11
Plasma treatments of fibres and textiles

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11.1   Introduction

Cold plasma technologies have found extensive application in material processing for over 30 years and they are now widely used in the manufacture of semiconductors, magnetic media and special glasses, and for metal coating, etc. The success of these techniques is related to their ability to change the surface properties of a material by physical or chemical modification of its most external layers ($\leq 1\,\mu m$), without modifying its bulk characteristics. In this way, reengineering of surface chemistry can open completely new fields of application to conventional polymers.

If we consider that, in many cases, the use of textiles is mainly determined by their surface properties, as a consequence of their very large specific areas, and that the traditional finishing methods usually involve high energy consumption, large amounts of chemical substances, frequently toxic or noxious, or use of organic solvents, as well as production of liquid and gaseous effluents which require expensive purification treatments, cold plasma processes seem to be very suitable for application in the textile industry. In fact, they are 'dry' processes; the amounts of chemicals required is very limited; in many cases the expected results are obtained just by using air, nitrogen, oxygen or other 'inert' gases. Moreover, they are rapid, extremely versatile and work at room temperature, thus limiting the amount of energy necessary for heating water or for inducing chemical reactions, typical for conventional processes, and can be applied to all kind of textiles, even to such delicate natural fibres as silk. All these points have induced, since the 1970s, a strong interest by various research groups, both academic and industrial. However, due to a multiplicity of factors, which will be discussed later in this chapter, plasma has not found the same success in the textile sector as it has in other industrial sectors.

On the other hand, the growing concern of final consumers and public authorities for environment and health aspects, the increasing requests for high-performance textiles, the extension of the use of textile materials to

new sectors (building, geotextiles, medical uses, etc.) with special exigencies, has stimulated, during the last decade, a renewed interest for these technologies. Nowadays, plasma treatments are used in specific textile market niches, but it is easy to forecast their adoption also for products intended for wider markets.

11.2   Principles of plasma processes

A commonly accepted definition of plasma is: a partially ionised gas composed of highly excited atomic, molecular, ionic and radical species, as well as photons and electrons. Plasmas are generally classified as thermal or non-thermal. Thermal ('hot') plasmas are characterised by a condition of thermal equilibrium between all the different species contained in the gas. In fact, if the gas density is sufficiently high, the frequency of collisions between electrons, ions, and neutral species composing the plasma is such that an efficient energy exchange is possible. In thermal plasmas, temperatures of several thousands degrees are reached. It is clear that these plasmas are, intrinsically, of a destructive nature and no material can stand their action.

Contrary to thermal plasmas, non-thermal plasmas are 'cold' plasmas and are produced at room temperature or a little above room temperature. In this case, electrons acquire higher energies than ions and molecules, their energies ranging from 0.1 to some electron volts, and, due to the low density of the gas, collisions with the other species are relatively rare and thermal equilibrium is not reached: the bulk temperature of the gas is comparable to room temperature. Electron collisions with neutral species produce additional electrons and ions. Thanks to the low operating temperatures, cold plasmas can be put in contact with any material, even delicate textiles, without problems.

Different types of cold plasma can be described:

* *Glow discharge*: This is obtained at low pressures, typically less than 10 mbar. The plasma is generated by antennas, fed with electromagnetic fields at frequencies of 40 kHz or 13.56 MHz or microwaves (2.45 GHz).
* *Corona discharge*: This is obtained at atmospheric pressure by applying d.c., low frequency or pulsed high voltage between two electrodes of very different sizes. The corona consists of a series of rapid, non-uniform, non-arcing discharges. Plasma density drops off rapidly with increasing distance from the electrode.
* *Dielectric barrier discharge*: This is an atmospheric-pressure plasma source. In this case a pulsed high voltage is applied between electrodes, one or both of which is covered by a dielectric layer. The purpose of

the dielectric layer is to terminate rapidly the arcs that form in the region between electrodes. The discharge consists of series of rapid microdischarges.

- *Atmospheric pressure plasma jet (APPJ)*: This a non-thermal, atmospheric pressure, glow discharge plasma produced in continuously flowing gases (Park, 2000).

The interaction between the very active chemical species (and photons) present in the plasma gas and a substrate is the basis of all industrial applications of the above technologies. As a consequence of the very complex and non-equilibrium nature of cold plasmas, a multiplicity of very different phenomena can occur, depending on the nature of the gas and the operating conditions (Figure 11.1). Being interested in textile plasma processing, our attention will be limited to polymeric materials.

- **Cleaning** or **etching**: For such a phenomenon to occur, 'inert' gases (Ar, He, etc.), nitrogen or oxygen plasmas are typically used. The bombardment of the substrate with the plasma species causes the breakdown of covalent bonds. As a consequence, detachment of low molecular weight species (ablation) takes place. In this way, contaminants or even thin layers of the substrate are removed, producing extremely 'clean' surfaces, modifications in the surface area, or controlled reduction of weight of the exposed substrate.
- **Activation**: Interaction with plasma may induce the formation of active sites on the polymer surface (radicals or other active groups, such as
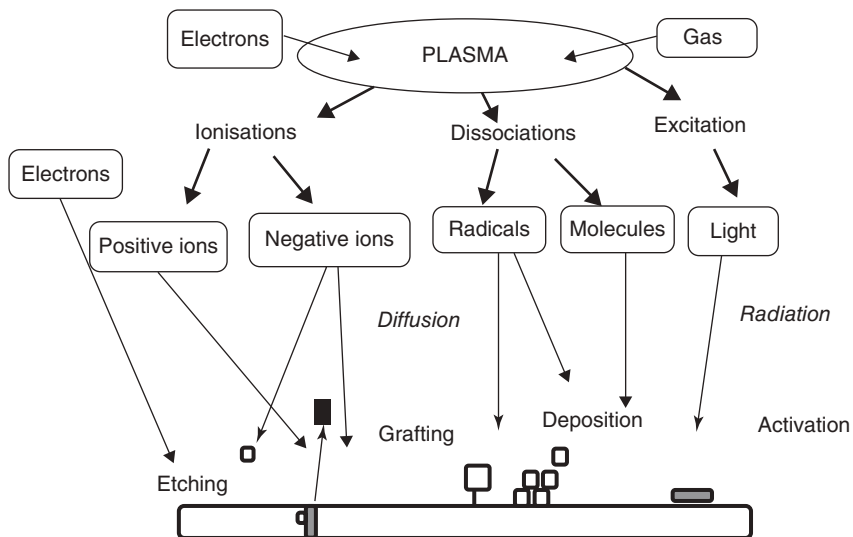
11.1 Cold plasma process.

hydroxyl, carboxyl, carbonyl, amine groups), which can give rise to chemical reactions, not typical of the untreated material, with substances brought in contact with the material after plasma processing.

- **Grafting**: Radical species present in the plasma may be directly grafted onto the polymer surface.
- **Polymerisation**: by using specific molecules, a process known as plasma-enhanced chemical vapour deposition (PECVD) may occur. These molecules, activated in the plasma, may react with themselves forming a polymer directly on the surface of the substrate. Depending on the different experimental conditions, chemically unique, nanometric polymeric coatings are obtained and chemical, permeation, adhesion and other properties of the starting material can be dramatically modified.

All these phenomena are limited to the most external layer of the substrate. Normally, the effects do not involve layers deeper than 10–100 nm. However, it must be noticed also that ultraviolet (UV) or vacuum ultraviolet (VUV) radiation (with wavelength <200 nm) is an important component of plasma. VUV radiation can give rise to a variety of photochemical interactions with the substrate, such as bond breakage and formation of free radicals, reaching inner layers (>10 nm) depending on the absorption coefficient of the substrate (Molina, 2003).

11.3   Plasma textile treatments

Plasma treatments of textiles, especially in the last ten years, have been extensively studied. A very large number of papers has been published and patents registered on this subject, all focussing on different aspects of plasma processing, such as:

- Generators and experimental set-ups
- Gas composition
- Types of textiles
- Plasma treatments for textile finishing
- Product innovation.

