

# Surface modification and preparation techniques for textile materials

M. J. JOHN and R. D. ANANDJIWALA  
CSIR, South Africa

**doi:**

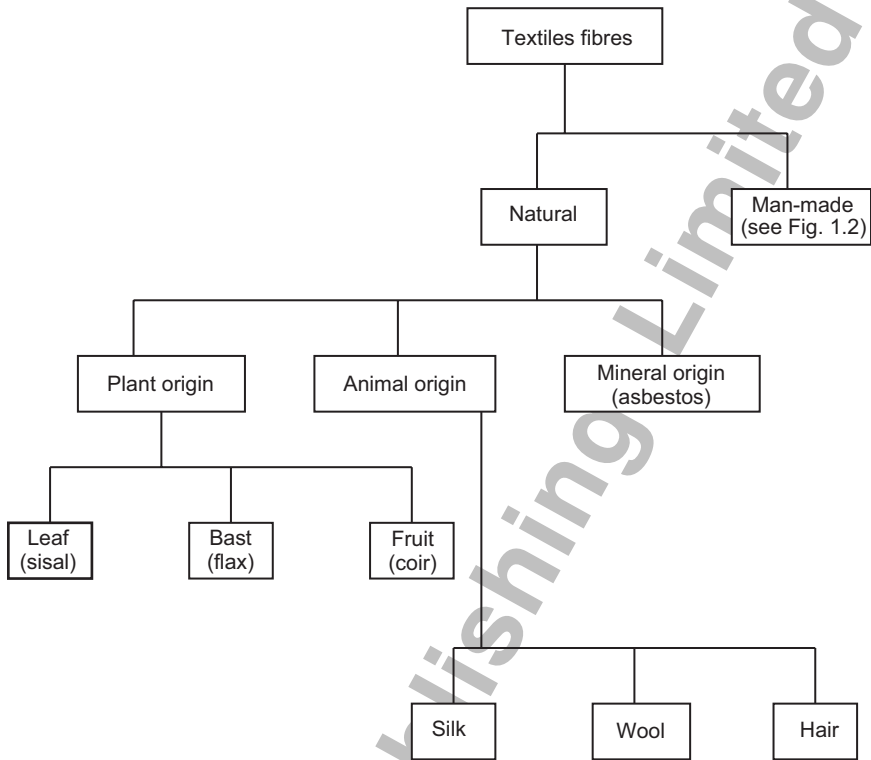
**Abstract:** This chapter presents an overview of some important surface modification techniques employed for improved functional behaviour of textiles. Textile materials are used in a variety of applications where surface modification is of profound importance as it improves various properties – such as softness, dyeability, absorbance and wettability. In this chapter, the most commonly used surface modification techniques, ranging from plasma treatment to nanocoatings, for both natural and synthetic fibres have been discussed. Recent studies involving the modification and characterisation of textiles have also been highlighted.

**Key words:** textile, modification, preparation techniques, wet processing

## 1.1 Introduction

Textile technology deals with several disciplines including: the structure, properties and behaviour of fibres; how fibres are assembled into fibrous structures and fabrics; surface modification of fibres; and the making, analysis, sale and end uses of fibres and fabrics. Of these disciplines, surface modification of textiles is of profound importance as it improves properties such as softness, adhesion and wettability. Functional properties can also be imparted to textile fibres. Textiles find use in a variety of applications, the most common of which are clothing, carpeting and furnishing. Textiles used for industrial purposes, and chosen for characteristics other than their appearance, are commonly referred to as technical textiles. Technical textiles include textile structures for automotive applications, medical textiles (e.g. bandages, pressure garments and implants), geotextiles (for reinforcement of embankments), agro-textiles (textiles for crop protection), protective clothing (e.g. against heat and radiation for fire-fighter clothing, against molten metals for welders, stab-proof clothing and bullet-proof vests). In all these applications, stringent performance requirements must be met.

Textile fibres are classified into two main groups, i.e. natural and man-made, depending upon their origin. Natural fibres can be mainly divided into protein fibres of animal origin (wool, silk), plant fibres of cellulosic origin and mineral fibres. Man-made fibres include three main categories:



25 1.1 Classification of textile fibres.<sup>1</sup>

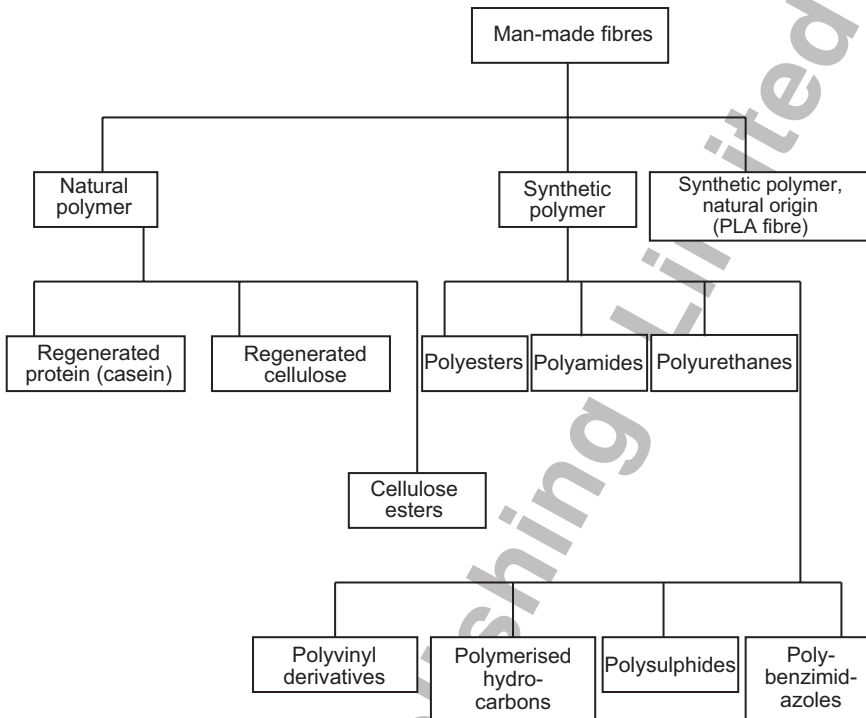
- 26  
27
- from synthetic polymers, such as polyester, nylon and acrylic;
  - from regenerated cellulose, such as viscose and lyocell;
  - cellulose acetates, such as diacetate and triacetate.

30 A number of reports on the classification of textile fibres have been published.<sup>1-4</sup>  
31 There are also newly synthesised fibres engineered for high-performance end uses,  
32 for example, aramid and polysulfide fibres. Figures 1.1 and 1.2 give the detailed  
33 classification of textile fibres.  
34

## 35 36 1.2 Natural fibres

### 37 38 1.2.1 Plant origin

39  
40 Plant fibres include bast (or stem or soft sclerenchyma) fibres, leaf or hard fibres,  
41 seed, fruit, wood, cereal straw, and other grass fibres. Plant fibres are composed of  
42 cellulose, hemicellulose and lignin. Common examples of plant fibres are flax (bast  
43 fibre), sisal (leaf fibre) and cotton and oil palm (seed). Table 1.1 presents a list of



1.2 Classification of man-made fibres.<sup>1</sup> PLA, poly-lactic acid.

commonly used plant fibres and their origin. The use of such plant fibres in reinforced composites has increased owing to their low costs, biodegradability and the fact that they can compete well with other fibres in terms of strength per weight of material.

### 1.2.2 Animal origin

Animal fibres include silk, wool and hair. Silk is the secretion product from silkworm. Wool is classified in the soft hair group while the coarse hair group comprises horse hair, cow hair and human hair. Animal fibres are composed mainly of proteins. Wool fibres are composed of keratin, a complex mixture of proteins characterised by the presence of a considerable amount of the amino acid cystine. The disulfide bond in this amino acid residue forms cross-linkages between different protein chains thereby making it more stable and less soluble than other proteins.<sup>5</sup> Table 1.2 presents a list of commonly used animal fibres. Deer hair and racoon dog hair are also used mainly for the bristles of paint brushes.

