



Heriot-Watt University  
Research Gateway

## Plasma modification of textiles: understanding the mechanisms involved

### Citation for published version:

McCoustra, MRS & Mather, RR 2019, 'Plasma modification of textiles: understanding the mechanisms involved', *Textile Progress*, vol. 50, no. 4, pp. 185-229. <https://doi.org/10.1080/00405167.2019.1637115>

### Digital Object Identifier (DOI):

[10.1080/00405167.2019.1637115](https://doi.org/10.1080/00405167.2019.1637115)

### Link:

[Link to publication record in Heriot-Watt Research Portal](#)

### Document Version:

Peer reviewed version

### Published In:

Textile Progress

### Publisher Rights Statement:

This is an Accepted Manuscript of an article published by Taylor & Francis in Textile Progress on 21/8/2019, available online: <http://www.tandfonline.com/10.1080/00405167.2019.1637115>

### General rights

Copyright for the publications made accessible via Heriot-Watt Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

### Take down policy

Heriot-Watt University has made every reasonable effort to ensure that the content in Heriot-Watt Research Portal complies with UK legislation. If you believe that the public display of this file breaches copyright please contact [open.access@hw.ac.uk](mailto:open.access@hw.ac.uk) providing details, and we will remove access to the work immediately and investigate your claim.

# **Plasma modification of textiles: understanding the mechanisms involved**

M. R. S. McCoustra & R. R. Mather

School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, Scotland

## **ABSTRACT**

Plasma treatments are acquiring growing commercial recognition as a highly practical means of altering the surface properties of textiles without detriment to their bulk properties. It is clearly desirable that processing conditions are formulated as accurately as possible, so that fewer trials are required to achieve a desired outcome. We discuss how better formulation is achievable from a clearer understanding of the mechanisms comprising the plasma process. This improved understanding comes from not only analysing surface chemical and topographical changes resulting from a plasma treatment, but also monitoring key processes taking place during the treatment. Furthermore, we highlight the application of computational approaches, statistical experimental design and process control as supporting tools and highlight the role that artificial intelligence may play in the future. We also consider three specific plasma treatments of textiles and propose how examples of these approaches extracted from the literature may be combined, to achieve more realistic formulations.

## **Keywords**

plasma, fibre, surface, spectroscopy, microscopy, Langmuir probe, statistical experimental design, computer modelling, process control

## **1. Introduction**

In 2007, over ten years ago, the book “Plasma Technologies for Textiles” [1] was published. In its introduction Roshan Shishoo, the editor, highlighted the enormous potential of plasma technologies for improving textile processing, enhancing textile properties and broadening textile applications. Chapter 2 of the book, by James Bradley and Paul Bryant [2], emphasised the use of plasma diagnostic tools as essential for the understanding and development of plasma technologies. With these tools, Shishoo noted, not only could plasma technologies be operated most efficiently, but conditions could be much more readily formulated for a particular process. In a review published in “Textile Progress” by Kan and Yuen [3] in the same year on plasma technology in wool, it was noted too that processing parameters in plasma treatments are highly system dependent: a successful

formulation devised for one system will usually need to be modified for the same treatment in another system. In this present review, we consider the approaches available now to progress the understanding of plasma treatments of textiles and indicate how these approaches, when used in conjunction, can progress the formulation of processing parameters for a desired plasma treatment in a particular system.

Gas plasma treatments produce changes to the surface properties of a solid without altering its bulk physical and mechanical properties. The technique was introduced half a century ago and has steadily been gaining traction since then. More recently it has been given additional impetus by the development of large-scale equipment, so that the technique has become widely applied in a number of commercial sectors.

Perhaps the best known, and certainly the oldest sector, to embrace plasma technologies is microelectronics; in particular for etching and deposition of thin films [4,5]. Plasma can be used too to enhance chemical vapour deposition (CVD) [6]. CVD enables coatings to be prepared from volatile precursors by chemical reaction and is widely used in the fabrication of semiconductor devices. Other important examples of plasma applications include surface treatment of polymers [7], paper [8,9], biomaterials [10] and the production of flexible packaging [11]. A recent paper even describes a plasma assisted one-step process for producing tiny capsules containing antibiotics [12].

Plasmas can be generated in a variety of different ways. For example, different types of power supply can be used to generate plasma [1], including:

- low frequency (LF), 1-500 kHz;
- radio-frequency (RF), 2-60 MHz, often 13.56 MHz or 27.12 MHz;
- microwave (MW), 915 MHz or 2.45 GHz.

The power needed to deliver a plasma treatment depends on the nature of the treatment and the size of the plasma reactor. Plasmas may be delivered continuously or in a series of intermittent pulses.

Both low pressure and atmospheric pressure technologies are available. Low pressure systems usually operate at pressures in the range 1-100 Pa (0.01-0.10 mbar) and in the RF or MW range. They are generally more expensive to install and operate, because of the need to attain and then maintain low pressure. On the other hand, low pressure systems tend to provide more uniform and reproducible treatments. In addition, they use far less gas, an aspect that is especially important for expensive gases. Low pressure systems are less amenable to continuous processing, though continuous roll-to-roll systems can be constructed where the unwind and rewind rolls are located outside the plasma reactor. A further consideration is the evaporation of water from textiles at low pressure, especially

from textiles containing natural fibres. This aspect is illustrated in Section 9.3 of this review. A detailed discussion of low pressure systems has been given by Lippens [13].

Atmospheric pressure systems fall broadly into three categories: corona discharge, dielectric barrier discharge (DBD) and atmospheric pressure glow discharge (APGD). These systems are very fully discussed by Herbert [14]. Corona discharges are seldom used for textile treatments, being too weak and inhomogeneous. Many fabrics are too thick for successful treatment with a corona discharge. Two forms of DBD exist: filamentary and homogeneous. Plasmas generated by filamentary DBD are not truly continuous, and the textile substrate is therefore not uniformly treated. Careful adjustment of processing controls can lead, however, to a homogeneous DBD, which provides a much more uniform treatment.

APGD systems possess many of the qualities of low pressure systems, for example in mode of generation and uniformity of textile treatment, but without the need to attain low pressures. A drawback is that the discharge is usually generated in helium, an increasingly scarce and expensive resource, though argon and even nitrogen can sometimes be successfully used instead. The disadvantage of helium can be largely overcome by recycling the gas through adjacent ancillary equipment.

It is evident that the individual equipment used is highly influential on the plasma treatment conferred. There are several important control factors. Apart from the composition of the plasma source gas and the type of textile, these factors include the pressure of the gas in the chamber – and any fluctuations in it, the power and frequency of the electrical supply, the duration of the treatment and the rate of flow of gas into the reactor. A process formulation that is successful in one system may well, therefore, have to be modified for another system.

The actual application of plasma treatments to textiles has been fully described before [1] and so does not need to be covered in detail in this review. The plasma technique offers a clean, dry approach that uses considerably less energy than traditional wet treatments. Depending on their nature, plasma treatments can render changes in hydrophilicity or hydrophobicity [15], assist dyeing [16,17], enhance the shrink resistance of wool [16], and promote flame retardancy, abrasion resistance, ballistic protection and many other technologically desirable properties [18,19]. Plasma treatments can be used on biomedical textiles: notably, sterilisation by inactivating infectious micro-organisms present on a fabric surface [20], and the adaptation of fabric surfaces so that they can anchor biological molecules to render a textile more biocompatible [21,22]. Another important advantage offered by plasma treatments is the increased scope for grafting polymers onto textile fibre surfaces [23-25]. Grafting not only permits the nature of the surfaces to be altered to suit the application for which the textile is intended; it also opens up the scope for further applications of the textile not available to it using traditional surface treatments and

can help in rendering textile surfaces more durable. Informative surveys of some of the practical applications of plasma treatments on textiles have been published by Morent *et al.* [26] and Zille *et al.* [27].

It is clear then that the plasma technique offers huge potential to textile technology and, in particular, to commercial textile processing and manufacture. A number of European Union projects have, for instance, been undertaken to encourage textile companies to adopt plasma technology. Examples are:

PLASMAPOR (2012-2017): Plasma penetration into porous materials for biomedical, textile and filtration applications [28]. Outcomes included:

- Development of an atmospheric plasma jet that could penetrate into flexible tubes constructed for medical applications;

- Demonstration of the positive influence that plasma treatment can have on cell adhesion and multiplication in porous scaffolds;

- Development of a plasma coated textile for the immobilisation of the enzyme, laccase, as a filter for decolourising dyes;

- Studies of stimuli-sensitive poly(N-isopropylacrylamide) grafted surfaces for wound dressings.

POWER (2013-2016): Atmospheric plasma treatment for enhancement of textile surfaces for more efficient treatment processes [29]. One outcome was:

- Development of a tailor-made roll-to-roll plasma treatment machine that was tested in real manufacturing conditions, with a specific emphasis on car seat upholstery.

ACTECO (2005-2009): Eco-efficient activation of hyper functional surfaces [30]. A major outcome was claimed to be:

- The design and operation of new plasma processes which can provide surface finishes that are durable during the lifetime of a textile product.

PLASMATEX (2016-): Investigation of new types of silver-containing antibacterial coatings on medical textiles. The project involves the plasma assisted deposition of these coatings to control the release of an antibacterial agent [31].

There was also an EU-funded project, 2BFUNTEX (2012-2015), for “boosting collaboration between research centres and industry to enhance rapid industrial uptake of innovative functional textile structures and textile-related materials in a

mondial [worldwide] market”; plasma technology played an important part in this project [32].

Nevertheless, despite such initiatives there appears to have been reluctance by many textile companies to embrace plasma technology at a commercial level. This reluctance may stem not just from the investment needed to acquire and operate plasma equipment but also from lack of familiarity and appreciation of the benefits that plasma treatments can bring. Moreover, technological innovation in a company will generally require management innovation as well, and so the structure and operation of a company may well have to be changed. The link between technological innovation and management innovation has recently been extensively analysed by Hervas-Oliver *et al.* [33]. Thus, the adoption of any major new technology, even a successful one such as plasma technology, may be viewed as a significant hurdle, even though plasma machinery that can be used for the industrial treatment of textiles is widely available. For example, low pressure systems are offered on the market by:

P2i (P2i Limited, Milton Park, Oxfordshire, UK) – a pulsed plasma process, focussed on all liquid repellency but expanding into a range of functional nano-coatings;

Europlasma (Europlasma NV, Oudenaarde, Belgium) – water/oil repellent coatings and other functional ultra-thin coatings;

Henniker Plasma (Henniker Plasma Treatment, Runcorn, UK) – activation of surfaces for several applications, including liquid repellency, improved wettability, enhanced fibre-matrix adherence and specific surface functionalities.

Atmospheric plasma systems are available from companies such as:

AcXys (AcXys Technologies, Grenoble, France) – surface treatments of textiles, for e.g. packaging, medical applications, technical wear;

Ahlbrandt® (Ahlbrandt System GmbH, Lauterbach, Germany) – corona treatments designed for coating and laminating narrow webs;

Arioli® (Arioli® SPA, Gerenzano, Varese, Italy) – general finishing of textiles;

APJet® (APJet®, Morisville, North Carolina, USA) – applications including water/oil repellency, biomedical applications, outdoor wear, flame retardancy, protective and safety wear;

MTIX (MTIX Limited, Huddersfield, UK) offers 'Multiplexed Laser Surface Enhancement', which the company markets as a combination of plasma and ultra-violet laser technologies;

Tri-Star Technologies (Tri-Star Technologies, El Segundo, California, USA) – predominantly medical, pharmaceutical and aerospace applications.

Clearly, the market for plasma machinery has become well established. In addition, there are products available for *in situ* plasma analysis (discussed in Section 5 of this review), e.g. from Hiden Analytical (Hiden Analytical Limited, Warrington, UK) and Air Products (Air Products PLC, Walton-on-Thames, - Regional HQ, UK).

As highlighted above, the nature of the plasma modification of a textile surface depends on a number of control factors. Nevertheless, despite all these disparate factors, several effects can be broadly identified. One of these is etching of fibre surfaces: the texture of the surface, and hence for example fibre wetting properties, is altered. Another important effect is the modification of a fibre's surface chemistry, through the introduction of particular chemical functional groups. Still another effect is plasma polymerisation, whereby very thin polymeric coatings are formed on the fibre surface. In many cases, these coatings possess highly cross-linked structures. Surface chemical changes and plasma polymerisation will nearly always be accompanied by changes in surface texture. The effects of some of the gas plasmas commonly applied to textiles are shown in Table 1. It should be noted that after a low pressure treatment, subsequent exposure of the treated sample to the atmosphere may trigger further changes to the fibre surfaces.

To better understand plasma treatment processes, one must consider the nature of plasmas and the mechanisms by which they alter textile surfaces. When a sufficiently large voltage is applied across a space containing a gas, the gas will break down into a mixture of ions, electrons and excited neutral atoms and molecules. The interactions of these species that may occur with one another and with the textile to be treated are consequently highly numerous. In addition, a thin neutral sheath is created between the plasma and the textile fibre surfaces, with the result that electrons tend to be reflected back into the plasma and ions are accelerated towards the surfaces [34]. It should also be taken into account that, in contrast to low pressure plasmas, atmospheric plasmas are likely to have a low concentration of ions and excited neutral species and may heat the textile substrate [7]. On the other hand, the plasma will be better able to penetrate the fibre interstices [35,36].

It is not surprising that, given the complexity of the species comprising a plasma, a huge number of reactions between them are possible [34], and just a few of these are shown in Table 2. In addition, a large number of reactions between the plasma

species and the textile fibre surface also appear possible (exemplified in Table 3), and it is these that will govern the nature of the treated fibre surface. Differences of behaviour between the plasma species in the gas phase and at the fibre surface also have to be taken into account [37]. Moreover, the topographical and chemical heterogeneity of the fibre surfaces, particularly in most natural fibres, will have significant influences, and the extent of a plasma treatment on a fabric can be uneven, depending on the nature of the fabric's construction [38]. For example, a treatment can be more pronounced at the edge of a fabric than elsewhere on it [39].

It is clear, therefore, that a quest to elucidate so many reactions for every individual plasma treatment applied to a textile fabric would be highly impractical. On the other hand, a full elucidation is unlikely to be needed to gain a detailed understanding of the important underlying mechanisms, since some reactions will be much more significant than others. Indeed in the examples discussed later in this review (Section 9), only a few key species appear to have significant reactions with the fibre surface, though the rate of reaction with the surface may well depend on the other plasma species present. The level of understanding necessary in practice is one that ensures that treatment conditions can be better formulated, with consequently fewer trials to achieve a particular desired result.

In this paper, we briefly survey the approaches that are available to better understand the mechanisms behind plasma treatments of textiles. A number of different approaches can be brought to bear, often in combination. The most widely reported approaches are concerned with topographical and chemical analysis of the fibre surface by advanced microscopic and spectroscopic techniques. The ability to identify key species in the plasma chamber and to follow changes in their concentrations during a treatment process is also important. More recent approaches utilise computer modelling. In addition, statistical experimental design and analysis is now being applied, particularly to determine the most significant chemical processes underpinning a plasma treatment. The application of artificial intelligence techniques, like artificial neural networks and genetic algorithms, could also eventually play a part. In Section 9, we consider three specific plasma/textile systems, and show how examples of these approaches taken from the literature may be combined, with the goal of obtaining more predictable and reproducible results.