It is practically impossible to review such an amount of information in a thorough way. Therefore, only a general classification will be attempted, starting from the nature of the modifications that may be produced on textile materials. It should be kept in mind that, thanks to the high reactivity of the plasma environment, special results can be obtained on all textile materials:

- *Enhancement of both hydrophilic and hydrophobic properties.* This is one of the most widely studied plasma applications. Oxygen, ammonia,

air, nitrogen, etc. plasmas have been used to increase the wettability of synthetic polymers (PA, PE, PP, PET, PTFE, etc.), while hydrophobic or oleophobic finishing of natural fibres (cotton, wool, silk, etc.) has been obtained by using siloxanes, perfluorocarbons, SF_6, acrylates, etc.

- *Adhesion promotion.* Good adhesion between fibres and matrix is essential in the production of composites and laminates. Plasma treatments can increase markedly the surface energy of synthetic fibres, improving the mechanical characteristics of the final products.

- *Dyeing and printing.* Several studies have shown that dyeability or printability of textiles can be markedly improved by plasma treatments. This effect can be obtained on both synthetic and natural fibres. Capillarity improvement, enhancement of surface area, reduction of external crystallinity, creation of reactive sites on the fibres and many other actions can contribute to the final effect depending on the operative conditions. Also production of colours on fibres exploiting diffraction effects has been attempted.

- *Electrical properties.* Antistatic properties have been conferred to artificial or synthetic polymers. Moreover, studies have been carried out for the creation of fabrics with very high conductive properties, suitable for integrating electronic devices into fabrics.

- *Intelligent filtration properties.* Filtration of gases or liquids is one of the most common technical applications of fibres, fabrics or non-wovens. Appropriate surface functionalisation can enhance chemical selectivity of traditional filters based on more conventional adsorption/absorption or physical separation processes.

- *Other properties.* The extreme versatility of the plasma processes is shown by a very large number of investigations concerned with a wide range of different properties of great importance for textiles, such as flame retardancy, crease resistance, antimicrobic, antimicotic, biological compatibility, antifelting for wool, UV-protection, as well as 'hand' modification, softening and antipilling.

Even if plasma treatments, in principle, may apply to all substrates, a clear description of the applications of plasma technologies to textiles requires a more specific examination from the point of view of the nature of the treated fibres. Due to the extreme variety of textiles, attention will be focussed on the most used materials and on synthetic fibres and silk in particular. As stated before, the number of papers dealing with plasma treatments of all types, and on practically all textile materials, is enormous and it is impossible to give an exhaustive report of all. Only a short survey will be attempted, trying to give a general picture of the state of the art of the research in this field. Table 11.1 reports a summary of some of the properties that plasma treatments can impart to material textiles.

Table 11.1 Some properties of textile materials that can be modified by plasma treatments

Property	Material	Treatment
Wettability	Synthetic fibres	Oxygen, air, NH_3
Hydrophobicity	Cellulosic fibres, wool, silk, PET	Fluorocarbons, SF_6, siloxanes
Dyeability	Synthetic fibres, wool, silk	Oxygen, air, nitrogen, argon, SF_6, acrylates
Flame retardance	Cellulosic fibres, synthetic fibres	Phosphorus compounds
Softness	Cellulosic fibres	Oxygen
Wrinkle resistance	Wool, silk, cellulosic fibres	Nitrogen, siloxanes
Antistaticity	Synthetic fibres	Chloromethylsilanes, acrylates
Adhesiveness	Synthetic fibres, cellulosic fibres	Air, oxygen, nitrogen, argon, acrylates
Antibacterial, antimicotic	Cellulosic fibres, synthetic fibres	
Bleaching	Wool	Oxygen
Antifelting	Wool	Oxygen, air

11.3.1 Synthetic fibres

In the field of synthetic fibres, plasma technologies have been mainly used for increasing hydrophilicity, conferring antistatic properties, improving dyeability and printability, as well as promoting adhesiveness for the preparation of composites and laminates.

Polypropylene (PP) is a widely used material, especially for technical applications. In many cases, an improvement of its hydrophilic properties would be quite useful; for instance, PP non-woven filters can be permeable to water only when high pressure is applied. The introduction of hydroxyl, carboxyl, carbonyl, amino groups by air, oxygen, nitrogen or NH_3 plasma can produce a very large increase in wettability. Both atmospheric and vacuum plasmas have been used (Sparavigna, 2002). The same effect is produced on all kinds of synthetic hydrophobic fibres such as polyethylene (PE), poly(ethylene terephthalate) (PET), polytetrafluoroethylene (PTFE), polyamides (PA), and so on. Usually the treated samples show also an improvement in antistatic and adhesive properties (Hautojarvi, 2000; Yip, 2002). Some experimental data of water contact angles are reported in Table 11.2 (Sparavigna, 2002).

The behaviour changes observed after oxygen plasma treatments are due to the formation of new polar groups on the surface, such as carbonyl

Table 11.2 Effect of air plasma treatment on water
contact angle of some synthetic fibres

Material	Water contact angle	
	Untreated	Air plasma treated
PP	87°	22°
PE	87°	42°
PA	63°	17°
PET	71°	18°
PTFE	92°	53°

(Sparavigna, 2002)

($>$C$=$O), carboxylic (—COOH), hydroxyl (—OH), and peroxide (—COO—R) groups. Nitrogen containing plasmas give rise to amino (—NH$_2$), imino (—CH$=$NH), cyano (—C$\equiv$N) groups. Moreover, plasma induces the activation of the surface, thus producing further carbon, oxygen and nitrogen functionalities as a consequence of the reactions of the activated layer when put in contact with atmospheric air. This effect is particularly evident on samples treated with inert gas plasmas (Denes, 1997).

The poor dyeability of PP and PE fibres, as well as many other fibres such as aramidic fibres, is one of the problems which impair a wider use of these fibres in non-technical textile sectors. It is well known that only the introduction of disperse dyes for coloration of PET opened an immense market to this fibre, so that now the production of synthetic fibres has overtaken that of natural fibres. Analogously, poly(acrylonitrile) (PAN) found good access to the market only when, instead of homopolymers, functionalised copolymers were used, so that dyeing with basic dyes could be carried out according to conventional methods.

As stated previously, plasma treatments are able to increase wettability of synthetic polymers in a dramatic way and are able to create specific reactive groups on the surface. These facts have been exploited to increase dyeability. In particular, PET, PA, PP have been the main object of interest. For PET, good results have been obtained with oxygen or air plasmas. An increase of colour depth with respect to untreated samples of up to 60% (Urbanczyk, 1983; Sarmadi, 1993; Yoon, 1996; Kan, 1998; Barni, 2005; Raffaele-Addamo, 2006) was observed. Interesting results have also been obtained, using argon plasma, for aramid fibres, where the increase in depth of shade seems to be due to a decrease in reflectivity of the surface as a consequence of the formation of micro/nanocraters (Kobayashi, 1995). Even if many research groups, working under widely different experimental conditions, have obtained remarkable dyeability increases, the reasons for

such behaviour are still the object of some discussion. Modification in crystallinity of the external layer of the fibres (Okuno, 1992), increase in surface area brought about by ion bombardment, increase of polar interactions between polymer and dyes, creation of active sites, simple optical effects due to a lower reflectivity of the polymer, have all been proposed in order to explain the experimental results. Probably, attribution of the observed behaviour to one single cause is not realistic. On the other hand, an increase of hydrophobicity may also be of great interest for special applications. PET fibres have been shown to increase adhesion strength to a PE matrix from 1 to 2.5 N/mm using an ethylene plasma (Höcker, 2002). Siloxane, perfluorocarbon, SF_6 have given very interesting results. The low resistance to hydrolysis of polyaramid fibres can be markedly reduced by application of a hexafluoroethene/hydrogen plasma, which creates a hydrophobic diffusion barrier layer at the surface of the fibre.

Grafting of vinyl monomers has also been the object of many studies for a very wide range of applications. This method, in fact, opens the way to the introduction of special functionalities with extremely diversified reactivities. Yarn or fabric properties can thus be re-engineered according to a specific project for special uses (Oktem, 1999; Hochart, 2003; Liao, 2004; Möller, 2006). Incorporation of vinyl monomers can be achieved following two different approaches. In the first, the fabrics are directly treated in a monomer plasma, while in the second, preliminary argon, or other non-depositing gas, plasma treatment is performed in order to activate the surface by producing active sites, and, immediately after treatment, the fabric is put in contact with monomer vapours or immersed in a bath containing the monomer. The second of these procedures has been the most studied. According to this method, flame-retardant properties (Shi, 2000), reduction of resistivity, modifications in wettability, dyeability, adhesivity, etc. have been given to synthetic fibres (Bhat, 1999; Tyan, 2002, Tyan, 2003, Cai, 2003).