Table 1.1 List of important plant fibres

Fibre source	Species	Origin
Abaca	<i>Musa textilis</i>	Leaf
Bagasse	–	Grass
Bamboo	(>1250 species)	Grass
Banana	<i>Musa indica</i>	Leaf
Broom root	<i>Muhlenbergia macroura</i>	Root
Cantala	<i>Agave cantala</i>	Leaf
Caroa	<i>Neoglaziovia variegata</i>	Leaf
China jute	<i>Abutilon theophrasti</i>	Stem
Coir	<i>Cocos nucifera</i>	Fruit
Cotton	<i>Gossypium</i> sp.	Seed
Curaua	<i>Ananas erectifolius</i>	Leaf
Date palm	<i>Phoenix dactylifera</i>	Leaf
Flax	<i>Linum usitatissimum</i>	Stem
Hemp	<i>Cannabis sativa</i>	Stem
Henequen	<i>Agave fourcroydes</i>	Leaf
Isora	<i>Helicteres isora</i>	Stem
Istle	<i>Samuela carnerosana</i>	Leaf
Jute	<i>Corchorus capsularis</i>	Stem
Kapok	<i>Ceiba pentrandia</i>	Fruit
Kenaf	<i>Hibiscus cannabinus</i>	Stem
Kudzu	<i>Pueraria thunbergiana</i>	Stem
Mauritius hemp	<i>Furcraea gigantea</i>	Leaf
Nettle	<i>Urtica dioica</i>	Stem
Oil palm	<i>Elaeis guineensis</i>	Fruit
Phormium	<i>Phormium tenax</i>	Leaf
Piassava	<i>Attalea funifera</i>	Leaf
Pineapple	<i>Ananus comosus</i>	Leaf
Roselle	<i>Hibiscus sabdariffa</i>	Stem
Ramie	<i>Boehmeria nivea</i>	Stem
Sansevieria (Bowstring hemp)	<i>Sansevieria</i>	Leaf
Sisal	<i>Agave sisilana</i>	Leaf
Sponge gourd	<i>Luffa cylindrica</i>	Fruit
Straw (cereal)	–	Stalk
Sun hemp	<i>Crotalaria juncea</i>	Stem
Cadillo/urena	<i>Urena lobata</i>	Stem
Wood	(>10 000 species)	Stem

### 1.3 Synthetic fibres

Synthetic fibres form an important part of the textile industry, with the production of polyester alone surpassing that of cotton. There are many different kinds of synthetic fibres but among them polyamide is widely used, for example nylon. The fibres of polyvinyl alcohol and polypropylene (PP) are also important. Given this importance, research into effective production of these fibres and improving fibre

Table 1.2 List of important animal fibres

Animal fibre	Origin
Silk (domestic silk, wild silk)	Silkworm
Wool	Sheep
Cashmere wool	Goat reared in Himalayan region
Camel wool	Camel
Mohair	Angora goat
Alpaca wool	Goat reared in Andes mountains in Peru
Rabbit hair	Angora rabbit
Cow hair	Cow

From reference 6.

properties is warranted. A great disadvantage of some synthetic fibres is their low hydrophilicity. This affects the processing of the fibres especially during wet treatments. The surfaces are not easily wetted, thus impeding the application of finishing compounds and colouring agents. In addition, a hydrophobic material hinders water from penetrating into the pores of fabric.

Nonwoven fabrics are formed by extrusion processes and may be manufactured inexpensively so that they can be used in disposable products that are discarded after only one or a few uses. For example, PP and polyester nonwoven fabrics are used in disposable absorbent articles, such as diapers, feminine care products and wipes. Moreover, they are also widely used as filtration media, battery separators and geotextiles. In all these applications, the PP and polyester nonwoven fabrics need to be wettable by water or aqueous liquids, which is not an inherent characteristic of the material.

Surface modification of textiles is performed to improve various properties such as softness, dyeability, absorbance and wettability. Recent advances in textile chemistry have resulted in imparting various functional properties such as antimicrobial activity, decreased skin irritation properties and also enhanced fragrance to textiles.

#### 1.4 Surface preparation techniques for textile materials

Surface preparation techniques are mainly used for the removal of foreign materials to improve uniformity, hydrophilic nature and affinity for dyestuffs and other treatments and relaxation of residual tensions in synthetic fibres. The surface preparation technique usually depends on the type of fibre (natural or synthetic) and the form of the fibrous structure (i.e. spun yarn, woven or knitted fabric). Some of the common preparation techniques are outlined below.

### 1 1.4.1 Singeing

2 Singeing is usually carried out on woven cotton fabrics and yarns to burn  
3 protruding fibres which affect subsequent processing, such as dyeing and  
4 finishing. The fabric is passed over a row of gas flames and then immediately  
5 dipped into a quench bath to extinguish the sparks and cool the fabric. The quench  
6 bath often contains a desizing solution, in which case the final step in singeing  
7 becomes a combined singeing and desizing operation.  
8

### 9 1.4.2 Desizing

10 Desizing is used for removing previously applied sizing compounds from woven  
11 fabric and is usually the first wet finishing operation performed on woven fabric.  
12 Different desizing techniques are employed depending upon the kind of sizing  
13 agent to be removed. Sizing agents are commonly based on natural polysaccharides  
14 (starch, protein and cellulosic derivatives) and synthetic polymers (polyvinyl  
15 alcohol (PVA), polyacrylates, polyesters and polyvinyl acetates). Depending on  
16 the sizing agent used, sizes can be removed using hot water, enzymes or hydrogen  
17 peroxide.  
18

19 Currently applied techniques can be categorised as follows:  
20

- 21 (a) removal of starch-based sizing agents (water-insoluble sizes);
  - 22 (b) removal of water-soluble sizes (PVA and polyacrylates).
- 23

### 24 1.4.3 Scouring

25 The purpose of scouring is to extract impurities present in the raw fibre or picked  
26 up at a later stage – such as pectins, fat and waxes, proteins, inorganic substances  
27 (e.g. alkali metal salts), calcium and magnesium phosphates, aluminium and iron  
28 oxides, sizes (when scouring is carried out on woven fabric as part of desizing),  
29 residual sizes and sizing degradation products (when scouring is carried out on  
30 woven fabric after desizing).  
31

32 Scouring can be carried out as a separate step of the process or in combination  
33 with other treatments (usually bleaching or desizing) on all kind of substrates:  
34 woven fabric (sized or desized), knitted fabric and yarn. The action of scouring is  
35 performed by an alkali (sodium hydroxide or sodium carbonate) together with  
36 auxiliaries that include non-ionic (alcohol ethoxylates, alkyl phenol ethoxylates)  
37 and anionic (alkyl sulfonates, phosphates, carboxylates) additives.  
38

### 39 1.4.4 Bleaching

40 Bleaching is used to remove colour impurities in natural and some man-made  
41 fibres to produce a whiter substrate. This is usually accomplished by oxidising the  
42 natural pigments of the fibre using an oxidising agent, for example, hydrogen  
43

peroxide. Cotton is usually bleached using hydrogen peroxide under alkali conditions, with the addition of sodium silicate and magnesium sulfate to stabilise the process and reduce fibre damage. Metal ions, such as iron and copper, can catalyse the decomposition of the hydrogen peroxide resulting in the formation of oxycellulose and localised damage to the fibres. Bleaching of cotton fabrics can be undertaken as continuous or pad batch processes. Newer research in this field is directed towards non-peroxide bleaching to reduce the adverse effects on the environment caused by effluent discharge. Non-peroxide bleaching agents like sodium hypochlorite and sodium chlorite are widely used but have lost favour because of environmental issues.

#### 1.4.5 Mercerisation

Mercerisation is another technique and is used for cellulosic and cotton fibres in particular.<sup>7</sup> The process involves the treatment of fabrics with sodium hydroxide and is named after John Mercer. It has been observed that compared with untreated cotton mercerised cotton has greater strength and lustre, is more absorbent and has a greater capacity to absorb dye. When natural fibres are treated with sodium hydroxide, it results in dissolution of hemicellulose and rearrangement of microfibrils in a more compact manner.

Surface preparation techniques for man-made composites would involve techniques like solvent cleaning with solvents such as isopropyl alcohol, surface abrasion, and conditioning and neutralisation with suitable chemical agents.

### 1.5 Surface modification techniques for textile materials

There are several surface modification techniques that have been developed to improve wetting, adhesion and other properties of textile surfaces by introducing a variety of reactive groups. Some of the common techniques are described below.

#### 1.5.1 Wet chemical processing

In wet chemical surface modification, the textile surface is treated with liquid reagents to generate reactive functional groups on the surface. This technique results in the penetration of the textile substrate by the chemical agent. The commonly used chemical processing agents are chromic acid and potassium permanganate which introduce oxygen-containing moieties to PP and polyethylene fibres. The degree of surface functionalisation is therefore not repeatable between polymers of different molecular weight and crystallinity. This type of treatment can also lead to the generation of hazardous chemical waste and can result in surface etching.

## 1 1.5.2 Ionised gas treatments

2  
3 *Plasma treatment*

4  
5 Plasma is a high-energy state of matter in which a gas is partially ionised into  
6 charged particles, electrons and neutral molecules. Gas plasmas were introduced  
7 in the 1960s but it is only recently that it has been possible to treat textiles on a  
8 commercial scale. Plasma is essentially a dry process providing modification of  
9 the top nanometre surface without using solvents or generating chemical waste.  
10 The type of functionalisation imparted can be varied by the plasma gas selected  
11 (e.g. Ar, He, N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub> and NH<sub>3</sub>) and operating parameters (e.g. pressure,  
12 power, time and gas flow rate). Oxygen plasma is used to impart oxygen-  
13 containing functional groups to polymer surfaces. Carbon dioxide plasma has been  
14 used to introduce carboxyl groups. Inert gases are used to introduce radical sites on  
15 the polymer surface for subsequent graft polymerisation.

16 Exposure to plasma results in the cleaning of the surface of materials and  
17 modification of surface energies. Active species from the plasma bombard or react  
18 with monolayers on the surface of materials and change the properties either  
19 temporarily or permanently. The advantages of plasma technology are its potential  
20 environmental friendliness and energy conservation benefits in developing high-  
21 performance materials.

22 The properties of natural and synthetic fibres are modified by processes such as  
23 polymerisation, grafting and cross-linking. As adhesion is a surface-dependent  
24 property, plasma technology can achieve modification of the near-surface region  
25 effectively without affecting the bulk properties of the materials of interest. The  
26 common benefits of plasma surface modifications on textile materials are enhance-  
27 ments in wettability<sup>8,9</sup>, printability<sup>10,11</sup>, adhesion<sup>12,13</sup> and sterilisation.<sup>14</sup>

28 Plasma can also be used as a precursor to other surface modification techniques;  
29 for example, plasma activation followed by ultraviolet (UV) graft polymerisation  
30 or plasma activation followed by silane treatment.

