use of textiles capable of blocking harmful UV radiation during outdoor activity. Recently much work has been done to develop special UV protective clothing and consideration has been given to factors affecting UV protection capability of fabrics like fibre type, cover factor, construction (weave/knit pattern), porosity, thickness, presence of dyes/pigments,^{44–45} etc. The ability of a particular textile to block UV radiation is measured in terms of SPF (sun protection factor) or UPF (ultra violet protection factor), which depends on the fibre type and various other fabric construction parameters. A value of 30 and above is supposed to provide good protection. Special UV protecting chemicals and processes have been developed^{46–48} that enhance the UV protective capability of the textiles. Ciba-Geigy has launched a number of UV absorbers for different textile fibres, which are available in the brand names like Cibatex W, Cibatex APS, Ciba Tinofast CEL, Ciba Tinofast PES, etc. and can be applied by exhaust or pad-batch methods. Similarly, a process developed by Textile Department of the University of New South Wales and launched by Clariant is known as Rayosan process.⁴⁹ The two products available are Rayosan C Paste and Rayosan CO Liquid. In this technology fibre reactive Rayosan products can be applied on cellulosic, wool and nylon fibres during dyeing.

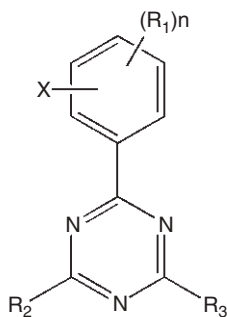
The active chemical responsible for the UV protection should be able to absorb solar UV radiation efficiently (esp. in high energy UVB region,



Benzophenones



Benzotriazoles



Phenyltriazines

R1=alkyl, alkoxy, halide, sulphoalkoxy

n=0, 1, 2

X=H, SO₃⁻

R₂=hydroxy, alkoxy, alkylthio, substituted alkyl, substituted phenyl, O-hydroxyphenyl

R₃=R₂ (Identical or different)

12.7 Structures of some common UV absorbers.

280–320 nm), convert the absorbed energy into vibrational energy and then into heat energy to the surroundings without causing photodegradation of the fibre or the finish itself. Structures of some common UV absorbers are given in Figure 12.7.

Some interesting UV resistant fibres have been developed with a sheath core structure wherein the core consists of polyester, polyether ester, polyester urethane, polyester amide,⁵⁰ polyamide,⁵¹ polyester with 10% TiO₂, ZnO and/or alumina⁵² and the sheath consists of similar polymers with UV absorbers i.e., carbon black, etc. Similarly titanium dioxide (TiO₂) that is sometimes incorporated in man-made fibres for delustring, also provides protection from UV radiation.

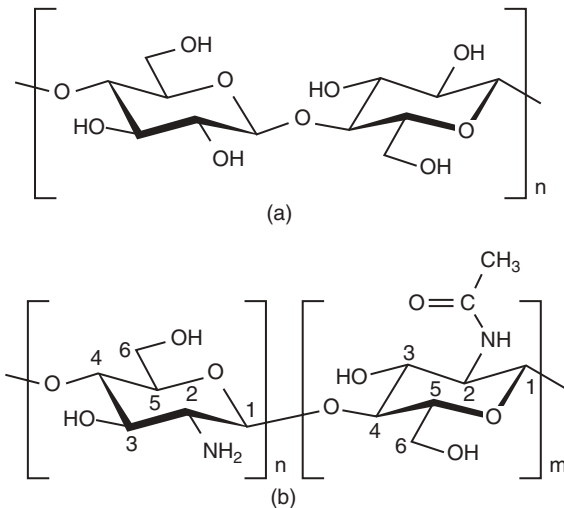
Inorganic UV blockers are preferable to organic UV blockers as they are non-toxic and chemically stable under exposure to both high temperatures and UV. Inorganic UV blockers are usually certain semiconductor oxides such as TiO₂, ZnO, SiO₂ and Al₂O₃. Among these semiconductor oxides, titanium dioxide (TiO₂) and zinc oxide⁴⁹ (ZnO) are commonly used. It was determined that nano-sized titanium dioxide and zinc oxide were more efficient at absorbing and scattering UV radiation than the

conventional size and were thus better able to block UV.⁴⁶ This is due to the fact that nano-particles have a larger surface area per unit mass and volume than the conventional materials, leading to the increase of the effectiveness of blocking UV radiation. For small particles, light scattering predominates at approximately one-tenth of the wavelength of the scattered light. Rayleigh's scattering theory states that the scattering is strongly dependent upon the wavelength, where the scattering was inversely proportional to the wavelength to the fourth power. 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.