The demand not only for antistatic textiles, but also for electrically conductive textiles, is rapidly growing for a number of applications, such as electromagnetic shielding materials, building materials and smart textiles. Introduction on the substrate surface of basic functionalities has been found to be very effective for promoting metal–fabric adhesion (Šimor, 2003). Very short contact times (0.1 s) have been shown to be sufficient for optimum results (Charbonnier, 1996). Plasma treatments have been also been used to promote compatibility with organic conductors, such as polythiophene, polyaniline and polypyrrole (Oh, 2001).

Grafting of various silane monomers has imparted to synthetic fibres increased thermal stability, scratch or crease resistance and colour depth (Akovali, 1990; Ganapathy, 1966; Lee, 2001). Air plasmas have been found to be very effective for sterilisation of PP non-woven fabric structures

(Kang, 2004). Bacterial proliferation on synthetic fibres is the object of strong interest not only for biomedical applications, but also for avoiding formation of bad smell or fibre degradation (Kim, 2002). The bacterial inactivation efficiency of silver metal and oxides is very well known. Ag-loaded PET-PA fabrics with very good permanent antibacterial properties have been prepared by activation with RF air plasma treatment followed by chemical reduction of silver salts (Yuranova, 2003). Acrylic acid grafted on PP activated by oxygen low-pressure plasma has been used as a support to promote chitosan immobilisation on the fibre through formation of amine bonds. The modified PP non-woven fabric showed marked antico-agulation and cell-adhesion properties (Tyan, 2003).

11.3.2 Cellulosic fibres

Cotton is one of the most used substrates for studying the application of plasma treatments to textiles. Low temperature plasmas of air, argon and oxygen are able to increase strongly water absorption, soil release, drying rate, crease resistance properties, but do not improve markedly the dye-ability of cotton (Goodman, 1960; Stone jr, 1962; Ward, 1979; D'Agostino, 1982; Benerito, 1981; Wakida, 1989; Chen, 1991; Chen, 1996).

Cotton fabrics treated with plasmas of fluorocarbon gases, such as tetra-fluoromethane (CF_4), tetrafluoroethane/hydrogen or hexafluoropropene (C_3F_6), show a strong increase in water contact angles and wet-out times (McCord, 2003; Zhang, 2003). Very good results were also obtained with SF_6 plasma (Raffaele-Addamo, 2003). In this case, direct binding of fluorine atoms to cellulose polymer chains occurs. The resulting effects are quite stable. Treatment with hexamethyldisiloxane (HMDSO) leads to a very strong hydrophobisation effect with a water contact angle of greater than 130° (Höcker, 2002).

In order to enhance dyeability, good results can be obtained by introduc-ing onto cotton cationic functionalities, so reducing the negative zeta-potential in water. Ammonia or other amine substances, such as ethylenediamine (EDA) or triethylenetetramine (TETA), have been used (Kamel, 1998; Blanchard, 1999; Ozdogan, 2002).

Surface activation and subsequent grafting of acrylic monomers on cel-lulosic fibres has been the object of many investigations (Zubaidi, 1996; Bhat, 1999; Andreozzi, 2005). Grafting of acrylamide was found to reduce significantly the surface resistivity of cotton, marginally increasing water absorption, while use of acrylonitrile monomers led to a slight increase of surface resistivity (Bhat, 1999). Use of vinyl laurate monomer gives rise to very high water repellence properties which induce strength losses much lower than those experienced with traditional resin finishing (Abidi, 2004; Abidi, 2005).

A further stage of cotton processing where plasma technologies can find useful applications is desizing. Atmospheric air, air/He and, especially, air/O_2/He plasma etching, followed by hot water washing, was found to be very effective for complete removal of polyvinyl alcohol (PVA), used as sizing agent, without affecting fabric properties. The positive action is due to breakdown of PVA molecular chains, thus facilitating swelling and dispersing in water (Cai, 2003).

11.3.3 Wool and silk

Wool was one of the first fibres for which industrial application of plasma technologies were attempted. In fact, the first patent describing a corona treatment on wool goes back to 1956. The main object of study is shrink-proofing of wool (Rakowski, 1996).

Air or oxygen plasma treatments, either at atmospheric and low pressure, have proven very effective in conferring antifelting properties to wool fabrics, even if, at the present state of research, the quality and durability of the fabrics treated by the chlorine/Hercosett method are still superior under various aspects. In particular, plasma-treated fabrics show a harsher hand, a decrease of tear strength and often an unpleasant odour that must be removed by subsequent washing. The latter effect is probably due to oxidation of wool fatty substances. Post-application of some silicone polymer softeners or resins can overcome these drawbacks and can further improve dimensional stability and wrinkle resistance (Kim, 2002) reaching quality levels not inferior to the chlorine/Hercosett system. Electron spin resonance (ESR) studies have shown that nitrogen, air and water vapour plasma treatments of wool produce two new signals, attributable to an organic (carbon or oxygen) radical and to a nitrogen radical (consistent with nitroxide radicals) whose central band is overlapped by the organic radical. No sulphur radical formation was detected (Molina, 2003).

Air and nitrogen plasmas produce significant effects on wool dyeing with acid dyes. Increased dyeing kinetics, improved bath exhaustion and enhanced depth of shade have been observed (Höcker, 1994). Formation of additional amino groups is likely to be at the origin of the phenomenon (Holme, 2000).

As far as silk is concerned, the number of studies regarding this fibre is much more limited. Nitrogen plasma induces formation of microcraters on the surface of the fibre if the treatment is carried out under relatively drastic conditions, while no effect is visible by scanning electron microscopy for short contact times (less than 1 min) or lower RF power (less than 50 W). However, even very short contact times induce large increases in colour depth (more than 30%) upon dyeing with acid dyes. This effect decreases with increasing exposure times. However, dye absorption in plasma-treated

samples was always greater than in untreated ones under the experimental conditions adopted (Massafra, 1996). Tetramethyldisiloxane (TMDSO) and TMDSO/O_2 plasmas give rise to a layer of silicon polymer or silica deposited over the surface of the fibres which, under the experimental conditions adopted, makes fibroin insoluble in conventional silk solvents (saturated LiBr solution) and improve significantly wrinkle recovery and flame resistance properties. Acid dye absorption is slightly increased in TMDSO plasma treated samples while it is slightly reduced by using TMDSO/O_2 plasma (Massafra, 1996).

Water repellence is produced, both on wool and silk, by fluorinating plasmas, such as SF_6 or fluorocarbons (Selli, 2001b; Chaivan, 2005). Water contact angles comparable (>130º) to those of polystyrene, poly(tetrafluoroethylene), silicone, etc. can be obtained with short treatment times, but the results are strongly influenced by the experimental conditions. It is interesting to note that the most hydrophobic samples reveal also an increase in surface fibroin crystallinity and in microroughness. Probably fluorine implantation is accompanied by etching, especially of the surface amorphous polymeric regions. The samples that show such a combination of effects are also characterised by the greatest increase in water contact angles and a longer stability of the water repellence properties.

Air and oxygen plasmas have also been used as a pre-treatment in the silk degumming process. The time necessary to remove completely sericin was dramatically reduced, both in the case of the traditional Marseilles soap bath method and in the case of the high-pressure water bath technique.

11.3.4 Influence of operative conditions

Even if the short survey reported above shows that plasma processing has all the characteristics for being successfully and profitably employed in textile manufacture, nevertheless textile industrial applications are still far from being common. Many factors are at the origin of this fact. When dealing with plasma treatments, it should be kept in mind that the effects obtained in practice, even on the same substrate, depend on a multiplicity of factors and not only on the gas used. The experimental set-up plays a major role. Variations in gas pressure, frequency and power of the generator, geometry of the electrodes and of the reaction chamber, treatment time, and so on, can affect the results in an extraordinary way. Plasma chemistry is extremely complex and cold plasmas are in a non-equilibrium state. Plasma is a state of matter, just like the liquid state, and cannot be considered as something exactly defined simply by its macroscopic composition. In order to obtain reproducible and predictable results, it is necessary to have a good knowledge of the nature of the reacting species present in the plasma, their concentrations and space distribution inside the reactor, as

well as of the reactivity of the various species with the substrate. Some examples can be described to clarify this point.