31 Dielectric barrier discharges (DBDs) or 'silent' discharges are widely used for  
32 the plasma treatment of polymer films and textiles.<sup>15,16</sup> These discharges demon-  
33 strate great flexibility with respect to their geometric shape, working gas  
34 composition and operational parameters (input power, frequency of the applied  
35 voltage, pressure, gas flow, substrate exposure time, etc.). A DBD is obtained  
36 between two electrodes, at least one of which is covered with a dielectric, when a  
37 high-voltage alternating current is applied between the electrodes. The most  
38 interesting property of DBDs is that in most gases the breakdown starts at many  
39 points, followed by the development of independent current filaments (termed  
40 'micro-discharges'). These micro-discharges are of nanosecond duration and are  
41 uniformly distributed over the dielectric surface.

42 A disadvantage of plasma treatment is that plasma generation requires a vacuum  
43 to empty the chamber of latent gases; this is complicated for continuous operation



in a large-scale industrial setting. In addition, there are several processing parameters to optimise – including time, temperature, power and distance of substrate from plasma source – which can affect the reproducibility of results. Morent *et al.*<sup>17</sup> have presented an interesting overview of the literature on the treatment of textiles with non-thermal plasmas.

#### *Corona discharge*

Corona discharge is a low-cost, simple process in which an electrically induced stream of ionised air bombards the polymer surface. It is usually used to promote adhesion in inert polymers. A disadvantage of the process is contamination of the polymer surface since vacuum conditions are not required.

#### *Flame treatment*

Flame treatment is a non-specific surface functionalisation technique that bombards the polymer surface with ionised air generating large amounts of surface oxidation products. The reactive oxygen is generated by burning an oxygen-rich gas mixture. Flame treatment has been shown to impart hydroxyl, aldehyde and carboxylic acid functionalities to polyethylene and is utilised to enhance printability, wettability and adhesion. One drawback of flame treatment is that it can reduce the optical clarity of polymers; in addition, there are many parameters (including flame temperature, contact time and composition) that must be accurately controlled to maintain consistent treatment and to avoid burning.

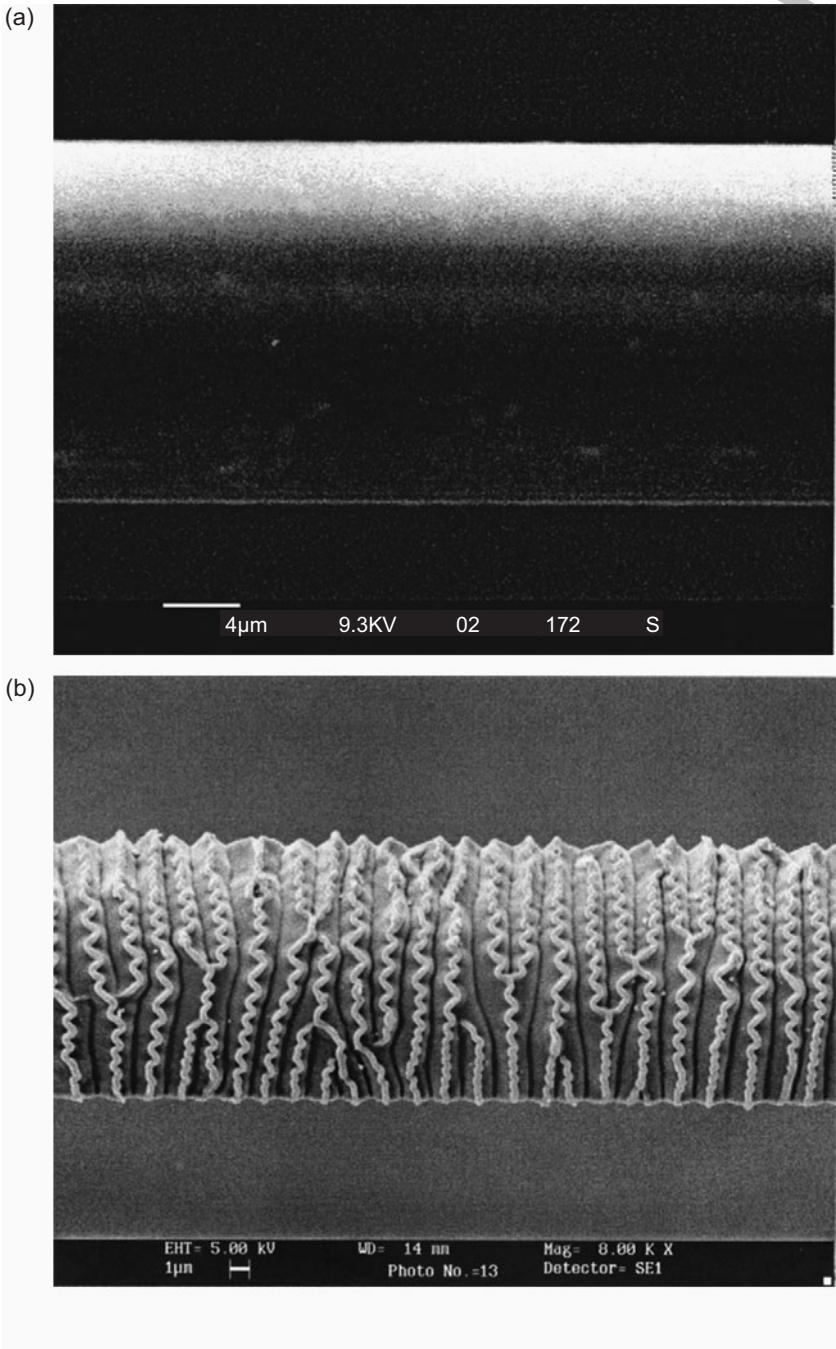
#### *Ultraviolet irradiation*

When polymer surfaces are exposed to UV light, polymer surfaces generate reactive sites which can become functional groups upon exposure. The difference between ionised gas treatments and UV irradiation is the ability to tailor the depth of surface reactivity by varying wavelength and absorption coefficient.

### **1.6 Recent studies on the modification of textiles**

Strnad *et al.*<sup>18</sup> investigated the effect of chitosan treatment on sorption and mechanical properties of cotton fibres. Cotton fibres initially underwent different pre-treatments (alkali treatment, bleaching, demineralisation) and were then oxidised using differing procedures containing  $KIO_4$  solutions and then treated with chitosan. The authors observed that all the oxidation procedures, even under very mild conditions, have a significant influence on the worsening of mechanical properties. The treatment of oxidised cotton with chitosan had no influence on breaking force and elongation, but increased the Young's modulus of fibres. This was attributed to the fact that chitosan bound itself to raw cotton through inter-

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43



1.3 Surface structure of polyester fibre (a) untreated (b) under high fluence (5 pulses at 100 mJ/cm<sup>2</sup>).<sup>19</sup>

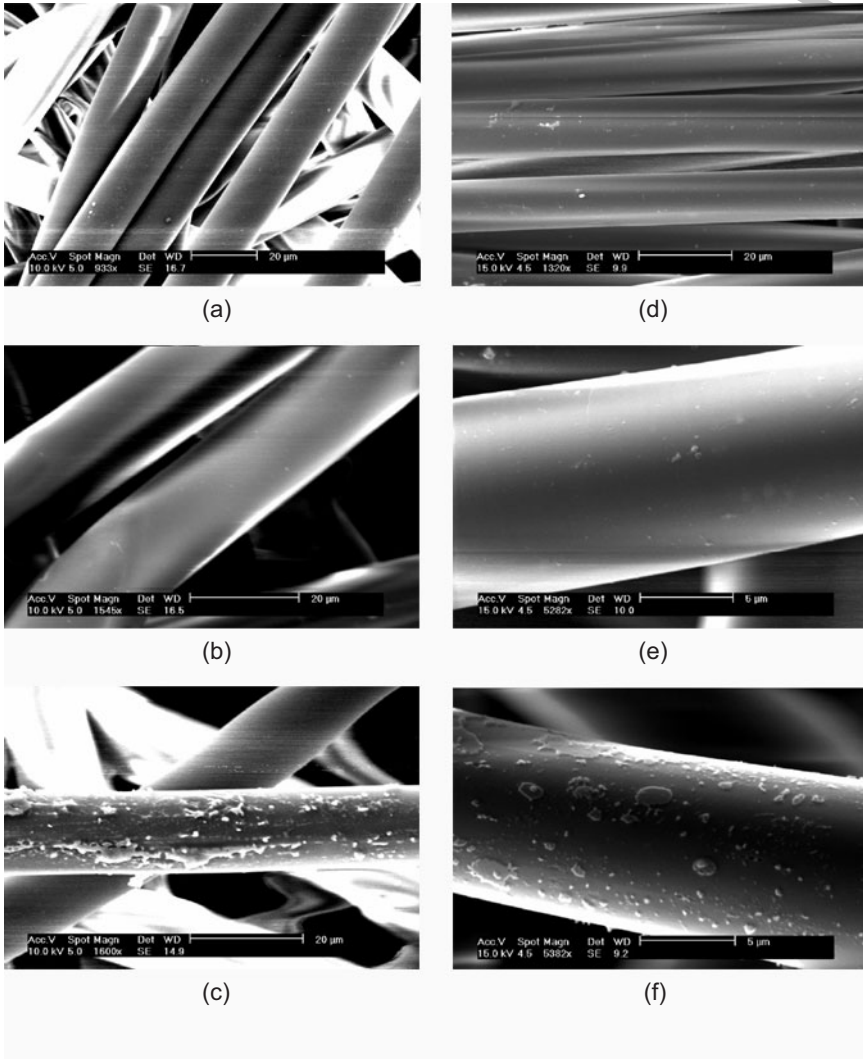
fibrillar linkages with the primary walls of the fibres. Chitosan adsorption was also found to increase the moisture absorption of the fibres.