12.3.8 Finishing with natural products/enzymes

Since eco-friendliness of a finishing process may determine its viability in future, researchers are increasingly looking to use natural products for finishing of textiles. One of the most versatile natural products is chitosan, which is a deacetylated derivative of chitin, which is the second most abundant polysaccharide found on earth next to cellulose. Chitin is the main component in the shells of crustaceans, such as shrimp, crab and lobster. It is also found in exoskeletons of molluscs and insects and in the cell walls of some fungi.⁵³

Chitin has the same backbone as cellulose, but it has an acetamide group on the C-2 position instead of a hydroxy group. The molecular structure of cellulose, chitin and chitosan are given in Figure 12.8. The presence of



12.8 The molecular structures of (a) cellulose and (b) chitin and chitosan.

amino groups in chitosan imparts hydrophilicity and antimicrobial character to it. A comprehensive review of use of chitosan as antimicrobial agent mostly for cotton and other natural fibres is available.⁵³

Matsukawa *et al.*⁵⁴ used chitosan as an antistatic agent for polyester (PET) fabric. To create bonding between chitosan and PET fabric, PET was first hydrolysed in NaOH solution to generate carboxyl groups on the PET surface. The PET fabric was then treated with chitosan in 1% acetic acid by a pad-dry-cure method. Simultaneously, the chitosan films on the fabric were insolubilized by the addition of a dicarboxylic acid to cross-link the chitosan molecules. It was observed that hydrolysed PET with chitosan treatment showed a considerably lower value (6 volts) compared to those of only hydrolysed PET (2600 volts) and untreated PET (4600 volts). Also, the decreased strength of the fabric by the NaOH treatment was recovered by the chitosan treatment. A similar antistatic treatment is reported by Eom, who observed that development of electrostatic voltage decreases below one tenth of that of untreated polyester.⁵⁵

Chitosan has also been used for imparting antibacterial character to PET fibres. Jung *et al.*⁵⁶ made nanofibres from the blends of PET and chitosan by electrospinning onto the PET micro-nonwoven mats for biomedical applications. The PET/chitosan nanofibres were evenly deposited onto the surface, and the diameter of the nanofibres was in the range between 500 and 800 nm. The nanofibres showed significantly enhanced wettability. The antibacterial activity of the samples was evaluated utilizing the colony counting method against *Staphylococcus aureus* and *Klebsiella pneumoniae*. PET/chitosan nanofibre mats showed a significantly higher growth inhibition rate compared with the PET nanofibre control.

Another natural resource, neem tree has been known to have antimicrobial properties and has been used in India for many centuries. Neem (*Azadirachta indica*) extract is widely used by Indian farmers to protect the cotton crop from pest and fungus. In a recent study Joshi *et al.*⁵⁷ have utilized this potential of neem for the development of biofunctional polyester/cotton blend fabric. Extract from the seeds of the Neem tree (*Azadirachta indica*) was used for imparting antibacterial properties to the blend fabric. Durability of the neem extract on the blended fabric was ensured with the help of simultaneous application of a resin finish to the blend fabric. Resin (glyoxal/glycol) and catalyst (aluminum sulfate and tartaric acid) concentrations were optimized to get the maximum cross-linking in the fabric blend. Quantitative analysis was carried out to measure the antimicrobial activity against Gram-positive and Gram-negative bacteria. The treated fabrics inhibited the growth of Gram-positive bacteria (*Bacillus subtilis*) by more than 90% as compared with the control sample. Antimicrobial activity against Gram-positive bacteria was retained up to five machine washes and decreased thereafter. The antibacterial activity

was higher against Gram-positive bacteria as compared to Gram-negative bacteria (*Proteus vulgaris*).

Most of the synthetic fibres are non-biodegradable. This means that the used and disposed articles made from such fibres keep building up in the environment. To overcome this problem, there have been attempts to develop biodegradable polymers. However such polymers have not been able to replace conventional fibre forming polymers due to the performance and cost factors. One attractive option is to use enzymes for biodegradation of such polymers.