As cited above, radio frequency (RF) low-pressure SF_6 plasma treatment is known to increase hydrophobicity of polymer surfaces (Riccardi, 2001; Selli, 2001a; Cruz-Barba, 2002; Raffaele-Addamo, 2003; Ranger, 2003; Barni, 2005). As shown in Figure 11.2, enhanced hydrophobic properties of PET could be observed only at pressures higher than 0.2 mbar. At lower pressures, on the contrary, a very sharp transition occurs and an unexpected increase in hydrophilicity takes place. If RF power or treatment times are changed, the above effects both increase, hydrophilicity under 0.2 mbar and hydrophobicity above that threshold limit (Figure 11.3). SF_6 plasma treatment can also produce modifications of dyeability of PET, as happens with other gases (air, argon, oxygen, etc.), but here again a strong increase of dyeability at low pressure and a decrease at higher pressures is observed (Figure 11.4). In the case of PET, dyeability has been related to hydrophilicity and/or increase or microroughness and surface area. The explanation of the observed phenomena is relatively simple only if a careful diagnostic of the plasma has been carried out and discharge local properties and prevailing reactions with polymer surface have been characterised.

Hydrophobicity is produced by fluorination of the polymer. The reactive species are fluorine atoms. Under relatively low pressure, the ionisation degree is higher and the surface is mainly affected by collisions with electrons and ions. Thus, etching and activation processes are prevalent, leading to an increase in surface area and formation of hydrophilic functional groups. Under higher pressures, the mean free path of electrons and ions is lower; the number of collisions with the surface and impact energy are
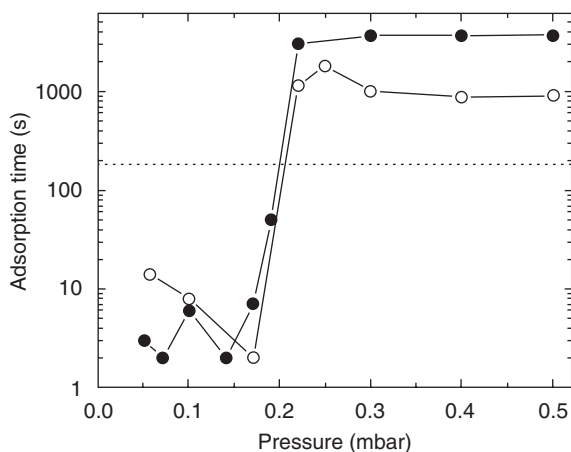
11.2 Water droplet adsorption time values of SF_6 plasma-treated PET samples at different pressures (• 100 W ○ 50 W).
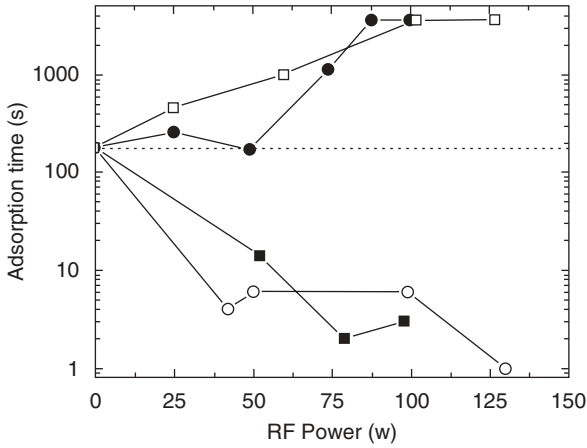
11.3 Water droplet adsorption time values of SF_6 plasma treated PET samples at different RF power (■ 0.05 mbar ○ 0.10 mbar ● 0.22 mbar □ 0.40 mbar).
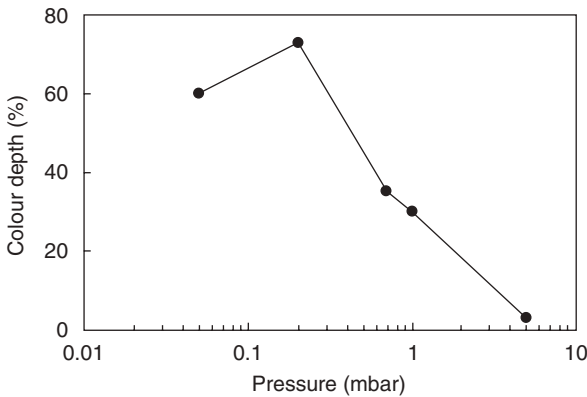
11.4 Percentage increase of colour depth of PET fabrics dyed after air plasma treatments at different pressures.

reduced. Fluorine grafting is now prevailing and surface area is comparable with that of untreated samples.

Also, the distance of the substrate from the electrodes can influence strongly the result, as well as can the form and size of the reactor, as a consequence of the variations in spatial distribution of reactive species.

Moreover, textiles are very complex materials. The textile production chain is very long and, usually, the operators of any single stage are not fully aware of the treatments previously undergone by the material they are working on. Therefore, the substrates can introduce into the plasma chamber

unexpected substances in unexpected quantities, which can modify substantially the final effects. Laboratory tests are usually carried out on carefully cleaned, washed and dried materials and do not take into account possible interferences brought about by the presence of contaminants. Even water can be considered, in some cases, as a contaminant and alter the results. Moreover, the structure, the weight and the texture of the treated material can markedly change the results when operating under the same experimental conditions.

Nowadays, in the textile field, atmospheric plasma treatments seem to attract more interest because they avoid complications and costs connected with vacuum production and greater possibilities of in-line continuous application. Corona discharge and, from the 1990s, dielectric barrier discharge and APPJ have been objects of great interest. However, all these processes, in different degree, produce less uniform effects and, usually, are not as rapid as vacuum processes. Furthermore, if the gas to be used is not simply air, the costs of reagents increase significantly. In any case, good knowledge of plasma chemistry and physics is still necessary in order to obtain the desired results.

11.4 Advantages and problems of plasma treatments for textiles

As has been demonstrated, plasma treatments of textiles look very promising. They can be used both in substitution of conventional processes and for the production of innovative textile materials with properties that cannot be achieved via wet processing. They are applicable, in principle, to all substrates, even to those that cannot be modified by conventional methods. In general, no significant alteration of bulk properties is produced. They are fast and extremely gentle, as well as environmentally friendly, being dry processes characterised by low consumption of chemicals and energy. When they cannot replace an existing wet process (dyeing and some finishing), if used as pre-treatments, they can reduce markedly the amount of chemicals required by the process and the concentration of pollutants in the effluents.

Nevertheless, the application of plasma treatments to textiles is still limited to technical products. Several explanations can be given. As specified above, correct application of plasma processes requires a good knowledge of the physical and chemical nature of plasmas, especially if the treatments have to be applied to different materials, as is the normal case for most textile small and medium enterprises. Therefore, skilled labour is required, which is, however, not generally available either in textile or in textile machinery companies. Without the capacity to understand the nature of the problems that can occur and to adopt the relevant correct actions,

plasma treatments may lack reproducibility and give rise to disappointment and delusion. Moreover, the very wide variety of plasma technologies makes it difficult to decide which is the best solution to be adopted.

As a second point, the offer of machinery is still limited and those on the market are not flexible enough to obtain good results in a relatively large range of possible applications. A strong effort should be made by machinery producers in order to really push this technology.

Finally, capital investment and processing costs must be carefully considered. Vacuum plasma reactors are considerably more expensive than atmospheric ones and, at the present stage, they cannot be integrated into a continuous line. However, they are more controllable, flexible, adaptable to new productions and require much smaller amounts of chemicals. A fast pay-off of the investment costs is possible only if something completely new and well-accepted by the market is produced. Substitution of conventional finishing treatments with plasma treatments has much longer pay-off times, especially if water, energy and waste treatment costs are not exactly taken into account. In Table 11.3 a schematic comparison of the characteristics of plasma and conventional processes is reported.