The effect of laser modification on the properties of polyester was investigated by Kan.<sup>19</sup> The properties studied included tensile strength, elongation, wetting and crystallinity. The author observed that laser irradiation did not affect the bulk properties owing to its low penetration depth. Morphological study of the untreated and treated polyester fibres revealed a ripple-like structure on the treated fibres. Figures 1.3(a) and (b) show the presence of a smooth surface while laser irradiation resulted in a roll-like to ripple-like structure. The orientation of this kind of ripple-like structure was found to be perpendicular to the fibrillar orientation of the fibre. The tensile strength and elongation were also found to decrease after irradiation. This was attributed to the fact that ripples created more weak points in the fibre leading to a reduction in tensile strength.

In a recent study, by Morent *et al.*<sup>20</sup> polyethylene terephthalate (PET) and PP nonwovens were modified by a dielectric barrier discharge in air, helium and argon at medium pressure (5.0 kPa). The helium and argon discharges contained an air fraction smaller than 0.1%. Surface analysis and characterisation were performed using X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). XPS measurements revealed the incorporation of oxygen-containing functional groups (C–O, C=O and O–C=O) on the PP and PET nonwovens. It was also observed that air plasma was more efficient at incorporating oxygen functionalities than argon plasma, which was in turn more efficient than helium plasma.

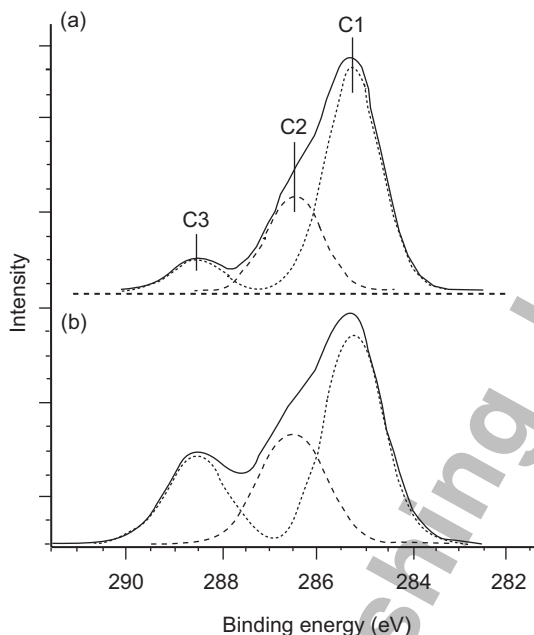
Figures 1.4(a) and (d) show SEM images of untreated PP and PET nonwovens, respectively. The untreated PP nonwoven consisted of PP fibres with a relatively smooth surface; the surface of the PET fibres was also relatively smooth, however small particles were present on the fibre surfaces. Energy-dispersive X-ray microanalysis (EDX) identified the particles as NaCl crystals. The presence of these crystals was due to the insufficient removal of chemicals during the production process of the nonwoven. Figures 1.4(b) and (e) show SEM images of the saturated PP and PET nonwovens, respectively, after plasma treatment in air. The SEM images show that the saturated PP and PET nonwovens had the same surface morphology as the untreated samples. Figures 1.4(c) and (f) show SEM images of the PP and PET nonwovens, respectively, after plasma treatment in air with a very high energy density (1.13 J/cm<sup>2</sup>). After extended plasma treatment, the surfaces of the PP and PET fibres showed a significant accumulation of PP and PET matter, respectively.

Borcica *et al.*<sup>21</sup> investigated the effects of plasma treatment of woven natural, synthetic and mixed fabrics, using a DBD run in various environments (air, argon and nitrogen) at atmospheric pressure. The experiments were conducted to determine the effects of the operating parameters (dielectric layer make-up, discharge energy density, gas flow, gas type and exposure time) on the measured changes to surface wettability, morphology and chemical composition. It was



34 1.4 SEM images of (a) the untreated PP non-woven, (b) the PP non-woven after plasma treatment in air (energy density = 420 mJ/cm<sup>2</sup>), (c) the PP non-woven after plasma treatment in air (energy density = 1.13 J/cm<sup>2</sup>), (d) the untreated PET non-woven, (e) the PET non-woven after plasma treatment in air (energy density = 230 mJ/cm<sup>2</sup>) and (f) the PET non-woven after plasma treatment in air (energy density = 1.13 J/cm<sup>2</sup>).

35  
36  
37  
38  
39  
40  
41 observed that surface modification of woven natural, synthetic and mixed fabrics  
42 showed that a DBD plasma can be used to modify the surface of textured textile  
43 materials, leading to enhanced hydrophilicity-dependent properties. The



1.5 Carbon (1s) XPS spectra for (a) untreated and (b) 1.0 s-treated polyester fabric.<sup>21</sup>

behaviour of the woven textile polymers was found to be very similar, under DBD treatment, to that of thin-film variants of the same polymers. The surface properties, such as the wickability and the level of oxidation, were increased markedly after the treatment.

Figure 1.5 shows the XPS spectra of untreated and treated polyester fabrics. The XPS spectra of untreated samples include high binding energy carbon peaks, as shown in Fig. 5.1(a) for the polyester fabric. The C1s spectrum for untreated polyester consists mainly of three distinct peaks: the hydrocarbon atoms C1 (285.0 eV), the methylene carbon singly bonded to oxygen C2 (286.7 eV) and the ester carbon atoms C3 (288.9 eV). Although the same chemical functionalities can be identified on the treated samples (Fig. 1.5(b)), the oxidation is demonstrated by the increase in intensity of the C2 and C3 peaks as compared with the C1 peak.

Masaeli *et al.*<sup>22</sup> investigated the effect of treatment time with low-pressure oxygen plasma on the wettability, surface characteristics and fine structure of spunbonded PP nonwoven. It was observed that oxygen plasma treatment increased the surface wetting of PP fibres significantly. This was the result of an increase in surface free energy as well as the etching effect of the plasma. The wetting properties were measured using contact angle measurements. Table 1.3 compares the contact angles of water and methylene iodide on plasma-treated and

1 **Table 1.3** Contact angle of oxygen-plasma-treated and untreated samples<sup>22</sup>

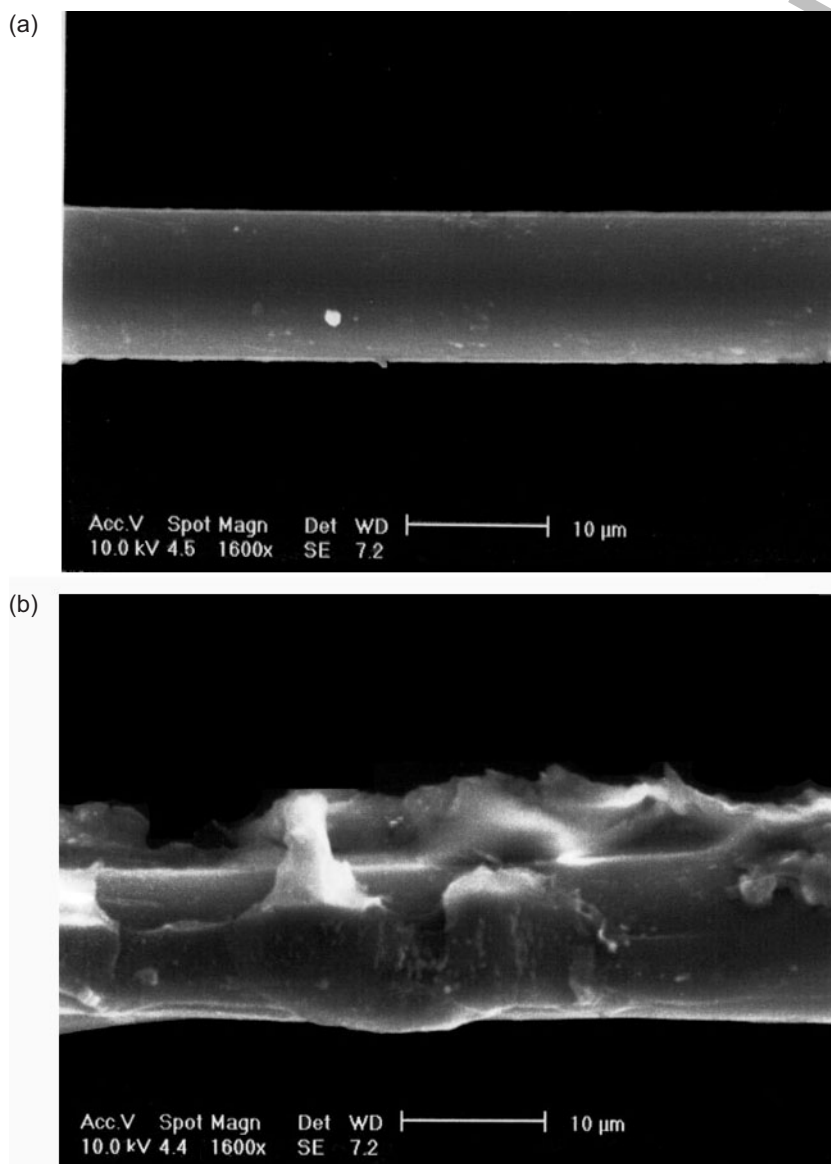
Sample	Contact angle	
	Water	Methylene iodide
Untreated	121.5	99.9
Oxygen plasma treated(30 min., 500 W)	83.9	88.2

untreated nonwoven fabrics. As a result of plasma treatment, the contact angle decreased from 121.5° to 83.9° and from 99.9° to 88.2° for water and methylene iodide, respectively, indicating an increase in wettability. It was also noted that a longer plasma exposure time can produce more hydrophilic functional groups on the PP surface. The SEM images of the plasma-treated and untreated PP fibres are shown in Fig. 1.6(a) and (b). It is clear that the plasma treatment etches PP fibres significantly. The etching effect is caused by the bombardment of the fibre surface by active species in plasma radiation. XRD spectra of the samples (Fig. 1.7) revealed that plasma treatment had no significant effect on the crystallinity of the treated fibres. This was expected because the plasma action is limited to the surface of the fibres.