Enzymes are today being used at many stages in textile wet processing. Hence amylases (desizing), cellulases (biopolishing/denim processing), pectinases (cotton scouring), proteases (wool surface modification/silk degumming/laundry detergents), catalases (H_2O_2 decomposition) are in use today. Attempts have been made to degrade polyester using lipases and esterases. Although the enzyme attack on the polyester to bring about hydrolysis is a rather slow process, which excludes the possibility of enzymes being used for polyester waste disposal at least in near future, some degree of surface hydrolysis can be achieved. Hence researchers are reconciled to using enzymes for surface modification of polyester fabric,^{58–62} which in a sense is similar to the surface hydrolysis by NaOH in that the formation of $-OH$ and $-COOH$ groups takes place. However the similarity ends there. As compared to alkaline treatment, the enzyme treatment takes place under much milder conditions of time, temperature and pH. The watability obtained is higher and the effect on mechanical properties is much milder.

12.4 Recent advances in finishing

12.4.1 Plasma processing

Textile materials are increasingly used in various industries. In these applications, the functions of textile materials are associated with phenomena such as wetting, biocompatibility, adsorption and electrical conductivity. Wetting, biocompatibility, adhesion, and many other performance properties all begin at the surface.⁶³ The properties of textile surfaces and interfaces play key roles in material processing and application technologies.⁶⁴ As with many other types of materials, the surface properties of textiles can be readily altered by the treatment of the materials with gas plasma, without impairment of their bulk mechanical properties.

The plasma treatment of textiles is a highly innovative technology in the field of superficial treatments of the material surfaces. It is based on a DBD electric discharge (dielectric barrier discharge). The use of electric

discharge creates radicals, active chemical species and ions which can modify the surfaces of textiles due to the high plasma reactivity in two ways. Surface bombardment by radicals may change the physical nature of the surface. This may result in partial destruction of scales on wool fibre surface or formation of structures or channels on other materials. The modifications applied to the surface are on the nanometre scale at room temperature, which can fundamentally change the properties like wetting, adhesion, etc. It operates under atmospheric pressure with air or inert gas and several gas mixtures. The nature of modification changes with the type of atmosphere, speed of the process, retention time, etc. The change may also be of chemical type; through formation of functional groups due to the chemical reactions taking place between the radicals and the surface molecules.

In any case it generates innovative materials and new surface properties. It does not modify the bulk properties of the material. The main advantages of plasma processing over conventional chemical finishing are:

- Negligible quantity of chemicals used
- Essentially a dry process, which does not require solvents or chemicals dangerous for the environment
- The DBD technology operates at atmospheric pressure, hence no need for sealing or vacuum pumps
- Production can proceed in continuous way
- Process times are highly reduced
- They can be applied to all textile-working phases from the fibre until fabric finishing process
- Treatment on one or both fabric sides. Hence multifunctional fabrics with hydrophilic nature on one side and hydrophobic on the other can be created.

Overall, the process provides higher energy saving and a lower environmental impact.

The following functionalities can be introduced into the treated substrates:

- Increase of wettability
- Increase of hydrophilicity
- Water-repellent and oil-repellent surfaces
- Biocompatibility (antibacterial properties of adhesion and affinity to proteins and other bio molecules)
- Dyeable (increase of dyeing rate)
- Print (increase of absorbed colour quantity by the textile fibres)
- Adhesion (increase of spreading adhesion with specific compounds)

- Polymer deposition in a gaseous phase as thin layer adherent to the surface (film deposition)
- Superficial ablation of the materials (etching).

12.4.2 Micro-encapsulation

Microencapsulation is a technique in which chemicals are released in a controlled manner over a long period.⁶⁵ In this process small particles or droplets are confined in a coating to give small capsules or microcapsules. The materials inside the capsules form the core and the outside coating becomes a barrier wall. Hence the core material is isolated from hostile outside environment⁶⁶ and can be released either slowly by diffusion through the wall or by rupture of the wall on demand. The microcapsules can then be attached to textiles, conferring various properties to them. This is an especially useful technique when the active component of a finish has high vapour pressure or when it needs to be activated only on specific occasions. The best example of a simple application of microencapsulation is carbonless copy paper. This paper has a thin coating of microcapsules on the back side. The microcapsules contain an ink which is released only under pressure. When something is written on the paper, the pressure of writing releases the ink from the layer of microcapsules and a copy of the original writing is created on a sheet kept below carbonless copy paper.

Although the industrial applications of microencapsulation began to appear almost 50 years ago in fields like pharmaceutical, cosmetics, food processing, etc., the textile industry has been a little slow in responding to this novel technique. It was only in the 1980s and 1990s that some applications started appearing on the textile front.