It should also be considered that the textile productive chain is very complex and is made of a great number of extremely specialised small operators. Penetration by completely new technologies is always difficult and takes place on a large scale only when they have proven clearly their advantages in respect to traditional ones.

11.5   Industrial applications

Despite the difficulties and obstacles described above, other aspects are pushing in favour of plasma. The great advances of the last decades in the field of the science of materials are now ready to enter into the field of textiles and it is already possible to envisage that, in the next ten years, the clothing–textile industry will undergo a dramatic revolution. Smart textiles, completely new fibres (nanofibres, etc.), and new textile applications in unexpected fields can be expected. Also, our way to consider clothing is going to change completely. Environmental aspects are going to play a more and more important role. Under these perspectives, plasma processes are certainly going to supersede many traditional finishing processes.

Actually, today, many companies, especially for technical and special applications, have already adopted plasma technologies and the interest in plasma is growing at a very fast rate. Following this increasing attention of the textile world, many machinery manufacturers are developing new plasma machines of various types, which will soon be on the market. It is easy, therefore, to envisage that, in the near future, plasma technologies will become commonplace in the textile-clothing chain. As far as the present

Table 11.3 Comparison of plasma and conventional processes

	Plasma	Conventional
Solvent	Dry	Water (or organic solvents)
Chemicals	Gases in limited amounts	Large amounts
Type of reactions	Very complex and not well known	Simple and well known
Energy consumption	Limited for atmospheric-pressure plasma. Greater for vacuum plasma	High
Temperature	Room temperature	High temperature
Type of treatment	Surface treatment (<10–20 nm); no modification of bulk properties	Mass treatment or surface treatment (>100 nm); often modifications of bulk properties
Substrates	The same equipment can be used on all textile materials under different operative conditions	Different textile materials require different processes
Type of process	Batch (vacuum plasma) Batch or continuous (atmospheric-pressure plasma)	Batch or continuous
Equipment	Complex and in evolution	Simple and very well known
Competency required	High specialisation	Standard
Investment costs	High for vacuum plasma; lower for atmospheric plasma	Wide range of costs depending on the type of process
Waste treatment costs	Extremely limited	High

situation is concerned, certainly it is not possible to give an exhaustive view of all the industrial applications already at work in the world. So, only a short survey, principally limited to the Italian experience, will be reported here.

Air, oxygen and nitrogen low-pressure plasmas are mainly used. Increasing adhesion of chemicals or polymers to fibres and providing fabrics with marked hydrophilic properties leaving all the other properties substantially unaltered are, by far, the most important applications. Industrial plasma pre-treatments are currently used for the following finishing processes in order to improve the properties, the quality, and the useful life of the final products and to reduce the amount of chemical substances needed to obtain a certain effect:

- hydrophobic or oleophobic finishing of Nomex fabrics
- hydrorepellent finishing for polyamide fabrics for skiwear
- antibacterial finishing for microfibre lining of shoes
- flame-retardant finishing for home textiles
- coupling of polyester fabrics and polymeric membranes for surgical wear
- coupling of polyester fabrics and polymers for industrial tapes.

Plasma treatments as real finishing steps are also increasingly used, as mentioned before, for improving hydrophilicity, water vapour transfer, and drying rate properties of fabrics, all characteristics that can ensure clothing with very high comfort levels. The principal examples are:

- cycling polyester knitwear
- knitted underwear
- lining fabrics for overalls of Formula 1 racing car drivers
- shirts for Formula 1 teams
- jackets for workwear
- cycling shoe lining fabrics
- polyester fabrics for surgical applications.

The above list is far from being complete and new items could be added everyday.

11.6   Acknowledgment

11.7   References

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12

Characterisation of plasma-treated textiles

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12.1 Surface reactions in plasma treatment

Plasmas are energetic sources of radiation and chemical species, having a complexity of interactions with their surroundings. It is clear that the intense plasmas produced with highly energetic sources at high pressures in almost any gaseous environment will emit copious amounts of ions and electrons, radicals and excited neutral species, photons (from UV to IR), as well as heating their surroundings to high temperatures, and thus can cause severe damage to many materials. Low-pressure, low-energy plasmas are more benign but are still capable of damaging some materials that are exposed to them, and are indeed widely used to erode (etch) solids. Between these extremes are a variety of plasmas giving various fluxes of species with various energies. The possible effects produced by plasmas on textiles therefore range from heating to UV degradation, and from electrical charging to chemical alteration. Selection of an appropriate plasma system for a desired effect and its subsequent optimisation therefore requires some means of measuring this effect, and preferably monitoring some correlated feature of the plasma in order to give reliable control over the effect. If the material is to be coated by a plasma interaction, then it may be possible merely to measure the coating thickness with time, but a more subtle alteration of the surface properties may be extremely difficult to measure *in situ*.

Characterising a plasma-treated surface might involve determining any or all of the following: surface topography, chemical composition, mechanical strength, reaction to the environment (e.g. liquids, ultraviolet radiation) and durability. Fibrous materials have at least two 'dimensional scales' for which these properties may be measured: those for individual fibres and those for the conglomerate as a whole. Such fabric properties as drape will depend on the behaviour of individual fibres as they interact with each other across the whole material. However, a localised measurement of

surface properties, such as on a single fibre, may not indicate the overall behaviour of a group of fibres, alteration of whose behaviour may be the purpose of the plasma treatment. Similarly, there may be inhomogeneities in the treatment if the plasma or its active ingredients do not penetrate the fibre network beyond the uppermost exposed surface. Nonetheless, it has been shown that oxygen plasma etching of woven PET was not affected by the fabric texture (Kuvaldina, 2000).

12.1.1 Plasma emissions

To see the relative significance of these problems, we should now consider the emanations from plasmas, including radiation, charged and neutral species, and how these may affect the properties mentioned above.

The most obvious feature of a plasma is its luminosity, which can extend from microwaves to deep UV. However, the ordinary cold fluorescent light tube produces visible light by generating UV photons in a low pressure gas that are then absorbed by a fluorescent coating on the inner surface of the tube, emitting specific colours in the process. Plasma TVs operate by a similar mechanism. Although the electrons in this type of plasma are highly energetic ('hot'), they do not transfer much heat to the surroundings because of their low mass: the gas molecules in this type of plasma have much lower energies ('cold') and so also carry little heat to the surroundings. High intensity arc discharge lamps operate at high gas pressure, and both electrons and ionised gas molecules are hot, so that the lamp envelope becomes very hot from the energy the gas transfers to it. Both hot and cold lamps can be designed as efficient UV sources. Therefore, if similar conditions are present in processing plasmas, the material being treated will receive a high flux of photons, especially as the shortest wavelengths are not filtered out by the presence of a glass envelope between plasma and material, as they are for fabric exposed to fluorescent light tubes. The energies carried by UV photons from plasmas in some pure gases and simple mixtures (e.g. Fozza, 1998) are similar to those of chemical bonds in materials: a photon with energy ~5 eV (wavelength of ~250 nm) has greater energy than the O—H bond (~460 kJ mole^{-1}) or the C—H bond (~420 kJ mole^{-1}). Even the visible emissions are similar in photon energy to C—C bond strengths. Polymers that are degraded by long-term exposure to UV may therefore be damaged to some extent even by brief exposure to the highly energetic photons produced in plasmas; the actual cross-section for photon absorption is small and so a high photon flux is generally required for a significant amount of C—C and C—H cleavage. The effect may be mitigated by down-stream processing. Note that UV radiation will penetrate further into a material than the other plasma emissions (ions, electrons, radicals, etc.).

The electric fields that create plasmas do so by generating free electrons. Whilst the electron flux does not convey significant thermal energy to surfaces that are exposed to plasma, electrons do carry kinetic energy and electrical charge that may affect the material. Electrons can excite, ionise or dissociate molecules, and may induce desorption of atoms or molecules if these are only loosely bound to the surface of a material. Electron interactions will decrease with exposure time for an insulator, as it becomes negatively charged, so that electron-induced desorption is more significant for metallic surfaces. Examples of this type of desorption include hydrogen and CO from metals and semiconductors. If a sample does become charged from exposure to plasma, the energy released by a subsequent electrostatic discharge may generate sufficient heat to damage the material.