Canal *et al.*<sup>23</sup> examined the role of (N<sub>2</sub>, N<sub>2</sub> + O<sub>2</sub> and O<sub>2</sub>) post-discharge plasma modification on wool and polyamide fabrics. Dynamic contact angle, XPS and SEM were used to characterise the modified wool surfaces and revealed an improved wettability that was attributed to the generation of new chemical groups and the reduction/elimination of the fatty layer on the surface of the wool. Wool exhibits hydrophobic properties as a result of the presence of a thin lipid layer, called a ‘fatty layer’, on the outermost part of the fibres, surrounding each cuticle cell (scale). The fatty layer is formed by fatty acids which are covalently bonded to the protein matrix of the epicuticle (with a global thickness of 5–7 nm) by thioester links.<sup>24</sup> The scales on the surface of wool fibres overlap one another like tiles on a roof, and are responsible for the directional frictional effect.

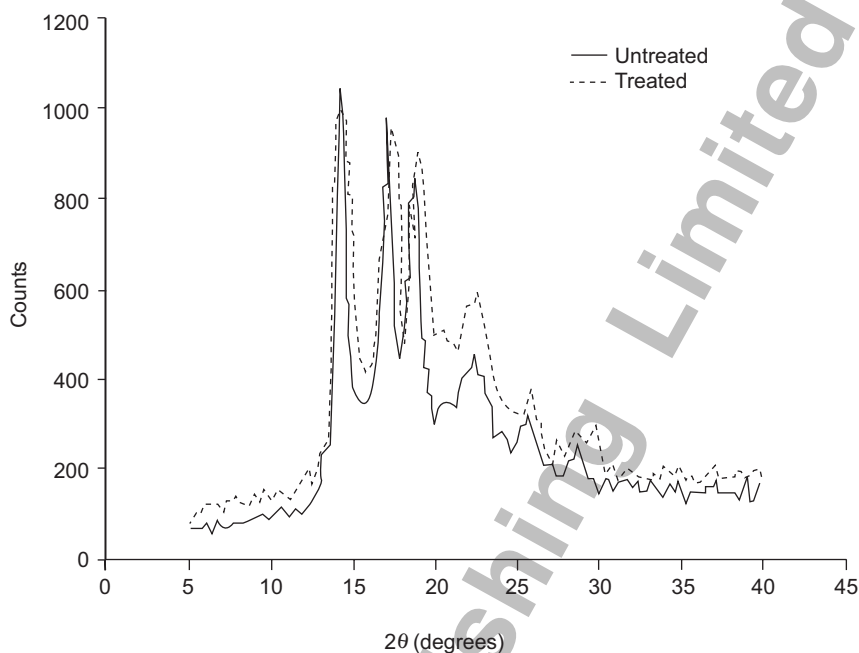
Figure 1.8(a) shows the SEM micrograph of an untreated merino wool fibre, it can be observed that the cuticular cells are flat, the roughness of the wool fibre comes from the overlapping of the cells. A N<sub>2</sub> post-discharge treatment did not produce remarkable changes on the surface of wool, except for the cleaning of the surface (Fig. 1.8(b)). In direct nitrogen plasma discharges there was no modification on the surface of wool, confirming the ineffectiveness of this kind of plasma gas treatment. In contrast, micrographs (Fig. 1.8(c)) of wool treated with oxygen post-discharge showed the presence of the visible etching effects through the presence of striations and micro-craters on the wool cuticle.

The treatment of textile fabrics with ozone has been of interest in the field of textile finishing from the standpoint of environmental preservation.<sup>25, 26</sup> Ozone bleaching of cotton fabric and ozone shrink-resistant finishing of wool fabric has



1.6 SEM images of (a) untreated fibres and (b) fibres treated with oxygen plasma for 30 min.<sup>22</sup>

been reported.<sup>27,28</sup> Lee *et al.*<sup>29</sup> investigated the ozone gas treatment of nylon 6 and polyester fabrics. The treatment incorporated much more oxygen into the fibre surface in the form of  $-COOH$  and  $-COOH$  as shown by XPS. Water penetration increased considerably with treatment, and the apparent dyeing rate and

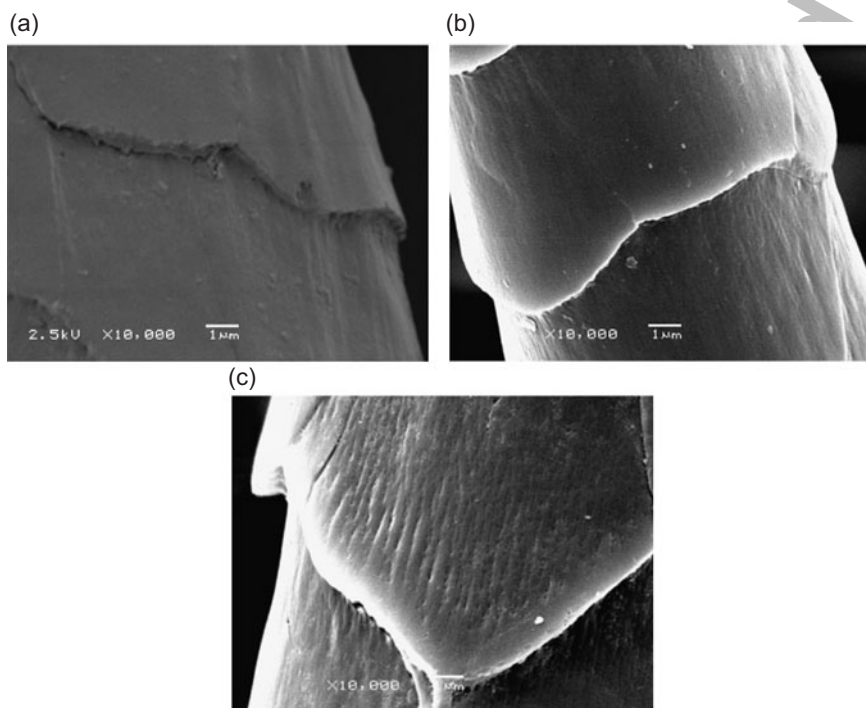


1.7 XRD results of untreated samples and samples treated with oxygen plasma for 30 min.<sup>22</sup>

equilibrium dye uptake were also improved, especially for the polyester fabric, despite an increase in the crystallinity. Thus, it was observed that the treatment brought about a change not only in the fibre surface but also in the internal structure of the fibres (the crystalline and amorphous regions) with regard to the dyeing behaviour. Table 1.4 shows the relative intensities of the C1s, O1s and N1s spectra in the wide-scanning XPS of the ozone-gas-treated nylon 6 and polyester fabrics. As shown in Table 1.4, the O1s intensity of the nylon 6 fabric apparently increased when treated at atmospheric pressure, whereas the intensity of the polyester fabric increased with increasing gas pressure.