## **2. Topographical analysis of plasma-treated textiles**

### ***2.1 Brief introduction***

Changes to the topographical nature of a textile fibre surface after plasma treatment can be readily revealed using microscopic techniques comparing the fibre's appearance before and after the treatment. Amongst the most widely used of these techniques are scanning electron microscopy and atomic force microscopy. However, it should be borne in mind that any microscopy involves localised analysis that is confined to a very small area of the fibres under investigation. The analysis of



this area may therefore not always be representative of the whole fibre, and still less of the fabric of which the fibre is a constituent.

## 2.2 Scanning electron microscopy (SEM)

SEM is well established and has been commercially available for fifty years or more. Details of the application of the technique to textiles are widely available [40-42]. High resolution images of at least  $\times 10^4$  magnification are achievable, with a large depth of field. A limitation of the technique for non-conducting samples, such as most polymers and textiles, is the need to apply a very thin layer of a metallic coating to provide a path for the discharge of electrons. Without this coating images of poor quality are obtained. Numerous examples of the application of SEM in studies of plasma treated textile surfaces have been reported, some of them more than twenty years ago [43-45]. More recently published examples include:

Improvements to the dyeing of polyethylene terephthalate (PET) fabric [46]. SEM demonstrated that roughening of PET fabric surfaces after atmospheric pressure oxygen plasma treatment was a contributing factor to improved wetting and dyeing capabilities.

Improvements to the ink-jet printing of PET fabric [47]. SEM revealed the distribution of pigment particles on the surfaces of PET fabrics after their exposure to atmospheric pressure air/helium plasma. The nature of the pigments was not specified.

Etching of nylon 6:6 fibres [48]. A variety of surface nanostructures was observed by SEM on nylon 6:6 fibres after treatments with low pressure oxygen plasma, which improved wettability, notably for filtration applications.

Improvements in antibacterial activity of nylon 6 fibres [49]. SEM revealed slight roughening of nylon 6 fibres after exposure to atmospheric air plasma. The uptake of the natural yellow antibacterial cationic dye, berberine, was increased, especially if the fibres had been treated with copper sulfate mordant after exposure to plasma.

Improved antistatic properties in acrylic fibres [50]. SEM showed the formation of grooves along the length of acrylic fibres after exposure to nitrogen plasma at low pressure. Considerably improved wettability and antistatic capability were observed. XPS results from this paper are summarised in Section 3.3.

Grafting polymers to promote dyeability of polypropylene fabric [51]. Atmospheric pressure argon plasma treatment was shown by SEM to

roughen the surfaces of polypropylene fibres, prior to their being grafted with compounds that then enable a degree of dyeing with selected acid and cationic dyes.

Improved adhesion between polypropylene fibres and matrices in cementitious composites [52]. SEM showed that extensive treatment of polypropylene fibres with low pressure argon and oxygen plasmas gave rise to some roughening of the fibre surfaces. Increased flexural strength and toughness of the composites were observed with the treated fibres, and attributed to improved fibre-matrix adhesion.

Improvements to the dyeing behaviour of cotton [53]. SEM revealed abrasion of cotton fibre surfaces as a result of atmospheric pressure air plasma treatment and the appearance of fibril-like formations following treatment with dichlorodifluoromethane plasma. The authors state that these formations contribute to the highly hydrophobic fibre surfaces.

Plasma modification of viscose textile [54]. SEM revealed roughened fibre surfaces after treatment with low pressure oxygen and hydrogen plasmas, whereas no obvious roughening was detected after exposure to nitrogen plasma.

Improvements in hydrophilicity and bleaching behaviour of linen-containing fabrics [55]. Linen, linen/cotton and linen/viscose fibres were examined by SEM after atmospheric plasma treatments with oxygen, air and nitrogen. Fibres exposed to oxygen and air plasmas exhibit clear etching. There was also some surface roughening after exposure to nitrogen plasma.

Characterisation of plasma-treated cashmere and wool-cashmere textiles [56]. SEM showed only a very small effect on the morphology of the fibres after their exposure to atmospheric pressure humid air plasma, although chemical analysis revealed fibre surface oxidation.

Improved absorption of lac dyes by silk [57]. Silk fibre surfaces were shown to be roughened by exposure to argon and oxygen plasmas. The plasma treatments improved the capacity of silk for absorbing lac dye, a red dye extracted from scale insects and applied to silk and wool.

These references well illustrate the range of uses to which plasma technology can be put and provide some insight into the morphological changes which contribute to the overall effects that plasma treatment may bring about. Moreover, many of the techniques described below, such as AFM, XPS and FTIR, were also used in these

examples. Most analyses are qualitative, in that they compare visual images of fibres before and after a particular treatment. However, software exists to measure changes in roughness and fractal parameters, although these parameters seem seldom to have been determined; examples include MeX by Alicona (Alicona GmbH, Graz, Austria) and MountainsMap® by DigitalSurf (Besançon, France). A paper illustrating how surface roughness can be measured and analysed using SEM has been written by Paluszynski and Słówko [58].

An important advance in SEM has been the development of environmental scanning electron microscopy (ESEM) [59]. In contrast to SEM, evacuation of the sample is not required and there is less need for a metallic coating. Wei *et al.* [42] have pointed out that a major drawback to conventional SEM is the inability to examine specimens in the wet state, a difficulty that ESEM largely overcomes. Nevertheless, the use of ESEM does not appear to be extensively reported in the textile literature, although Tao and Collier [60] highlighted its potential for examining textiles a quarter of a century ago. Studies of changes in the wetting behaviour of nylon 6 nanofibres as a result of plasma treatment have been followed using ESEM [61], as has the effect of oxygen plasma treatment to remove organic size from ceramic fibre surfaces [62].

ESEM can also be used to observe dynamic processes, at the  $\mu\text{m}$  scale. For example, Wei *et al.* [42] have examined the progress of the absorption of water by alginate fibres. No water droplets are formed on the fibre surfaces, even at 100% relative humidity. Instead significant increases in fibre diameter can be progressively observed. Wei & Wang [63] have reported how the installation of a micro-tensile stage in an environmental scanning electron microscope can also allow dynamic tensile behaviour to be observed under controlled conditions.

### 2.3 Atomic force microscopy (AFM)

AFM is a member of an extensive family of scanning probe microscopies and is now by far the most applied of them in the analysis of textile surfaces. The surface of the textile sample is scanned with a sharp tip a few  $\mu\text{m}$  long, typically made of silicon nitride, at the end of a cantilever. The probe is operated by an intricate control system, with the tip so close to the surface that changes in van der Waals forces are readily detected. From measurements of the forces generated between the sample and the tip during scanning, the contours of the surface are mapped and images can be produced. Indeed, AFM is now so sophisticated that it can be used to break molecular bonds and move atoms around on a surface [64]. A technique sometimes used in conjunction with AFM, lateral force microscopy (LFM), which measures lateral deflections of the scanning tip, has also been applied successfully to textiles [65]. More detailed descriptions of AFM in the study of textile surfaces are available elsewhere [42,66].

A particular advantage of AFM is that no surface treatment is required prior to imaging, and yet it potentially provides substantially higher morphological detail than SEM. Moreover, a sample can be imaged in air at atmospheric pressure, and even in water. A variety of papers have been published demonstrating the use of AFM to analyse the surfaces of plasma treated textiles, including:

Wetting behaviour of plasma treated PET fibres [67]. AFM showed the progressive roughening of PET fibre surfaces with increasing exposure to low pressure oxygen plasma. Initially, aggregates are formed on the surfaces but prolonged exposure produced marked etching.

Improved adhesion of poly(pyrrole) to PET fabric and conferment of electrical conductivity [68]. A progressive increase in the root mean square surface roughness of PET thin films and fabric was observed by AFM with increasing duration of a low pressure oxygen plasma treatment. Fig 1 shows the sequence of AFM images obtained. The roughness of the surface also appears more uniform after longer treatments. The increased roughness was a contributing factor to improved adhesion of poly(pyrrole) on the fabric.

Modification of the surfaces of nylon 6 nanofibres [61]. AFM revealed the formation of nanosized structures on electrospun nylon 6 nanofibres on exposure to low pressure oxygen plasma. Longer exposures also resulted in the formation of grooves on the fibre surfaces. The topographies influence the shapes of the water droplets condensed on the fibres.

Improvement of oil and water absorbency on nylon 6 [69]. Nylon 6, PET and cotton fabrics were treated with helium, argon, air and oxygen plasmas at atmospheric pressure. AFM revealed roughening of the surfaces of the fibres, with the formation of nano-sized channels along the fibre surface in PET fibres and at right angles to it in nylon 6 fibres.

Improved performance of polypropylene meshes containing antibiotics [70]. Corona discharges were used to increase the loading of the antibiotic, ampicillin, on PP surgical meshes, and AFM revealed considerably roughened fibres. Subsequently, low pressure argon plasma treatment was applied to allow the surface formation of polyethylene glycol, which permitted the higher drug loading to be maintained. The roughness of the fibre surface was increased.

Enhancement of adhesion strengths of polypropylene nonwoven fabrics [71]. After treatment with low pressure oxygen plasma, the fibre surfaces of nonwoven PP fabrics were observed by AFM to be

rougher. There was also a considerable enhancement of peel strength of fabrics laminated using acrylic and polyurethane based adhesives.

Improvement of wettability of cotton [72]. Cotton fabrics were first pre-treated with oxygen, argon or hydrogen plasmas. AFM showed marked roughening after all three plasma treatments, but with some differences in the surface morphologies. Plasma enhanced chemical vapour deposition (PECVD) of methane-hydrogen-argon mixtures was then carried out to obtain highly hydrophobic surface structures arising from a 'diamond-like carbon' (DLC) coating. Where there had been oxygen and argon pre-treatments, cauliflower-like structures were observed by AFM. Where there had been a hydrogen pre-treatment, structures were formed which mirrored those present before the DLC coating.

Effects on ink-jet printing of cotton [73]. By means of AFM progressively increasing roughness values were determined on cotton surfaces after low pressure treatments with oxygen, nitrogen, and sulfur hexafluoride ( $\text{SF}_6$ ) plasmas, respectively. The absorption of inks from inkjet printing was influenced by fibre surface roughness and also by changes in the chemical nature of the fibre surfaces.

Oxygen plasma treatment to reduce temperatures for wool dyeing [74]. Low pressure oxygen plasma treatment on wool fabric samples was shown by AFM to roughen their fibre surfaces. Longer treatments led to increased roughness. Plasma treatment allowed effective dyeing at  $85^\circ\text{C}$ , rather than at a temperature near boiling point normally used for dyeing untreated wool.

Improvement of cell adhesion to silk [75]. The topography of silk fibre surfaces was hardly altered, if at all, when they were exposed to low pressure nitrogen plasma. The accelerated adhesion of mouse fibroblast cells, as a result of plasma treatment, was attributed to the higher surface content of nitrogen and oxygen.

Again, this range of papers illustrates the wide range of uses of plasma treatments on textiles, and indeed many of these examples also include the use of SEM. In several cases, changes in the mean roughness of the fibre surface were also determined from the AFM images. A detailed discussion of the calculation of Wenzel roughness factors and the application of surface fractal analysis for analysing changes in the surface roughness of cellulose film as a result of exposure to oxygen plasma has been provided by Calvimontes *et al.* [76], using AFM images. Image Metrology (Image Metrology A/S, Lyngby, Denmark) provide market software

specifically for analysing surface roughness from AFM images, though the company states that its software can also be applied to SEM images.

AFM can also be used to evaluate surface mechanical properties quantitatively at the nanoscale level, through the determination of so-called force-distance curves, although an expert AFM operator would generally be required. These properties would be impossible to evaluate by SEM. In this application of the technique, the tip approaches the textile surface at a known rate, until it contacts the surface. The resulting deflection of the cantilever is recorded as a function of the position of the tip relative to the surface. The reverse procedure is then adopted, with the tip moving away from the surface. The resulting traces provide information on the mechanical properties of the textile surface. A very full discussion of force measurement using AFM has been written by Butt *et al.* [77] and useful illustrations of the application of AFM to nanoscale mechanical performance mapping has been published by Vansco *et al.* [78]. An interesting application of force-distance analysis arises where specific sensors are bound to the cantilever tip. Sensor molecules on the tip can be used to target molecules on the sample surface [42].

Although the determination of force-distance curves has still to find widespread use in studies of textile surfaces, it has yielded valuable information where it has been applied, notably with wool fibre surfaces [79,80]. Surface mechanical properties will almost certainly be altered by a plasma treatment, especially in the case of most natural fibres, and force-distance analysis would provide a means of assessing these changes. Such changes could, for example, be exploited to influence sensory aspects of fabric handle [81]. There are, however, some inherent difficulties with the analysis of force-distance curves [80]. One particular problem lies in determining the extent of interaction between the tip and the sample, from which the modulus of the sample is calculated. In addition, there are uncertainties in the methods available to determine the spring constant of the cantilever. Nevertheless, comparisons between untreated samples and those that have been given a treatment, such as a plasma treatment, can yield valuable information about any changes in surface mechanical properties. AFM can also now be coupled with bulk measurements of fibre electrical and mechanical properties, but we are not aware of this approach being used yet on textiles.

### **3. Surface chemical analysis of plasma-treated textiles**

#### **3.1 Brief introduction**

Chemical changes to fibre surfaces as a result of a plasma treatment can be followed using a number of techniques. Prominent amongst these are secondary ion mass spectrometry (SIMS), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) spectroscopy [66,82,83]. Full accounts of these techniques are included in a book by Vickerman & Gilmore [84].

### 3.2 Secondary ion mass spectrometry (SIMS)

SIMS possesses the advantages of extreme sensitivity towards a surface and hence the capability of identifying a wide variety of functional groups. An excellent review has been written by Delcorte *et al.* [83] of the application of SIMS to the study of plasma treatments of organic surfaces, such as the surfaces of most textile fibres. The surface is bombarded *in vacuo* by a focused beam of primary ions. This bombardment causes the release not only of atoms and molecular fragments from the surface but also of a small proportion of secondary ions. The mass/charge ratios reveal the nature of the individual chemical constituents at the surface. Analysis of the secondary ions is normally conducted in a time-of-flight (TOF) analyser which separates the ions according to their time of flight from the sample to a detector. SIMS has also recently been applied to depth profiling, in which chemical groups just under the surface up to a depth of 5 nm or more can additionally be identified. Depth profiling on a number of polymers has been reported [83]. However, whilst SIMS is useful for identifying the individual chemical constituents of a surface, it is less reliable for determining their relative proportions, as the fraction of ions released from the surface will vary from one type of ion to another. For this reason, SIMS is often applied in conjunction with XPS (discussed in the next section). To the authors' knowledge, only a few examples of plasma-treated textiles investigated using SIMS have been published, *e.g.* by Naebe *et al.* [85] and Panda *et al.* [86], a consequence perhaps of the expensive equipment required. Detailed accounts of TOF-SIMS have been compiled in a book edited by Vickerman and Briggs [87].

### 3.3 X-ray photoelectron spectroscopy (XPS)

XPS is now a well-established quantitative analysis technique for determining the elemental composition of a surface and the chemical and electronic states of these elements. XPS analysis can be restricted to the top 2 nm of a surface, but by means of etching processes chemical characterisation up to a depth of 10 nm can be achieved. Like SIMS, XPS is performed *in vacuo*, though recent developments in the technology have driven up the upper pressure limit to ca. 10 mbar.

