9

Plasma modification of wool

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9.1   Introduction

Though one of the oldest raw materials for clothing, wool cannot be regarded as an old fashioned textile fibre. Wool still represents one of the most fascinating materials, a masterpiece of design which could never be duplicated in a factory. This is due to a highly complex chemical and physical structure which is responsible for superior natural fibre properties.

The wool fibre exhibits a typical core–shell structure consisting of an inner protein core, the cortex, which is covered by overlapping cuticle cells with scale edges pointing in the direction of the fibre. The cortex is built up of spindle-shaped interdigitated cells, consisting mainly of *ortho* and denser *para* cells, which divide the stem of a fine fibre into two halves. This bilateral asymmetry results in a natural crimp of the fibre being jointly responsible for crease resistance and, due to permitting enmeshed air, for insulation against loss of heat or protection from heat. The cortex contains macrofibrils formed by fibril-structured α-helical keratin proteins embedded in a cystine-rich protein matrix. Whereas the α-helical material is responsible for the fibre resilience, a diamino acid, cystine, cross-links the protein chains and thus stabilises the wool fibre towards environmental influences. Cystine is also responsible for the high wet strength, moderate swelling and insolubility of the fibre. Wool is hygroscopic and the amount of water taken up corresponds to the relative humidity and temperature of the surrounding air. However, only the interior of the wool fibre is able to absorb water vapour to an extent of up to 30% o.w.f., whereas the fibre surface is water repellent due to the hydrophobicity of the outer surface of the cuticle. This apparently contradictory behaviour results in an intelligent moisture management system being responsible for the well-known wearing comfort of wool.

The hydrophobic nature of the wool fibre is caused by covalently bound, branched fatty acids, which form the outer cuticle layer. Both the hydrophobic nature of the fibre surface and the high cross-linking density of the protein layer immediately below the lipid layer act as a natural diffusion

barrier. This can complicate wool finishing processes and can necessitate a modification of the fibre surface by applying special auxiliaries and, in some cases, acid chlorination.

Scientific and technical progress, which is closely linked to innovative potential and to technological know-how, is the key for sustainable growth. Due to their broad application potential in almost all areas, surface modification techniques are an important factor in developing key technologies. Surface technologies offer a virtually unlimited potential for modifying the surface characteristics of a material in accordance with its specific requirements. Low-temperature plasmas (barrier and glow discharges) are of special interest, not only to replace less environmentally friendly finishing processes but also to create new surface characteristics and thereby open up new fields of application for various materials. Though being already established in many areas of industry, low-temperature plasmas are being explored for their application in the textile industry due to particular advantages which can be expected for different uses. Therefore, in the last decade, the plasma-induced modification of natural and man-made fibre surfaces has been investigated in different fields of applications for clothing and technical textiles.

Apart from inducing permanent hydrophilicity, fibre matrix adherence in fibre-reinforced composites and fibre protection towards chemical attack and soiling in technical textiles, the application of low-temperature plasmas can significantly influence the finishing and usage properties of clothing textiles. In particular, for wool finishing, plasma technology offers an enormous potential ranging from improved dyeing, printing and spinning performance to reduced felting tendency. Since concern for the environment and introduction of strict ecological legislation has caused environmental pressure on industry, the application of low-temperature plasmas to wool has recently become of increasing interest, particularly with regard to an improvement of dye-uptake and to replace the chlorination stages in commercial shrink proofing and printing.

9.2   Plasma systems relevant for application to wool

Low-temperature plasmas (barrier- and glow-discharge plasmas), which are only relevant to textile applications, are characterised by a thermal non-equilibrium between heavy particles (ions, metastables, neutrals) and light particles (electrons). With these plasmas, surfaces can be modified at low temperatures, an effect which is related to the low temperature of heavy particles combined with high electron energies that are typically found in low-temperature plasmas.[1]

The barrier discharge (BD) plasma is characterised by a low current discharge under atmospheric conditions, generated by application of high

voltages. Barrier discharges consist of transient micro-discharges whose distribution can be controlled by matched voltage wave forms.[2] Insulators, at least at one of the electrodes, prevent an electrical breakdown which would lead to the formation of an arc and burns the substrate. In order to discharge a corona under atmospheric conditions, a high electrical field at one electrode has to be generated. Electrons leaving the electrode are accelerated by a high voltage in the direction of the insulator, which is situated immediately below the material to be treated. On their way to the substrate, the electrons collide with air molecules leading to the formation of ozone and nitrogen oxides. Those electrons which hit the counter electrode have high energies (average energy level: $5\,eV^3$) and are able to split covalent linkages in the surface of the substrate, resulting in the formation of radicals. Their subsequent reaction with products in the corona atmosphere leads to a surface specific oxidation.

In contrast to the BD plasma, the glow-discharge plasma (GD) generally operates at reduced pressures (10^{-3}–10^{-4} bar) at lower voltage inputs and is characterised by a higher current discharge. As a consequence of the low pressure, the electron energies are higher when compared to barrier discharges (up to $10\,eV$), resulting in a faster and deeper surface modification. In addition, the electron densities in radio frequency- and microwave-induced GD plasmas were known to be many times higher than that of a BD plasma. The same relationship exists for the concentration of active particles produced in such discharges. A GD plasma it is therefore expected to assist in achieving the desired results in much shorter treatment times. Furthermore, the mean free paths of reactive plasma species are higher when compared to those generated at atmospheric conditions. This results in a more complete surrounding of each individual fibre by the plasma, leading to a more even modification, especially when higher weight fabrics, yarns or tops are treated. Voluminous wool tops can therefore be more evenly treated in their delivered form with GD, whereas homogenous treatment results with BD require a reduction of the original top weight by drafting as well as by a double-sided treatment.[4,5] However, the main advantage of BD over GD is that wool can be treated at atmospheric pressure, thus avoiding the use of low-pressure equipment.

Apart from other plasma systems constructed for textile treatment, there are two plasma systems which have been mainly developed for the treatment of wool that allow a larger scaled continuous air-to-air-treatment. In the 1980s, Rakowski[4] developed a continuous operating machine for the application of GD on wool top. This system operates at 13.56 MHz and is fitted with a four-step vacuum system to achieve and keep a pressure of 50 Pa during a production rate of up to 10 m/min. At the end of the last century, Softal[5] developed a continuous operating machine for wool using atmospheric pressure dielectric barrier discharges (DBD), which can be

coarsely regarded as a further development of the machinery described by Belin in 1976.[6] The DBDs in this system are generated in the plasma unit between parallel arranged ceramic-coated roller electrodes by application of pulsed high alternating voltages. The station is designed for a double-sided treatment of wool consisting of two motor-driven, earthed backing rolls and rotating electrode rolls connected to the high voltage. The wool is guided between the electrodes and is penetrated by the discharges perpendicular to the transportation direction of the substrate. The system allows treating both, wool tops and fabrics. For top treatment, a spreading unit enabling a simultaneous treatment of 16 tops is connected to the inlet and to wool top containers at the outlet of the plasma unit. For full-scale fabric treatments, a batch unwinder with a fabric spreading and guiding system at the inlet and a batch winder at the outlet of the plasma unit can be implemented.[5,7]

## 9.3   Plasma-induced chemical and morphological changes

Wool has a very complex fibre surface which is responsible for the majority of wool properties, such as water repellence, soil resistance, resistance to chemical attack and felting behaviour. The fibre surface (cuticle) shows a characteristic scale structure, built of flattened cells overlapping each other. The cuticle can be subdivided into four coaxial layers of different chemical composition: (i) the outermost hydrophobic epicuticle, mainly consisting of covalently bound fatty acids, (ii) the exocuticle immediately below the epicuticle, which is divided into an A- and B-layer and is highly cross-linked via cystine bridges, (iii) the less cross-linked endocuticle beneath the exocuticle and (iv) the cell membrane complex (CMC), a proteinaceous membrane between cuticle and cortex.

Though the hydrophobic nature of the fibre surface and the high cross-linking density in the outermost fibre surface act as a diffusion barrier and protect the native wool fibre from environmental influences, wool finishing processes can be complicated by the natural structure of the cuticle. Therefore, in wool finishing processes, such as printing, dyeing or shrink-proofing, surface modification plays an important role. To date, the required surface modification is mainly accomplished by wet chemical processes using special auxiliaries or chemical surface oxidation, e.g. the chlorination processes. An appropriate alternative to conventional treatments is given by the pre-treatment of wool with low temperature plasmas (LTPs).

A number of investigations into the effect of plasma treatments on wool have shown that the observed changes in finishing and care performance of wool are related to surface-specific changes of the protein fibre by the plasma treatment. Surface analyses of wool fibres treated with different

plasma gases have shown that the content of hydrophilic groups increases and that part of the cystine in the surface layer is converted to cysteic acid.[8–12] The increase in hydrophilic groups is based on surface oxidation during LTP treatment. The surface oxidation can be regarded as the consequence of water desorption from the fibre during the plasma treatment, resulting in a predominant presence of oxygen and its highly energetic (reactive) derivatives in the discharges, even when inert gases are used as reaction gases. However, the resulting degree of surface oxidation strongly depends on the reaction gas used and increases significantly when oxygen-bearing gases are used instead of N_2, Ar and H_2, respectively.[10,13,14] This applies for LTP treatment both at reduced pressure and under atmospheric conditions.[13,14] In addition, the resulting degree of surface oxidation depends on the type of plasma applied.

Conventional amino acid analyses of plasma-treated wool reveal only little change because reaction is restricted to the fibre surface.[10] Chemical changes can be detected by surface-sensitive X-ray photoelectron spectroscopy (XPS) being able to provide elemental analysis and determination of the binding state of the elements at the wool surface and in the immediate subsurface down to a depth of about 10 nm. In the XPS survey spectrum peaks related to carbon, oxygen, nitrogen and sulphur are observed.[9,10,13,14] As shown in Figure 9.1, plasma treatments cause changes in the chemical composition of the wool fibre surface, an effect that is mainly related to a decrease in carbon content, whereas increasing amounts of oxygen, nitrogen and sulphur are detected to an extent that is more intensive for GD than for BD treatments. The high-resolution carbon spectra show that the aliphatic carbon species are significantly reduced by the action of plasma. Figure 9.2 shows that the strongest changes are observed, as expected, for
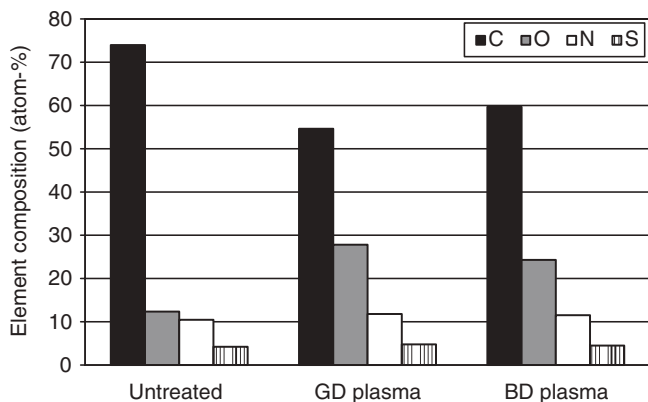
9.1 Changes in the element composition of the wool fibre surface after application of GD and BD plasma.
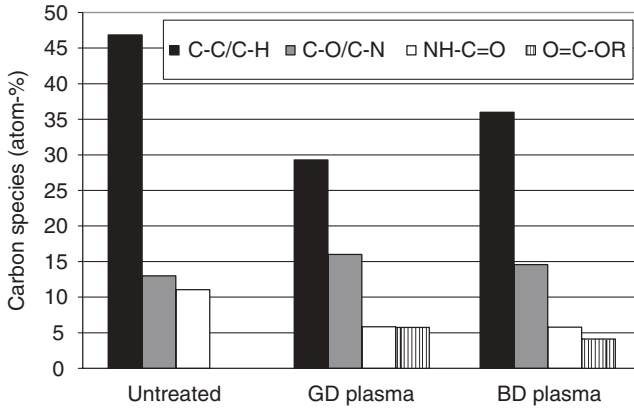
9.2 Changes in the content of carbon species of the wool fibre surface after application of GD and BD.
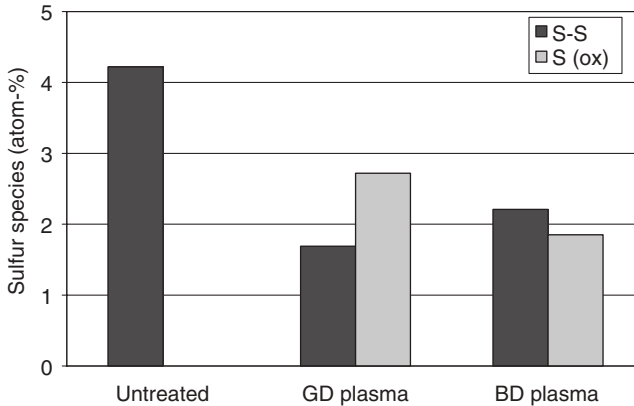
9.3 Changes in the content of sulphur species of the fibre surface after application of GD and BD to wool.

the GD-treated samples. The decrease in aliphatic carbon is associated with an oxidation of sulphur, present in disulfide linkages, to sulfonic acid groups. As shown in Figure 9.3, the oxidation of cystine residues present in the A-layer of the exocuticle is more complete after treatment of wool with GD than the corresponding changes detected after treatment with BD.