An interesting approach to surface modification is the use of enzymes for this purpose.<sup>30-32</sup> Examples of applicable enzymes are lipases and cutinases.<sup>33-35</sup> They have been reported to increase hydrophilicity of polyesters by hydrolysis of ester bonds. Owing to the size of enzymes, they are only active at the surface so that the bulk characteristics of fibres remain unchanged. Reactions generally occur under mild conditions, no complicated machinery is required, as is the case for plasma treatments or etching procedures, and little or no additional chemicals are necessary. Cutinases and carboxylesterases have both shown the potential to hydrolyse ester bonds in a similar manner to lipases.<sup>36</sup> The enzymatic surface modification of PET with cutinase from *Fusarium solani pisi* was investigated by



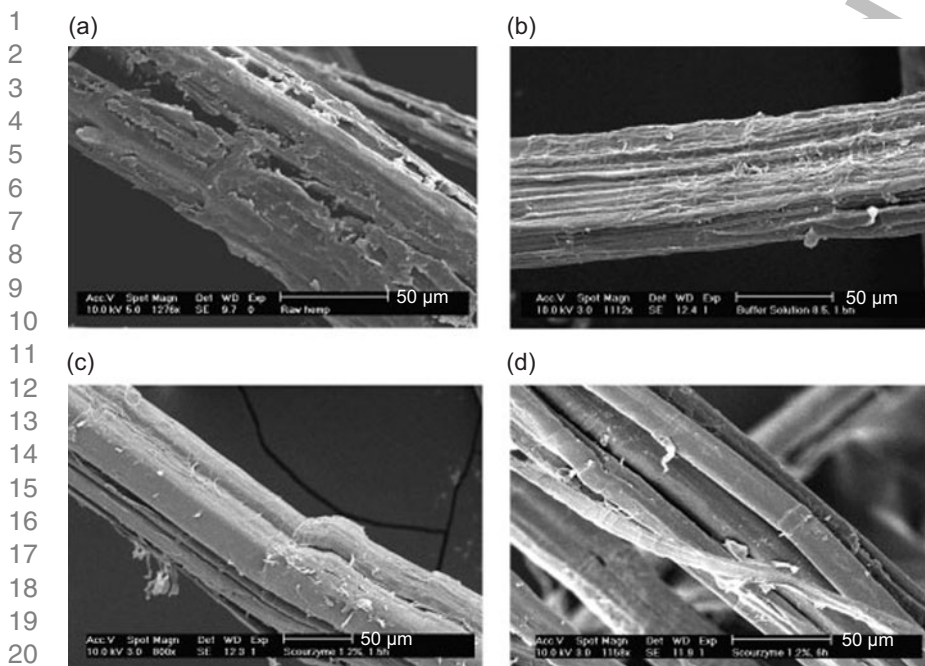


1.8 SEM micrographs of wool fibres: (a) untreated; (b) treated for 900 s in an  $N_2$  post-discharge; (c) treated for 900 s in an  $O_2$  post-discharge.<sup>23</sup>

Table 1.4 Relative intensities of C1s, O1s and N1s in wide-scanning XPS analysis of nylon 6 and polyester fabrics treated with ozone gas<sup>29</sup>

Treatment	Surface chemical composition (%)		
	C1s	O1s	N1s
<i>Nylon 6</i>			
Untreated	83.5	12.7	3.8
Ozone gas treated AP, 20 °C/10 min	79.8	15.5	4.7
<i>Polyester fabric</i>			
Untreated	75.2	24.8	–
Ozone gas treated AP, 20 °C/10 min	74.8	25.2	–
0.1 MPa, 20 °C/10 min	74.2	24.8	–

AP, atmospheric pressure.



25 1.9 SEM micrographs of Scourzyme-treated hemp fibres.

26 Vertommen *et al.*<sup>37</sup> It was observed, by direct measurement and identification of  
27 the different products, that cutinase from *F. solani pisi* displayed significant  
28 hydrolytic activity towards amorphous regions of PET.

29 In another interesting study, Ouajai and Shanks<sup>38</sup> looked into the bioscouring of  
30 hemp fibre using pectate lyase (EC 4.2.2.2) (Trade name: Scourzyme L). Greater  
31 enzyme concentration and a longer treatment improved the removal of the low  
32 methoxy pectin component as indicated by UV spectroscopy. Removal of pectate  
33 caused no crystalline transformation in the fibres, except for a slight decline in the  
34 crystallinity index.

35 Figure 1.9(a) shows fibre bundles of untreated hemp covered by non-cellulosic  
36 materials. The fibre bundles were 80–100 mm in diameter. Figure 1.9(b) indicates  
37 that a treatment without the pectate lyase enzyme was not sufficient to remove all  
38 of the non-cellulosic materials from the fibres; fibres treated by buffer solution  
39 (pH 8.5) alone exhibited a considerable surface roughness. Only the fractions that  
40 were soluble in the buffer were partially extracted. The surface of 1.2% Scourzyme  
41 L-treated fibres (Fig. 1.9(c)) appears smooth, but the fibres are still assembled in  
42 bundles. A further elimination of pectin was exhibited after an extended treatment  
43 time of 6 h (Fig. 1.9(d)), resulting in a smoother surface and deeper inter-fibrillar  
disintegration of the bundle.

The influence of a chitosan application on wool fabric before a treatment with a proteolytic enzyme was investigated by Vílchez *et al.*<sup>39</sup> The enzymatic treatment enhances whiteness and confers shrink resistance to wool, but an increase in the enzyme concentration leads to a detrimental effect on the physico-mechanical properties. A chitosan treatment before the enzymatic treatment was also found to improve the shrink resistance and increase the weight loss.

Ibrahim *et al.*<sup>40</sup> attempted to enhance the antibacterial properties of cotton fabrics via pre-cross-linking with trimethylol melamine followed by subsequent treatment with iodine solution to create new active sites. The treated fabric showed the ability to inhibit as well as to arrest the growth of both *Bacillus subtilis* and *Escherichia coli*. The antibacterial activity is determined by the degree of modification and the extent of iodine retention, as well as the ease of iodine liberation.

Another concept for the modification of synthetic and natural fibres is based on the permanent fixation of supramolecular components, e.g. cyclodextrins, on the surfaces by functional groups using common technologies of textile processing. An advantage of this method is that the textile fibres achieve specific properties by means of inclusion of inorganic molecules within the cyclodextrin cavities.<sup>41, 42</sup> Cyclodextrins possess a hydrophobic cavity in which a number of chemicals can form inclusion complexes. They have been grafted to cellulosic and polyamide fabrics in order to investigate their use as textile finishing agents. Fourier transform infra red (FTIR), spectroscopy SEM and absorbance spectra confirmed their immobilisation, and standard textile tests established that surface modification treatments did not affect mechanical integrity. An antimicrobial agent (benzoic acid), an odour-producing compound (vanillin), and an insect repellent pesticide (*N, n*-diethyl-meta-toluamide (DEET)) were some of the chemicals investigated for inclusion in these bound cyclodextrins.<sup>43–45</sup> The unique ability of cyclodextrins to form reversible complexes with a range of chemicals makes them attractive in a number of polymer-bound applications, including drug delivery, odour removal and fragrance applications.

In a study by Denter and Schollmeyer<sup>46</sup> both synthetic and natural fibres were subjected to cyclodextrin fixation. It was reported that properties such as hydrophilicity, physiological and electrostatic power, reactivity and complexing power were significantly affected by ligand fixation.

The surface modification of PP fibres by the addition of non-ionic melt additives (nonyl phenol ethoxylates and stearyl alcohol ethoxylates) has been reported by Vasantha *et al.*<sup>47</sup> Melt additives can be blended with the polymers prior to or during melt spinning and they are bound in the polymer matrix when the polymer cools. The melt additive can migrate to the surface imparting durable hydrophilicity without altering the bulk properties of polymer.

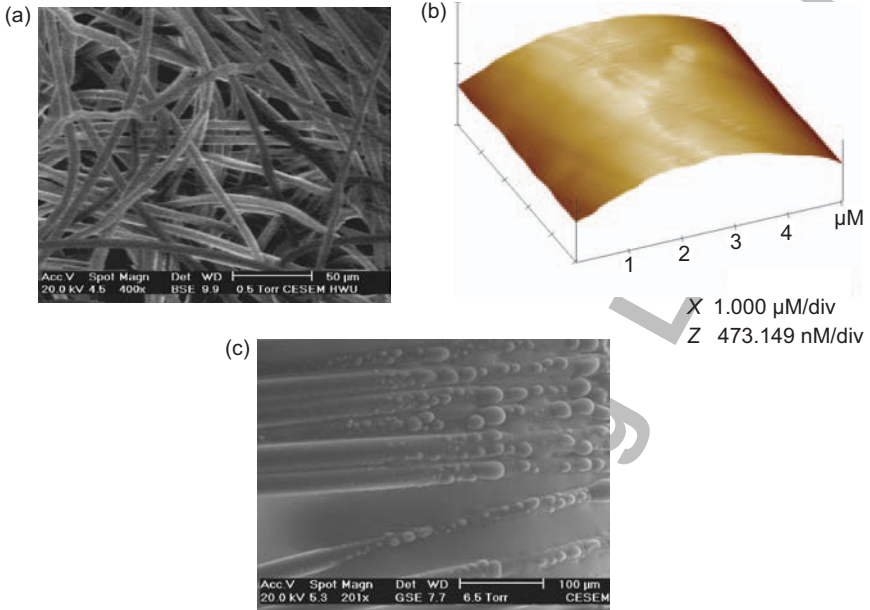
An interesting approach is the functionalisation of textile fibres by making use of concepts of nanotechnology.<sup>48</sup> Coatings based on nanosols and inorganic–organic hybrid polymers, derived from the sol-gel process, have immense potential

1 for creative modifications of surface properties of textiles and can be applied with  
2 a comparatively low technical effort and at moderate temperatures. Coatings of a  
3 thickness of less than one micron can act as effective barriers against chemical  
4 attacks, super-repellent surfaces can be created, or the wear-resistance of textile  
5 materials improved. Coatings incorporating nanoparticles as employed in sun  
6 creams protect sensitive polymers against decomposition due to UV radiation.  
7 Ballistic bodywear based on fabrics with protection against gun attacks and fabrics  
8 that are resistant to knife cuts can be developed. For these products, thin coatings  
9 based on inorganic–organic hybrid polymers filled with alumina nanoparticles  
10 were found to give good stab-resistance. Further approaches deal with reversible  
11 photochromic coatings – coatings that change colour if irradiated with sunlight –  
12 magnetic hybrid polymers or medical systems based on porous sol-gel coatings  
13 with immobilised drugs that are released in contact with skin.