In the textile industry, microencapsulation has been mainly done for innovative and novel application for value addition. Much less of it is being targeted as a replacement for conventional finishing. One of the most popular applications has been addition of fragrance to the textiles by microencapsulation.

Several manufacturers have already launched such products in the market. Welbek fabrics launched its CX series of scented fabrics towards the end of the twentieth century. Similar products have also been produced by RT Dodge, Celanese International, Matsui Shikiso Chemical Co, LJ Specialities, El Dorado International Co., etc. In addition to the fragrances, another type of textiles known as Wellness Textiles based on microencapsulation are being offered. Hence there is a product: Biocap Series from Specialty Textiles Products which has microcapsules containing vitamins A, D, E and Aloe Vera. The vitamins are slowly released into the body of the wearer through the skin.

Microencapsulation is also being used for making intelligent textiles which can regulate the temperature using phase change materials (PCMs). The PCMs are compounds which have their melting temperature near the ambient temperature. When they are brought to higher temperatures, the PCMs melt and absorb heat. When they are brought down below ambient temperature, they solidify and release heat. Hence the wearer using clothes having PCMs is protected from sudden thermal shocks.

12.5 Future trends

In future one can expect some new trends in the way the textile finishing is carried out. With cost of energy, effluent treatment and competition becoming increasingly critical factors by the day, the emphasis is going to be on efficiency and cost effectiveness in finishing. With environment being a key issue, a lot of emphasis is going to be on the environmental impact of the processes.

This makes plasma processing an important technique for future textile finishing, as the process uses no water and few chemicals and causes little pollution. The role of nanotechnology in finishing will be more dominant than it is today. The main reason is that the functionalities can be created without spoiling the feel and the breathability of the garments. We are also going to witness more value addition in the products through use of techniques like micro- and nanoencapsulation.

The role of smart textiles or smart finishes will grow significantly. The finishes which can change their character according to the changes in the external stimuli, like temperature and humidity, will be more in demand. One such finish was discussed in the waterproof/breathable textiles section.

Lastly, the customers are going to look for multiple functionalities in the textile products they buy. Hence a finisher should be ready to provide easy care, soil release, antimicrobial, UV protection and breathability in a single textile product.

12.6 Sources of further information and advice

For those interested in the basic principles of textile finishing processes, there are some very good books available. The list of these is given below:

1. *Textile Finishing*, ed. Derek Heywood, Society of Dyers and Colorists, Bradford, UK 2003.
2. *Chemical Finishing of Textiles*, W D Schindler and P J Hauser, Woodhead Publishing Limited, 2004.

3. *Handbook of Fibre Science and Technology: Volume II Chemical Processing of Fibres and Fabrics, Functional Finishes Part A and B*, Ed Menachem Lewin and Stephen B Sello, Marcel Dekker Inc, 1984.
4. *Encyclopedia of Textile Finishing*, Vol. 1, 2 and 3. Prof. Dr. rer. Nat. Hans-Karl Rouette, Springer 2001.

For information related to the research and latest developments in textile finishing processes, chemicals and machinery, the following journals may be referred to:

1. *Melliand International* (Quarterly), Deutscher Fachverlag GmbH, Mainzer Landstr. 251, 60326 Frankfurt am Main, Germany.
2. *AATCC Review*, American Association of Textile Chemists and Colorists, PO Box 12215, Research Triangle Park, N.C. 27709.
3. *Textile Research Journal*, SAGE Publications, 2455 Teller Road, Thousand Oaks, CA 91320, Phone: (805) 499 9774.
4. *Journal of the Textile Institute*, The Textile Institute, 1st Floor, St James's Buildings, 79 Oxford Street, Manchester, M1 6FQ, UK.
5. *International Dyer*, World Textile Publications Ltd, Perkin House, 1 Longlands Street, Bradford, West Yorkshire, BD1 2TP, UK.
6. *Coloration Technology*, Society of Dyers and Colourists, PO Box 244, Perkin House, 82 Grattan Road, Bradford BD1 2JB, England.
7. *Journal of Applied Polymer Science*, John Wiley & Sons Ltd., Journals Fulfilment, 1 Oldlands Way, Bognor Regis, West Sussex PO22 9SA, UK.

These journals also advertise any books in the field of textiles which may be due for publication from any publisher.

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