The application of oxygen-bearing plasmas results first of all in an oxidation of adhering and covalently fixed surface lipids. This counts for both plasma treatments and is demonstrated in the IR spectra of adhering lipids isolated from glow-discharge treated wool showing a strong increase in the amount of carbonyl as well as single-bonded CO groups (Figure 9.4). In addition to the changes detected by IR spectroscopy, a decreasing amount
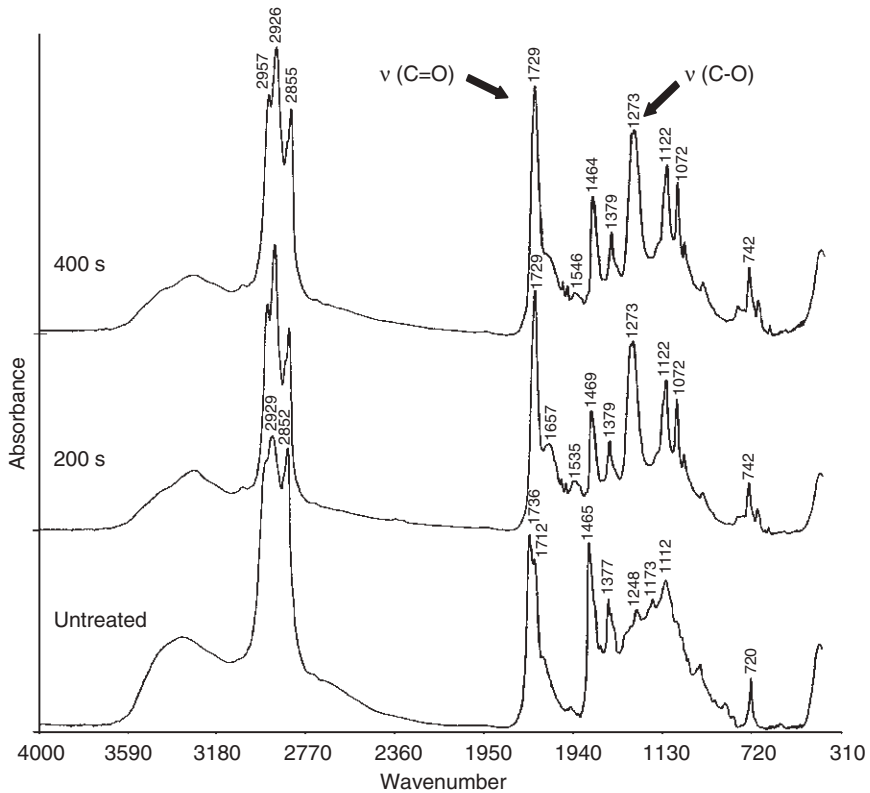
9.4 IR spectra of extracted surface-adhering lipids before and after GD plasma treatment.

of surface lipids is observed with increasing treatment time, indicating a plasma-induced removal of surface lipids by etching. This applies to both plasma treatments investigated and is exemplified in Figures 9.5 and 9.6, for surface lipids isolated from BD-treated wool. To identify the reaction pathways of plasma-induced lipid oxidation, Merten[13] analysed model lipids after glow discharge treatment. The weight determination of plasma-treated icosanoic acid, palmitic acid, 19-methylicosanoic acid, triolein and cholesterol showed that the etching rate decreases with increasing molecular mass of the lipid. As determined by IR spectroscopy and mass spectrometry (MALDI-MS), the initial step of lipid degradation is an oxidation of the aliphatic hydrocarbon chain resulting in the formation of carboxylic groups, which are also detected in fatty acids isolated from plasma-treated wool (Figure 9.4). In the case of ramified hydrocarbon chains (e.g. 18-methylicosanoic acid), the oxidative degradation and subsequent formation of carboxyl groups is initiated mainly at the tertiary carbon.
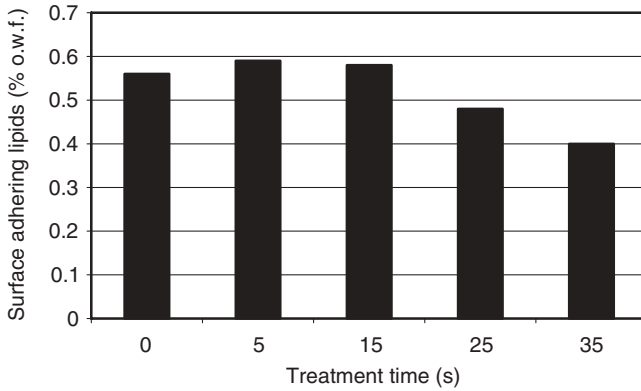
9.5 Amount of surface-adhering lipids as a function of the treatment time in BD (determined by solvent extraction and subsequent weight determination).
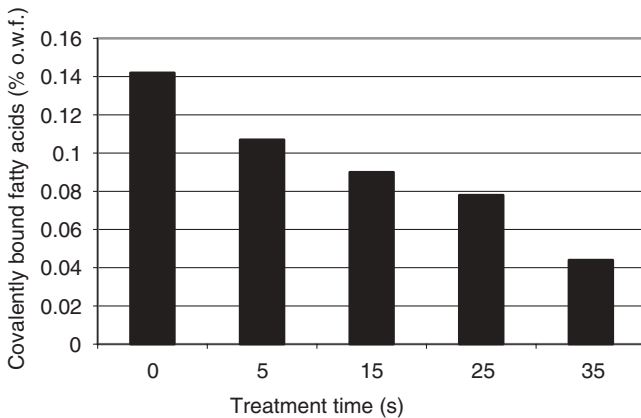

9.6 Amount of covalently bound fatty acids as a function of the treatment time in BD (determined by gravimetry after isolation via transesterification).

Scanning electron microscopic (SEM) images show no noticeable differences when compared with the corresponding untreated samples. The extent of surface modification can be visualised by transmission electron microscopy (TEM) of fibre cross-sections. As shown in Figures 9.7–9.9, a plasma treatment modifies the A-layer of the cuticle, indicating that the degree of modification depends on the plasma technique applied.

Figure 9.7 shows an electron micrograph of the untreated fibre with its untouched cuticle region. The extent of plasma-induced surface modification is demonstrated in Figure 9.8 for a BD-treated sample and in Figure
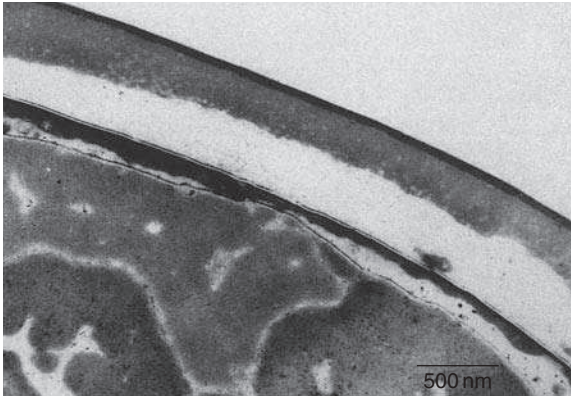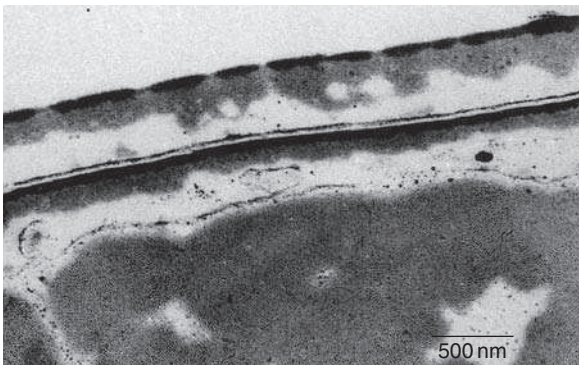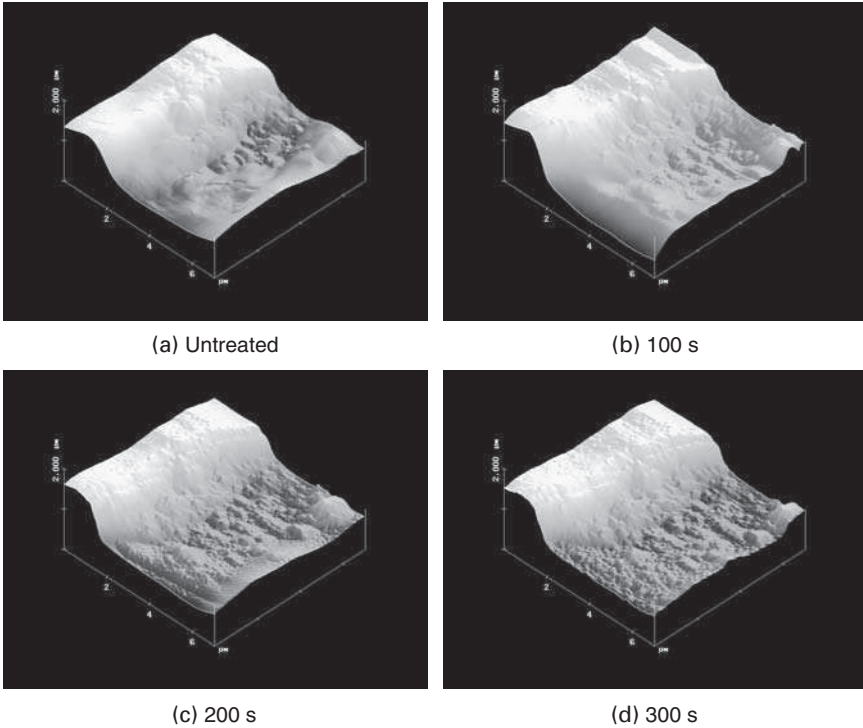
9.7 TEM image of an untreated wool fibre.[22]
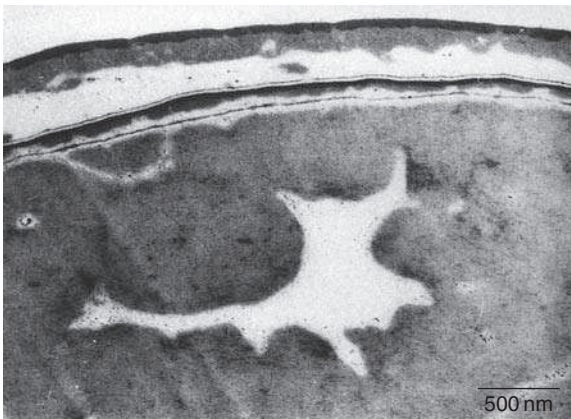
9.8 TEM image of a DBD-treated wool fibre.

9.9 TEM image of a GD-treated wool fibre.[22]

(a) Untreated   (b) 100 s

(c) 200 s   (d) 300 s

9.10 AFM images of the same section of a wool fibre surface with different exposure times to GD.[13]

9.9 for a corresponding GD-treated fibre. From these pictures it becomes evident that a plasma treatment can modify the A-layer of cuticle to varying degrees, resulting in a partly considerable swelling. In contrast to the application of BD, the staining intensity in GD-treated fibres (Figure 9.9) is in places considerably reduced, and parts of the A-layer have been sputtered off, leading to the formation of grooves in this layer. This underlines (i) the influence of more reactive species present in this type of plasma, and (ii) that chemical reactions induced by the action of reactive plasma species can be accompanied by etching of the fibre surface, resulting in a rougher and larger surface area. The latter is corroborated by images from atomic force microscopy (AFM) which reveal more surface detail of the plasma-treated wool samples (Figure 9.10).

9.4   Textile properties of plasma-treated wool

The partial removal of surface lipids, the increase in carbonyl and single-bonded CO groups, the conversion of cystine to cysteic acid in the fibre
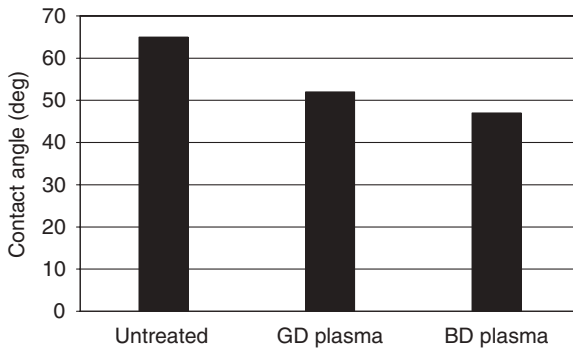
9.11 Influence of the plasma treatment on wettability of wool. (Contact angle measurements according to Wilhelmy[37].)

surface and the increase in surface roughness results in an increase in the wettability of wool. As expected, the magnitude of wettability is higher for the GD-treated sample when compared to the corresponding data determined for BD-treated wool (Figure 9.11).

Apart from the wettability increase, the plasma-induced surface oxidation is accompanied by a decreased handle performance and higher fibre–fibre friction. As demonstrated by Ryu and Wakida,[15] the dry and wet frictional coefficients of plasma-treated wool fibres are significantly increased in the with- and against-scale directions to an extent which is higher for the GD- than for the BD-treated samples. For GD-treated wool tops, Rakowski[4] has shown that the dry and wet frictional differences in both scale directions are reduced.

Felting is a special property of wool that occurs when wool is subjected to mechanical agitation in water. Though this behaviour is required for creating felts or fabrics with special optical appearance, the well-known irreversible shrinkage during washing is one of the principal drawbacks of textiles made of wool. Felting and shrinkage are the result of movements of individual fibres within the textile, always taking place towards the fibre root. The phenomenon of unidirectional fibre movement primarily is related to the unique scale structure (from the root to the tip) of the wool fibre surface, which is responsible for a different coefficient of friction in the with-scale and against-scale direction. As a consequence of the reduction in the difference in the coefficient of friction, plasma-treated wool shows a significantly diminished felting behaviour.[4,5,13–17]

In addition to the reduced felting behaviour of wool, the increase in fibre friction after application of GD or BD leads to an increased cohesiveness of plasma-treated wool fibres, resulting in considerably improved abrasion resistance, sliver tenacity and yarn strength.[4,6,18,19] According to Rakowski,[4] the latter is improved to an extent of 16% when compared to the corre-

sponding values determined for yarns of the untreated material. Since fibre strength measurements on plasma-treated wool indicate that the action of reactive plasma species is strictly restricted to the fibre surface and do not alter the fibre quality,[17] this allows the generation of finer yarns and thus, of lighter weight textiles from wool at a high quality level.