XPS spectra are obtained by irradiating the surface with a beam of monochromatic X-rays. As a consequence electrons are emitted from the surface and their kinetic energies are analysed. A spectrum is determined from a count of the emitted electrons over a range of kinetic energies. The intensities of the peaks at particular energies allow the elements at the surface to be identified and relative abundances to be determined. Deconvolution analysis of individual peaks reveals the chemical and electronic states of the elements. A very useful account of the characterisation of plasma-modified surfaces by XPS has been published by Vandencastele and Reniers [88]. These authors emphasise, however, that XPS is insufficient for plasma polymerised films, and that other techniques such as SIMS and FTIR (see Section

3.4) are also required. A number of the papers already cited in Sections 2.2 and 2.3 include the application on XPS. Other papers include:

Surface modification of polyester fabrics for inkjet printing [89]. XPS showed an increase in the oxygen content of PET fabric surfaces after their exposure to atmospheric pressure plasmas consisting of air and 10% argon. Inkjet printing with pigment inks of the treated fabric surfaces gave enhanced colour yields and much improved print sharpness. The nature of the pigments was not disclosed.

Air plasma treatment of polyester textiles [90]. Increases in the contents of hydroxyl and carboxyl groups at the surfaces of PET film, woven and nonwoven fabrics were revealed by XPS. The creation of these extra polar groups enhanced the adhesion of two poly(dimethylsiloxane) resins to the substrates.

Surface modification by plasmas of nylon 6 fibres and films [91]. Nylon 6 fibres were treated with plasmas containing nitrogen and ethyne (acetylene) in helium at atmospheric pressure. XPS showed increases in the hydroxyl and carboxyl contents of the fibres. The treated fibres and films appeared quite resistant to ageing.

Plasma treatment of polypropylene fabric to promote dyeability with vat dyes [92]. XPS demonstrated some oxidation of the PP fibre surfaces after atmospheric pressure treatment with argon or air, which the authors attribute largely to exposure of air following plasma treatment. The surface nitrogen content also increased. For leuco-form application of a vat dye, better dyeing was obtained after argon plasma treatment. For application of a dye in pigment form, an air plasma treatment was more effective.

Surface properties of plasma treated acrylic fibres [50]. After treatment with nitrogen plasma at low pressure, the surfaces of acrylic fibres had a reduced content of nitrile (-CN) and ester groups and a virtually unchanged content of methylene and methyl groups. New amide and carboxyl groups appeared, probably from conversion of nitrile and ester groups respectively. SEM results from this paper have been summarised in Section 2.2.

Preparation of hydrophobic viscose fabric using a nitrogen plasma treatment [93]. After a low energy atmospheric pressure nitrogen treatment, viscose fabric became, perhaps surprisingly, more hydrophobic. From XPS data, it was concluded that large numbers of hydroxyl groups had been removed from the surface. Increased



roughness of the surface was also observed. Binding of copper (II) cations to the plasma-treated surface conferred a 'petal effect', whereby drops of water adhered to the fabric surface when the fabric was turned upside down.

These examples illustrate the prominence of XPS in analysing chemical changes at fibre surfaces resulting from plasma treatments. Indeed many of the papers cited in Sections 2.2 and 2.3 also include XPS analysis.

### *3.4 Fourier Transform Infrared (FTIR) Spectroscopy*

Infrared spectroscopy has been a standard analytical technique for 80 years or more. An infrared spectrum displays the frequencies of vibrations in the bonds between the atoms comprising the sample being studied. The technique has been considerably advanced and simplified by the introduction of Fourier Transform instrumentation in the early 1980s. In FTIR individual chemical groups, for example C=C, C-O and O-H, can be observed at characteristic fingerprint wavelengths.

Using reflectance techniques, infrared analysis of surfaces can also be undertaken. The appearance and diminution of surface chemical functional groups as a result of plasma treatment can be detected with suitable instrumentation, and specific bonding characteristics at the surface can then be determined. However, some reports of the application of FTIR suggest that it can reveal little or no information about the surface chemical changes resulting from plasma treatment [94,95], though this difficulty may arise from the level of equipment used. Indeed, a technique combining AFM and infrared spectroscopy has now been developed, from which nanoscale infrared in conjunction with AFM images can be displayed. The technique has been applied, for example, to the characterisation of single polymer nanofibres [96]. Examples of plasma-treated textiles investigated using FTIR are numerous, including several of the papers already cited above. Other papers include:

Air plasma treatment of PET fibres [97]. Atmospheric air plasma treatment produced some changes to the FTIR spectra of PET fibres. There was an increase in -CH group surface content, attributed by the authors to scission of PET chains. There also appeared to be increases in the surface contents of -CH<sub>3</sub> groups and -CHO groups. The plasma treatment improved the efficiency of a nano-emulsion silicone softener deposited on the PET fibres.

Plasma treatments of cotton to improve surface functionality [98]. Cotton was treated with atmospheric air and argon plasmas, to study their effects on the waxes, pectins and proteins present on the fibre surfaces. FTIR revealed the appearance of methylene (-CH<sub>2</sub>-) groups after plasma treatments, attributed to the partial decomposition of

waxes. In addition, ester groups present in the pectins appeared more prominent after argon plasma treatment.

Plasma polymerisation of hexamethyldisiloxane (HMDSO) on cotton fabric [99]. Atmospheric plasma polymerisation of HMDSO was carried out on cotton fabric. FTIR showed that the plasma polymer contained Si-CH<sub>3</sub> moieties in its structure, and the methyl (CH<sub>3</sub>-) groups conferred water repellency on the fabric. The longer the exposure time to the plasma, the greater was the methyl content. The methyl content and consequent water repellency decreased gradually with increased number of washing cycles. The authors state that a polymer with a high cross-linking density is required to improve stability.

Formation of a plasma polymer of HMDSO on wool fabrics [100]. Low pressure PECVD was applied to produce a plasma polymer of HMDSO on wool fabric surfaces. FTIR revealed the presence of Si-O and CH<sub>3</sub>-groups in the polymer. The plasma polymer reduced pilling.

Analysis of the effects of oxygen plasma treatment on wool fibre [101]. FTIR showed that low pressure oxygen plasma treatment confers a higher cysteic acid (-SO<sub>3</sub>H) content in wool. Interestingly, Raman spectroscopy revealed that some  $\alpha$ -helices in wool keratins were changed to  $\beta$ -pleated sheets.

#### **4. Other approaches**

Although microscopic and spectroscopic techniques provide the most intricate insights into the effects of a plasma treatment, other complementary techniques are often used alongside them. These techniques are more 'broad-brush' in that they do not analyse surface physical or chemical changes directly. However, many are of particular importance to application technologists. Examples are abrasion resistance [102], adhesion promotion in fibre-matrix composites [103] and biocompatibility [22]. Some of these techniques can, however, provide a more direct link. One important example is the measurement of changes in contact angle of (usually) water on a textile, either by static or dynamic wetting tests, from which information about changes in surface free energy can be derived. Indeed, in many of the references already cited measurements of contact angle form part of the overall study. However, such tests are also important in the assessment of changes in a textile's hydrophilicity or hydrophobicity. In addition, as noted above, there are examples of the use of ESEM to examine the behaviour of tiny water droplets on individual textile fibres.

## 5. Understanding the plasma itself

### 5.1 Brief introduction

It is evident then that a wide variety of surface analysis techniques can be combined to examine the effect of a particular plasma treatment on the surface of the textile of interest. Whilst such a combination serves to identify changes to the textile surface, other approaches are available which can provide further valuable insights into the treatment. Such insights would be particularly useful when conditions for new plasma treatments are to be formulated, especially at a commercial level. It would be invaluable therefore to be able to follow a plasma treatment during its actual application, by determining changes continually in the composition of the plasma. Techniques to achieve this aim are certainly available, although so far they appear to have made little overall impact on textile science and technology. Available techniques include quadrupole mass spectrometry, optical emission spectroscopy and the use of Langmuir probes.

### 5.2 Quadrupole mass spectrometry (QMS)

In the mass spectrometric analysis of plasmas, ions and neutral species present in the plasma are initially extracted through a sampling orifice or narrow 'sniffer' tube, and then differentially pumped before being introduced into the spectrometer. Differential pumping is necessary because the spectrometer has to be operated at very low pressure ( $< 10^{-4}$  mbar). This approach can also be extended to examine the distribution of the composition of a plasma in three dimensions. Plasmas of any pressure can generally be analysed. Neutral species in the plasma have to be ionised first, a process that can be achieved by electron impact ionisation.

The type of mass spectrometry often applied is QMS. A quadrupole mass analyser consists essentially of four parallel rods of hyperbolic cross-section, coupled to a detector. Each opposing pair of rods is electrically connected. A radio frequency voltage, together with a direct current offset voltage, is applied between one pair of rods and the other pair, and ions travel along the quadrupole between the rods. For a particular ratio of voltages, only ions of a certain mass/charge ratio reach the detector. By continuously varying the voltage applied, a range of ions can be identified. Comprehensive reviews of the QMS of reactive plasmas have recently been published [104,105].

The use of QMS to characterise species within a plasma chamber at low pressure goes back over 20 years. In a paper by Alexander *et al.* [106] for example, hexamethyldisiloxane, HMDSO, was subjected to low pressure plasma treatments, and thin films were deposited onto silicon substrates. HMDSO plasma treatments confer hydrophobicity to substrate surfaces, and there is nowadays increasing interest in their application to textiles. The species within the plasma chamber were analysed by QMS. It was found that cationic oligomers of HMDSO were formed in the gas phase, and indeed the deposited material appeared to possess a structure

closer to these oligomers than to the original HMDSO. More recently QMS has been extended to atmospheric plasma treatments. One example is a study of the plasma treatments of a series of polyolefins, including polyethylene and polypropylene [107].

### 5.3 Optical emission spectroscopy (OES)

Although mass spectrometry can provide a highly sophisticated analysis *in situ*, it is arguably less readily implemented at a commercial level than some other techniques. One of these other techniques is OES, which analyses the spectral lines radiated from plasma sources. Line radiation results from photons emitted by the transition of electrons between discrete energy levels in ions, atoms and molecules. In technological plasma, line radiation predominantly arises from processes resulting from collisions between these species [2], many of which give rise to chemical reactions, as exemplified in Tables 2 and 3.

The light emitted from a plasma chamber, therefore, is a collection of the spectral lines generated by these species within the chamber, and there is a unique emission spectrum specific to each of these species. A diffraction grating splits the light, so that the emission spectrum of each constituent element can be extracted. The intensity of each spectrum is governed by the proportion of the element in the chamber. Those processes occurring in the presence of a textile substrate can then be readily compared with those taking place in its absence. Relevant examples of the use of OES include studies of the action of oxygen plasma on polypropylene [108] (Section 9.1), sulfur hexafluoride plasma on silk [109,110] (Section 9.2), and carbon tetrafluoride plasma on cotton fibres [111] to tailor their surface morphology. A particular feature of this last example was the observation of CO spectral lines during etching of the cotton fibres.

If the plasma is sufficiently thin in optical terms, radiation from all parts of the plasma can escape, with little being reabsorbed. Thus, the spectrum provides a continual insight at an atomic level into the processes occurring within a plasma chamber, and even in different parts of the chamber. At higher pressures, however, there can be the risk that emission spectra are derived solely from the outer part of the plasma. In such cases, more sophisticated methods based on optical absorption may be needed.

### 5.4 Langmuir Probes

The Langmuir probe is probably the commonest practical method for measuring the electrical properties of plasmas. In particular, the method also reveals information about the electrons present in the plasma. In this respect the technique complements QMS and OES, which determine the ionic and neutral species present. The electronic properties that can be measured include electron density and temperature, the distribution of electron energies and plasma potential. Ion density can also be assessed. The technique is quite straight-forward in that it involves

placing a wire or disk in the plasma and measuring the current in it over a range of applied voltages. It is therefore an intrusive technique, so the probe has to be designed such that it does not interfere in any way with the plasma. Whilst this difficulty has largely been overcome, some refinements are nevertheless required where changes in the character of the plasma need to be followed over a period of time. The most serious problem with the Langmuir probe technique lies in the interpretation of the current-voltage curves obtained, owing to the number of probe theories that have been proposed. Details of the types of current-voltage curves obtained and of their interpretation have been extensively reported in the literature [2, 112].

The application of the Langmuir probe technique to studies of the plasma treatments of textiles appears not to have been extensively reported in the literature. This sparsity of reporting can perhaps be attributed to the problems inherent in analysing current-voltage curves, despite the relative simplicity of the actual application of the technique. Nevertheless, some examples have been reported in the literature for textiles and related substrates, and in conjunction with other techniques have yielded some useful information about conditions in the plasma chamber, e.g. in a paper by Chaivan *et al.* [110]. A detailed illustration of the use of Langmuir diagnostics in the plasma treatment of textiles has been shown by Riccardi *et al.* [113], and this illustration is discussed in Section 9. 2 later in this review.

## **6. Statistical experimental design and analysis**

It is evident that not only can a textile surface be examined for the effect a plasma treatment will have had on it, but that the course of the treatment itself can be followed. These considerations imply then that there is a basis for devising particular process control strategies for desired plasma treatments. Nevertheless, these strategies need not be based solely on the approaches discussed so far. As mentioned in the Introduction, there are a variety of process control factors that can in practice govern the effect of a given plasma treatment on a given textile substrate. Another valuable approach, therefore, is the design of plasma treatment trials on a statistical basis using factorial experimental design. Key process control factors for a particular treatment, and any significant interactions between them, can then be evaluated using established statistical tests. Not only can optimum treatment conditions be formulated, but also important insights into the mechanisms behind the treatments can be gained. Both aspects can then also be included for creating process treatment strategies.

A good example has been published, concerning the optimisation of process control factors in the low pressure oxygen plasma treatment of polylactic acid (PLA) fabrics, to improve their wicking rate [114]. The control factors used in the experimental design were pressure, power applied and treatment time. By varying these factors and identifying interactions, the authors could determine optimal values for the

factors that produced the highest wicking rate. XPS revealed that the primary effect was the formation of carboxyl groups. In addition, SEM revealed etching of the PLA fibre surfaces, especially in non-crystalline areas.

A similar study has been reported on improvements to the hydrophilicity of a specially modified polyester fabric as a result of oxygen plasma treatment at atmospheric pressure [115]. The process control factors comprising the experimental design were discharge power, treatment time and the spacing between the two electrodes. Hydrophilicity was assessed from wicking trials and measurements of spreading rate. By using a so-called Box-Behnken statistical methodology, they determined the optimal values for the control factors.

An interesting use of statistical methodology to plasma treatments has recently been published by Delcorte *et al.* [83] in the analysis of SIMS data. Although this application does not concern textiles directly, it shows that spectroscopic data can also be treated statistically to assist process control formulation. Delcorte *et al.* describe a comparison of plasma polymer films of polystyrene, formed under different conditions of plasma treatment. Two commercial polystyrene samples were also included in the study: one linear and the other cross-linked. Using principal component analysis, an established statistical method, they determined that just two components contain nearly all the information in the SIMS analyses. The first of the components revealed that for the plasma polymers, the protonated styrene monomer and some oxygen-containing fragment ions dominated. For the two commercial polystyrene samples, the tropyllium ion,  $C_7H_7^+$ , stood out. The structural differences between the plasma polystyrene samples and the commercial samples are highly significant. The second component clearly revealed differences in the chemical nature of the plasma polystyrene films, depending on whether the films had been obtained above or below a power of 50-60 W. Films formed at powers above this threshold possessed less aromaticity and greater cross-linking and oxidation. Below this threshold aromaticity was retained in the films. The power applied is therefore particularly significant in determining the plasma polymer structure.