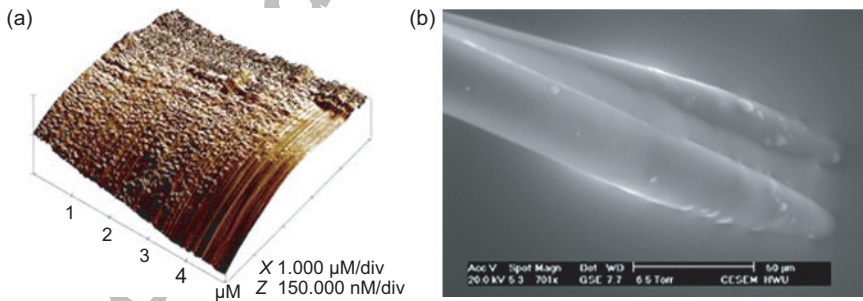
14 In an interesting study, Becheri *et al.*<sup>49</sup> reported on the synthesis and  
15 characterisation of nanosized ZnO particles and their application on cotton and  
16 wool fabrics for UV shielding. The effectiveness of the treatment was assessed  
17 through UV–visible light spectrophotometry and the calculation of the UV  
18 protection factor (UPF). The authors observed that the performance of ZnO  
19 nanoparticles as UV absorbers, can be efficiently transferred to fabric materials  
20 through the application of ZnO nanoparticles on the surface of cotton and wool  
21 fabrics. The UV tests indicate a significant increment in the UV absorbing activity  
22 in the ZnO-treated fabrics. Such results can be exploited for the protection of the  
23 body against solar radiation and for other technological applications.

24 In a recent study by Leroux *et al.*<sup>50</sup> a fluorocarbon nanocoating was deposited on  
25 polyester (PET) woven fabric using pulse discharge plasma treatment by injecting  
26 a fluoropolymer directly into the plasma DBD. The objective of the treatment was  
27 to improve the hydrophobic properties as well as the repellent behaviour of the  
28 polyester fabric. The study showed that adhesion of the fluoropolymer to the  
29 woven PET was greatly enhanced by the air plasma treatment.

30 In another interesting study, Wei *et al.*<sup>51</sup> investigated the functionalisation of  
31 PET by plasma modification. The surface topography and wetting characteristics  
32 were studied using environmental scanning electron microscopy (ESEM) and  
33 atomic force microscopy (AFM). Figure 1.10(a) shows an ESEM photomicro-  
34 graph of the untreated PET nonwoven material. The image reveals the fibrous  
35 structure of the material, but at this magnification the surface morphology of  
36 individual fibres in the web is not clear. The AFM image at higher magnification  
37 clearly indicates the surface characteristics of the untreated PET fibre in the web.  
38 As illustrated in Fig. 1.10(b), the surface of the PET fibre is quite smooth with  
39 some groove-like structures on the surface before plasma treatment. The groove-  
40 like surface is the fibril structure of the fibre. The wetting of the PET fibres  
41 observed in the ESEM image reveals that water droplets are formed on the fibre  
42 surface, which is shaped like the segments of spheres (as illustrated in Fig. 10(c)),  
43 and so the fibres are not properly wetted. This observation reflects the hydrophobic



1.10 Images of PET nonwoven and fibres: (a) ESEM image of PET nonwoven, (b) AFM image of the PET fibre surface and (c) wetting of water on the PET fibre surface.<sup>51</sup>



1.11 Activated PET nonwoven: (a) AFM image of the fibre surface and (b) ESEM image of the wetting of the fibres.<sup>51</sup>

1 behaviour of the PET fibres. However, after exposure to oxygen the fibre surface  
2 becomes pitted, as shown in Fig. 1.11(a). The surface of the fibre is roughened due  
3 to the etching effect of oxygen plasma. Oxygen plasma treatment also significantly  
4 affects the behaviour of the PET fibre surface towards water. The effects of plasma  
5 treatment are clearly discerned from the ESEM photomicrographs, as shown in  
6 Fig. 1.11(b). After oxygen plasma treatment, the profiles of the water droplets are  
7 considerably altered. The droplets are spread along the fibre surface, and the water  
8 droplets formed on the fibre surface show much lower contact angles, indicating  
9 the much better wetting properties of the treated fibres.

## 11 1.7 Future trends

13 A considerable amount of research is taking place in the field of surface modifica-  
14 tion of textiles with a view to improving properties and processes. In the case of  
15 conventional textile wet processes, the trend will be to reduce water and energy  
16 consumption and eliminate environmentally harmful effluent discharges resulting  
17 from the use of synthetic chemicals. Of the different kinds of surface modification  
18 techniques applied, plasma treatment appears to be the commonly used and with  
19 good results and environmental benefits. Both equipment manufacturers and  
20 researchers are making concerted efforts to improve the commercial viability of  
21 plasma processes; however, doubts remain about the durability of the plasma  
22 treatments and their commercial viability. Enzymatic modification of textiles  
23 usually occurs at the surface of textiles owing to the large structures of enzymes  
24 and the use of enzymes will penetrate into different areas of the industry in the  
25 future. The use of naturally abundant substances, such as chitin and chitosan, will  
26 also be researched further. Nanotechnology offers promise owing to its potential to  
27 improve functional properties, for example super-hydrophobicity and  
28 hydrophilicity. Both intrinsic and surface modifications using nano-additives will  
29 be researched and the processes will be modified accordingly. The super-  
30 hydrophobicity effect is seen in plants like lotus, taro and nasturtium and is termed  
31 the Lotus-Effect<sup>®</sup>. The effect arises because lotus leaves have a very fine surface  
32 structure and are coated with hydrophobic wax crystals of around 1 nm in  
33 diameter. Surfaces that are rough on a nanoscale tend to be more hydrophobic than  
34 smooth surfaces because of the reduced contact area between the water and solid.  
35 In the lotus plant, the actual contact area is only 2–3% of the droplet-covered  
36 surface. The nanostructure is also essential to the self-cleaning effect – on a smooth  
37 hydrophobic surface, water droplets slide rather than roll and do not pick up dirt  
38 particles to the same extent. Researchers are currently using this technology in  
39 developing Lotus-Effect<sup>®</sup> aerosol spray and clothing ([http://nanotechweb.org/  
40 cws/article/tech/16392](http://nanotechweb.org/cws/article/tech/16392)).

41 The ideal surface modification techniques will introduce a monolayer of a  
42 desired functional group without causing irregular etching or producing signifi-  
43 cant hazards.

## 1.8 References

- 1 GOSWAMI B. C., ANANDJIWALA R. D. AND HALL D. M. (2004), *Textile Sizing*, Marcel Dekker Inc., New York. 3
- 2 COOK J. G. (1984), *Handbook of Textile Fibres*, Parts 1 and 11, 5th Edition, Merrow, Durham, UK. 4
- 3 MONCRIEF R. W. (1975), *Man-made Fibres*, 6th Edition, Wiley, New York. 5
- 4 MAUERSBERGER H. R. (Ed.) (1954), *Mathews Textile Fibres*, 6th Edition, John Wiley & Sons, New York. 6
- 5 SCHICK M. J. (1975), *Surface Characteristics of Fibers and Textiles*, Part 7, Marcel Dekker Inc., New York. 7
- 6 NAKAMURA A. (2000), *Fiber Science and Technology*, Science Publishers Inc., Enfield, USA. 8
- 7 HILL D. J., HALL M. E., HOLMES D. A., LOMAS M. AND PADMORE K. (1993), *An Introduction to Textiles, Volume IV- Textile Wet Processing*, Eurotex, Guimarães, Portugal. 9
- 8 DE GEYTER N., MORENT R. AND LEYS C. (2006), Surface modification of a polyester non-woven with a dielectric barrier discharge in air at medium pressure, *Surf. Coat. Technol.* **201**(6), 2460–2466. 10
- 9 CHENG, C., ZHANG, L. Y. AND ZHAN, R. J. (2006), Surface modification of polymer fibre by the new atmospheric pressure cold plasma jet, *Surf. Coat. Technol.* **200**(24), 6659–6665. 11
- 10 RADETIĆ M., JOČIĆ D., JOVANIĆ P., TRAJKOVIĆ R. AND PETROVIĆ Z. L. (2000), The effect of low-temperature plasma pretreatment on wool printing, *Text. Chem. Color. Am. Dyest. Rep.* **32**(4), 55–60. 12
- 11 RYU J., WAKIDA T. AND TAKAGISHI T. (1991), Effect of corona discharge on the surface of wool and its application to printing, *Text. Res. J.* **61**(10), 595–601. 13
- 12 SHAKER M., KAMEL I., KO F. AND SONG J. W. (1996), Improvement of the interfacial adhesion between Kevlar fiber and resin by using RF plasma, *J. Compos. Technol. Res.* **18**(4), 249–255. 14
- 13 SHENTON M. J., LOVELL-HOARE M. C. AND STEVENS G. C. (2001), Adhesion enhancement of polymer surfaces by atmospheric plasma treatment, *J. Phys. D Appl. Phys.* **34**(18), 2754–2760. 15
- 14 HEISE M., NEFF W., FRANKEN O., MURANYI P. AND WUNDERLICH J. (2004), Sterilization of polymer foils with dielectric barrier discharges at atmospheric pressure, *Plasma Polym.* **9**(1), 23–33. 16
- 15 DE GEYTER N., MORENT R. AND LEYS C. (2006), Surface modification of a polyester non-woven with a dielectric barrier discharge in air at medium pressure, *Surf. Coat. Technol.* **201**(6), 2460–2466. 17
- 16 BORCIA G., ANDERSON C. A. AND BROWN N. M. D. (2003), Dielectric barrier discharge for surface treatment: application to selected polymers in film and fibre form, *Plasma Sources Sci. Technol.* **12**(3), 335–344. 18
- 17 MORENT R., GEYTER N. D., VERSCHUREN J., CLERCKE K. D., KIEKENS P. AND LEYS C. (2008), Non-thermal plasma treatment of textiles, *Surf. Coat. Technol.* **202**(14), 3427–3449. 19
- 18 STRNAD S., SAUPER O., JAZBEC A. AND KLEINSCHKE K. S. (2008), Influence of chemical modification on sorption and mechanical properties of cotton fibers treated with chitosan, *Text. Res. J.* **78**, 390–398. 20