9.5   Finishing performance of plasma-treated wool

9.5.1   Dyeing and printing behaviour of plasma-treated wool

From the work of Leeder and his co-workers who could follow the uptake of pre-metallised dyes by wool via TEM, it is evident that, due to the virgin diffusion barrier, the dye molecule does enter the untreated fibre via cuticle cell junctions.[20] However, it is not the same for plasma-treated wool. Light microscopic studies of the initial stage of the dyeing process with Sulforhodamine G showed significant differences between untreated and plasma-treated wool. Whereas in the case of the untreated wool the dye almost selectively stained the outer scale edges in accordance with the results reported by Brady,[21] no such concentration of dye in these regions was observed for the plasma-treated fibre.[22] Instead, already in this initial dyeing stage, a staining of the cuticle scales extending from the scale edges to the ends of the scales was observed. Examinations on fibre cross-sections of correspondingly treated samples showed that plasma-treated wool is more easily penetrated by the dyes, which were more evenly distributed over the cross-sections.[22] This can be attributed to the plasma-induced removal of surface lipids and to cystine oxidation in the A-layer of the exocuticle, and thus to a degradation of the natural diffusion barrier in the fibre surface, which obviously facilitates the transcellular dye diffusion besides the intercellular dye diffusion postulated for the untreated wool.[20]

The improved dye-uptake of plasma-treated wool described by different authors[4,7,15,18,22–28] can be therefore related to the plasma-induced degradation of the natural diffusion barrier of the fibre. This obviously facilitates an accelerated, more even and more complete dye-uptake, resulting in significant enhanced final bath exhaustion and thus in significantly reduced effluent discharges during dyeing. The latter is concluded from analyses of effluents from industrial dyeing trials with chromium-bearing 1:1-premetallised dyes.[7] As shown in Table 9.1, a considerable reduction in chemical (COD) and biochemical (BOD_5) oxygen demand is detected in the exhausted dye-bath from the DBD-treated fabric. Since this is further accompanied by a reduced chromium content and translucent coloration number, the detected reduction in COD and BOD_5 load of the effluent is obviously partly caused by a more complete dye-uptake of the DBD-treated

Table 9.1 Effluent load of the exhausted dye-baths from DBD treated and untreated wool fabrics during industrial dyeing with 1:1-premetallised dyes under comparable conditions

	Untreated fabric			DBD treated fabric		
COD	12 500 mg/l			6500 mg/l		
BOD$_5$	852 mg/l			1170 mg/l		
COD/BOD$_5$	14.67			5.56		
Translucent coloration number	*620 nm*	*525 nm*	*436 nm*	*620 nm*	*525 nm*	*436 nm*
(DFZ) (ε at $d = 1$ m)	40.0	31.6	30.7	25.2	13.2	8.1
Cr$_{total}$ after digestion	1.97 mg/l			1.84 mg/l		

fabric when compared to that of the non-pretreated reference. As a consequence of the improved dye-bath exhaustion, the final shade of the DBD-treated fabric appears darker than that of the correspondingly dyed reference material,[7] clearly indicating that a plasma-treated fabric may require less amount of dyestuff for a given shade. Since dye exhaustion strongly depends on the initial dye concentration, a reduction in the amount of dye used will potentially further contribute to a diminished effluent load.[7]

Due to the low permeability to dyes, wool shows only poor printability. Thus, in order to satisfactorily print wool, it is necessary to prepare the wool for printing by degradation of the virgin diffusion barrier. This is traditionally achieved by mild chlorination. Due to the resulting effluent load with adsorbable organic halides (AOX), there is a quest for environmentally more acceptable print-preparation processes. For this reason, plasma treatment of wool has also been investigated with special regard to its potential to replace the conventional chlorination techniques. For this purpose the effects of differently intensive BD- and oxygen-atmosphere GD-treated fabrics on the resulting printability with colour pastes of acid dyes have been elucidated.[15] Whereas the dye-uptake during subsequent steaming increases with the treatment intensity, the resulting colour depth decreased, thus indicating that only a slight surface modification with BD is particularly effective for printing of wool fabrics.[15] Further, BD-treated wool fabrics can meet the colour depth of conventionally chlorinated samples during printing.[29] The results shown in Table 9.2 demonstrate the improved depth of shade (L*) after printing with an acid milling dye, to an extent which meets the corresponding values for the chlorinated sample. This clearly underlines the propensity of plasma treatments for imparting printability to wool and thus, the feasibility of replacing conventional chlorination processes for print preparation.

Table 9.2 Colour development (CIE values) after printing of differently pretreated fabrics with an acid milling dye

Pretreatment	CIE-values			
	L*	A*	B*	ΔE
Untreated	31.3	−0.7	−23.4	0
Chlorinated	26.5	−2.0	−25.8	3.51
CD-treatment	26.8	−2.4	−25.7	3.80

9.5.2 Plasma-induced shrinkproofing of wool

Apart from print preparation, commercial shrinkproofing causes tremendous environmental problems by using chlorine as an oxidising agent. Today, nearly 75% of the overall production of machine-washable wool is carried out at the stage of wool top being the base material for yarn production. State-of-the-art so far is the Chlorine/Hercosett treatment, a continuously operating combined process using chlorination as a preliminary step to polymer coating of the fibre with a polyaminoamide (Hercosett). The disadvantage of this process is again its contribution to the overall discharge of AOX in effluents. Chlorinated organic substances are recognised as being mostly toxic, and a number of countries have established maximum concentration levels for these compounds in effluents. Since the AOX generation during conventional shrinkproofing of wool exceeds the permitted levels by up to 40 mg/l,[30] an environmentally acceptable, chlorine-free process for imparting full machine washability is required.

For shrinkproofing of wool, a plasma-induced surface oxidation as well as a direct coating of the fibres by plasma polymerisation is found also to reduce, but not to eliminate, felting. Since plasma polymers deposited on wool fibres are known to decrease the dye uptake by the fibre,[31,32] a plasma polymerisation does not meet the requirements for treatments at the stage of top. Therefore, generation of non-shrinkable wool has been mainly concentrated on the plasma-induced surface oxidation. This requires an additional coverage of the fibre surface to further decrease the difference in coefficient of friction by masking the scale edges. Since commercially available resins do not show the expected positive influence on the felt-free performance of plasma-treated wool, new resins have been tailored for the plasma-treated fibre surface.[7,33]

Two different wool-compatible resin types have been developed by BAYER, allowing the generation of machine-washable wool after GD or BD treatment. One type consists of a water-dispersible isocyanate-bearing resin which is able to permanently coat each individual fibre. As a consequence, the scale heights of the fibre surface are significantly reduced,
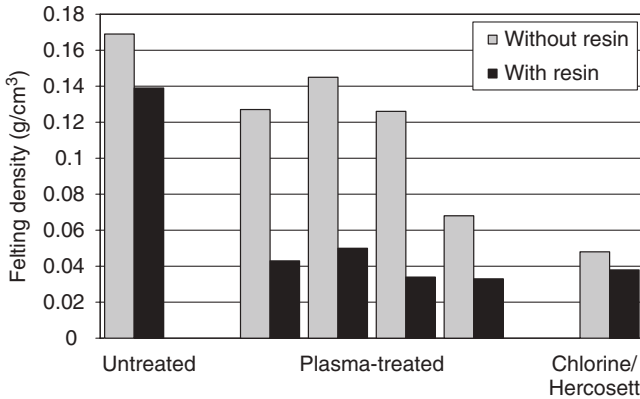
9.12 Felting densities (IWTO 20-69) of differently plasma-treated wool before and after resin application in comparison to the corresponding data for the untreated and Chlorine/Hercosett treated material.

resulting in nearly equalised with- and against-scale friction values.[17] As shown in Figure 9.12, the differences in the degree of felting observed after different plasma-only treatments can be equalised by the resin application, to an extent which meets the value correspondingly determined for Chlorine/Hercosett-treated samples. The second resin is a polyurethane type which does not coat the fibre completely, but is deposited at the scale edges instead. This also results in significantly decreased shrinkage behaviour. DBD treatment of tops followed by application of one or both resins guarantees the specifications set by the Woolmark Company in their Technical Method 31 (TM 31). This requires that the area felting shrinkage of knitted fabrics must not exceed a value of 10% after 50 simulated washing cycles in a domestic washing machine. With a reduction in area felting shrinkage from 69% for the untreated and over 21% for the DBD-treated, to 1–3% for the additionally isocyanate- or polyurethane-treated samples, this can be completely fulfilled. The result has led to the development of a completely AOX-free shrinkproofing process for wool tops[5,17,33] and has thus opened up a new possibility for the wool industry to have an environmentally acceptable, plasma-based shrinkproofing process in the near future.

9.5.3 Softening of plasma-treated wool

The oxidation of surface lipids, and their partial removal, results in poor handling performance to some extent, which requires an additional softening of plasma-treated wool. Investigations on commercially available softeners of different chemical compositions (cationic and non-ionic fatty acid

condensates with and without polysiloxane additions, fatty acid amides and polyethylene derivatives, cationic polysiloxanes as well as reactive aminosiloxanes) have shown that a softening step can interfere with the plasma-induced antifelt finish.[7] Though most of the softeners improved the handle performance significantly, the plasma-generated antifelt-finish is simultaneously decreased by softening to an extent that exceeds the felting tendency of the untreated material.[7]

One reason for the increased felting tendency of plasma-treated wool by softening is the increase in hydrophobicity. As a consequence of the hydrophobic effect, the fibres aggregate in aqueous medium and, under mechanical action, move to their root end to form a felt. The second reason is the reduction in fibre–fibre friction, thus allowing an increased movement of the individual fibres towards to their root, which further contributes to an increase in felting behaviour. Since the plasma-induced shrinkproofing effect is mainly based on (i) a hydrophilisation of the fibre surface and (ii) an increase in fibre–fibre friction, the application of softeners was believed to be incompatible with a plasma-induced shrinkproofing effect.

The only exception from this general trend determined for a series of softeners was given for softeners which were able to coat the fibre surface permanently and thus, to further reduce the differential friction coefficient. This was shown for a reactive aminosiloxane, which was able to additionally reduce the felting behaviour of plasma-treated wool (Fig. 9.13).[7] From these actual results, it can be concluded that a plasma-induced antifelt finish for wool is not necessarily accompanied by a non-reparable decrease in handling performance. Softeners being able to coat the fibre have the potential to overcome this well-known problem.
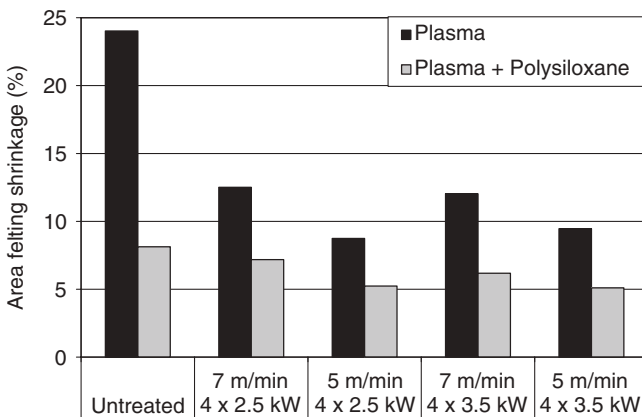
9.13 Influence of the plasma, and subsequent treatment with a reactive polysiloxane, on the felting behaviour of wool fabrics at various power-inputs and production speeds during DBD-treatment.

9.6   Future trends

Plasma treatment leads to selective modification of the outermost wool fibre and has many implications for improved dyeing, printing, shrinkproofing and subsequent chemical finishing. Plasma treatments of wool represent a most innovative approach to replacing chlorination stages in wool finishing and to improving existing processes with special regards to an economical–ecological optimisation. The apparent potential of plasma technology for wool finishing processes led to the development of machinery allowing a treatment under atmospheric conditions for different fibre make-ups. This can be regarded as a large step towards industrial implementation that will help the wool industry to benefit in the near future from a technology that is extremely surface-specific, totally effluent free, and thus less destructive and more environmentally friendly. The implementation of plasma technology into the wool industry is closely connected to further developments towards larger-scaled machinery, allowing a cost-efficient treatment with special regards to a high material throughput, as well as to the development of highly efficient tailored auxiliaries for achieving special effects.

9.7   Sources of further information

For readers who wish to obtain more detailed information about wool, only a few key books can be advised describing the wool fibre science and technology from the morphological to the chemical and finally to the technological point of view of this exciting fibre material.[34,35,36] Wool science is continuing to grow, leading to new innovations. The status quo on actual developments of experts all around the world is presented at the International Wool Conference, which takes place every 5 years and was last held in 2005 in Leeds, UK. The proceedings of these conferences, as well as the relevant journals, are of special interest to readers searching for special topics.

9.8   Acknowledgments

Thanks are due to Deutscher Fachverlag GmbH for permission to reproduce the photographs shown in Figures 9.7 and 9.9.

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10

Plasma modification of natural cellulosic fibres

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10.1   Introduction

This chapter provides a general summary of the current state of knowledge of plasma modification of various natural cellulosic fibres. Much of the information reported here is taken from the references cited at the end of the chapter, which should be consulted for a more in-depth treatment. Several aspects of plasma modification of various natural cellulose fibres are thoroughly treated in a number of excellent works.[1,2]

Although the literature is abundant with descriptions of plasma-enhanced synthesis of macromolecular structures and surface modification of synthetic polymeric substrates, plasma treatment of natural macromolecular compounds has received less attention for the following reasons:

- The abundance, low cost, and availability of petrochemical precursors of synthetic polymers during and after World War II
- The remarkable physiochemical characteristics (processability, chemical inertness, mechanical strength, etc.) of synthetic polymers.