## **7. Computer and Mathematical Modelling**

Computer modelling is another approach that can assist our understanding of textile plasma processing. Some interesting examples have been published by Bogaerts and her colleagues [116,117]. They point out that several modelling approaches for plasmas are available: notably fluid models, Monte Carlo (MC) models and a combination of these models. Reactions in the gas phase at atmospheric pressure within a plasma chamber can be modelled using fluid modelling, and the densities of reacting species and species formed in the chamber, including free radicals, can be calculated as a function of time. For low pressure plasma reactions, Bogaerts *et al.* [117] emphasise the importance of the densities of electrons within the chamber and argue that, whereas a fluid modelling approach can still be applied to the other

plasma species present, an MC model should be applied to electrons. They combine the electron MC model with a fluid model for the other species, using a so-called hybrid plasma equipment model [118].

These types of computer modelling approaches to gas phase reactions in the plasma chamber are now gaining some traction. However, in the case of plasma treatments of textiles, or of any other materials, their presence in the chamber obviously has to be taken into account. A computer model also needs to accommodate reactions of plasma species with the textile. According to Bogaerts *et al.* [117], this input can, for example, be satisfactorily obtained from molecular dynamics simulations, in which the behaviour over time of a few thousand atoms within a few nm<sup>3</sup> volume is followed. Successive impacts can also be modelled, as the nature of the surface changes.

A good illustration of the utility of computational modelling is provided in a study by Dufour *et al.* [119] of the treatment of the surfaces of high density polyethylene (HDPE) foil with an atmospheric helium-oxygen plasma post-discharge generated by a radiofrequency plasma torch. HDPE surfaces provide a model for gel spun polyethylene (PE) fibre surfaces, and it is useful to consider this example in further detail. In this study, the effects of the treatment on HDPE surfaces were analysed experimentally by dynamic water contact angle measurements and by XPS. Changes were monitored in the wettability of the surfaces and in the nature of the functional groups responsible for these changes. An increased surface oxygen content was noted, attributable to the formation of polar groups, principally C-O bonds (which constitute ether groups), C=O (carbonyl) bonds and O-C=O (carboxylic) bonds. The fraction of C-C bonds, which constitute the backbone of the HDPE chains, was correspondingly reduced. In addition, depth profiles were determined, to assess any changes in the sub-surface: *i.e.* just below the HDPE surface. It was found that for none of these groups was the fraction significantly changed down to a depth of 9 nm.

An ageing study was also conducted to determine whether or not the increase in the level of polar groups was reversible. After a period of one month or so, the fractions of C-O and C=O bonds declined by 5% at most, irrespective of depth of sub-surface. The decline in the fraction of O-C=O bonds, however, was greater: 7-10%, but again largely irrespective of depth of sub-surface. The fraction of C-C groups by contrast rose, especially at greater depths. Therefore, whereas a rearrangement of functional groups might be expected initially at the HDPE surface before extending into the sub-surface, there is instead a movement of functional groups in the reverse direction. This observation can be explained by the formation during plasma treatment of oxidised compounds of low molar mass, which gradually migrate to the surface before being released to the environment.

The experimental results were complemented by computer modelling, notably molecular dynamics. Simulations were conducted of oxygen atoms impacting on and reacting with a polyethylene surface, and also the behaviour of oxygen atoms that had diffused below the surface. Additionally, these simulations were supported by so-called nudged elastic band calculations, applied to calculate activation energies for plausible reaction pathways. These simulations were able to explain the differences between the levels of the functional groups, as determined by XPS. Of all the plausible reactions that could be triggered by the plasma treatment, just three were identified as particularly important for the surface formation of oxygen-containing functional groups: a C-C cleavage reaction, hydrogen abstraction to form an aldehyde and the oxidation of the aldehyde to a carboxylic acid. Therefore, with outcomes of the simulations applied, the principal mechanisms involved could be identified. The simulations also threw some light on the ageing process. In particular, they revealed the comparatively low activation energies for the formation of low molar mass compounds containing C=O or O-C=O bonds.

This example illustrates then how computer modelling can be successfully applied to support and enhance practical results to provide better understanding of the process changes involved. Further examples are given later in this review. Thus, whilst computer modelling may seem highly theoretical to the practical textile technologist, it can have its place as an adjunct to actual practical approaches, provided the boundary conditions are recognised by which all modelling techniques are limited.

## **8. Process Control**

For plasma treatments of textiles to take off as a versatile technology on a commercial scale, process control strategies will be required [120]. It is our aim in this review to demonstrate that, despite the obvious complexities underlying plasma treatments, judicious application of the many approaches available, such as those described above, should provide considerable assistance in formulating process control strategies. Nevertheless, in the time since the publication of "Plasma Technologies for Textiles", edited by Shishoo [1], there appears to have been little movement towards embedding even simple process control technologies in the plasma treatment of textiles. However, implementing even a simple process control strategy could offer production cost savings as well as enhancing uniformity and quality of products, potentially adding significant value to those products [121].

At its simplest, and perhaps anecdotally predominant, process control in plasma application to textiles relies on visual monitoring and applied plasma power control by a skilled human operator. Additional control flexibility may be introduced to such a system through operator control of process gas pressure and composition. Replacing the operator with a photosensor-based electronic control system would be an easy step if the operator is only monitoring the intensity of the light from the plasma. However, it is more likely in such applications that the operator has the



experience to sense colour changes and this is where OES would be invaluable. An OES-based control system integrating the knowledge base of the operator and managing applied plasma power and gas pressures and composition would therefore represent a basic approach to process control. Beyond this electrical potential measurements *via* a Langmuir probe, which is nowadays both robust and relatively easy to implement in an industrial environment, could be integrated into the control system. More sophisticated plasma analysis using mass spectrometry, commonly used in the laboratory to probe plasma composition, is likely much harder to potentially implement online, as noted above. It may perhaps, however, be worth the effort where complex gas mixtures are employed in the process *e.g.* in polymer deposition. Coupling these with control of the plasma process control parameters outlined in the Introduction then provides the necessary feedback to establish process control.

Of course, such a simple strategy ignores the textile. Additional monitoring options might exist in terms of textile reel-to-reel tension and speed and even, for woven fabrics, the use of fast image processing methods to define weave density. Furthermore, it is clearly highly desirable to quantify the surface characteristics of a treated textile online, but such surface characterisation is likely to remain technologically limited for the near future. Thus, a direct link to the conditions within the plasma and the textile itself may be very difficult to establish online in a process. What may be easier, however, is to explore the phase space of the textile parameters and surface characteristics of the treated textile through sufficient laboratory work to establish a good microkinetic model phenomenologically describing the plasma treatment process. This approach is already well-established in other technologically significant areas where microkinetic methods have blossomed in recent years, *e.g.* catalysis [122], and could, we suggest, be applied in textile treatment with only modest effort.

## **9. Some examples**

### ***9.1 Treatments of polypropylene fibres with oxygen-containing plasmas to confer hydrophilicity***

We now consider some specific textile-plasma systems and show how results gathered from the literature serve to provide practical information to textile scientists and technologists wishing to apply plasma treatments. The first example concerns the treatment of polypropylene textiles with oxygen-containing plasmas, to render their fibre surfaces more hydrophilic.

Polypropylene (PP) textiles have many technical applications. Nevertheless, the low surface energy of their fibres and consequent hydrophobicity, together with the smoothness of the fibre surfaces, affects processing, especially during wet treatments, and reduces their efficacy in a number of applications. For example, the inherent hydrophobicity impedes the surface application of finishes, such as spin finishes, during processing. PP fabrics are used in absorbent products such as

nappies and feminine hygiene products and in geotextiles and filtration media. They are even used in biomedically implantable products such as hernia patches, and it is desirable that these products are biocompatible with blood cells and surrounding tissue. Aqueous fluids must therefore be able to wet the fabric, and the hydrophobicity of PP fibre surfaces militates against this. In addition, PP textiles are widely used for reinforcing concrete. Good adhesion between the PP fibres and the concrete matrix is very important. However, there is little chemical compatibility between the two. Rendering the PP fibre surfaces hydrophilic would help to overcome the problem.

Oxidation of the fibre surfaces through suitable plasma treatments overcomes these difficulties to a considerable extent, and indeed plasma oxidation of PP surfaces was reported over half a century ago [123]. For example, adhesiveness is promoted in composites, laminates and fibre reinforced concretes, and biocompatibility is considerably enhanced. It is well known too that PP fibres cannot be dyed unless they contain specific additives. Treatment of the fibre surfaces with oxygen-containing plasmas can promote dyeability with disperse dyes to some extent [124].

The efficacy of treatments in which PP fibres are exposed to oxygen-containing plasma, including air, has been known for several decades. More specifically, it was established in the 1990s that oxidation of the PP fibre surfaces occurs, predominantly through the introduction of C-O, C=O and O-C=O bonds [125-127]. The formation of C-OH and C=C functionalities was also recognised. In addition, the fibre surfaces are roughened. There have, however, been doubts about the durability of these treatments. There is evidence that the outer polymer layers of the fibres consist of oxidised and unoxidised segments and that, in contact with air, these layers rearrange themselves over time, in such a way that hydrophilicity is somewhat lowered [128]. This apparent ageing can be compared with the ageing of plasma-treated HDPE surfaces discussed in Section 7. Loss of hydrophilicity can be considerably reduced by prior treatment of the PP fibres with a noble gas plasma, through crosslinking of the polymer chains at the surface, a treatment known as CASING (crosslinking by activated species of inert gases). Surface durability is important for the subsequent wear and tear in the use of the PP textile and its permanence against washing, light and other external influences.

Since these reports were published, much effort has been expended in studying in greater detail the effects of these plasma treatments and, to some extent, the processes that give rise to these effects. The approaches discussed in the previous sections have nearly all been reported in the literature. Whilst many of these studies relate to non-textile forms of PP, the information gained from the studies of surface chemical changes may well still be largely relevant to textile forms. Conclusions derived from changes observed in the surface topography of non-textile substrates can also be transferred to PP fibres, but here a degree of caution is needed. For example, these changes will be highly dependent on the initial topography of the

sample surface and on the proportion and distribution of crystalline and non-crystalline regions at the surface. The curvature of fibres may also have to be taken into account.

Turning first to the surface topography of PP fibres, we note then that treatments with plasmas containing oxygen roughen the surfaces, the extent and nature of roughening depending on the processing conditions. Roughening can involve etching, pitting of the surface, rippling effects and the formation of tiny (nanoscale) grooves [23,129]. The appearance of aggregated particles in the range 100-400 nm or more has also been observed, and the formation of these aggregates may well be equivalent to that of well-defined angular structures of similar size when PP tape has been treated with low pressure oxygen plasma [65]. In addition, the presence of cross-shaped structures in clusters on the tape surfaces was noted. The appearance of these angular and cross-shaped structures was attributed to the recrystallization of PP in parts of the tape surface. This recrystallization would very probably have been preceded by localised surface melting, as observed by Collaud Coen *et al.* [130] in the plasma treatment of PP plates. It is noteworthy too that after oxygen plasma treatment, the profiles of water droplets on PP fibre surfaces become much less regular. The droplets become flattened along the curvature of the fibre surface at right angles to the fibre axis [23].

It is evident, therefore, that complex changes in PP fibre surface topography can arise, and these changes need to be taken into account when designing a plasma treatment process, particularly for those applications where fibre surface topography will be important, such as fibre-matrix adhesion in coatings and laminates. The efficacy – or inefficacy – of these different surface topographies in promoting adhesion could be tested using statistical experimental design. Whereas studies have been conducted on the influence of overall roughness at a nanoscale level, to the authors' knowledge the effects of different forms of surface roughness in PP fibres have not so far been reported. In addition, the determination of force-distance curves in the atomic force microscopy of PP fibre surfaces would also prove useful, to pursue desired improvements in surface mechanical properties. An example of the application of force-distance analysis to PP surfaces was reported by Nie *et al.* [131].

Changes in surface topography are accompanied by surface chemical changes, notably the formation of oxidised functional groups and of C=C bonds, as noted above. More recently reported work has confirmed these findings [132-134], and in some reports the proportion of each functional group has been determined. The types of plasma system used have been varied, but taken together they can point the way towards the formulation of a suitable plasma process using a particular set of processing conditions. Not surprisingly perhaps, much of the work has focussed on chemical analysis of the PP surface before and after a plasma treatment. In this

respect, XPS has figured prominently, with a few supporting results from SIMS [135] and FTIR [136].

The associated increase in hydrophilicity has been confirmed through measurements of the contact angle of water droplets. Some examples are provided in Table 4, from which it can be noted that the values of the contact angles for both the untreated and treated samples vary widely. However, contact angle values are influenced not just by the chemical nature of the substrate surface but also by its topography.

It is well established that surface roughness makes the contact angle,  $\theta$ , further removed from  $90^\circ$ : either lower than for a smooth surface where  $\theta < 90^\circ$  or much higher, where  $\theta > 90^\circ$ . As PP is a hydrocarbon, water is normally repelled from its surface, and  $\theta > 90^\circ$ . The value of  $86^\circ$  reported by Carrino *et al.* [137] may suggest the presence of a few hydrophilic groups already present on the surfaces of the samples they studied. After plasma treatment,  $\theta$  becomes much lower than  $90^\circ$ . Figure 2 shows a plot of  $(90^\circ - \theta_f)$  against  $(\theta_i - 90^\circ)$ , with values taken from Table 4. An approximately linear relation is revealed. The plot thus provides evidence for the additional effect of surface roughness.

Some more recent studies have begun to focus on *in situ* investigations, notably using optical emission spectroscopy (OES). Kregar *et al.* [108] investigated the treatment of PP samples with low pressure oxygen plasma. They noted that, in the absence of PP, the plasma is dominated by oxygen atoms. In the presence of PP samples, however, several other species can be detected, including CO, OH and CH. The appearance of CO and OH species could be readily attributed to the oxidation of the PP surface. The presence of the CH radicals in the plasma could be explained by degradation of the PP surface. Kregar *et al.* [108] also noted the slow increase in concentration of these species up to a critical time, when their concentrations increased much more rapidly and there was a marked fall in the concentration of oxygen. The authors concluded that at lower pressures there is predominantly reaction of molecular oxygen cations with the PP surface, whereas at higher pressures there is reaction of oxygen atoms with the PP surface. Thus, their work begins to show how the important reactions in the plasma treatment can be identified.

Nisticò *et al.* [138] applied OES and XPS in their investigation of the treatments of PP fibres using plasma mixtures of helium and oxygen at atmospheric pressure. They found an increase in the concentration of molecular oxygen cations and the formation of oxygen atoms, which they attributed to the decomposition of molecular oxygen. XPS confirmed the presence of C-O and C=O functional groups on the fibre surfaces. From their results they proposed some reaction pathways both in the plasma phase and with fibre surfaces.

Although the reports cited so far throw considerable light on the plasma treatment process they are, arguably, still insufficient to lead to the provision of practical formulations. It would be of help to have more detailed understanding of:

- the mechanisms underlying the formation of these groups;
- what proportions of these groups are best for achieving a desired application of the PP textile;
- how these proportions can be achieved.