- 1 19 KAN C.W. (2008), Impact on textile properties of polyester with laser. *Optics Laser Technol.* **40**, 113–119.
- 2 20 MORENT R., DE GEYTER N., LEUS C., GENGEMBRE L. AND PAYEN E. (2007), Surface  
3 modification of non-woven textiles using a dielectric barrier discharge operating in air,  
4 helium and argon at medium pressure, *Text. Res. J.* **77**(7), 471–488.
- 5 21 BORCIA G., ANDERSON C. A. AND BROWN N. M. D. (2006), Surface treatment of natural  
6 and synthetic textiles using a dielectric barrier discharge, *Surf. Coat. Technol.* **201**, 3074–  
7 3081.
- 8 22 MASAELI E., MORSHED M. AND TAVANAI H. (2007), Study of the wettability properties  
9 of polypropylene nonwoven mats by low-pressure oxygen plasma treatment, *Surf.*  
10 *Interface Anal.* **39**, 770–774.
- 11 23 CANAL C., GABORIAU F., MOLINA R., ERRA P. AND RICARD A. (2007), Role of the active  
12 species of plasmas involved in the modification of textile materials, *Plasma Process.*  
13 *Polym.* **4**, 445–454.
- 14 24 NEGRI A. P., CORNELL H. J. AND RIVETT D. E. (1993), A model for the surface of keratin  
15 fibers, *Text. Res. J.* **63**, 109–115.
- 16 25 KARAKAWA T., UMEHARA R., ICHIMURA H., NAKASE K. AND OHSHIMA K. (2002),  
17 Continuous shrink-resist process of wool top sliver with ozone 1 performance, *Sen'i*  
18 *Gakkaishi.* **58**, 135–142.
- 19 26 WAKIDA T., LEE M., JEON J. H., TOKUYAMA T., KURIYAMA H. AND ISHIDA S. (2004),  
20 Ozone-gas treatment of wool and silk fabrics, *Sen'i Gakkaishi.* **60**, 213–219.
- 21 27 WAKIDA T., LEE M., JEONG D. S., ISHIDA S. AND ITAZU T. (2003), Ammonia-gas  
22 treatment of cellulosic fabrics, *Sen'i Gakkaishi.* **59**, 443–447.
- 23 28 WAKIDA T., TOKUYAMA T., DOI C., LEE M., JEONG D. S. AND ISHIDA S. (2004),  
24 Mechanical properties of polyester/cotton and polyester/rayon fabrics treated with  
25 ammonia-gas, *Sen'i Gakkaishi.* **60**, 34–38.
- 26 29 LEE M., SUN LEE M. S., WAKIDA T., TOKUYAMA T., INOUE G., ISHIDA S., ITAZU T. AND  
27 MIYAJI Y. (2006), Chemical modification of nylon 6 and polyester fabrics by ozone-gas  
28 treatment, *J. Appl. Polym. Sci.* **100**, 1344–1348.
- 29 30 ALISCH M., FEUERHACK A., BLOSFELD A., ANDREAUS J. AND ZIMMERMANN, W. (2004),  
31 Biocatalytic modification of polyethylene terephthalate fibres by esterases from actino-  
32 mycete isolates, *Biocatal. Biotransform.* **22**(5), 347–352.
- 33 31 ANDREAUS J., NAU C. T., KISNER A., BUDAG N. AND BARCELLOS, I. O. (2004),  
34 Biocatalytic modification of polyamide fibers. In Proceedings of the 3rd International  
35 Conference on *Textile Biotechnology*, abstract 11.
- 36 32 MATAM´A T., SILVA C., O'NEILL A., CASAL M., SOARES C., GÜBITZ, G. M. AND  
37 CAVACO-PAULO, A. (2004), Improving synthetic fibers with enzymes. In Proceedings of  
38 the 3rd International Conference on *Textile Biotechnology*, abstract 5.
- 39 33 KHODDAMI A., MORSHED M. AND TAVANI, H. (2001), Effects of enzymatic hydrolysis  
40 on drawn polyester filament yarns. Iran, *Polym. J.* **10**(6), 363–370.
- 41 34 YOON M. Y., KELLIS J. AND POULOUSE A. J. (2002), Enzymatic modification of  
42 polyester. *AATCC Rev.* **2**, 33–36.
- 43 35 MIETTINEN-OINONEN A., SILVENNOINEN M., NOUSIAINEN P. AND BUCHERT J. (2003),  
44 Modification of synthetic fibres with laccase. In Proceedings of the 2nd International  
45 Symposium on *Biotechnology in Textiles*, abstract 13.
- 46 36 GENECOR INTERNATIONAL (2001), Enzymatic modification of the surface of a polyes-  
47 ter fiber or article, International Patent WO 0014629.
- 48 37 VERTOMMEN M. A. M. E., NIERSTRASZ V. A., VAN DER VEER M. AND WARMOESKERKEN



- M. M. C. G. (2005), Enzymatic surface modification of poly(ethylene terephthalate), *J. Biotechnol.* **120**, 376–386. 1
- 38 OUAJAI S. AND SHANKS R. A. (2005), Morphology and structure of hemp fibre after bioscouring, *Macromol. Biosci.* **5**, 124–134. 2
- 39 VÍLCHEZ S., JOVANCIC P., MANICH A. M., JULIA M. R. AND ERRA I. P. (2005), Chitosan application on wool before enzymatic treatment, *J. Appl. Polym. Sci.* **98**, 1938–1946. 3
- 40 IBRAHIM N. A., ALY A. A. AND GOUDA M. (2008), Enhancing the antibacterial properties of cotton fabric, *J. Ind. Text.* **37**, 203–212. 4
- 41 BUSCHMANN H.-J., KNITTEL D. AND SCHOLLMMEYER E. (1992), German patent DE 40 35 378 A 1. 5
- 42 KNITTEL D., BUSCHMANN H.-J. AND SCHOLLMMEYER, E. (1992), Neuartige Ausrüstungseffekte für Natur- und Chemiefasern, Mal-geschneiderte Eigenschaften, *Bekleidung Textil.* **44**(12), 34–40. 6
- 43 NOSTRO P. L., FRATONI L AND BAGLIONI P. (2002), Modification of a cellulosic fabric with  $\beta$ -cyclodextrin for textile finishing applications, *J. Inclusion Phenom. Macrocyclic Chem.* **44**, 423–427. 7
- 44 LEE M. H., YOON K. J. AND KO S. W. (2001), Synthesis of a vinyl monomer containing-cyclodextrin and grafting onto cotton fiber, *J. Appl. Polym. Sci.* **80**, 438–446. 8
- 45 GAWISH S. M., RAMADAN A. M., MOSLEH S. AND MORCELLET M. (2006), Synthesis and characterization of novel biocidal cyclodextrin inclusion complexes grafted onto polyamide-6 fabric by a redox method, *J. Appl. Polym. Sci.* **99**, 2586–2593. 9
- 46 DENTER U. AND SCHOLLMMEYER E. (1996), Surface modification of synthetic and natural fibres by fixation of cyclodextrin derivatives, *J. Inclusion Phenom. Mol. Recognit. Chem.* **25**, 197–202. 10
- 47 VASANTHA M. D., EUNKYOUNG S. AND BEHNAME P. (2006), Surface modification of fibers and nonwovens with melt additives, in International Nonwovens Technical Conference, INTC 2006, pp 684–699. 11
- 48 TORSTEN T., SCHOTER F. AND ECKHARD S. (2006), Functionalisation of textiles with nanotechnology, in Materials Research Society Symposium Proceedings, vol. 920, *Smart Nanotextiles*, pp 1–11. 12
- 49 BECHERI A., DURR M., NOSTRO P. L. AND BAGLIONI P. (2008), Synthesis and characterization of zinc oxide nanoparticles: application to textiles as UV-absorbers, *J. Nanopart. Res.* **10**, 679–689. 13
- 50 LEROUX F., CAMPAGNE C., PERWUELZ A. AND GENGEMBRE L. (2008), Fluorocarbon nano-coating of polyester fabrics by atmospheric air plasma with aerosol, *Appl. Surf. Sci.* **254**(13), 3902–3908. 14
- 51 WEI Q., WANG Y., YANG Q. AND YU L. (2007), J., Functionalization of textile materials by plasma enhanced modification, *Ind. Text.* **36**(4), 301–309. 15