However, an increasing awareness of the benefits and advantages of lignocellulosics, which are the most significant renewable natural polymeric resource, has increased the interest in improving their surface properties further using plasma surface modification. A brief presentation of various cellulosic fibres (Section 10.2) is followed by a section devoted to exploring the mechanisms of the interaction between various plasmas and cellulosic fibres, including generation of free radicals and oxidation of cellulose surfaces using argon and oxygen plasmas (Section 10.3). Section 10.4 deals with plasma modification of cotton fibre, which is the purest cellulosic fibre, for improved surface properties in various textile applications.

The lignocellulosics, especially various vegetable fibres, are natural composites built up of cellulose and lignin and are light-weight, strong, abundant, biodegradable and relatively inexpensive, which makes them ideal components for creating advanced materials in conjunction with synthetic

thermoplastic polymers. High lignocellulosic-content composites combine the attributes of natural macromolecules (e.g. supramolecular order, non-hazardous, renewability) with the chemical inertness, processability, high tensile strength, etc. characteristics of the synthetic counterparts. Section 10.5 describes how plasma surface modification of the lignocellulosic fibres (and also the thermoplastic counterpart) can improve the mechanical and adhesion properties of the resulting composite.

Plasma surface modification of solid wood and wood pulp fibres is discussed in Section 10.6 and the final section deals with plasma modification of regenerated cellulose fibres such as, for example, cellophane and rayon viscose fibres.

10.2   Description of natural and man-made cellulosic fibres

This section provides a short description of the different types of cellulosic fibres as they appear in this chapter.

10.2.1 Cellulose

Cellulose is the most widely known fibrous polysaccharides and it occurs in higher plants and in some algae. Cellulose is widely used in the form of wood, agricultural fibres and paper products and in the form of cotton throughout the world. The basic structural repeating unit for cellulose is the cellobiose unit. The second ring in the cellobiose unit is chemically identical to the first ring. The important difference is that the second ring is inverted from the general plane of the first ring. The rings are not planar but puckered. Each ring is called an anhydroglucose unit. Since each one is identical chemically, it is more convenient to express cellulose as a polymer with the anhydroglucose unit as the repeating unit. Each unit contains three alcohol hydroxyls (—OH). These hydroxyls form hydrogen bonds inside the macromolecule itself (intra-molecular) and between other cellulose macromolecules (intermolecular). Cellulose is highly crystalline, regardless of source. The highly crystalline regions represent a tight packing of ordered chains wherein the hydrogen bonding is at a maximum. Cellulose also contains amorphous regions in which there can be a variation from complete disorder of the chains to some order.

10.2.2 Cotton

The origin, development, morphology, chemistry, purification and utilisation of cotton have been discussed by many authors.[3,4] Cotton is the most important textile fibre, as well as cellulosic textile fibre, in the world, despite

inroads made into its markets by synthetic fibres. Worldwide, about 38% of the fibre consumed is cotton. The cotton plant grows naturally as a perennial, but for commercial purposes it is grown as an annual. Cotton fibres used in textile commerce are the dried cell walls of formerly living cells. Cotton is a unique textile fibre because of the inter-relationships of its subunits. Typically, cellulose in all the cell walls is in small crystalline microfibrils that are arranged in multilayer structures. However, only in the cotton fibre have so many organisation levels been discovered, and the special properties of cotton depend on this complexity. From its multi-component primary wall, through the pure cellulose secondary wall to the lumen, the organisation of sub-fibre units provides the fibre with characteristic properties that make it a processable, strong and comfortable textile fibre. The cotton fibre is composed mostly of the long-chain carbohydrate molecule cellulose (the sugar of cell walls). Of all existing natural cellulose fibre sources, cotton cellulose is the purest. Raw cotton fibre, after ginning and mechanical cleaning, is essentially 95% cellulose. After treatments to remove the naturally occurring non-cellulosic materials, the cellulose content of the fibre is over 99%. The non-cellulosic constituents are nitrogen-containing compounds (proteins), wax, pectic substances (e.g. pectic acid, iron pectates, etc.), organic acids (malic and citric acids), sugars and ash-producing inorganic salts.[3]

10.2.3 Other vegetable fibres

In a broad sense, the source of vegetable fibres, as the name suggests, is the rich plant life of mother earth. In a narrower sense, different fibres come from different parts of different plants. A widely accepted classification of fibres is one that is based on their location in the plant. Accordingly, the three principal categories are seed fibres, bast fibres and leaf fibres. Those that do not fit into one of these three categories are lumped together as miscellaneous fibres. Vegetable fibres include sisal, jute, hemp, flax, ramie, etc.[5,6]

   The chemical composition of vegetable fibres has attracted the attention of many investigators and it is generally agreed that the fibres contain one or more of the following:[7]

- Fats and waxes, mostly found on the surface
- Water solubles, extracted by boiling the dewaxed fibres in water
- Pectin, on the water-insoluble form of calcium, magnesium or iron salts of pectic acid.
- Hemicelluloses, which are amorphous short-chaine isotropic polysaccharides and polyuronides
- Cellulose, which is the principal constituent of the fibre ultimates

- Lignin, a short-chain isotropic made up of units derived from phenyl-propane, which is found in the middle lamella of the fibre bundle.

Of the components listed above, the cellulose, hemicellulose and lignin are considered the three principal constituents. Most vegetable fibres also contain a proportion of acetyl groups that are readily hydrolysed by dilute alkali to acetic acid. Estimation of the quantity of acetic acid produced per unit weight of fibre then provides an index of the acetyl content. Most vegetable fibres are strong fibres but exhibit brittle fracture and have only a small extension at break. They have a high initial modulus, but show very little recoverable elasticity. Vegetable fibres are often used in handicraft industries, to make textiles, to make paper products, or to produce a variety of composites. The largest potential markets are in composite products. Vegetable fibre-based composites are often classified by their uses, e.g. geotextiles, filters, sorbents, structural composites, non-structural composites, moulded products, packaging, etc.[5]

10.2.4 Wood-pulp fibres

Fibres derived from wood-pulp are used in large quantities in the hygiene industry because of their absorbing properties. Wettability, absorption and liquid-holding capacity are important properties related to the physical nature of the capillary system and the chemical and physical nature of the exposed fibre surfaces, and these have to be optimised in order to meet the demands on the product The main natural fibre source worldwide comprises various softwood and hardwood species. Apart from small amounts of inorganic material, wood pulp fibres consist of carbohydrates (cellulose and hemicellulose), lignin and small amounts of organic low molecular weight material.[8]

10.2.5 Man-made cellulosics

There are different types of man-made cellulosics. Cellophane and viscose are probably the most well known and most frequently subjected to surface modification.

Cellophane was invented by Jacques E. Brandenberger, a Swiss textiles engineer, in 1908. Cellophane is a thin, transparent sheet made of processed cellulose. Cellulose fibres from wood or cotton are dissolved in alkali. This solution is extruded through a slit into an acid bath to reconvert the viscose into cellulose. A similar process, using a hole instead of a slit (a spinneret), is used to make a fibre called rayon.

Cellophane's low permeability to air, grease and bacteria makes it useful for food packaging. Cellulose film has been manufactured continuously

since the mid-1930s and is still used today. As well as packaging a variety of food items, there are also industrial applications, such as a base for self-adhesive tapes such as Sellotape and Scotch Tape, a semi-permeable membrane in certain types of battery, and as a release agent in the manufacture of fibreglass and rubber products. Typically, however, the use of the word 'cellophane' has been genericised, and is often used informally to refer to a wide variety of plastic film products, even those not made of cellulose.[9]

Viscose is a regenerated cellulosic fibre, which is widely used in apparel, home furnishing and industrial materials.[10,11] Basically, all methods for producing rayon filaments or fibres depend on the solubilising of cellulose by alkali (aqueous sodium hydroxide), then reshaping it into long-fibred products by extrusion through the small holes of a spinnerette, immediately followed by conversion into solid cellulose. Although there are a number of ways in which this can be done, the viscose process is by far the most important and widely practised. The basic chemical unit of viscose is the anhydroglucose unit of the cellulose molecule. Viscose consists primarily of type II anti-parallel crystalline structure, rather than type I parallel crystalline structure in natural cellulosic fibres. Viscose has a much lower degree of polymerisation than cotton, and 40% crystallinity versus 60% for cotton.[12,13] Viscose is mainly based on wood pulp fibres and cotton.

Chemically modified regenerated celluloses can be spun, moulded and cast into films. Examples of these are cellulose acetate fibres, which have high luster and sheen and are frequently utilised in garment linings, and cellulose acetate films, which find applications ranging from photography and sausage casings to dialysis membranes. Cellulose acetate butyrate and cellulose acetate propionate can be used to make strong, resistant, plastic tool handles.[1]

10.3 Mechanisms of interactions between plasmas and cellulose-based fibres

Cellulose, as have all polysaccharides, has traditionally been modified through reactions of the hydroxyl group, the only functional group generally available for reaction. This has generally limited the reactions to esterification and etherification. The hydroxyl groups on the anhydrosugar units vary in reactivity and, with polyglucans for example, the C6 hydroxyl is favoured in esterification and the C3 is favoured in etherification reactions. It has also been demonstrated that the accessibility of the OH groups is controlled by the relative ratios of crystalline and amorphous regions of the cellulose suprastructure. The hydroxyl reactivity can be quantified by exposure to TFAA (trifluoroacetic anhydride) vapour followed by XPS analysis. The ease with which a hydroxyl centre can be derivatised was found to be

directly dependent upon its crystallinity. Amorphous celluloses can be functionalised much more readily than their crystalline counterparts.[14]

The use of cold plasma is a new approach to cellulose modification, varying significantly from the traditional esterification and etherification routes. Plasma gas substituents can be reacted directly with the anhydrosugar units by abstraction of hydrogens from either carbon or oxygen atoms in the plasma reactor. Thus, cellulose can be oxidised, reduced and/or substituted in new, unique ways. Cellulose can also be grafted with vinyl monomers by using the plasma as a free-radical initiator at the cellulose surface. Because the monomer is introduced as a gas, no wasted homopolymer is formed and the grafting is restricted to the surface.[1]

10.3.1 Free radical formation and stability at cellulose surfaces

The interaction of the active species of a plasma with cellulose (and other polymer) surfaces, involves several electron-mediated processes, as well as positive ion-induced reactions. Some of these reactions can promote homolytic bond cleavages leading to the formation of free-radical sites. These reactive centres can lead to a variety of functionalisation mechanisms, depending on where in the cellulose structure they are created. Free radical sites usually contain unpaired electrons which are not involved in chemical bonding, and this determines their extremely high instability and high reactivity. As a consequence, free radicals generated on a polymer surface, e.g. as a result of the interaction with a plasma in a closed vacuum environment, and which are subsequently exposed to atmospheric conditions, disappear almost instantaneously through water vapour or moisture-driven recombination mechanisms, which make their identification and detection very difficult. However, some of these free radicals can be quite stable below the surface layers of the substrates through sterical hindrance and 'caging' effects. It is possible to investigate these active species, both by chemical (e.g. reaction with sulphur dioxide or diphenylpycryl-hydrazil) and physical (electron spin resonance (ESR)) techniques.[1]

ESR measurements indicate that significant free radical concentrations can be created on polymeric surfaces under cold plasma environments, regardless of the nature of the substrates or plasma gases.[14] Argon, O_2, N_2, H_2, CO, CH_4 and CF_4 plasma-generated relative free-radical intensities from cellulose fibre surfaces such as cotton, linen, viscose rayon and polynosic fibres, and from wool, silk, nylon 6 and poly(ethylene terephthalate) have been measured by the ESR technique. It was shown that trapped free radicals can survive in the polymer matrix and that their intensities vary significantly with the nature of the fibres and the plasma gases. The following order of free-radical intensities was established for various substrates

and plasma gases: cotton > linen > mercerised cotton > nylon 6 > polynosic fibres = viscose rayon, and $CF_4 > CO > H_2 > Ar > CH_4 > N_2 = O_2$. It was also found that longer treatment times induce higher free-radical concentrations. In addition to the plasma parameters, the fine structure of the fibres plays an important role in the generation and stability of plasma-created free radicals. It has also been concluded that there is no direct relation between free-radical intensity and the extent of surface modification. XPS evaluation of the relative surface atomic compositions of CF_4 plasma-treated cellulosic fibres demonstrated that exposure to the CF_4 discharge induces similar surface chemistry (i.e. comparable relative surface atomic compositions) regardless of the nature of the substrate. However, the free-radical intensities of natural and regenerated cellulose fibres differ significantly.

The stability of living free radicals 'trapped' in cotton fibres after exposure to O_2, CF_4, and CO plasmas at different temperatures has been investigated under open laboratory conditions, see Figure 10.1. The activated fibres were conditioned at room temperature, as well as in a temperature range of 120–200°C. It was shown that the relative free-radical intensities
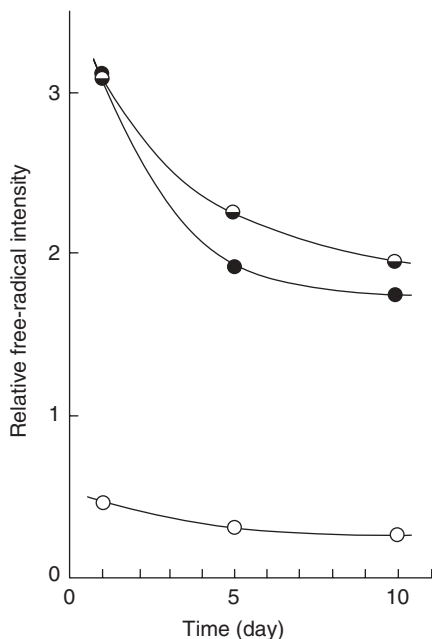
10.1 Stability of free radicals generated on cotton by O_2, CO, and CF_4 plasmas in air at room temperature. (Reproduced with permission from Ref. 15.)

of the CF_4 and CO plasma-treated fibres decreased markedly with an increase in temperature and exposure time to air, whereas free-radical intensities of oxygen plasma-treated substrates did not undergo substantial changes. Similar free-radical instabilities have been observed on argon plasma-treated jute and cellulose.[16] Tests with non-extracted and plasma-treated jute and plasma-exposed ethanol-extracted lignin indicate that the lignin plays a significant role in the free-radical formation, and that the low-molecular weight extractives inhibit the free-radical formation.