The free electrons in a plasma may ionise the gas or vapour, or cause a diatomic or polyatomic gas or vapour to dissociate, or may just create excited species from it. It is the transitions of bound electrons in atoms or molecules from excited states to lower energy states that produce the radiation seen from plasmas. (Not all such transitions radiate energy.) Most chemical effects from plasma treatment arise from the excited neutral species. These may be diatomic radicals, such as OH, CF_x, NH_x, or atoms such as H, O, F, N or polyatomic species such as higher hydrocarbons or ozone. An oxygen plasma may contain a mixture of ions and neutrals, such as O, O^+ and O^-, O_2^+ and O_2^-, O_3, and other active species, but the ions will be in a minority in most plasma conditions. Ions are encouraged in plasma etching, for instance of semiconductors, because they provide a directional beam on the sample that leads to anisotropic etching, through a combination of circumstances. Ions can, of course, sputter or ablate the surface layer by transferring kinetic energy to it. Compared with neutral species, ions may enhance the surface reaction kinetics. Thus the electrons and other species colliding with the surface of the material can create free radicals on the surface that will interact with the gaseous species to alter the surface of the material.

Although it is usually considered that the feedstock gas is the source of reactive species for plasma treatment of materials, there may be by-products from surface reactions that are vaporised and then either supplement or reduce the intended surface effect (e.g. oxygen plasma on wool can redeposit etched material if over-done: Molina, 2004). Almost inversely, it is possible for feedstock species to be implanted into the surface, even if these are chemically inactive: argon, in particular, is known to become embedded into some materials from plasmas, for instance during argon ion sputtering of another material from a solid target with the intention of coating the surface with this material alone. If these are ions, they may generate more damage in the material than would uncharged species.

12.1.2 Surface reactions

It is not commonly known which of these entities is responsible for altering any particular property of the material, and combinations of them are likely to be involved in many cases. Since a plasma is such an active soup of ingredients it is difficult to distinguish the influence of, say, the radicals from that of the neutrals, except in well-characterised cases. Although it is straightforward to monitor a particular wavelength of emission that may be known to arise from a particular electronic transition in a certain molecule (e.g. the strong green Swan band emission at 516 nm that comes from C_2 or the blue emission from CH or CH^+), the active ingredient in a particular plasma process may not have a radiative transition (e.g. CH_3 does not emit). Thus a plasma process for adding a carbonaceous layer may be controllable through an optical emission monitor if the process involves CH or C_2, but not if it relies on CH_3 unless some correlation has been proven first. If carbon-related emission is seen in a plasma when there are no carbon-containing gases, then this would indicate degradation of a carbon-containing fabric or the removal of carbon contamination from the surface, which is likely in energetic oxygen-containing plasmas.

Plasma deposition of a coating involves not only supplying the requisite mix of elements to the surface of the material, but also ensuring that it has active sites where these elements can bond. Attachment will occur by a balance of adsorption and desorption, often determined by the substrate temperature in physical vapour deposition, followed by surface diffusion and reaction. Each step will be affected by the plasma, and trouble-shooting an unsuccessful procedure by post-characterisation of the coating should attempt to discover which of these steps was ineffective. For instance, the balance of ions and radicals will affect the uniformity, structure and composition of the coating: the ion flux modifies the number of dangling bonds and the across-surface diffusion, and radicals can attach to dangling bonds or insert into the surface (Chang and Coburn, 2003). Complete characterisation of plasma deposition may require a chemical kinetics model, and for this the rates of the different processes and competing reactions must be known.

A frequent application of plasma treatment is to chemically functionalise the surface of organic materials, often by addition of OH, NH, CO, COOH, CH_x or CF_x groups. These can provide attachments for adhesives, biochemicals, or cells, without modifying the underlying structure of the material. The plasma abstracts hydrogen or breaks into the typical organic backbone without vaporising it into oligomers or monomers. Unless sufficient radicals are provided to attach to the break, it may cross-link with adjacent broken molecules. Over-exposing a polymeric fabric will risk damaging the surface so much that it is converted into short chains and vaporises. Plasmas

containing oxygen or CF are known to alter the surface morphology of some fabrics (e.g. polyester: Sarmadi, 1993; polyaniline–Nylon 6: Kyung Wha Oh, 2001; carbon fibre–PEEK composites: Jang, 2004) but successful treatments can still be produced on many fabrics if they are not over-exposed (e.g. cotton copolymerised with vinyl groups: Abidi, 2004; wool keratin fibres: Molina, 2003).

With the increasing interest in atmospheric pressure plasmas for textile and polymer treatment (e.g. for surface cleaning, surface energy modifica-tion, or texturing), it should be recognised that, in contrast to low-pressure plasmas, these systems are likely to have a lower concentration of ions, lower numbers of highly energetic species and a smaller flux of UV photons, but may heat up the substrates more (Shenton and Stevens, 2001). On the other hand, at these higher pressures, the plasma should be more able to penetrate the fabric interstices (M Simor *et al.*, 2003, De Geyter *et al.*, 2006). De Geyter and coworkers showed that medium-pressure dielectric barrier discharge plasmas in air do indeed penetrate into non-woven polyester at higher pressures, but the active species must diffuse through the fabric from a plasma existing above the surface at somewhat lower pressures: in both cases, the fabric's surface energy was increased by oxidation. Fluorocarbon plasma generated by a cascade arc torch has also been shown to penetrate into PET non-woven fabric (Krentsel, 2003).

These contrasting examples of the plasma influence on fabrics demon-strate the potential difficulty in determining the 'active ingredient' from post-treatment characterisation of the fabric.

12.2   Techniques for characterisation of plasma-treated textiles

The field of surface engineering has been growing in the last 2–3 decades, primarily as sophistication of surface treatments and their potential for providing enhanced functionality to near surface regions has improved. Modification of surfaces while maintaining bulk material properties has obvious attractions in engineering applications across a wide range of mater-ials from metals to ceramics to polymers. The current chapter is related to the plasma treatment of textiles – a surface modification methodology which has the potential to change functional characteristics such as wetta-bility (Lai *et al.*, 2006), biocompatibility (Nuutinen *et al.*, 2003), strength (Sun *et al.*, 2006), surface reflectivity (Kaless *et al.*, 2005) and dyeability (Costa *et al.*, 2006) – these changes being induced by modification of a range of physical (e.g hardness, modulus), chemical (e.g. bonding) and topo-graphical (e.g. roughness) properties.

Surface treatments of metals and other engineering materials are nor-mally conducted with the intention that the bulk material properties are

left intact. In some surface treatments, as a result of desired chemical changes there can be resulting physical changes and *vice versa*. Plasma treatment of textiles is known to induce chemical changes in the near surface regions and these can be due to incorporation of species in the surface or due to surface melting and resolidification – often these occur at conditions away from equilibrium. Characterisation of plasma-treated textiles requires techniques that will assess the above properties in the near surface region. 'Near surface' is a general description for the treated layer and, as will be described in this chapter, the analysis depth for various techniques defines '*near surface*'. The techniques for surface analysis will be divided into two main categories – those that assess physical and topographical properties and those that assess chemical properties.

## 12.2.1 Physical and topographical

Scanning electron microscopy

The scanning electron microscope (SEM) was developed in the 1930s and brought about a different way of imaging solids (Knoll, 1935). By 1965, the first commercial instruments were in general use and this represented a revolution in microscopy. Using electrons to focus, it has the benefit of providing a great depth of field as well as extremely high resolution images at magnification levels of in excess of ×10000. The SEM has been extensively used in analysis of the surface characteristics of plasma-treated textile fibres (Figure 12.1(a) and (b)) and woven materials. The information obtained from SEM is normally qualitative, simply providing an image of the surface at extremely high magnification. However, some software can be used to determine quantitative surface properties such as average roughness (R_a), rms roughness (R_{rms}) and fractal parameters.