For the first of these, computational analysis has been shown to be particularly helpful, as illustrated in a paper by Dorai and Kushner [139]. Using a well validated plasma kinetics model, they examined the reaction kinetics both in the plasma phase and at the PP surface when PP is treated with a humid air plasma. Clearly nitrogen and water vapour were present as well as oxygen, yet the action of oxygen generally dominated. They identified many of the individual reactions occurring at the PP surface, and could categorise them into initiation, propagation and termination reactions and set out a complex reaction mechanism. Indeed many reactions are similar to those identified in the thermal oxidation of PP. Dorai and Kushner [139] could also estimate the rate of each constituent reaction. On this basis they devised a reaction scheme to describe the plasma treatment. They noted that reaction with the PP surface takes place primarily with  $O\cdot$  and  $\cdot OH$  free radicals in the gas phase. They noted too that the roughening of the PP surface occurs through chain scissions and the formation at the surface of oxidised compounds of low molar mass. The more volatile of these compounds are emitted from the surface, but these compounds may also aggregate into globules at the surface.

The work of Dorai & Kushner was followed by that of Bhoj & Kushner [140], using a more sophisticated kinetics model. They investigated the actions of repetitively pulsed  $He/O_2/H_2O$  plasma discharged on moving PP sheets. They also noted the generation of  $O\cdot$  atoms and  $\cdot OH$  radicals during each pulse and the reaction of these radicals with the PP surface. Between pulses the radicals were largely consumed, with most of the oxygen atoms being consumed to form ozone, which tended to accumulate over many pulses. Again, a highly complex reaction mechanism was set out.

These two papers demonstrate that the mechanisms underlying the formation of oxygen containing functional groups at the PP surface have already been described. Moreover, the reaction schemes set out by Kushner and his colleagues assist in the prediction of the relative proportions of the groups. The task then remains to determine the optimum proportions in a particular plasma system for achieving a desired PP textile application.

This goal can be approached using statistical experimental design, as outlined above. A simple example is provided by the work of Carrino *et al.* [137], who sought

to determine which plasma process control parameters significantly affect the contact angle of water droplets on air plasma treated PP surfaces. They deduced that the voltage across the plasma chamber had a significant influence on reducing the contact angle, as did the interaction between voltage and treatment time and between voltage and flow rate of air. Although these results on their own throw little light on underlying mechanisms, an analogous approach could be adopted to determine which parameters significantly determine the proportion of oxygen containing surface functional groups and which proportion is best suited for a particular application of the textile.

## *9.2 Treatments of silk with SF<sub>6</sub> plasma to confer water and oil repellency*

It is of course no secret that silk fabrics have been widely regarded for centuries - and even millennia - as luxurious and glamorous, and indeed silk is one of the most delicate of natural fibres. Although more recently technical applications have also been found for silk fabrics, such as materials for parachutes and biomedical applications, it is as 'high-end' clothing and home furnishing fabrics that they are still particularly regarded, even despite the appearance of cheaper 'sand-washed' silk garments on the market over the past 30 years [141]. Most silk products do, however, need a lot of careful attention during use, notably during cleaning, on account of their delicate nature. The removal of stains from silk fabrics often requires particular care, and silk deteriorates markedly when exposed to perspiration, chlorine-based bleaches and also detergents that contain even mild alkalis. If silk can be rendered more water repellent, then some of these adverse properties will be largely removed.

There have been many approaches in the textile industry to confer water repellency, and detailed discussions of them can be found in, for example, books by Schindler & Hauser [142] and Mather & Wardman [143]. Early water repellent treatments involved the use of waxes and melamine-based products, but around the 1980s treatments based on the silicone, polymethyldisiloxane, became popular. The structure of polymethyldisiloxane is given in Fig. 3. The chains of this polymer become oriented on textile fibre surfaces such that the methyl groups in the polymer face outwards and the fibre surface is rendered hydrophobic, as also shown in Fig. 3. In the last 20 years, treatments using fluorocarbon agents have gained popularity in that they also confer oil repellency. This property renders the silk resistant to oily stains as well. The fluorocarbons contain perfluorinated acrylate polymer as the active component, which is linked to long-chain, lauryl or stearyl, acrylate comonomers, as illustrated in Fig 4. The fibre surface thus becomes highly hydrophobic owing to the formation of an outer layer of CF<sub>3</sub>- groups. However, more recently doubts have grown about health problems that may arise from exposure to fluorocarbons, notably the C8 fluorocarbon, perfluorooctanoic acid, C<sub>7</sub>F<sub>15</sub>COOH, which appears in trace amounts as a by-product in the manufacture of these fluorocarbon agents. Although shorter chain C6 derivatives are currently considered

acceptable as an alternative, the development of conventional types of treatment based on fluorine-free agents is nevertheless gaining some momentum. Commercial processes to confer both oil and water repellency are discussed by Coulson [15].

To minimise the level of fluorine required to confer hydrophobicity, low pressure plasma treatments with fluorine-containing compounds can be applied. This approach also serves to reduce damage to the silk substrate, an important consideration in view of the delicate nature of its fibres. These treatments can be effected with fluorocarbons, such as carbon tetrafluoride ( $\text{CF}_4$ ), hexafluoroethane ( $\text{C}_2\text{F}_6$ ) or trifluoromethane ( $\text{CHF}_3$ ), or with sulphur hexafluoride ( $\text{SF}_6$ ). A fluorocarbon treatment results in the formation of a thin film of fluoropolymer on the silk fibre surface but, because of its fluorinated nature, the film may not adhere strongly enough to the surface during subsequent treatment and use of the silk. It has also been asserted that the film reduces water permeability, and so makes garments less comfortable to wear [109].  $\text{SF}_6$  plasma has therefore often been applied to circumvent formation of fluorocarbon film [144], and its use also circumvents concerns associated with fluorocarbons.

The growing pressure to reduce or even eliminate the use of fluorocarbons on a commercial scale could be expected to extend to  $\text{SF}_6$ , in view of its fluorine content.  $\text{SF}_6$  is, however, a dense unreactive gas that is considered harmless to its immediate environment. It is not toxic and can be readily handled. Nevertheless, there are fears that because of its use on a commercial basis, it will in time become a significant greenhouse gas. Currently, however, its contribution to global warming is very small, and it will be kept small if it is effectively recycled. Moreover, for low pressure plasma treatments the amounts of  $\text{SF}_6$  consumed are tiny.

$\text{SF}_6$  plasmas have been used for some time in the microelectronics and solar cells industries [145] and the chemical reactions between the reactive species within the plasma chamber have been documented by Riccardi *et al.* [146], along with rates of reaction in low pressure conditions. Indeed, Riccardi *et al.* [146] were able to present a very detailed description of an  $\text{SF}_6$  plasma, through a combination of experimental results and computer simulation, and the design of a low pressure plasma reactor, suitable for applications to textiles on a small commercial scale, has also been published [113].

It is noteworthy that much of the information about the conditions inside the plasma reactor has been obtained through the use of the Langmuir probe technique, though care has had to be exercised in the analysis of the results obtained, for the reasons discussed in Section 5.4. The papers by Riccardi *et al.* [113,146] are especially pertinent in this respect, as both papers provide extensive discussions of the application of Langmuir probes. The authors showed, for example, that there was an unexpectedly high concentration of negative ions and an unusually low concentration

of electrons, owing to the attachment of electrons to plasma species. Attachment of electrons will have special significance for fluorine-containing gases, which are highly electronegative. The authors were also able to take account of the rates at which these species are transported in the plasma chamber.

The value of computer simulations of the composition of the plasma, depending on both treatment time and distance of the sample from the point where the plasma is generated, has also been demonstrated [146]. These simulations have been performed through the application of a numerical method based on the reaction kinetics of the plasma species and their transport properties. A combination of the experimental use of Langmuir probes and computer simulations has thus led to quite a detailed description of the processes occurring in different parts of a plasma reactor. In particular, it was concluded that reaction of excited fluorine atoms with the silk fibre surface is the key to surface fluorination. The concentration of fluorine atoms in different parts of the reactor can be monitored, and even predicted, and the level of fluorination of silk fibre surfaces can then be regulated. High levels of fluorine on the treated surfaces can then give rise to extensive hydrophobicity [113]. Levels of fluorine atoms in a plasma chamber can also be assessed using OES [109,110].

The chemical change occurring at the silk fibre surface seems moderately straightforward, despite the many reactions occurring in the bulk of the plasma chamber reactor. Hydrogen atoms bound to carbon atoms in the silk fibroin chains are first abstracted from the silk fibroin chains and then replaced by excited fluorine ( $F\cdot$ ) atoms present in the plasma chamber [145]. This mechanism therefore contrasts with the diversity of polar groups that oxygen-containing plasmas confer on PP fibre surfaces, as discussed in Section 9.1. Moreover, XPS traces reveal no reaction with surface nitrogen and oxygen atoms [144] though it appears that the level of surface oxygen, whilst not influenced by the duration of the plasma treatment, is significantly higher compared with that of untreated silk. No sulfur becomes bonded to the fibre surfaces. Successful fluorination of silk fibre surfaces is strongly influenced by the position of the silk sample in the plasma chamber [144]. The sample should be located some distance away from the point of plasma generation, because high concentrations of ions rather than of free radicals predominate at the point of generation. Thus for a given plasma reactor the optimum rates and extent of a surface plasma treatment could be assessed by means of statistical trials.

The value of computer simulation has been further provided by Sangprasert *et al.* [147]. Bearing in mind that the amino acids, glycine (Gly) and alanine (Ala), together comprise ca. 74% of the amino acid content of silk fibre, they utilised density functional theory to investigate several possible mechanisms for the action of fluorine atoms on the model compounds, Gly-Ala and Ala-Gly. The structures of the two compounds are illustrated in Fig. 5, from which it can be noted that, in contrast to Gly, Ala possesses pendant methyl ( $CH_3-$ ) groups. The lowest activation energies



calculated by Sangprasert *et al.* were for substitution of hydrogen atoms by fluorine atoms at the pendant methyl groups of both model compounds. It is worth pointing out that, of course, silk also contains a significant content of the amino acid, serine (Ser), ca. 12%. However, Ser contains pendant hydroxyl (-OH) groups and it has been noted above that no reaction of SF<sub>6</sub> plasmas with surface oxygen atoms seems to occur [144]. It therefore appears to be the alanine content of the silk fibre that is important for successful treatment by SF<sub>6</sub> plasmas.

Nevertheless, the chemical structure of the silk fibre surface is more complex than that of the PP fibres discussed in Section 9.1. It is clear too that the fluorine atoms are much larger than the hydrogen atoms they have replaced. Moreover, etching and changes in surface crystallinity should also be considered. These factors are all likely to have a bearing on the level and rate of formation of C-F groups at the surface, as well as the stability of the fluorinated polymer chains once they have been formed.

Indeed results on the stability of the fluorinated silk fibre surface, even after treatment with SF<sub>6</sub> plasma rather than with fluorocarbon plasmas, are conflicting. On one hand, Selli *et al.* [144] have observed that the high hydrophilicity initially obtained can be partly lost a week or so after the treatment, though there is little or no subsequent loss and there is still a good degree of hydrophobicity. They suggest that after exposure of the treated silk fibres to air, there is a gradual rearrangement of some of those surface polymer chains to which fluorine atoms have been bonded. Some of the fluorine atoms become oriented away from the fibre surface, in order to minimise surface energy. Such a change could result from the larger size of the fluorine atoms. However, the same authors also note that surface crystallinity can increase as a result of plasma treatment, probably due to preferential etching of regions of unoriented silk polymer chains. An increase in surface crystallinity then serves to maintain high hydrophobicity over a longer period of time, as the polymer chains are much more constrained from undergoing rearrangement. On the other hand, Suanpoot *et al.* [109] have noted that hydrophobicity can be maintained for at least 30 days. There therefore seems to be a conflict between the tendency of the fluorinated polymer chains to rearrange themselves, or partly so, and the restraint on chain rearrangement imparted by increased surface crystallinity. An increase in surface crystallinity is therefore desirable to stabilise the hydrophobicity conferred. It is thus illustrative to probe further the mechanisms by which SF<sub>6</sub> plasma treatments operate and how knowledge of these mechanisms can assist process control in a particular plasma treatment unit.

An additional consequence of etching is roughening of the silk fibre surface at a nanometre level, a factor that will also contribute to increased hydrophobicity. It has been suggested, in addition, that a contributing factor could be the much larger size of the surface fluorine atoms compared to that of the hydrogen atoms they have replaced [145]. As with the example in Section 9.1, we are not aware, however, of

any analysis of different forms of surface roughness, nor to our knowledge has force-distance analysis been applied to examining any changes in surface mechanical properties. Such studies would be beneficial in assisting the formulation of suitable process control parameters, for applications where the surface physical and mechanical properties of hydrophobic silk could be important, such as fabric handle.

It is noteworthy that several of the authors cited in the preceding paragraphs of this section report that the contact angle of water droplets on treated silk fibres is generally about 130-140°. This observation may be contrasted with the range of contact angles shown in Table 4 for PP samples. Although the nature of the untreated silk fibre surface will be the same – or very nearly so - for all these authors, it could be expected that different plasma conditions would have resulted in different features of surface roughness and hence influence the contact angles determined. However, Hodak *et al.* [145] claim that in their studies AFM images revealed the surface morphologies of their treated samples to be similar, irrespective of treatment condition, a result that is in keeping with the broad consistency of the contact angles. In all cases, the root-mean-square roughness increased from 10 nm to 30 nm. These results suggest then that the fluorinated nature of the treated silk fibre surface is the predominant contributor to hydrophobicity but that increased crystallinity at the surface is also desirable to preserve the hydrophobicity obtained.

### ***9.3 Plasma treatments of wool to confer shrink resistance***

It is well known that wool fabrics shrink irreversibly during use, and particularly during washing, unless they have been given a preventative treatment. Shrinkage very largely arises from the innate ability of wool to felt. Felting involves the progressive entanglement of wool fibres when they are subjected to mechanical action, especially agitation in water, and the fabrics become thicker and bulkier. A major factor contributing to felting is the scale structure of the wool fibre surface, arising from the overlap of adjacent cuticular cells. This cuticular structure is shown diagrammatically in Fig 6. The overlapping scales in turn give rise to the so-called directional frictional effect (DFE), whereby the coefficient of friction from the root to the tip of a fibre is much less than that from the tip to the root. Although the scale structure is exploited in the production of such products as overcoats and the playing surfaces of snooker and pool tables, it is also the prime cause of the shrinkage of woollen garments during washing.

Shrinkage can be considerably reduced or even prevented through oxidative treatments, which soften, degrade or even destroy the cuticular scales. An alternative approach involves the deposition of a suitable polymer: the polymer can mask the scale structure, weld junctions between fibres, or even apply both mechanisms. Conventionally, an oxidative treatment is often applied first, before the deposition of a polymer onto the treated fibre surfaces. In some commercial treatments only a polymer is applied, though the flexibility of a wool fabric can then

be compromised. A particularly successful commercial example is the chlorine-Hercosett wool top process, first commercialised by Villawool (Australia) in 1967 in collaboration with the Australian Wool Corporation, whereby the fibre surfaces are oxidised by a chlorinating agent prior to polymer coating of the fibre with a reactive polyamide-epichlorohydrin resin, Hercosett® (Hercules). Without the subsequent polymeric treatment, shrink resistance is progressively lowered in successive washings [148]. A drawback of this two-step process is the reduction in wet fastness of applied acid dyes [148]. The mechanisms underlying felting and resistance to felting have been extensively reviewed by Rippon [149]. Techniques for commercial shrinkproofing treatments are discussed by Kettlewell *et al.* [150].

There have, however, for some time been considerable environmental concerns about the discharge of organic chlorine compounds in waste liquor, and alternative strategies have been pursued. One viewpoint is that because modern washing machines use reduced mechanical action, the problem of felting is in practice less severe. Whilst this argument may prove to have validity, the problem of felting is still not properly resolved: felting then requires more washes to become as severe.