Detailed and systematic evaluation of the nature and intensity of free radicals generated on polysaccharides, by coupling ESR kinetics with computer simulation, allowed identification of the precise nature of the plasma-created free-radical sites.[17] It was demonstrated that all possible four hydroxyalkyl radicals (1, 2, 3, and 7) are generated as primary structures through the hydrogen abstraction mechanism, but with a preference at C2 and C5 carbon atoms. The radicals formed at C4 and equivalent C6 were unstable, i.e. they underwent spontaneous thermal dehydrogenation resulting in acylalkyl radicals, whereas radical C1 was stable even at temperatures as high as 120 °C.[18]

An in-depth ESR study of Ar plasma-induced polycarbohydrate radicals in powdered cellulose and amylose demonstrated a significant difference between the ESR spectra from the two anomeric polymers.[19] The spectra of the plasma-exposed cellulose contained a large amount of an isotropic triplet (*ca* 2.8 mT hyperfine splitting constant (HSC)) in addition to the doublet, whereas plasma-irradiated amylose contained only a negligible amount of the triplet. This triplet is assignable to the hydroxylalkyl radical C2 and/or C3 of the glucose units of cellulose. The lack of triplet formation in the amylose was considered due to the suppression of hydrogen abstraction at C3 in the helical tertiary structure of amylose. It was also shown that the polycarbohydrate radicals react rapidly with oxygen under open laboratory conditions, whereas monocarbohydrate radicals are stable even at elevated temperatures. This difference was ascribed the difference in the polymorphic forms between poly- and monocarbohydrates.[19] The structure of the plasma-induced radicals in cellulose and the reaction sequence are illustrated in Figure 10.2.

10.3.2 Generation of high surface energy cellulose substrates – Ar and O_2 plasma treatments

Surface functionalisation of natural polymeric substrate surfaces from non-polymer forming plasmas (inert- and reactive-gas plasmas) are of special interest in theoretical and applied investigations for the following reasons:
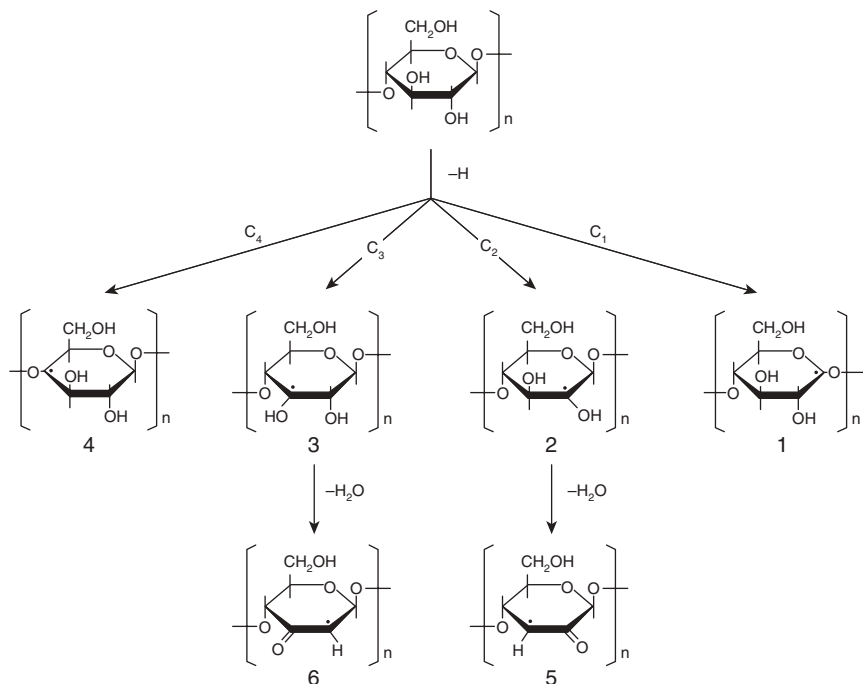
10.2 Structure of plasma-induced radicals in cellulose, and the reaction sequence. (Reproduced with permission from Ref. 18.)

- These processes are by-product free. The reactions are not accompanied by the deposition on the substrate or reactor wall surfaces of undesired macromolecular layers. Small quantities of gas phase components from ablation mechanisms or from plasma-induced molecular dissociation reactions usually do not create significant environmental problems.
- The plasma installations do not require periodic difficult cleaning procedures, which make this approach suitable for continuous-flow systems.
- The starting components usually are volatile, low molecular weight gases which can easily be fed into the reaction chamber.

The approach of Ar and O_2 plasma treatments is generally directed to create polar functionalities other than hydroxyl groups on the cellulose surfaces.
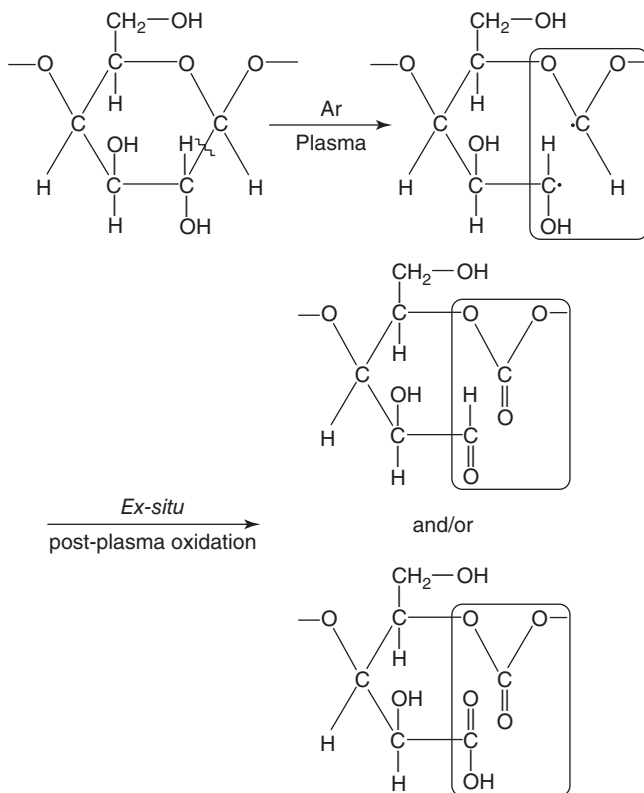
Argon plasma-treated cellulose surfaces

Several studies of O_2 and Ar plasma treatments of Whatman filter paper indicate that identical surface functionalities are created but through

different reaction mechanisms. Relative percentage surface areas of non-equivalent carbon peaks of high resolution XPS data collected from argon plasma-treated samples, indicate that new surface functionalities are formed compared with unmodified cellulose. In addition to the C—OH, C—O—C (286.6 eV) cellulose peaks, the existence of O=C=O (288.7 eV) and O—CO—O (290.4 eV) binding energy can also be noticed. Plasma-induced surface modification at higher RF powers involves mainly the diminution of the O—C—O linkages of the pyranosidic unit through the cleavage of the C1–C2 bonds. The formation of ketone and aldehyde functionalities as a result of the ring opening process, demonstrated by high resolution XPS data from Ar-plasma-treated samples, substantiate the suggested reaction mechanisms (see Figure 10.3). The oxidation processes of Ar plasma-treated cellulose are related to plasma-created free radicals, which initiate post-plasma oxidation reactions under open laboratory conditions.[20,21] The suggested reaction mechanism for argon plasma-induced molecular fragmentation of cellulose is shown in Figure 10.4.
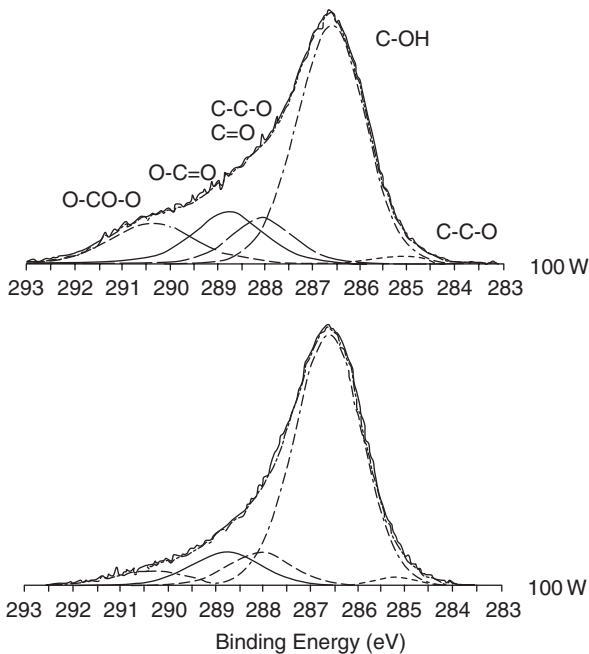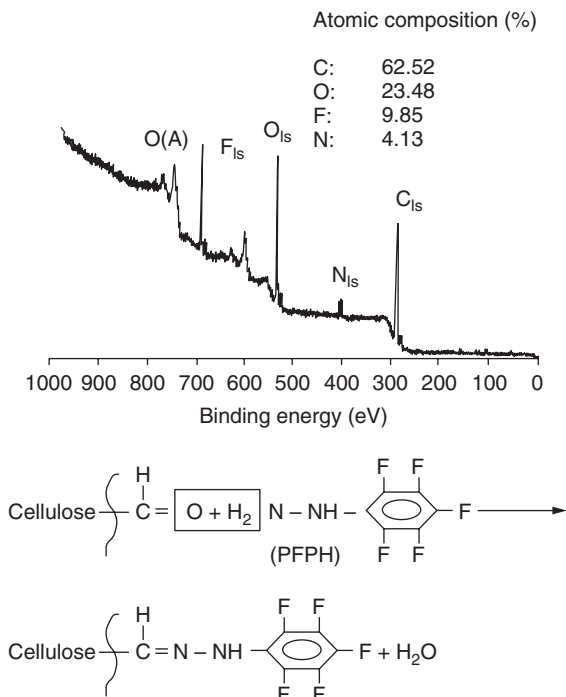

10.3 High resolution deconvoluted XPS spectra of cellulose (Whatman paper) treated at 100 and 500 W under argon-RF-plasma conditions. (Reproduced with permission from Ref. 21.)

10.4 Suggested reaction mechanism for argon plasma-induced molecular fragmentation of cellulose. (Reproduced with permission from Ref. 21.)

Oxygen plasma-treated cellulose surfaces

Similarly to the Ar plasma-modified cellulose, XPS data collected from O_2 plasma-modified and PFPH-(pentafluorophenylhydrazine) and TFAA-(trifluoroacetic anhydride)-derivatised cellulose substrates clearly indicate the presence of O—C—O in all plasma-modified samples, but also formation of new O=C—O, C=O and O—CO—O functionalities. However, in this case C—OH and C—O—C linkages are involved in plasma-induced reaction mechanisms. It has been suggested that the relative increase of O—C—O concentration is related to the diminution of C—OH and C—O—C concentrations. The intensified reaction mechanisms involving C—OH and C—O—C groups at higher pressure values were suggested to be associated with cross-linking mechanisms. High resolution XPS data from PFPH-derivatised samples also indicate the presence of C=O functionalities.[21] The suggested mechanisms for the reactions of PFPH and TFAA

Atomic composition (%)

C:	62.52
O:	23.48
F:	9.85
N:	4.13

O(A)　F$_{ls}$　O$_{ls}$

N$_{ls}$

C$_{ls}$

1000 900 800 700 600 500 400 300 200 100　0

Binding energy (eV)

H
Cellulose —(— C = | O + H$_2$ | N — NH — ⟨C$_6$F$_4$⟩ — F ⟶
(PFPH)　F F

H
Cellulose —(— C = N — NH — ⟨C$_6$F$_4$⟩ — F + H$_2$O

10.5 Survey ESCA spectrum of a typical argon plasma-treated and pentafluorophenyl hydrazine-derivatised cellulose substrate and the derivatisation reaction mechanism. (Reproduced with permission from Ref. 21.)

with both C=O and C—OH functionalities are illustrated in Figures 10.5 and 10.6, respectively.