A two-stage surface treatment process to graft acrylic acid functional groups on to plasma-modified poly(ethylene terephthalate)/polyethylene (PET/PE) was used by Chen and Chiang (2006) to increase biocompatibility. The post-test analysis involved examination of the fibroblast cell density on the fibre surface, detail that is routinely achievable with SEM. The curvature of the fibre surface and the cells adhered to the surface are clearly shown without loss of focus. There are numerous examples in the literature where SEM has been used to characterise surfaces treated by plasma processes; some recent examples are papers by Liu *et al.* (2006) on acrylic fibres, Lin *et al.* (2006) on nylon fabrics and on polyester fabrics by Costa *et al.* (2006).

A very important development in SEM came in the 1990s when the first environmental SEM was developed. This was an important technological advance in the area of polymer science, given the restrictions in SEM for

(a)
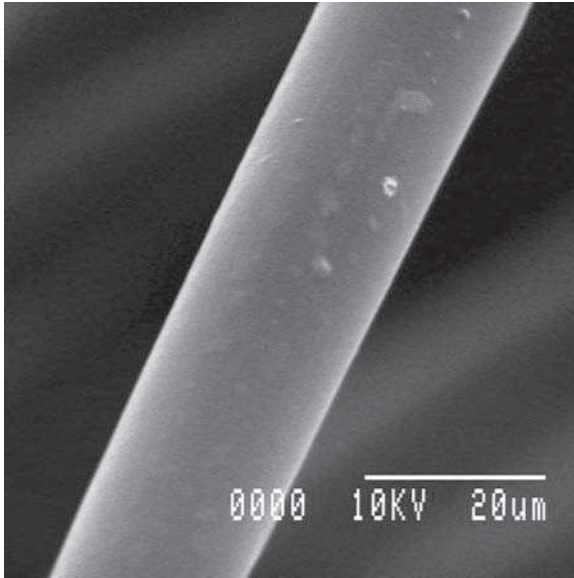
(b)
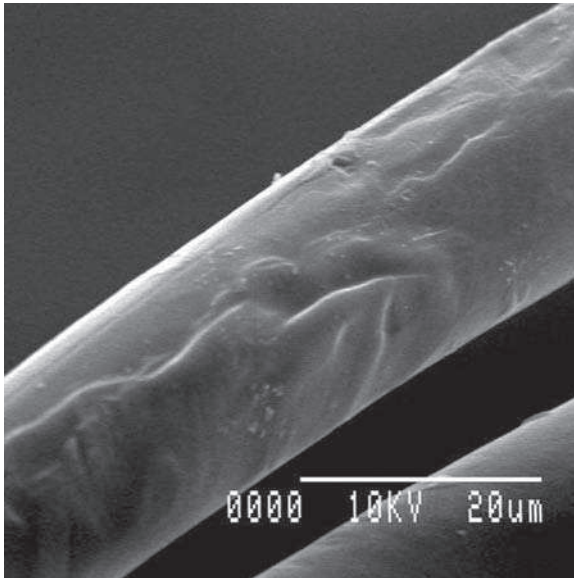
12.1 (a) SEM image of untreated PP fibre (b) SEM image of introgen treated PP fibre. (Courtesy of J. Warren, Heriot-Watt University.)
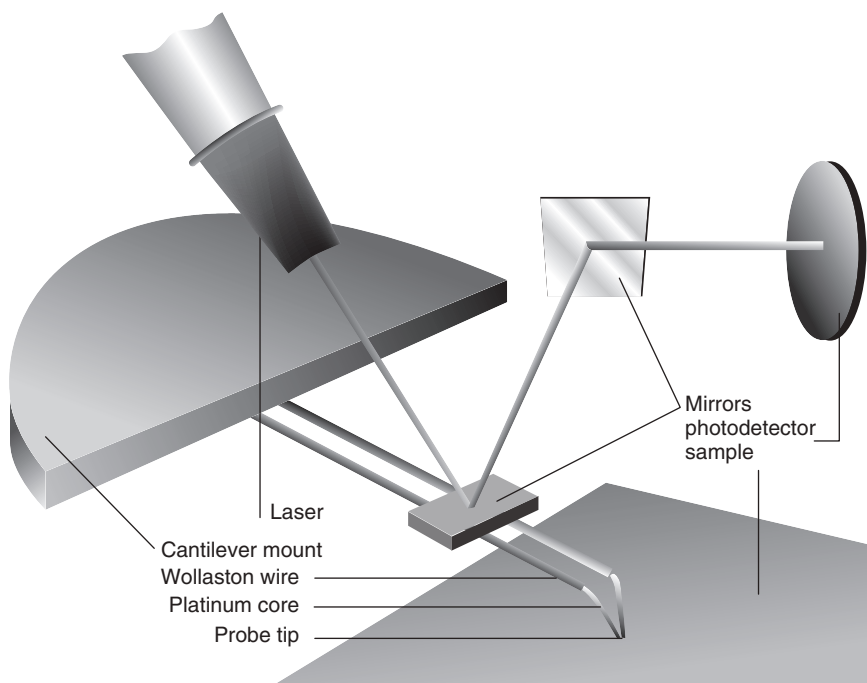
analysis of non-conducting samples. For examination of polymers using SEM, there is a need to apply a very thin sputtered layer of a metallic coating (normally gold) to provide a path for the discharge of electrons. Without this, the surface 'charges' and the image quality is extremely poor. With the introduction of ESEM, the need for coating was reduced, and sometimes eliminated, since the accelerating voltage could be reduced. The ESEM operates at much higher pressures than conventional SEM, which also brings benefits in terms of the ability to conduct experiments *in situ*. In the area of plasma treatment of textiles, the potential for observing the changes in the surface wettability by measurements *in situ* was realised by Hocker, 2002.

Atomic force microscopy

The development of the scanning tunneling microscope in 1981 earned Binnig and Rohrer the Nobel prize for physics. Scanning tunneling microscopy is one of the family of scanning probe microscopies (SPM) of which atomic force microscopy (AFM) is by far the most commonly used for analysis of plasma-treated textiles. Based on a relatively simple concept, the AFM has been partly responsible for the nano-revolution in materials science. Figure 12.2 shows the arrangement of the AFM. It comprises a scanning probe, with a tip (which is typically Si_3N_4) at the end of a cantilever. The probe is made to scan in the very near surface region (in the van der Waals forces) of a surface and an intricate control system enables the tip to follow the contours of the surface in great detail. Imaging of individual atoms has been possible, although in most applications this level of resolution is not normally required.

The AFM and other variants of the scanning probe techniques which emerged in parallel, or have been derived from, AFM have enabled unprecedented levels of detail to be reached on numerous surfaces across many fields of science. One major benefit of the AFM is the ability to image surfaces without the need for any complicated surface treatment process. It is a technique that can be used in air, and also imaging can be done in water, which makes it of particular usefulness in studies where the effect of liquids on surface structure (e.g. by swelling) are assessed. Crossley *et al.*, 2000 reported changes in the near-surface mechanical properties of wool when exposed to solvent cleaning by using high resolution force–distance (F–d) curves. These curves essentially enable the cantilever deflection on approaching and coming into contact with the surface, to be measured, hence giving a quantitative measure of the resistance to deflection.

In fibre science several papers making use of the AFM have been published to date. These have concentrated on wool (Titcombe *et al.*, 1997; Jovancic and Jocic, 1998; Parbhu *et al.*, 1999; Crossley *et al.*, 2000),

Laser

Cantilever mount

Wollaston wire

Platinum core

Probe tip

Mirrors
photodetector
sample

12.2 Schematic representation of the Atomic Force Microscope.

polypropylene (Leijala and Hautojarvi, 1998; Hautojarvi and Leijala, 1999; Hautojarvi and Niemi, 2000; De Rovere *et al.*, 2000); polyethylene (Magonov *et al.*, 1991; Magonov *et al.*, 1993); carbon (Dilsiz and Wightman, 1999); Kevlar (Li *et al.*, 1993; Rebouillat *et al.*, 1997, 1999; Graham *et al.*, 2000); and various composite fibres such as nylon or polypropylene reinforced with carbon or aramid fibres (Klein *et al.*, 1996; Vancso *et al.*, 1997; Wu *et al.*, 1998). The surface properties of a textile fibre play a fundamental role in governing some key technical properties, and these properties are, to a large extent, related to the processing conditions (Rebouillat *et al.*, 1997). SPM offers the potential to probe surface characteristics at a level not previously achievable and, as such, it is likely that existing structural models will be confirmed or changed as the technique sees more application in textile characterisation.