Alternative methods of oxidation of the scale surface have been the focus of interest for some time. Potassium permanganate ( $\text{KMnO}_4$ ) and Caro's acid ( $\text{H}_2\text{SO}_5$ ) have been successfully applied, but again their presence in waste liquors is environmentally dubious. Another approach is the use of enzymes, specifically proteases and even lipases [151,152]. However, their application requires care. Because proteases specifically degrade protein chains, soluble proteins can readily be formed, with a consequent loss of fibre weight and fibre strength [150]. A further option is the adoption of plasma treatments. Plasma treatments are proving to be acceptable alternatives, especially as such treatments are attractive environmentally and economically, although different polymers are needed for the subsequent treatment stage.

The idea of applying a plasma treatment is far from new and was, for example, proposed by Rakowski [153] thirty years ago. Resistance to felting that could be achieved by a 'clean' process was a key driver in this development. Later, Rakowski described a machine for the plasma treatment of wool top [154], as it is often wool top on which shrink resistant treatments are conferred. He noted that an aftertreatment by a suitable polymer further increased shrink resistance, although the polymers conventionally used on pre-chlorinated wool were ineffective. Fabric handle was also impaired, but could be improved by careful treatment using a suitable enzyme. Since then numerous papers have appeared on the application of plasmas to reduce felting in wool, and indeed one company, Südwole, based in Germany, has launched a technology it calls Naturetexx Plasma for the plasma treatment of wool fibres. Nevertheless, the question still is: why have plasma treatments not yet taken off widely in an industrial context? One reason, as noted above, is the investment required to install plasma treatment equipment. It also has

to be borne in mind that the surface of a wool fibre is highly complex both topographically and chemically, and is subject to considerable variation. Different qualities of fibre are obtained from different breeds of sheep, and even from a single fleece. The sheep's nutrition may have a bearing as well. Thus, statistical trials have shown that propensity for felting in cashmere fabrics is influenced by the animals' nutrition [155]. Poorly fed goats grew cashmere that possessed a lower propensity to felt compared with better fed goats. It has also been shown that for atmospheric plasma treatments the absorbed moisture content of the wool has an influence [156]. Thus a plasma processing treatment, particularly on a commercial scale, may well have to be subject to carefully controlled conditions. For these reasons it is therefore instructive to delve more closely into the mechanisms underlying reduction of wool felting by plasma treatments, at the same time noting that these treatments will also affect other properties of wool. The benchmark to be met for shrinkproofing using plasma treatments can be considered to be the chlorine-Hercosett® process.

It would be useful initially to examine what structural and chemical differences at the wool fibre surface arise from chlorination and plasma treatments, and what roles are needed for the subsequent treatment with polymer. Chlorination is generally carried out either by exposure of the wool fibres to a salt of dichlorocyanuric acid, DCCA, [157] or by the Kroy process [158], which uses an acidic solution of sodium hypochlorite, NaOCl. A series of SEMs shown by Cardamone *et al.* [159] reveals that at pH~4 DCCA steadily erodes the scale structure, depending on the strength of the DCCA solution and the duration of the treatment. In the process, the scale edges are progressively softened [150]. Cardemone *et al.* [159] observed that a sufficiently strong solution gives rise to a virtually smooth fibre surface, but detected no cleavage of the cuticle. The Kroy process also induces some loss of cuticular structure [160]. Chlorination thus appreciably reduces the DFE.

Both sets of authors used XPS to monitor the chemical changes at the fibre surface. The principal oxidation process triggered by these chlorinating agents is cleavage of the disulfide (-S-S-) bonds linking adjacent protein (keratin) chains, to yield sulfonic acid (-SO<sub>3</sub>H) groups. A small proportion of carboxylic acid (-COOH) groups also appear to be formed. In addition, the thin lipid layer of predominantly 18-methyleicosanoic acid present in the epicuticular membrane covering each cuticle cell is degraded. The softening of the scale structure can be attributed to absorption of water by newly formed peptide fragments, which contain -SO<sub>3</sub>H groups. One consequence of these changes is that the wool fibre surface becomes more hydrophilic.

XPS and FTIR have revealed that a number of the changes brought about by treatments with oxygen-containing plasmas are broadly similar to those effected by chlorinating agents. Thus, sulfonic acid groups, and also sulfosulfonic acid (-SSO<sub>3</sub>H) groups, are formed from cleavage of disulfide crosslinks [161,162]. A variety of hydrophilic bonds are introduced as well: these include C-O, C=O, O=C-O, O-H and

O=C-N [163,164]. The levels of C-C and C-H are reduced. Increased hydrophilicity is confirmed by reductions in the contact angles of water droplets. For example, Canal *et al.* [165] observed a fall from 103° to 58°, and then after an extended treatment to 35°. Cheng *et al.* [166] noted a fall from 116° to 59° in their experiments.

The extent of the reduction in contact angle will depend not just on surface chemical changes but also on changes in surface topography. Thus, the edges of the individual scales become less distinct [44], though even after extensive exposure to plasma a scale structure is still discernible [3]. However, it is particularly noteworthy that in addition to these changes, the scales themselves become pitted [3,44,161], a feature not observed after chlorination of the fibres. Nitrogen plasma treatment appears to be more benign: Kan & Yuen [3] and Shahidi *et al.* [164] observed some pitting, but Canal *et al.* [165] observed no obvious changes to the scale surface. Pitting leads to a greater coefficient of friction at the fibre surface. There is also some degree of rounding off of the scale edges. Thus the scope for increased fibre entanglement and consequent felting as a result of mechanical agitation is considerably reduced.

An important paper by Dai *et al.* [167] discussed *in situ* studies to analyse the reactive species present in the plasma. Their work was conducted mainly on oxygen plasmas at low pressures, and analysis was conducted predominantly using Langmuir probes. The reaction chamber was separated from the plasma source. Vacuum ultraviolet (VUV) emission measurements were also made to determine the level of molecular oxygen in the plasma. The density of atomic oxygen was estimated from the reduction in molecular oxygen concentration caused by the plasma discharge, on the basis that under the plasma treatment conditions being used, oxygen atoms were primarily produced from dissociation of oxygen molecules [168]. Increases in surface energy were also determined, in order to follow the transition of the wool fibre surfaces from hydrophobic to hydrophilic. Dai *et al.* [167] demonstrated that the key species in promoting the transition was atomic oxygen. Charged species seemed to have little effect, and the role of excited oxygen molecules appeared insignificant.

Dai *et al.* [167] also reported XPS measurements comparing the treated and untreated fibre surfaces, which revealed concomitant increases in hydrophilic bonds linking carbon and oxygen, such as C-O, C-O-C, C=O and O-C-O, and corresponding reductions in C-H, C-C and C=C bonds. The modification of the fibre surfaces results from their direct reaction with excited atomic oxygen. It may be noted here that modification of PP fibre surfaces is very often the result of their reaction with atomic oxygen, as noted in Section 9.1. A parallel may also be drawn with the treatment of silk with SF<sub>6</sub> plasma (Section 9.2), where the reacting species was shown to be atomic fluorine, despite the complex mixture of plasma species. It is noteworthy too that in locating the wool samples some distance away from the

plasma source they were subjected predominantly to excited atomic oxygen. It will be recalled that silk samples need to be similarly located for atomic fluorine to react with the fibre surfaces. Interestingly, no significant changes were noted from SEMs between the topographical features of the treated and untreated wool fibres under the experimental conditions applied. The authors concluded that only the outermost surface layers of the fibres had been affected, primarily the lipid layer. More extensive exposure to oxygen plasma would destroy the lipid layer and start to oxidise the underlying protein structures.

As with the examples of HDPE, PP and silk (discussed above in Sections 7, 9.1 and 9.2 respectively), there is evidence that wool too is subject to ageing after plasma treatment. Naebe *et al.* [169] reported that, immediately after helium plasma treatment at atmospheric pressure, there were significant increases in oxygen and nitrogen concentrations at the fibre surfaces, as revealed by XPS. A reduction in carbon surface concentration was also observed. After 14 days, however, the oxygen and nitrogen surface concentrations fell by ca. 6% and 9% respectively, and the carbon surface concentration was raised by ca. 6%. No change in sulfur concentration over this period was observed. The concentrations of all these elements then remained stable, except for that of oxygen, which fell by a further 3% or so until it too remained stable. No change in fibre morphology was apparent during this period of ageing. It was concluded that the plasma treatments had degraded the lipid content of the fibre surfaces, and that the subsequent ageing process involved the rearrangement of some protein-lipid chains. After 28 days, however, the plasma-treated surface became stable and was still markedly different from the surface of the untreated wool fibre.

A practical benefit of applying *in situ* techniques was well demonstrated by Osenberg *et al.* [170]. They treated wool in a large plasma chamber that had been pumped down to low pressure. They noted that, although increased energy input during a plasma treatment led to reduced felting, the wool started to burn if the energy input was too great. An online control procedure was therefore devised. However, given that online control of felting behaviour was impractical, suitable plasma diagnostics were trialled instead: QMS, OES and Langmuir probes.

For much of their work the authors adopted a 'static treatment', equivalent to a batch process. After the equipment had been pumped down but before plasma treatment had commenced, QMS revealed that the mass spectrum was dominated by the spectral line at 18 atomic mass units (amu), attributable to the release of moisture from the wool sample. Lines corresponding to molecular hydrogen (2 amu), oxygen (32 amu) and nitrogen (28 amu) were also observed. It should be noted that carbon monoxide, CO, would also give rise to a line at 28 amu, but no CO was likely to be present prior to plasma ignition. Once plasma treatment was under way, the spectral line for water at 18 amu decreased slightly, and those corresponding to H<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub> (2, 32 and 28 amu respectively) increased. There was also a steady rise in an

OH line at 17 amu and a carbon dioxide, CO<sub>2</sub>, line at 44 amu. The increase in the signal observed at 28 amu was attributed to the production of CO rather than to N<sub>2</sub>. As plasma treatment proceeded, the O<sub>2</sub> line reached a maximum intensity, before falling away significantly. The H<sub>2</sub> line revealed similar, but less marked behaviour.

Osenberg *et al.* [170] determined that if plasma treatment was halted just before the crossover of the intensities of the lines at 28 and 32 amu, no burning of the wool was observed, while felting resistance was considerably improved. The QMS results were supported by OES, but Osenberg *et al.* stated that measuring a complete spectrum took too long a time for OES to be adopted as a process control tool. Langmuir probes were tried with a view to finding a correlation between ion density and felting behaviour. There were, however, several problems. The authors pointed out that ion mass was needed to evaluate ion density, but as the plasma is a mixture of several species whose concentrations are continually changing, estimation of overall ion mass would prove difficult. In addition, the measurement of Langmuir probe data was also too slow for the online process control system in use, and the tips of the probes were reported to degrade rapidly.

For a 'dynamic treatment', which simulated a continuous process, Osenberg *et al.* arrived at a slightly different result. They concluded that wool samples would not start to burn if the intensity of the line at 28 amu were kept below 20% of the line at 32 amu.

This paper illustrates the real benefits and some drawbacks of the adoption of plasma diagnostics for online process control. Measurements must be sufficiently rapid to apply with a given control system, but if they are, then plasma diagnostics can be successfully applied. Osenberg *et al.* – in 1999 - argued that that OES and Langmuir probes were too slow as process control tools, whereas QMS worked well. However, in the case of OES there have since 1999 been significant developments in fibre-coupled CCD (charged coupled device) and CMOS (complementary metal-oxide semiconductor) array-based spectrometers, such as from Ocean Optics (Ocean Optics Inc., Largo, Florida, USA) [171], that allow for fast (sub-second) spectral acquisition and relative intensity measurements that would be sufficient for process control. Likewise, developments in Langmuir probe technology related to process control could be promoted if there were significant impetus from relevant industries.

There seem to be few examples of computer simulation of plasma treatments of wool in the literature, but simulation is likely to be quite problematic. As already discussed, the surface structure of wool fibres is highly complex. In chemical terms, no individual amino acids are especially abundant in wool keratins, and adjacent keratin chains are covalently linked by disulfide bonds. These properties are in marked contrast to those of silk fibres. It is consequently difficult to determine to what amino acids oxygen atoms in the plasma become bonded. In addition, the

untreated wool fibre surface contains an appreciable lipid content. In topographical terms, the surface possesses a complex scale structure. One interesting paper, however, by Kuzuya *et al.* [172] includes computer simulations of electron paramagnetic resonance (EPR) spectra of wool fibres after argon plasma treatments. The simulated spectra were found to agree well with the equivalent spectra determined experimentally, and it was noted that a broad asymmetric multiplet in the spectrum could be assigned to sulfide radicals, derived from scission of the disulfide bonds. There was also evidence of cross-linking at the fibre surface between bulky amino acid constituents which, Kuzuya *et al.* proposed, contributed to increased friction between fibres and hence reduced felting. The authors also suggested that the complex topography served to retard the formation of radicals in keratin structures.

Whilst it is clear then that some plasma treatments are highly effective in imparting shrink resistance to wool, a particular problem is the development of a notably harsh handle. This effect can be readily attributed to pitting of the scales, but the problem can be extensively overcome by subsequent treatment with a suitable polymer. Thus, the roles of polymer treatments after chlorination and after plasma treatment are not completely identical. As noted above, polymeric treatment given after a chlorination process enables shrink resistance to be maintained after a succession of washings. A polymer added after plasma treatment must mask the pitting and etching resulting from that treatment. It is therefore not surprising that polymers developed for the after-treatment of chlorinated wool fibres are much less successful on fibres that have been plasma treated.

Some polymers have been specially developed for deposition onto plasma-treated wool fibre surfaces. For example, two have been developed by Bayer [16]. One of these is a polymer containing isocyanate groups that can be dispersed in water. The polymer coats the individual fibres, with the result that the heights of the scales on the fibre surfaces are considerably reduced, and the DFE is almost eliminated. Another example is a polyurethane that is deposited on the edges of the scales, an approach that also leads to reduced shrinkage. Thus, an oxidative plasma treatment followed by deposition of a suitable polymer is available for chlorine-free shrink-proofing. In particular, the process has been successful for wool tops.

## **10. Artificial Intelligence/Neural Networks**

A further approach to assisting the formulation of plasma processes for textiles will undoubtedly be the use of artificial intelligence, which entails the development of machines behaving like human brains and performing tasks that would otherwise require human intelligence. Examples include learning, planning, reasoning and solving problems. Although as yet in its infancy, it already powers internet searches, enables voice-activated personal assistants such as Alexa and Siri, and together with other technologies enables driverless cars and robots. There is little doubt that



artificial intelligence will play a big part in textile processing generally in future, and not least in textile plasma processing.

The path leading to progress towards artificial intelligence at a human level is likely to be through machine learning in which, without being explicitly programmed, systems learn from data presented to them and then make a set of predictions. Machine learning is already commonly applied to internet searches, for example, and is enabled by learning algorithms called neural networks – or, more strictly artificial neural networks – that crudely mimic the capabilities of the human brain.

The application of neural networks is hardly new in the world of textiles. Indeed the original concept of neural networks themselves goes back over seventy years [173]. A neural network is modelled on the network of neurons that exist in the brain and involves a very large number of processors arranged in tiers and operating in parallel. The first tier receives the information supplied to the network. Each successive tier receives the output from the tier preceding it. The last tier produces the output from the network.