ATR-FTIR analysis of O$_2$ plasma-treated cellulose correlates well with the XPS data. A typical IR spectrum of virgin cellulose shows all the typical characteristic vibrations: OH wagging at 670 cm^{-1}; C1 group vibration, C—C stretching, C—C—O stretching, C—O—C symmetric stretching, and CH$_2$ bending at 893, 1000, 1060, 1120 and 1370 cm^{-1}, respectively; in-plane OH bending at 1400 cm^{-1}; CO$_2$ at 2359 cm^{-1}; C—H stretching at 2900 cm^{-1}; OH and intermolecularly bonded OH at 3100–3400 cm^{-1} and water at 3742 cm^{-1}. O$_2$ plasma-treated cellulose substrates show more intense in-plane OH vibrations (at 1390–1420 cm^{-1}) and the presence of weak unsaturation absorption (at 1600 cm^{-1}) in comparison with the spectrum of untreated cellulose. Analyses of TFAA-derivatised versions of untreated and O$_2$ plasma-treated cellulose show that the in-plane OH vibrations at 1390–1420 cm^{-1} disappear almost totally and the C=O vibrations of aryl esters appear at 1640–1680 cm^{-1} upon plasma exposure. The ATR-FTIR data support the XPS data and indicate that macromolecular chain-breaking

Atomic composition (%)

C: 49.03
O: 42.85
F: 8.15

1000 900 800   700 600 500   400 300 200 100   0

C—OH

C—C—O

CF₃   O—C=O   C—C—O

295 294 293 292 291 290 289 288 287 286 285 284 283 282

Binding energy (eV)
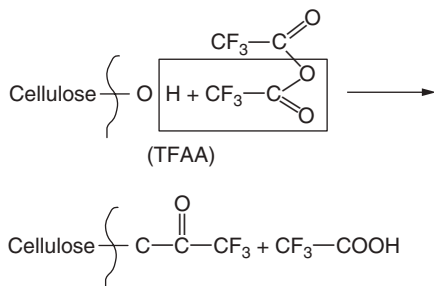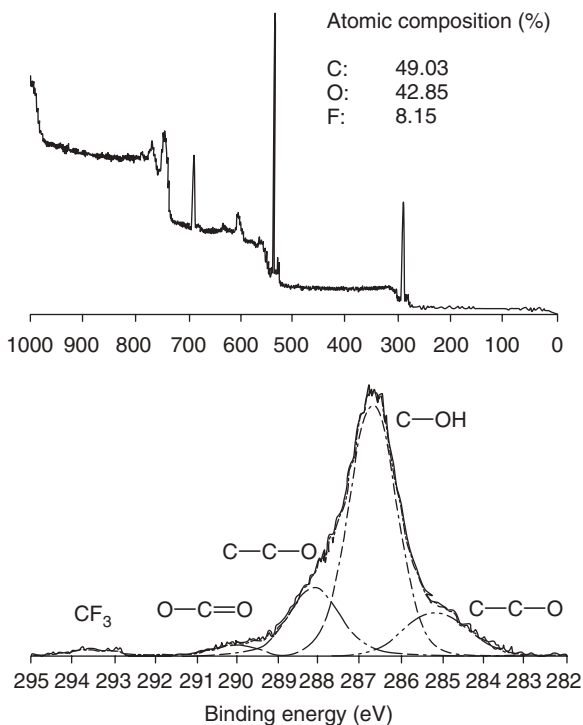
10.6 Survey ESCA spectrum of a typical argon plasma-treated trifluoroacetic anhydride-derivatised cellulose substrate and the derivatisation reaction mechanism. (Reproduced with permission from Ref. 21.)

mechanisms and plasma-induced etching processes control the number and availability of OH functionalities at the surface of the plasma-modified samples. In other words, the O_2 plasma treatment seems to cause more intense C—O—C scission reactions on the cellulose surface. The suggested cross-linking mechanism for O_2 plasma-exposed cellulose is shown in Figure 10.7.[21]
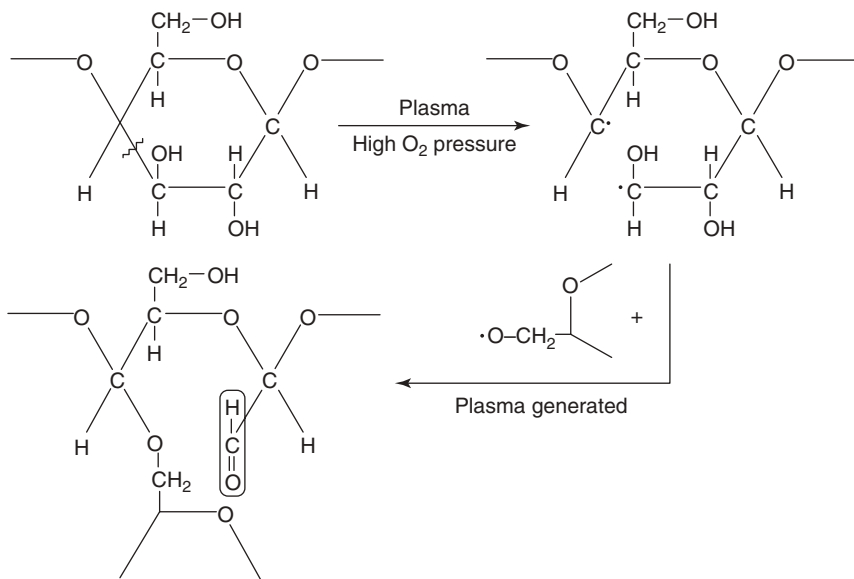
10.7 Suggested cross-linking mechanism for O_2 plasma-exposed cellulose. (Reproduced with permission from Ref. 21.)

10.4   Plasma modification of cotton for textile applications

The textile industry has long been concerned about water consumption and environmentally hazardous chemicals in effluents.[22] The method used to graft monomers onto cellulosic fabric, for instance was, for many years, based on the use of initiators (such as ceric ions) for copolymerisation between cellulose and the monomer. The main drawback of this method is the generation of highly toxic wastes.[23] In recent years, low-temperature plasma technology for surface modification of textile substrates has attracted increasing attention. It has been established that plasma treatment plays a key role in the enhancement of textile fibres and fabrics properties, such as improved wettability, dyeing, water repellency, lowered moisture content, and decreased surface resistivity.[24] Several studies on plasma surface modification of cellulose-based textiles have been conducted, using glow-discharge technology at low pressure[22–40] as well as barrier discharge and corona treatments at atmospheric pressure.[41–50] In both cases, active particles such as radicals, ions, electrons and photons are generated, which under reduced pressure have a much larger free path length as compared with the process at atmospheric pressure. Consequently, the treatment at atmospheric pressure normally occurs in a narrow slit, while the treatment at

low pressure is performed in a reactor with a volume adapted to the size of the samples.

10.4.1 Plasma surface modifications of cotton at low pressure

Air and oxygen plasma treatments of cotton fibres were studied under variation of the most important plasma parameters, such as discharge power, treatment time and nature and flow rate of the gas. The chemical effect of the treatments on the cotton fibres was evaluated by means of a variety of different methods, including the Cuprammonium fluidity test, weight loss measurement, determination of carboxyl groups, carbonyl group identification, FTIR analysis and ASTM yellowness. In addition, vertical wicking, the effect of ageing of the plasma treatments and amount of dye uptake were investigated. It was found that the plasma treatments led to surface erosion of the cotton fibres, which generated a weight loss, accompanied by an increase in the fibre carboxyl group and carbonyl group contents. The increase in carboxyl group concentration led to a more wettable fibre and the rate of fabric vertical wicking was increased. The direct dye (chloramine Fast Red K) uptake increased almost linearly with the increase in fibre carboxyl group content, but decreased progressively with increased ageing time after the oxygen plasma treatment. It was also shown that the fabric yellowness increased with time after treatment.[33]

Several attempts have been made to introduce different functionalities/properties to the cotton fibre surface by means of plasma-induced graft polymerisation. Often hydrophilic monomers have been polymerised on the cotton surface, previously activated by, e.g. an inert-gas plasma, in order to improve the mechanical properties of the cotton.[37] The most commonly used hydrophilic monomers are various methacrylates and acrylates (e.g. HEMA (2-hydroxyethyl methacrylate), GMA (glycidylmethacrylate), MEA (2-methoxyethyl acrylate), HEA (2-hydroxyethyl acrylate)) and other vinyl monomers such as acrylic acid acrylamide, N-isopropyl acrylamide, etc.

A variety of these hydrophilic monomers were grafted onto cotton and other textile fibres that had been pre-treated by glow discharge plasmas. A piece of textile fabric was exposed to an argon plasma generated at 13.56 MHz frequency. Previously degassed monomer solutions were then poured into the reactor without contact with air. The graft polymerisations were thus carried out in an aqueous phase under shaking in a water bath at a controlled temperature (60–65 °C) for 2 hours. It was found that HEMA was graft-polymerised more readily than the other monomers investigated. The grafting yield decreased with increasing air-exposure time and it was

concluded that vacuum processing is crucial for successful graft polymerisation. The mechanical properties, in terms of breaking strength, of the poly(HEMA)-grafted cotton yarns were improved. The increase in breaking strength was attributed to the binding of fibrils in the yarn by the graft polymer. The Ar plasma treatments alone caused a reduction in strength due to etching.[37]

Low temperature plasma was used to activate mercerized cotton fabrics, to be followed by grafting of various methacrylates.[51] Preliminary trials using glycidylmethacrylate (GMA) onto plasma-treated cotton fibres were carried out to select the most suitable gas and plasma conditions in order to obtain the highest possible graft yield of GMA. Argon was found the most efficient gas with respect to induced graft yield. ESR was used to study the formation of the different radical species generated on the plasma-treated cellulose of mercerised cotton substrate. The ESR results were in accordance with the graft yield results and showed proportionality between the total concentration of radical species and applied discharge power. The suggested reaction mechanism of surface-initiated free-radical polymerisation consists of an initiation step involving primary radicals generated directly by action of the Ar plasma on the cotton substrate, or indirectly by action of peroxides formed by interaction between radicals and atmospheric oxygen.[51]

It is also possible to graft hydrophobic, water-repellent functionalities onto the cotton fibres.[22,26,37] Radiofrequency-driven plasma processes are the most commonly used processes for textile substrate modification. However, the use of 2.45 GHz microwave generator plasma for surface modification of cotton fabrics has also been reported. One study demonstrated that an argon plasma at 2.45 GHz generated more active groups on cotton than either N_2 or O_2 plasma treatments.[51] It was also reported that vinyl laurate was successfully plasma-induced grafted onto lightweight cotton fabric, thereby imparting a hydrophobic character to the fabric surface.[52] Another study investigated the effect of microwave plasma treatment on fabric weight loss and breaking strength and the durability to repeated home laundering of the plasma-induced grafting of vinyl laurate on the fabric. Microwave plasmas using O_2, N_2 and argon, at various discharge powers and exposure times, were applied to the lightweight cotton fabric. The results showed that O_2 plasma generated higher weight loss than N_2 and Ar plasmas. The fabric breaking strength was not affected by the microwave power or by the type of plasma. However, longer exposure time to plasma may result in significant strength loss due to excessive etching and depolymerisation. Plasma-induced grafting of vinyl laurate monomer onto the fabric surface resulted in stable cellulose–vinyl laurate copolymers. Water contact angle measurements after repeated home laun-

dering did not show any significant effect on the water repellence of the grafted cotton fabric. The fabric strength losses due to the plasma treatments were only a fraction of the losses experienced with traditional textile finishing resin.[24]

Besides plasma activation with non-polymerisable gases and plasma-induced grafting of various monomers, it is also possible to modify cotton surfaces by means of plasma polymerisation, i.e. deposition of ultra-thin layers directly from the gas phase in the plasma.[26,27] The character of the deposited layer depends on the precursor (monomer) and can be anything from very hydrophilic to very hydrophobic.

Plasma polymerisation of dichloromethane (DCM) was found to be extremely effective with respect to improving properties such as moisture content and dyeability of cotton fabrics.[26] However, at polymerisation times beyond 20 seconds, an adverse effect was seen: the moisture content decreased along with colour strength. The decrease in moisture content showed a hydrophobic behaviour of the cotton fabric with a consequent effect on the dyeability of the modified fabric. An increase of yellowness in the plasma-coated cotton sample with increasing deposition time of DCM was also observed. The other properties remained unchanged. It was suggested that increased generation and deposition of free radicals of both plasma and DCM vapour onto the cotton surface with increased deposition time, were the causes of the yellowness of the surface.[26]

Several studies have shown that exposure of the cotton fibres to fluorinated gas plasmas results in a decrease of water absorption or wettability.[22,25,53] Fluorocarbon gas plasmas can change surface properties via either surface treatment or polymerisation and deposition of a thin film.[22,53–55] Cotton fabrics were treated by RF plasma with tetrafluoromethane (CF_4) and hexafluoropropylene (C_3F_6) gases at different plasma conditions[22] in order to make the fabric surface hydrophobic. The hydrophobicity and water repellence were determined by measurements of the cosine of the contact angle ($\cos \theta$) and wet-out time. The hydrophobicity was enhanced with treatments by either gas but XPS analyses revealed a significantly higher fluorine content on the cotton surface after the C_3F_6 plasma compared with after the CF_4 plasma treatment. It was also found that the increase in contact angle and wet-out time achieved by C_3F_6 plasma treatment were substantially higher than those after treatments in CF_4 gas plasma. These differences were mainly due to the fact that C_3F_6 plasma can generate polymers on the substrate through both plasma polymerisation and plasma-induced polymerisation mechanisms, whereas CF_4 gas plasma is limited to only plasma polymerisation. In addition, CF_4 plasmas produce more atomic fluorine than C_3F_6 plasmas, and it is well known that CF_4 is a highly effective etchant and ablates the deposited fluorinated polymer

layer. This results in a reduction in surface fluorine and a decrease in hydrophobicity over time. Using C_3F_6 plasma to make cotton fibres and other surfaces hydrophobic therefore appears to be the preferred choice over CF_4 plasma.[22]

10.4.2 Plasma surface modifications of cotton at atmospheric pressure

Despite the high efficiency of low-pressure plasma treatments, the wide use of vacuum-based plasma technologies has been discouraged by high investment costs, batch-wise processing and relatively long treatment times (on the order of minutes). The basic advantages of atmospheric-pressure plasma processing consist of comparatively simple implementation, no need for maintaining vacuum and possibility to organise the process based on continuous technology. A more extensive description of atmospheric-pressure plasma processes is given in Chapter 4 of this book ('Atmospheric-pressure cold plasma processing technology').