In a recent paper by Kwon *et al.*, 2006 the hydrophobicity of PP films was altered by plasma treatment in argon and in a mixed Ar/O_2 atmosphere. The AFM was used to quantify the change in surface roughness of the treated surface as well as provide high resolution images showing the topography (Figure 12.3). The AFM has therefore been used in numerous studies to assess the topographical and physical changes in structure as a result of plasma treatment. In other areas of surface engineering, the AFM has been
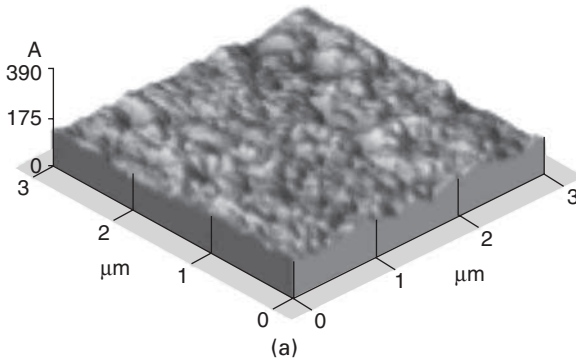
12.3 AFM contact mode scanning image of the Ar-plasma treated surface of PP film (Kwon *et al.*, 2006).

used to quantitatively assess the near-surface mechanical properties. The AFM can be used to perform what are referred to as force–distance curves, which are essentially a type of indentation experiment at ultra-low loads. The cantilever tip is made to approach the surface at a given rate and then it contacts the surface. As it contacts the surface, the cantilever deflects and this deflection is recorded as a function of the tip position relative to the surface. To date, this has not been used in assessment of plasma-treated textiles as far as the authors are aware, yet there is potential to access very localised changes in surface hardness and also in surface chemistry as the adhesion force of the tip to the treated surface varies.

12.2.2 Chemical

X-ray photoelectron spectroscopy (XPS)

XPS is a very powerful surface analysis technique in which chemical states can be determined in near surface regions. Near surface in XPS can be as localised as the top 1–2 nm of the surface, and chemical characterisation as a function of depth is achievable through an etching processes (using argon ion bombardment). XPS is an ultra-high vacuum (UHV) technique and so the normal restrictions that this imposes apply. However, the analysis of plasma-treated textiles has yielded a wealth of very useful information relating to the chemical changes that induce functionality changes (e.g. wettability). In a recent paper by Liu *et al.* (2006), the plasma treatment of acrylic fibres and the mechanism by which anti-static properties were induced were reported and this work relied heavily on a detailed analysis using XPS. Amide and carboxyl hydrophilic groups were identified on the surface. Oxidation pathways were shown to occur at the cyanogen and ester groups on the polymer backbone. This study represents an example of a

fully quantitative analysis of XPS, where curve-fitting procedures were used to fully identify the chemical species. In many other works (e.g. Su *et al.*, 2006), XPS is used to qualitatively show the change in chemical state through a shift in binding energy – in this paper the changes in C 1s, N 1s and O 1s were reported without full deconvolution of the peaks.

Fourier transform infrared (FT-IR)

FT-IR is often used alongside XPS to provide a comprehensive analysis of how the surface of the polymer is changed as a result of plasma treatment. The vibrational spectroscopy enables important information on the C=C, C—O bonds to be determined and, in addition, the presence of important functional groups such as —OH, COO—, —OOH, —COOH, which can provide hydrophilic functionality at the surface (Cheng *et al.*, 2006). These groups have a fingerprint wavelength, and determination of the FT-IR spectra enables the surface bonding characteristics to be determined. This complements the chemical speciation information from XPS.

12.3   Future trends – Nanoindentation

Although nanoindentation has emerged as a very prominent technique in materials science since *ca.* 1975, in particular in surface coating technology, it has not been adopted widely in textiles. The technique relies on an accurate loading and unloading cycle where the resulting deflection of a nanoscale tip is measured as it is loaded and released. In the paper by Gindl *et al.* (2006), it was used to measure the surface characteristics of regenerated cellulose fibres. The loading and unloading cycle is represented in Figure 12.4 and can be used to determine properties such as (i) elastic modulus (ii) yield strength (iii) normalised hardness. Given that plasma-treated surfaces have experienced a temperature cycle and often some chemical changes by integration of species at the surface, it is very likely that both the AFM, for measurement of local force–distance curves, and the nanoindenter have great potential in surface characterisation of plasma-treated textiles and it is likely that this will be seen in the next few years.

12.4   Surface characterisation challenges

It is apparent that a whole variety of physical and chemical techniques can be brought to bear on the comparison of textile samples before and after gas plasma treatments. The link between the advances in scientific understanding which are gained from application of these techniques, particularly in combination with one another, and the improvements in technological performance brought about by gas plasma treatments, have now to be
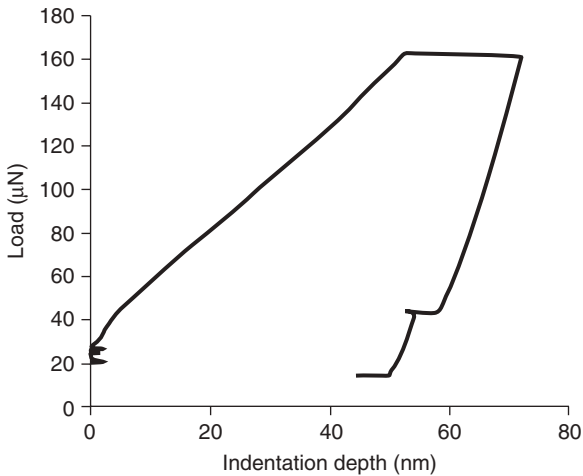
12.4 Load–displacement curve for cellulose fibres (Gindl *et al.*, 2006).

forged. Many technological requirements of textiles depend on their surface character, e.g. abrasion resistance, ease (or difficulty!) of wetting, and ease of incorporation of additives such as dyestuffs.

The advent of advanced microscopies, such as ESEM and SPM, has already considerably progressed our understanding of the effects of specific gas plasma treatments on particular types of textile. However, as with the study of any sample by microscopy, there is the problem of the scale of the targeted sample. Microscopies, such as electron and probe microscopies, focus on only a tiny area of sample, compared with the far larger areas used in actual applications. In particular, these areas, with possibly significant edge lengths, may well not be homogeneous. This sampling problem can, to some extent, be sometimes overcome by the use of a micro- or nano-probe with rapid deployment over any part of the sample.

Textiles present some unique problems as samples for investigation. Textile fibre surfaces are curved, a factor that can present problems with depth of focus in optical microscopy, and even in electron microscopy. In the case of SPM, it is essential that the tip of the cantilever be placed as close as possible to the top of the fibre curvature. For both electron and probe microscopies, examination of a textured fabric sample, e.g. at the junction of two fibres, requires even greater care.

The effect of a given gas plasma treatment on a particular type of fibre can vary according to its cross-section. As stated above, plasma treatments induce changes in the near surface regions of fibres, usually down to a particular depth. For thicker fibres, such as monofilaments (diameters of the order of 100 μm), this depth will represent only a tiny fraction of their cross-

section. With much thinner fibres, however, the effect of the plasma treatment could begin to impact on the fibres' bulk properties. This problem would be especially apparent in nanofibres, although investigations into the plasma treatments of nanofibres are still in their infancy.

Some technological concerns about the plasma treatments of textiles relate to the longevity and durability of the resultant surface changes. However, whilst even quite subtle changes may occur in the character of the treated surfaces, these changes may have marked effects on the performance of the textile. This aspect is pertinent right across the spectrum of textile usage: from the finish of a garment to the biological compliance of a medical device implanted in the body. For example, in the treatment of polypropylene fibre with oxygen plasma, a random copolymer of oxidised and unchanged units may result at the fibre surface (Gross *et al.*, 1994). The layer rearranges itself, however, depending on the medium with which the fibre is in contact, in order to minimise the free energy at the interface. The changes effected by plasma treatments in polypropylene, polyester and polyamide fibres may also be gradually eroded over a period of time (Radu *et al.*, 2000).

12.5   References

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