Each tier of processors contains an arrangement of interconnected nodes, which possess their own (relatively) small range of knowledge. This knowledge includes the information given to a node and any rules with which it has already been programmed or which it itself has developed. The tiers are also highly interconnected with one another. Importantly too, neural networks are adaptive in that, as they learn from initial ‘training’, they modify themselves, so that subsequent runs through the network should provide more reliable information. Each node assesses the importance of the input from each of its predecessors, so-called weighting. Inputs that contribute to obtaining the correct answers are weighted more highly. The predictive quality of the network is dependent on the amount of training data.

Detailed reviews of neural networks and their applications to textile technology have been written by Chattopadhyay & Guha [174]. The topic is also covered by Veit in a book he has edited [175]. Veit has also written in the same book accounts of the applications of genetic algorithms and fuzzy logic to textile technology. Examples of the application of neural networks to textile plasma treatments include the application of a repellent coating to surgical garments [176] and the modelling of plasma surface modification of textile fabrics using neural networks [177].

## **11. Concluding remarks**

The three quite disparate examples in Section 9 well illustrate how different methodologies can be combined to provide a more structured understanding of a particular textile plasma treatment and how together they can facilitate the

identification and formulation of the principal processing parameters required for that treatment in the equipment available. The examples cover:

The conversion of a hydrophobic textile surface (PP) to a hydrophilic one;

The conversion of a hydrophilic textile surface (silk) to a hydrophobic one;

The special case of rendering wool fibres resistant to felting.

Together the examples highlight overall practical strategies for which a range of disciplines is utilised: chemistry, physics, statistics, computing, chemical and process engineering. The combination of such disciplines, often in conjunction with art and design, is by no means novel to textile practice.

The methodologies highlighted in this review include:

Experimental determination of the topographical and surface chemical changes to a textile that have occurred as a result of a particular plasma treatment (Sections 2, 3 and 4);

Experimental observations of the process itself during a plasma treatment (Section 5);

The application of statistical experimental design and analysis (Section 6);

The application of computer simulation and modelling (Section 7).

Section 8 highlights the importance of using these methodologies in process control strategies. Whilst we certainly do not claim to set out a recipe of combined strategies for any particular plasma textile treatment, this review should nonetheless serve to demonstrate that the application of plasma technology need not be daunting despite the appreciable set-up costs that may be involved. Plasma technology can provide clean, dry, efficient processing that is environmentally friendly, reduces or even eliminates the need for aqueous and organic solvents and does not harbour toxicological risks. It is, as Shishoo [1] has remarked, a versatile and flexible approach for conferring desired functionalities on textiles. It can also, especially through grafting onto plasma treated surfaces, impart functionalities much less readily obtainable by more traditional means.

The examples in Section 9, although disparate, do indicate some common aspects that stand out. For example, there are likely to be just a very few plasma species

that are the predominant reactants with a textile surface, despite the complexities of the processes occurring within a plasma chamber. In the case of SF<sub>6</sub> plasma treatments of silk, there appears to be just one important species, the fluorine atom, F·. Sections 9.2 and 9.3 have shown that the location of the textile in relation to the plasma source is important. Indeed the location can be adjusted to fine-tune the extent of a plasma treatment.

Another obvious feature is that a plasma treatment roughens the fibre surface. Indeed surface topography plays a considerable role in influencing the effect of a plasma treatment, and quantitative measurements of roughness (usually from AFM) are especially important. However, it is clear that there are many different forms of surface topography, even in the same sample, and it would be useful if these different types could be differentiated or even categorised. Categorisation would certainly be challenging, but nevertheless we suggest that it could materially assist plasma process formulation.

A major concern that is often expressed about plasma treatments is their durability, both during subsequent processing and during the lifetime of the end product. For example, how many wash cycles will the treated textile be able to withstand? This concern arises principally from the thinness of the plasma-treated surface, compared with surface coatings conferred by traditional means. However, different types of product have different requirements for durability, and durability to laundering is arguably one of the most challenging, though also one of the most important in application terms. Indeed, as noted in the Introduction, durability was a key outcome of the EU project ACTECO [30]. This review has shown that instability arises largely from reorientation of polymer chains at fibre surfaces. In addition, volatile components of low molar mass formed during a treatment may migrate to the surface and then be released from it. Ageing at fibre surfaces is particularly acute in polymers with low glass transition temperatures, such as PP and HDPE, as these polymers possess innately high chain mobilities.

Several approaches are available for improving surface durability. In Section 9.1, it was noted that prior cross-linking of PP polymer chains considerably stabilises PP fibre surfaces using the CASING process, and it was also noted by Kale & Palaskar [99] that a highly cross-linked plasma polymer of HMDSO would increase its stability on cotton fibre surfaces. Crosslinking severely hinders the ability of polymer chains to reorient themselves or be sloughed off the surface, provided the chains are sufficiently strongly linked to the bulk of the fibre. The presence of traces of oxygen in a plasma, however, tends to hinder the cross-linking process [128]. Section 9.2 has indicated that reorientation of surface polymer chains is hindered if they are present in largely crystalline domains. Thus, increased surface crystallinity can also promote durability. A third approach is to graft a polymer onto the freshly treated surface, thereby restricting any reorientation. As already noted in the Introduction,

grafting possesses the additional advantage of opening up the scope for further applications not available by traditional treatments.

Plasma technology is already assuming key roles in textile technology. A formulation of conditions for a plasma treatment of a textile to impart to it desired applicational features need not be 'hit-and-miss' but can be founded on a wide range of information that can be acquired from a whole gamut of approaches working together.

## Acknowledgements

The authors would like to acknowledge the help and support provided by the editor, Richard Murray, during the compilation of this review. They also wish to thank Michael Brookes, Leeds University, for helpful discussion on the analysis of micrographs.

## References

- [1] R. Shishoo, ed., *Plasma Technologies for Textiles*, Woodhead Publishing Limited, Cambridge, 2007.
- [2] J.W. Bradley and P.M. Bryant, *The diagnosis of plasmas used in the processing of textiles and other materials*, in *Plasma Technologies for Textiles*, R. Shishoo ed., Woodhead Publishing Limited, Cambridge, 2007, p.25.
- [3] C-W. Kan and C-W.M. Yuen, *Text. Prog.*, 39 (2007) p.121.
- [4] D.B. Graves, *AIChE J.*, 35 (1989) p.1.
- [5] F.F. Chen, *Phys. Plasmas*, 2 (1995) p.2164.
- [6] J.I.B. Wilson, *Textile surface functionalisation of chemical vapour deposition (CVD)*, in *Surface Modification of Textiles*, Q. Wei ed., Woodhead Publishing Limited, Cambridge, 2009, p.126.
- [7] M.J. Shenton and G.C. Stevens, *J. Phys. D: Appl. Phys.*, 34 (2001) p.2761.
- [8] F. Denes, Z.Q. Hua, E. Barrios, R.A. Young and J. Evans, *J. Macromol. Sci.*, 32 (1995) p.1405.
- [9] A. Vesel, M. Mozetic, A. Hladnik, J. Dolenc, J. Zule, S. Milosevic, N. Krstulovic, M. Klanjsek-Gunde and N. Hauptmann, *J. Phys. D: Appl. Phys.*, 40 (2007) p.3689.

- [10] P.K. Chu, J.Y. Chen, L.P. Wang and N. Huang, *Mat. Sci. Eng.: R: Reports*, 36 (2002) p.143.
- [11] S.K. Pankaj, C. Bueno-Ferrer, N.N. Misra, V. Milosavljevic, C.P. O'Donnell, P. Bourke, K.M. Keener and P.J. Cullen, *Trends in Food Sci. and Technol.*, 35 (2014) p.5.
- [12] C. Lo Porto, F. Palumbo, G. Palazzo and P. Favia, (2017). *Polym. Chem.*, 8 (2017) p.1746.
- [13] P. Lippens, *Low-pressure cold plasma processing technology*, in *Plasma Technologies for Textiles*, R. Shishoo ed., Woodhead Publishing Limited, Cambridge, 2007, p.64.
- [14] T. Herbert, *Atmospheric-pressure cold plasma processing technology*, in *Plasma Technologies for Textiles*, R. Shishoo ed., Woodhead Publishing Limited, Cambridge, 2007, p.79.
- [15] S. Coulson, *Plasma treatment of textiles for water and oil repellency*, in *Plasma Technologies for Textiles*, R. Shishoo ed., Woodhead Publishing Limited, Cambridge, 2007 p.183.
- [16] H. Thomas, *Plasma modification of wool*, in *Plasma Technologies for Textiles*, R. Shishoo ed., Woodhead Publishing Limited, Cambridge, 2007, p.228.
- [17] B. Marcandalli and C. Riccardi, *Plasma treatments of fibres and textiles*, in *Plasma Technologies for Textiles*, R. Shishoo ed., Woodhead Publishing Limited, Cambridge, 2007, p.282.
- [18] R.R. Mather, *Surface modification of textiles by plasma treatments*, in *Surface Modification of Textiles*, Q. Wei ed., Woodhead Publishing Limited, Cambridge, 2009, p.296.
- [19] D. Sun and X. Chen, (2012), *Text. Res. J.*, 82 (2012) p.1928.
- [20] P. Cools, R. Morent and N. de Geyter, *Plasma modified textiles for biomedical applications*, in *Advances in Bioengineering*, P.A. Serra ed., InTech, 2015, p.117.
- [21] M.W. Huh, I.-K. Kang, D.H. Lee, W.S. Kim, D.H. Lee, L.S. Park, K.E. Min and K.H. Seo, *J. Appl. Polym. Sci.*, 81 (2001) p.2769.
- [22] U. Vohrer, *Interfacial Engineering of functional textiles for biomedical applications*, in *Plasma Technologies for Textiles*, R. Shishoo ed., Woodhead Publishing Limited, Cambridge, 2007, p.202.
- [23] Q.F. Wei, R.R. Mather, X.Q. Wang, and A.F. Fotheringham, *J. Mater. Sci.*, 40 (2005) p.5387.
- [24] G. Rosace and M.R. Massafra, *Text. Res. J.*, 78 (2008) p.28.

- [25] N. Abadi, *Surface grafting of textiles*, in *Surface Modification of Textiles*, Q. Wei ed., Woodhead Publishing Limited, Cambridge, 2009, p. 91.
- [26] R. Morent, N. De Geyter, J. Verschuren, K. De Clerck, P. Kiekens and C. Leys, *Surf. Coatings Technol.*, 202 (2008) p.3427.
- [27] A. Zille, F.R. Oliveira and A.P. Souto, *Plasma Process. Polym.*, 12 (2015) p.98.
- [28] <https://cordis.europa.eu/project/rcn/102168/reporting/en>
- [29] <https://ec.europa.eu/environment/eco-innovation/projects/en/projects/power>
- [30] <https://cordis.europa.eu/project/rcn/75759/factsheet/en>
- [31] <https://cordis.europa.eu/project/rcn/35499/factsheet/en>
- [32] <https://cordis.europa.eu/project/rcn/102082/reporting/en>
- [33] J.-L. Hervas-Oliver, F. Sempere-Ripoli, C. Boronat-Moll and R. Rojas-Alvarado, *Technology Analysis and Strategic Management*, 30 (2018) p.569.
- [34] W.G. Graham, *Plasma science and technology*, in *Plasma Technologies for Textiles*, R. Shishoo ed., Woodhead Publishing Limited, Cambridge, 2007, p.3.
- [35] M. Simor, J. Ráhel', M. Cernák, Y. Imahori, M. Stefecka and M. Kando, *Surf. Coat. Technol.*, 172 (2003) p.1.
- [36] N. De Geyter, R. Morent and C. Leys, (2006). *Plasma Sources Sci. Technol.*, 15 (2006) p.78.
- [37] A.G.M. Abdulgalil, D. Marchione, J.D. Thrower, M.P. Collings, M.R.S. McCoustra, M.E. Islam, E. Congiu and F. Dulieu, *Phil. Trans. Roy. Soc. A*, 2013, 371:20110586.
- [38] H.U. Poll, U. Schladitz and S. Schreiter, (2001). *Surf. Coat. Technol.*, 142-144 (2001) p.489.
- [39] J. Verschuren and P. Kiekens, *AUTEX Res. J.*, 5 (2005) p.154.
- [40] W.R. Goynes, *Surface characterization of textiles using SEM*, in *Modern Textile Characterization Methods*, M. Raheel ed., Marcel Dekker, New York, 1996, p.145.
- [41] C.C. Giri, *Colourage*, 49 (2002) p.9.
- [42] Q. Wei, F. Huang and Y. Cai, *Textile surface characterization methods*, in *Surface Modification of Textiles*, Q. Wei, ed., Woodhead Publishing Limited, Cambridge, 2009, p.26.
- [43] A.M. Sarmadi and Y.A. Kwon (1993). *Text. Chemist Colorist*, 25 (1993) p.33.

- [44] A. Hesse, H. Thomas and H. Höcker (1995). *Text. Res. J.*, 65 (1995) p.355.
- [45] S.D. Lee, M. Sarmadi, F. Denes and J.L. Shohet, (1997). *Plasmas and Polymers*, 2 (1997) p.177.
- [46 ] M.M. Kamel, M.M. El Zawahry, H. Helmyand and M.A. Eid, *J. Text. Inst.*, 102 (2011) p. 220.
- [47] C. Zhang, M. Zhao, L. Wang and M. Yu, *Vacuum*, 137 (2017) p.42.
- [48] H.S. Salapare, T. Darmanin and F. Guittard, *Appl. Surf. Sci.*, 356 (2015) p.408.
- [49] A. Haji, A.M. Shoushtari and M. Mirafshar, *Col. Technol.*, 130 (2014) p.37.
- [50] Y-C. Liu, X. Yan and N.D. Lu, *Appl. Surf. Sci.*, 252 (2006) p.2960.
- [51] N. Yaman, E. Ozdogan, N. Seventekin and H. Ayhan, *Appl. Surf. Sci.*, 255 (2009) p.6764.
- [52] B. Felekoglu, K. Tosun and B. Baradan, *J. Mater. Processing Technol.*, 209 (2009) p.5133.
- [53] N.V. Bhat, A.N. Netravali, A.V. Gore, M.P. Sathianarayanan, G.A. Arolkar and R.R. Deshmukh (2011). *Text. Res. J.*, 81 (2011) p.1014.
- [54] A. Vesel, M. Mozetic, S. Strnad, Z. Persin, K. Stana-Kleinschek and N. Hauptman, *Vacuum*, 84 (2010) p.9.
- [55] N.A. Ibrahim, M.M. Hashem, M.A. Eid, R. Refai, M. El-Hossamy and B.M. Eid, *J. Text. Inst.*, 101 (2010) p.1035.
- [56] S. Zanini, E. Grimoldi, A. Citterio and C. Riccardi, *Appl. Surf. Sci.*, 349 (2015) p.235.
- [57] K. Boonla and S. Saikrasun, *Text. Res. J.*, 83 (2013) p.288.
- [58] J. Paluszynski and W. Słówko, (2009). *J. Microsc.*, 233 (2009) p.10.
- [59] G.D. Danilatos, *Microscopy Res. and Technique*, 25 (1993) p.354.
- [60] W. Tao and B.J. Collier, *Text. Chemist Colorist*, 26(2) (1994) p.29.
- [61] Q.F. Wei, W.D. Gao, D.Y. Hou and X.Q. Wang, *Appl. Surf. Sci.*, 245 (2005) p.16.
- [62] Q.F. Wei, X.Q. Wang, R.R. Mather and A.F. Fotheringham (2003). *Appl. Surf. Sci.*, 220 (2003) p.217.
- [63] Q.F. Wei and X.Q. Wang, *J. Ind. Text.*, 33 (2003) p.101.