The first studies on corona treatment[56] (the first and most simple form of atmospheric pressure plasma) of cotton were reported at the beginning of the 1960s.[42] Corona treatment of cotton and its effect on spinnability, strength, abrasion resistance, friction properties, etc., have been investigated by several research teams.[41,43–45] It was found that corona treatments increased yarn strength (particularly for soft twisted yarns) by modifying the fibre surfaces to increase friction between fibres. It was demonstrated that the properties of the cotton fibre surface were permanently modified without any change in fibre strength.[45] It has also been demonstrated that the cohesion of twistless cotton slivers can be increased substantially by continuous corona-discharge treatment. It was also claimed that the most efficient method for a given total power input is to use multiple treatments at a number of separated treatment points rather than to rely on a single treatment in a single, concentrated corona field.[41]

In more recent years, other, more sophisticated, atmospheric pressure plasma processes (e.g. various dielectric barrier discharges,[50,57–60] have been developed. Cotton yarn was treated with an airflow-stabilised DC (direct current) discharge in the glow regime. It was demonstrated that the wicking rate of the treated cotton yarn increases with treatment time and discharge power. It was also indicated that the wicking rate was higher when the yarn was positioned in the vicinity of the electrodes. Some ageing of the treatment, i.e. decrease in wicking rate, was observed during the first 5 hours, but the decrease levelled off and the remaining wicking rate was significantly higher than the wicking rate for the untreated yarn.[50]

10.5   Plasma surface modification in cellulosic fibre-based composites

To create composites of polysaccharide and thermoplastic-based materials, at least one of the two dissimilar materials should be modified to make it compatible with the other. It has been shown that cold plasma environments are suitable for tailoring surface characteristics of cellulosic substrates and for increasing adhesion with their synthetic counterparts.[61–63] However, surface treatments of thermoplastics were also found to be effective in creating composites.[64] Results from hydrogen and oxygen RF-plasma treatments of filter paper (open texture and free from low-molecular-weight materials) and grease-proof paper (closed texture and the presence of low-molecular-weight compounds) indicated that hydrogen plasma environments reduce the cellulose surfaces and generate low molecular weight degradation products, whereas oxygen plasma exposure increases the relative surface oxygen content and improves adhesion (see Figure 10).[61] It was shown that reduction of cellulose surfaces does not influence the adhesion significantly. However, the presence of degradation products strongly diminishes this characteristic. The increased adhesion of oxygen plasma-treated cellulosic substrates to polyethylene is related to the ablation of low molecular weight components (resins in the case of greaseproof paper) and to the formation of hydroperoxide-mediated covalent bonds across the interface. It was also shown that the lamination temperature of the cellulose/thermoplastic composites significantly influences the adhesive strength only in the case of the filter paper.

Wood fibres from 60% beech and 40% birch, containing 86% cellulose, 13% hemicellulose, and a very small fraction of lignin, were treated in different microwave discharges.[63] By controlling the plasma environment, the acid/base interaction balance can be shifted towards acidity or basicity. Acidic character of the fibres was achieved by plasma polymerisation of methyl methacrylate, and the basic character was obtained by ammonia and nitrogen plasma treatments. It was emphasised that the surface treatments were incomplete, although the plasma reactor used was provided with a fibre-mixing system. It was shown that the mechanical properties of composites from plasma-modified cellulose fibres and polystyrene and chlorinated polyethylene were improved when a strong acid–base interaction between the matrix and the fibres was favoured. The properties of PP-based composites were not affected by the acid–base characteristics.

The effect of plasma treatments on the mechanical properties of composites made up from cellulosic fibres, in particular sisal fibres, and thermoplastics such as polypropylene and polyethylene, has been investigated by several authors.[65–73] Most studies showed that air and argon plasma treatments improved the compatibility between sisal fibres and polypropylene.

Both treatments, and air plasma in particular, improved the mechanical properties of the resulting composites in terms of strengths and moduli in both tensile and flexural modes. However, it was demonstrated that the plasma conditions are very critical. Optimised plasma treatment parameters were found at short (≤30 seconds) treatment times, and medium power and medium chamber pressures. Dynamic Mechanical Thermal Analysis (DMTA) showed that the storage modulus of the plasma-treated sisal fibre–PP composites improved over the whole temperature range (−60 to +160 °C), indicating better adhesion between the sisal fibre and the PP matrix. In particular, the interfacial shear strength increased more than 20% after an air plasma treatment for 30 seconds. Longer treatment times resulted in a significant reduction in interfacial shear strength. Surface characterisation by XPS showed that the O/C ratios of the sisal fibres increased after both Ar and air plasma treatments. The air plasma treatment yielded higher O/C ratios than Ar plasma. It was proposed that this higher O/C ratio, plasma-generated surface C=O and O—C=O functionalities, and selective etching of the surface by plasma, all contribute to better adhesion characteristics, which in turn results in better composite performance.[69,70] SEM analyses revealed that obvious corrugations and granules developed on the surface of the Ar plasma-treated fibres, and a number of cracks and an amount of scouring appeared on the fibre surface at prolonged air plasma treatment times. It has also been demonstrated that the plasma discharge frequency has a pronounced impact on plasma-induced degradation and chain scission in both polypropylene and sisal fibres during oxygen plasma treatments. Results showed that polypropylene–cellulose adhesion forces are about an order of magnitude higher for treatments at 13.56 MHz than at 40 kHz, owing to a much higher degree of chain scission at lower frequencies. Sisal fibres and PP powder treated in conditions of surface degradation did not improve in flexural or tensile properties but had higher impact resistance, comparable to the improvement obtained with the addition of compatibiliser.[66]

Sisal fibres and finely powdered high-density polyethylene (HDPE) were surface-functionalised with dichlorosilane in a RF-plasma reactor and the mechanical properties of composites made from the plasma-treated materials were investigated. In contrast to other studies, it was found that the best mechanical performance generally was obtained for composites where only the thermoplastic matrix (HDPE) was plasma-functionalised, which led to good interfacial adhesion between fibres and matrix. Plasma treatment of lignocellulosic fibres induced decomposition processes of the surface layer structures exposed to the plasma, which generally does not contribute to significant improvement of the mechanical behaviour of the composite. It was therefore suggested that only the thermoplastic substrate should be plasma-functionalised.[67,68]

Attempts have also been made to improve the compatibility and adhesion to polypropylene by making the cellulose fibre surface polypropylene-like.[72] Cellulose filter paper was treated with cyclohexane plasma under various conditions to evaluate this approach. Plasma polymerisation of cyclohexane is known to produce hydrocarbon-type polymer coatings. ESCA (XPS), dynamic contact angle measurements and SEM analysis were used to determine the nature of the chemical changes on the plasma-coated cellulose surfaces. The cyclohexane plasma treatments resulted in the deposition of an oxidised and dehydrogenated hydrophobic polymer film, similar in structure to polyethylene. Although compatibility with polypropylene was improved by covering the polar groups on the cellulose surface with non-polar plasma-generated polymer materials, adhesion was not at all improved. A cyclohexane plasma may increase the compatibility and intimate molecular contact between polypropylene and filter paper, but the lack of hydrogen and/or covalent bonding results in no strength development in the laminated structures.[72]

Various wood fibres (e.g. high temperature mechanical pulp (HTMP) and high alpha hardwood) have also been plasma-treated in order to improve their adhesion to thermoplastics, and mechanical properties of the resulting composites.[71,74,75] Also, here, air and argon plasma treatments improve the tensile strengths and moduli of woodfibre–polypropylene composites. It was shown that the best result was obtained when both the wood fibre and the PP surface were treated. It was suggested that dispersive forces are mainly responsible for the increased interfacial adhesion.[71] Atomic Force Microscopy (AFM) analyses revealed that oxygen plasma treatment caused changes in the morphology of the materials. The treated PP surface was covered by a nodular structure, which was not seen on the untreated film. Similar nodular structures have also been observed after corona treatment of PP films.[76] These structures were also detected on the lignocellulosic material. The diameter of the nodules increased with increasing treatment time. The nodules seemed to have poor interaction with the PP surface, resulting in a weak interface between the plastic film and the wood. Consequently, the maximum adhesion was reached with the shortest plasma exposure time applied.[75]

Lately, some studies have reported on chemical modification of cellulose fibres for improvement of their interaction with rubber matrices. Allyl acrylate and allyl methacrylate were grafted on short cellulose fibres, resulting in improved wetting and increased adhesion to a natural rubber (NR) matrix.[77] Butadiene and divinylbenzene were plasma-grafted onto kraft pulp cellulose fibres in order to improve the mechanical properties of natural rubber–cellulose fibre composites. There was no difference in apparent cross-link density but the initial modulus was increased more than 150%. This effect was attributed to an increased adhesion/dispersion as a

result of the plasma treatment.[78] Corona-treated wood flour was evaluated as a filler for nitrile butadiene rubber (NBR) compounds. The mechanical properties were investigated and it was found that corona treatment at optimal conditions improved these properties. The effect increased with increasing treatment time and discharge voltage. The improvement of the mechanical properties was explained by changes in the geometric area of the wood flour particles, caused by surface etching of the corona treatment, and the accumulation of surface oxygen-containing groups that changed the surface polarity of the wood flour particles.[79]

## 10.6   Plasma modification of solid wood and wood pulp fibres

10.6.1 Plasma modification of solid wood surfaces

Wood is a heterogeneous material consisting of two major components, carbohydrates and lignin, and minor components in the form of organic extractives and inorganic minerals.[80] Wood is a popular construction material due to its high physical strength, easy machinability, aesthetic appeal and low price. At the same time, wood has several disadvantages, such as biodegradability, dimensional instability with varying moisture content, significant reduction in physical strength at high moisture content and degradability by UV light, acids and bases.[81,82] Since most of these undesired properties are closely related to the hygroscopic nature of wood, reduction of water penetration into the pores is vitally important, especially when wood is exposed to outdoor environments. Lacquering, painting or oil impregnation are the most commonly used surface protection methods in order to ensure the retention of surface properties of wood in outdoor applications. The performance of these coatings is strongly influenced by the presence of liquid water since it can penetrate into the interface between the wood substrate and the coating and reduce the bond strength (wet adhesion) between the coating and the wood. This is especially critical for water-borne acrylic dispersions, where the wet adhesion occasionally is so critical that blistering, adhesive failure and other damages often occur.[83]

Low-temperature plasma technology offers, in principle, two routes to improved outdoor performance of wood: (i) plasma deposition of highly cross-linked hydrophobic coatings directly on the wood surface in order to prevent penetration of water into the wood pores,[84–88] and (ii) plasma cleaning and activation of the wood surface for improved adhesion of various protective coatings.[85,89–92] A few examples of each approach are given below.

Plasma-induced hydrophobisation of wood surfaces has been investigated to improve dimensional stability and biodegradability.[84] Pine sapwood

samples were coated in a tubular RF-plasma reactor under methane (CH_4), tetrafluoroethylene (C_2F_4) and hexamethyldisiloxane (HMDSO) discharge environments. It was found that, due to the released water vapour and/or low-molecular-weight components from the wood under low pressure, the efficiency of plasma treatment was dependent on the evacuation time; that is, longer evacuation times resulted in more efficient treatments (see Figure 10.8). The nature of the plasma gases also influences the water uptake. C_2F_4 plasmas reduce the water uptake more than CH_4 and HMDSO plasmas after long evacuation, whereas at short evacuation times, HMDSO depositions result in the lowest water uptake values. The hydrophobised wood surfaces exhibited poor adhesion to paint. This characteristic could be improved through post-hydrophilic treatments, such as oxygen plasma treatment and plasma polymerisation of acrylic acid. The adhesion was improved at the sacrifice of the reduction of water uptake. However, a large reduction in water uptake and good adhesion to the paint could be achieved by a proper combination of the hydrophobic treatment and the hydrophilic post-treatment.[84] In another study, defect-free pine blocks were coated with plasma polymer films from vinyl acetate vapour, ethylene, acetylene and 1-butene. The plasma polymerisation proved to be a very promising technique to change the hydrophilic characteristics of wood surfaces without changing the bulk properties. The best hydrophobic effect was obtained by plasma polymerisation of 1-butene. However, the plasma-deposited film was
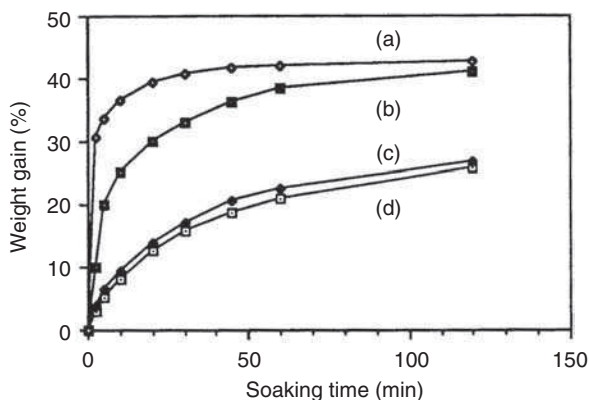
10.8 Weight gain in water of pine sapwoods (50 × 10 × 2 mm) treated with C_2F_4 plasma (5 sccm, 10 W, 10 minutes) as a function of soaking time. The plasma treatment is carried out at different evacuation pressures with corresponding evacuation time in parenthesis: (a) untreated sample, (b) 33 mTorr (5 minutes), (c) 18 mTorr (10 minutes), (d) 12 mTorr (30 minutes). The advancing water contact angles are for sample (a) 15°, (b) 94°, (c) 111° and (d) 128°. (Reproduced with permission from Ref. 84.)

unable to prevent absorption and desorption of water vapour since, it was concluded, the plasma technique was unable to coat wood capillaries.[86]

Wettability or intimate contact of a liquid adhesive to a solid substrate is necessary for durable bonding. The bond quality between a paint and a solid surface is also affected by the wettability. However, some wood species contain extractives that interfere with the adhesive bonding of the wood to other materials. They consist of hydrophobic resins, esters of fatty acids, waxes, etc. These substances form a structure of low surface energy at the wood surface. For this reason many papers concerning the pre-treatment of wood to improve its wettability and adhesive bonding have been reported.[90,91,93] Oxidative activation of resinous wood surfaces by a corona treatment to improve adhesive bonding was studied. It was found that the wettability of the veneers, including hardwoods, softwoods and tropical woods, increased with increasing treatment dose, and the gluability increased rapidly after the initial mild treatment. To elucidate the nature of any chemical change occurring on the wood surface, the dyeing of the wood and its components was performed and examined using Schiff's reagent. The results showed a higher dyeing ability for the corona-treated samples compared to the untreated ones, indicating that aldehyde groups were formed by the corona treatment. These were formed by oxidation of alcohol–benzene extractives on the wood surface. The untreated and corona-treated samples adsorbed basic dye to the same extent of coloration, indicating that no measurable carboxyl groups were formed by the treatment.[91] Atmospheric plasma, corona and fluorination were used to modify pine sapwood samples to improve the wet adhesion of water-borne acrylic dispersions.[89] All three methods improved the wet adhesion of the dispersions. This was attributed to the increased polar portion of the surface free energy. However, opposite to the observations made for the acrylate dispersions, the wet adhesion of the solvent-based internal comparison product (ICP) (according to EN 927-3) was reduced by the plasma treatment. The reason for this was not clarified, but it was stated that the plasma treatment has to be carefully fine-tuned to the coating material.[89]

10.6.2 Plasma surface modification of wood pulp fibres

Wood pulp fibres are traditionally characterised by bulk measurements, i.e. determination of chemical as well as physical characteristics of bulk fibres. However, since the surface of the fibres interact with each other and with other materials such as adhesives and barrier coatings and other liquids or gases, it is clear that controlling the surface composition and surface properties of such fibres and understanding their relation with the macroscopic physical properties is critical for further improvement of wood pulp fibres. Surface modification of the fibres is therefore an important tool for

increasing this knowledge. Comparative evaluation of the effects of oxygen air, nitrogen and argon cold plasma treatments of chemithermomechanical pulp (CTMP) showed that, whereas oxygen and air plasmas increase substantially the wettability (in some cases more than 100%), nitrogen and argon discharges reduce wettability.[94,95] It was demonstrated that the oxygen plasma treatment increases the oxygen content of fibre surfaces. The wettability increase was related to the oxidation and removal of hydrophobic materials (e.g. fatty acids, resin acids) from fibre surfaces and to the simultaneous oxidation and scission of the lignin and carbohydrates from substrate surfaces. It was suggested that the highly oxidised low-molecular-weight materials might act as surfactants, decreasing the contact angle between the liquid and the pulp and thus enhancing the permeation rate into the fibre network. The effectiveness of oxygen plasma treatments on various cellulosic fibres (cotton, kraft pulp) under different discharge conditions was also evaluated.[96,97] It was shown that microwave plasma conditions can induce very significant improvements in wetting properties of kraft paper strips and that water-migration velocity depends greatly on the length of treatment time and on the nature of plasma gases. Oxygen plasmas produced the most significant effects, in treatment times as low as 5 seconds. However, argon and nitrogen discharges also lead to wettability improvements. It was suggested that oxidation is not the only reaction responsible for the process involving wettability changes. As shown in Figure 10.9, hydrogen plasma treatments cause the opposite effects on pure cellulosic and greaseproof paper substrates in comparison to oxygen-RF discharges.[98] It was demonstrated that hydrogen plasma reduces the oxygen-to-carbon
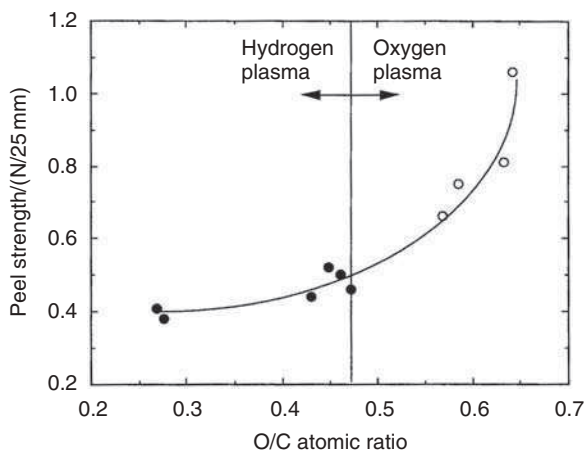
10.9 Adhesive strength of greaseproof paper–polyethylene laminates. Greaseproof paper exposed to hydrogen plasma (●) and to oxygen plasma (○). (Reproduced with permission from Ref. 61.)
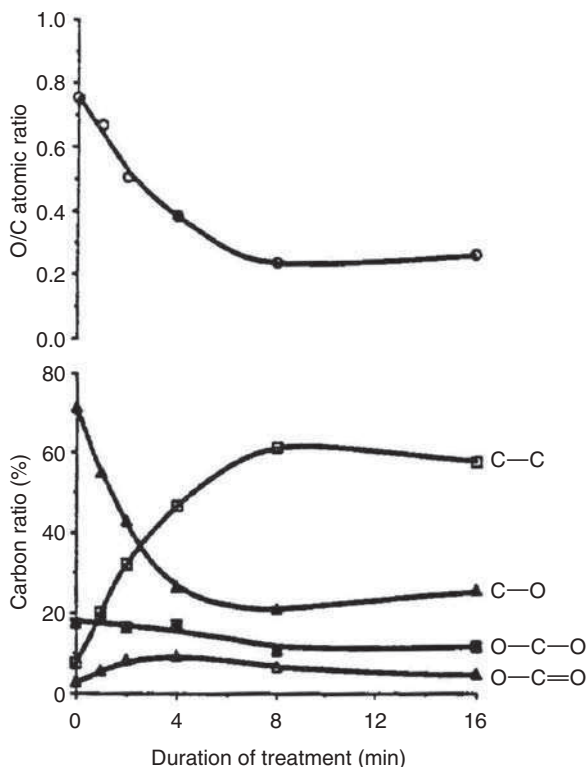
10.10 Hydrogen plasma treatment of filter paper. Changes in O/C atomic ratio and in the amount of the different carbons as a function of treatment time. (Reproduced with permission from Ref. 98.)

ratio and the number of hydroxyl groups on the cellulose, and generates low-molecular-weight compounds, see Figure 10.10. The water wettability of hydrogen plasma-modified pure cellulose is reduced as a result of lower surface polarity. However, the effect is opposite on paper substrates containing high amounts of resin. The oxygen plasma treatment of pure cellulose both oxidises and reduces the surface (macromolecular scissoring mechanisms associated with the formation of unsaturated and cross-linked structures), whereas hydrophobic-nature resin-rich paper substrates show improved water wettability after both oxygen and hydrogen plasma treatments.

10.7   Plasma modification of man-made cellulosics

The energetic particles of cold plasmas interact intensely with the surface topographies of polymeric substrates in addition to free-radical generation and surface functionalisation mechanisms. It is well known that more- or

less-ordered supramolecular structures (crystalline and amorphous zones) coexist in the polymeric substrates, and that the plasma-mediated etching reactions are morphology selective. This behaviour opens up possibilities for creating enhanced surface crystallinity and, consequently, new ways for initiation of template graft polymerisation reactions from plasma-activated surfaces. It has been demonstrated that argon-RF-plasma conditions can generate enhanced crystallinity and active sites (e.g. free radicals) simultaneously on cellophane film surfaces.[99] The free radicals can readily initiate template growth of polyacrylonitrile (AN) and styrene (ST) under *in situ* conditions, allowing for the creation of very thin and controlled-uniformity, ordered polymeric layers with potential applications in the optical industry. Detailed information on the ordered surface morphologies of the oxygen plasma-treated and AN- and ST-grafted cellophane was obtained by AFM investigations. Figures 10.11 and 10.12 show the AFM images of acetone-washed commercial cellophane, the oxygen plasma-exposed washed cellophane film and the oxygen plasma-treated and subsequently AN- and ST-grafted cellophane. It was concluded that acetone extraction of commercial cellophane clearly exposes the ordered nature of the cellulosic fibrils, and that the orientation of the grafted polymer crystallites strictly follows the orientation of the fibrils.[99] AFM was also used to evaluate the adhesion properties of untreated and plasma-modified cellophane films.[100] Both standard silicon nitride tips, as well as self-assembled monolayer (SAM) modified gold-coated tips containing a variety of specific functional groups, including —COOH and —CH$_3$ terminated tips, were used. Plasma treatments were used to modify the surface chemistry and surface roughness. However, neither oxygen nor argon plasma treatment caused significant changes in surface adhesion. It was apparent that the increased surface roughness caused by the plasma treatments cancelled out the enhancement
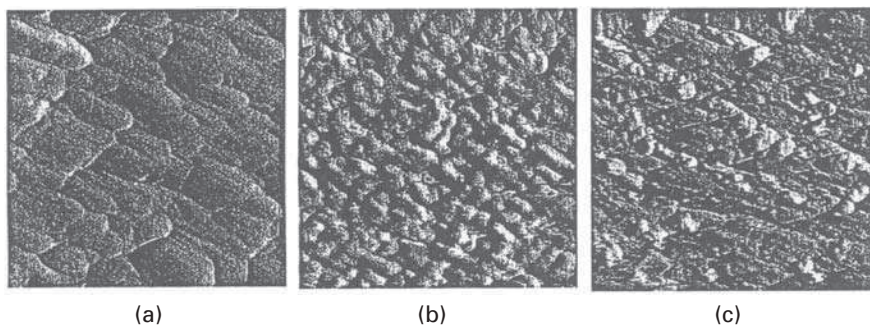
10.11 Atomic Force Microscopy images of cellophane (a) untreated, (b) argon plasma-treated for 30 seconds, and (c) argon plasma-treated for 9 minutes. (Reproduced with permission from Ref. 99.)
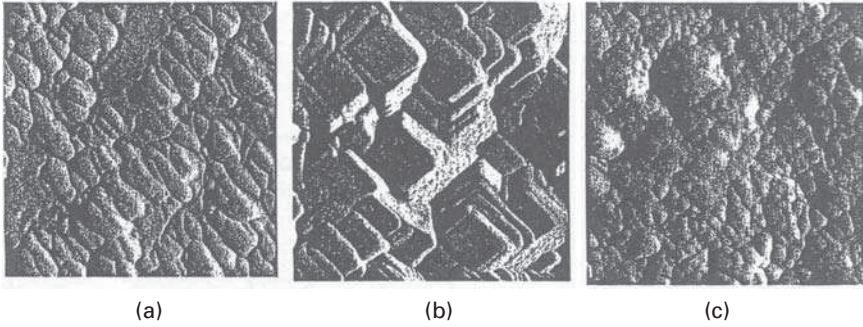
10.12 Atomic Force Microscopy images of cellophane grafted with polyacrylonitrile initiated from (a) argon plasma-treated cellophane surfaces for 30 seconds (b) argon plasma-treated cellophane surfaces for 9 minutes, and (c) cerium ion activation (conventional grafting) cellophane surfaces. (Reproduced with permission from Ref. 99.)

of the plasma-induced changes in surface chemistry. On the other hand, it was found that hydrazine plasma treatment of cellophane, introducing — NH_2 groups on the surface, resulted in strong adhesion forces to the — COOH-modified AFM tip due to acid–base interactions.[100]

Sheets of cellophane were corona-treated and the strength of water-induced bonds between the sheets was related to changes in solid surface free energy accompanying the treatment.[101] A significant increase in the surface free energy was primarily due to an increase in the polarity of the surface and a corresponding slight decrease in the magnitude of dispersion-type forces. Oxidation was found to be the primary chemical effect of the corona treatment and the modifications were confined within very thin surface layers.[101]

As already mentioned, cellophane has a low permeability to air, grease and bacteria, which makes it useful for food packaging. Cellophane films are often laminated with thermoplastics, such as polyethylene films, to further improve its protective properties, e.g. water and moisture barrier properties. However, the hydrophobic plastic matrix is inherently incompatible with the hydrophilic natural polymer. Therefore, surface treatments, including plasma and corona treatments, have been performed and evaluated by numerous authors.[1,102–104]

Viscose is a regenerated cellulosic fibre widely used in apparel, home furnishing and industrial materials.[12] Its characteristics include relatively low resiliency (particularly when wet), high moisture absorption, and soft hand. Viscose can be in either filament or staple form, and warp yarns must be sized before weaving to increase weavability. In general, a larger amount of size is used for viscose or viscose blends than for cotton yarns, and the size must be removed by wet processing prior to dyeing and finishing of the

woven fabrics. From the chemical processing point of view, viscose requires a more careful treatment than, e.g. cotton, as it is more susceptible to chemical attack.[105] Since plasma treatments do not involve as large quantities of chemicals and water as conventional desizing, it is preferable to use this technique to desize viscose. Air–oxygen–helium and air–helium atmospheric-pressure plasma treatments were employed to desize polyvinyl alcohol (PVA) on a viscose fabric.[10] Both plasma treatments were able to remove some of the PVA on the viscose fabric and increase PVA solubility in cold water, resulting in higher weight loss in cold washing. The efficiency of the treatments increased with increasing treatment time. Plasma treatment followed by one cold and one hot wash had the same effect as conventional chemical treatments followed by two cycles of cold and hot washing. In addition, the atmospheric plasma did not have any negative effect on viscose tensile strength.[10]

Information on the adhesion characteristics (interfacial shear strength) of RF-oxygen plasma-treated viscose fibres and polyethylene have been obtained by using single-fibre fragmentation estimations evidenced by shear strength values and birefringence patterns.[62] It was found that the oxygen plasma treatments enhanced the interfacial shear strength and critical fibre length considerably. Fibre fragmentation occurs in a matrix until the critical fibre length is reached by fragmentation (i.e. when the fibre is too short to bear the load). It was demonstrated that the plasma-generated relative surface atomic composition (surface chemistry), surface energetics (dynamic contact angles) and surface topographies (SEM analyses) do not improve the adhesion. Instead, the enhanced adhesion was related to the covalent bond formation between the fibre and the matrix, a mechanism which was suggested to be mediated by hydroperoxide groups generated under oxygen plasma condition.[62] However, this theory has been questioned since the development of cross-linking reactions and the formation of covalent bonds between interfaces are difficult to relate only to the presence of hydroperoxide functionalities evaluated by SO_2 tagging. This is due to the fact that trapped free-radical sites also react spontaneously with sulphur dioxide.[1]

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