- [64] M. Gunther, Chemistry World, (May 2017) p.32.
- [65] J.M. Warren, R.R. Mather, A. Neville and D. Robson, J. Mater. Sci., 40 (2005) p.5373.
- [66] A. Neville, R.R. Mather and J.I.B. Wilson, *Characterisation of plasma-treated textiles*, in *Plasma Technologies for Textiles*, R. Shishoo ed., Woodhead Publishing Limited, Cambridge, 2007, p.301.
- [67] Q. Wei, Y. Liu, D. Hou and F. Huang, J. Mater. Processing Technol., 194 (2007) p.89.
- [68] T. Mehmood, A. Kaynak, X.J. Dai, A. Kouzani, K. Magniez, D.R. de Celis, C.J. Hurren and J. du Plessis (2014). Mat. Chem. Phys., 143, (2014) p.668.
- [69] K.K. Samanta, M. Jassal and A.K. Agrawal, Surf. Coat. Technol., 203 (2009) p.1336.
- [70] C. Labay, J.M. Canal, M. Modic, U. Cvelbar, M. Quiles, M. Armengol, M.A. Arbos, F.J. Gil and C. Canal (2015). Biomaterials, 71(2015) p.132.
- [71] O.G. Armagan, B.K. Kayaoglu, H.C. Karakas and F.S. Guner, J. Ind. Text., 43 (2014) p.396.
- [72] D. Caschera, A. Mezzi, L. Cerri, T. de Caro, C. Riccucci, G.M. Ingo, G. Padeletti, M. Biasiucci, G. Gigli and B. Cortese, Cellulose, 21, (2014) p.741.
- [73] P. Pransilp, M. Pruettiphap, W. Bhanthumnavin, B. Paosawatyanong and S. Kiatkamjornwong, Appl. Surf. Sci., 364 (2016) p.208.
- [74] F. Rombaldoni, A. Montarsolo, R. Mossotti, R. Innocenti and G. Mazzuchetti, J. Appl. Polym. Sci., 118 (2010) p.1173.
- [75] P. Amornsudthiwat, R. Mongkolnavin, S. Kanokpanont, J. Panpranot, C.S. Wong and S. Damrongsakkul (2013). Coll. Surf. B: Biointerfaces, 111 (2013) p.579.
- [76] A. Calvimontes, P. Mauersberger, M. Nitschke, V. Dutschuk and F. Simon, Cellulose, 18 (2011) p.803.
- [77] H.-J. Butt, B. Cappella and M. Kappl, Surf. Sci. Reports, 59 (2005) p.1.
- [78] J. Vansco, P. Schön and J. Duvigneau, Microscopy and Analysis, (May 2009) p.5.
- [79] J.A.A. Crossley, C.T. Gibson, L.D. Mapledoram, M.G. Huson, S. Myhra, D.K. Pham, C.J. Sofield, P.S. Turner and G.S. Watson, (2000). Micron, 31 (2000) p.659.
- [80] J.M. Maxwell and M.G. Huson, (2005). Micron, 36, (2005) p.127.



- [81] R.R. Mather, D. Robson, A.F. Fotheringham, A. Neville, Q. Wei and J.M. Warren, *Surface modification of textiles by plasma treatments*, in *Proceedings of the International Textile Design and Engineering Conference (INTEDEC)*, Heriot-Watt University, Edinburgh, 2003.
- [82] R.N.S. Sodhi, (2004). *Analyst*, 129 (2004) p.483.
- [83] A. Delcorte, V. Cristaudo, M. Zarshenas, D. Merche, F. Reniers and P. Bertrand, *Plasma Process. Polym.*, 12 (2015) p.905.
- [84] J.C. Vickerman and I.S. Gilmore, *Surface Analysis - The Principal Techniques* (2<sup>nd</sup> edition), John Wiley & Sons, Chichester, 2009.
- [85] M. Naebe, P.G. Cookson, J. Rippon, R.P. Brady, X. Wang, N. Brack and G. van Riessen, *Text. Res. J.*, 80 (2010) p.312.
- [86] P.K. Panda, D. Rastogi, M. Jassal and A.K. Agrawal, *J. Appl. Polym. Sci.*, 124 (2012) p.4289.
- [87] J.C. Vickerman and D. Briggs, *TOF-SIMS: Materials Analysis by Mass Spectrometry*, 2<sup>nd</sup> ed., IM Publications, Chichester, and SurfaceSpectra, Manchester, 2013.
- [88] N. Vandencastele and F. Reniers, *J. Electron Spectrosc. And Related Phenom.*, 178-179 (2010) p.394.
- [89] C. Zhang and K. Fang, *Surf. Coat. Technol.*, 203 (2009) p.2058.
- [90] F. Leroux, C. Campagne, A. Perwuelz and L. Gengembre, *Surf. Coat. Technol.*, 203 (2009) p.3178.
- [91] D. Pappas, A. Bujanda, J.D. Demaree, J.K. Hirvonen, W. Kosik, R. Jensen and S. McKnight, 201 (2006) p.4384.
- [92] N. Yaman, E. Ozdogan and N. Seventekin, *Fibers and Polymers*, 12 (2011) p.35.
- [93] A.D. Kramar, B.M. Obradovic, A. Vesel, M.M. Kuraica and M.M. Kostic, *Plasma Process. Polym.*, 12 (2015) p.1095.
- [94] R.C. Lima da Silva, C. Alves Jr., J.H. Nascimento, J.R.O. Neves and V. Teixeira, *J. Phys.: Conf. Ser.*, 406 (2012) 012017 (10 pp).
- [95] M. Mirjalili and L. Karimi, *J. Text. Inst.*, 104 (2013) p.98.
- [96] A. Dazzi, C.B. Porter, Q. Hu, D.B. Chase, J.F. Rabolt and C. Marcott, (2012). *Appl. Spectroscopy*, 66 (2012) p.1365.
- [97] M. Parvinzadeh and I. Ebrahimi, *Appl. Surf. Sci.*, 257 (2011) p.4062.

- [98] H.A. Karahan and E. Özdoğan, *Fibers & Polymers*, 9 (2008) p.21.
- [99] K.H. Kale and S. Palaskar, *Text. Res. J.*, 81(2011) p.608.
- [100] R. Mossotti, G. Lopardo, R. Innocenti, G. Mazzuchetti, F. Rombaldoni, A. Montarsolo and E. Vassallo, *Text. Res. J.*, 79I (2009) p.853.
- [101] H. Barani and A. Haji, *J. Molecular Structure*, 1079 (2015) p.35.
- [102] G. Rosace, R. Canton and C. Colleoni, *Appl. Surf. Sci.*, 256 (2010) p.2509.
- [103] M.J. Shenton, M.C. Lovell-Hoare and G.C. Stevens, *J. Phys. D: Appl. Phys.*, 34 (2001) p.2754.
- [104] J. Benedikt, A. Hecimovic, D. Ellerweg and A. von Keudell, *J. Phys. D.: Appl. Phys.*, 45 (2012) 403001 (23pp).
- [105] S. Grosse-Kreul, S. Hübner, S. Schneider, D. Ellerweg, A. von Keudell, S. Matejčík and J. Benedikt, *Plasma Sources Sci., Technol.*, 24 (2015) 044008 (15pp).
- [106] M.R. Alexander, F.R. Jones and R.D. Short, *J. Phys. Chem. B.*, 101(1997) p.3614.
- [107] A.J. Beck, Y. Aranda Gonzalvo, A. Pilkington, A. Yerokhin and A. Matthews, *Plasma Process. Polym.*, 6 (2009) p.521.
- [108] Z. Kreger, M. Biscan, S. Milosevic and A. Vesel, *IEEE Trans. Plasma Sci.*, 39 (2011) p.1239.
- [109] P. Suanpoot, K. Kueseng, S. Ortmann, R. Kaufmann, C. Umongno, P. Nimmanpipug, D. Boonyawan and T. Vilaithong, *Surf. Coat. Technol.*, 202 (2008) p.5543.
- [110] P. Chaivan, N. Pasaja, D. Boonyawan, P. Suanpoot and T. Vilaithong, *Surf. Coatings Technol.*, 193 (2005) p.356.
- [111] M. Gorjanc, K. Jazbec and R. Zaplotnik, *J. Text. Inst.*, 105 (2014) p.1178.
- [112] R. Merlino, *Amer. J. Phys.*, 75 (2007) p.1078.
- [113] C. Riccardi, R. Barni, M. Fontanesi, B. Marcandalli, M. Massafra, E. Selli and G. Mazzone, *Plasma Sources Sci. Technol.*, 10 (2001) p.92.
- [114] A. Abdrabbo, H.M. El-Dessouky and A.F. Fotheringham, *J. Text. Inst.* 104 (2013) p.28.
- [115] T. Karthik, R. Murugan and M. Vijayan, *J. Text. Inst.*, 104 (2013) p.481.
- [116] A. Bogaerts, E. Bultinck, M. Eckert, V. Georgieva, M. Mao, E. Neyts and L. Schwaederlé, *Plasma Process. Polym.*, 6 (2009) p.295.

- [117] A. Bogaerts, C. De Bie, M. Eckert, V. Georgieva, T. Martens, E. Neyts and S. Tinck, *Pure Appl. Chem.*, 82 (2010) p.1283.
- [118] M.J. Grapperhaus and M.J. Kushner, *J. Appl. Phys.*, 81 (1997) p.569.
- [119] T. Dufour, J. Minnebo, S. Abou Rich, E.C. Neyts, A. Bogaerts and F. Reniers, *J. Phys. D: Appl. Phys.*, 47 (2014) 224007 (12 pp).
- [120] A.K.R. Choudhury, *Process control in finishing of textiles*, in *Process Control in Textile Manufacturing*, V. Kothari, R. Alagirusamy, A. Das and A. Majumdar eds., Woodhead Publishing Limited, Cambridge, 2013, p.363.
- [121] V.V. Jain, *Basics of process control in textile manufacturing*, in *Process Control in Textile Manufacturing*, V. Kothari, R. Alagirusamy, A. Das and A. Majumdar eds., Woodhead Publishing Limited, Cambridge, 2013, p.3.
- [122] J.K. Nørskov, F. Studt, F. Abild-Pedersen and T. Bligaard, *Fundamental Concepts in Heterogeneous Catalysis*, Wiley, New York, 2014.
- [123] R.H. Hansen, J.V. Pascale, R. De Benedictis and P.M. Rentzepis, *J. Polym. Sci.: Part A: Polym. Chem.*, 3 (1965) p.2205.
- [124] R. Shamey, *Improving the coloration/dyeability of polyolefin fibres*, in *Polyolefin Fibres: Structure, Properties and Industrial Applications*, 2<sup>nd</sup> ed., Elsevier, Duxford, 2017, p.359.
- [125] E. Occhiello, M. Morra, G. Morini, F. Garbassi and P. Humphrey, *J. Appl. Polym. Sci.*, 42 (1991) p.551.
- [126] Th. Gross, A. Lippitz, W.E.S. Unger, J.F. Friedrich and Ch. Wöhl, *Polymer*, 35 (1994) p.5590.
- [127] F. Denes, R.A. Young and M. Sarmadi, *J. Photopolym. Sci., Technol.*, 10 (1997) p. 91.
- [128] C.-D. Radu, P. Kiekens and J. Verschuren (2001). *Surface modification of textiles by plasma treatments*, in *Surface Characteristics of Fibers and Textiles*, C.M. Pastore and P. Kiekens eds., Marcel Dekker Inc., New York, 2001, p.203.
- [129] M.G. McCord, Y.J. Hwang, P.J. Hauser, Y. Qiu, J.J. Cuomo, O.E. Hankins, M.A. Bourham and L.K. Canup, *Text. Res. J.*, 72 (2002) p.491.
- [130] M. Collaud Coen, G. Dietler, S. Kasas and P. Gröning, *Appl. Surf. Sci.*, 103 (1996) p.27.
- [131] H.-Y. Nie, M.J. Walzak, B. Berno and N.S. McIntyre, *Appl. Surf. Sci.*, 144-145 (1999) p.627.

- [132] Ch. Bichler, T. Kerbstadt, H.-C. Langowski and U. Moosheimer, *Surf. Coatings Technol.*, 112 (1999) p.373.
- [133] Yu. Akishev, M. Grushin, N. Dyatko, I. Kochetov, A. Napartovich, N. Trushkin, T.M. Duc and S. Descours, *J. Phys. D: Appl. Phys.*, 41 (2008) 235203 (13pp).
- [134] K.N. Pandiyaraj, V. Selvarajan, R.R. Deshmukh and C. Gao, *Appl. Surf. Sci.*, 255 (2009) p.3965.
- [135] B. Boschmans, M. Vanneste, L. Ruys, E. Temmerman, C. Leys and L. Van Vaeck, *Appl. Surf. Sci.*, 252 (2006) p.6660.
- [136] R. Morent, N. De Geyter, C. Leys, L. Gengembre and E. Payen, *Surf. Interface, Anal.*, 40 (2008) p.597.
- [137] L. Carrino, G. Moroni and W. Polini, *J. Mater. Process. Technol.*, 121 (2002) p.373.
- [138] R. Nisticò, G. Magnacca, M.G. Faga., G. Gautier, D. D'Angelo, E. Ciancio, R. Lamberti and S. Martorana, *Appl. Surf. Sci.*, 279 (2013) p.285.
- [139] R. Dorai and M.J. Kushner, *J. Phys. D: Appl. Phys.*, 36 (2003) p.666.
- [140] A.N. Bhoj and M.J. Kushner (2007). *J. Phys. D: Appl. Phys.*, 40 (2007) p.6953.
- [141] R. Currie, (2001). *Silk*, in *Silk, Mohair, Cashmere and Other Luxury Fibres*, R.R. Franck ed., Woodhead Publishing Limited, Cambridge, 2001, p.1.
- [142] W.D. Schindler and P.J. Hauser, *Chemical Finishing of Textiles*. Woodhead Publishing Limited, Cambridge, 2004.
- [143] R.R. Mather and R.H. Wardman, *The Chemistry of Textile Fibres*, 2<sup>nd</sup> ed., The Royal Society of Chemistry, Cambridge, 2015.
- [144] E. Selli, C. Riccardi, M.R. Massafra and B. Marcandalli, *Macromol. Chem. Phys.*, 202 (2001) p.1672.
- [145] S.K. Hodak, T. Supasai, B. Paosawatyanong, K. Kamlangkla and V. Pavarajarn, *Appl. Surf. Sci.*, 254 (2008) p.4744.
- [146] C. Riccardi, R. Barni, F. De Colle and M. Fontanesi, *IEEE Trans. Plasma Sci.*, 28 (2000) p.278.
- [147] W. Sangprasert, V.S. Lee, D. Boonyawan, K. Tashiro and P. Nimmanpipug, *J. Molecular Structure*, 963 (2010) p.130.
- [148] D.M. Lewis, *Ancillary processes in wool dyeing*, in *The Coloration of Wool and Other Keratin Fibres*, D.M. Lewis and J.A. Rippon, eds., John Wiley and Sons Limited, Chichester, and Society of Dyers and Colorists, Bradford, 2013, p.99.

- [149] J.A. Rippon, *Friction, felting and shrink-proofing of wool*, in *Friction in Textile Materials*, B.S. Gupta, ed., Woodhead Publishing Limited, Cambridge, 2008, p.253.
- [150] R. Kettlewell, A. De Boos and J. Jackson, *Commercial shrink-resist finishes for wool*, in *Functional Finishes for Textiles: Improving Comfort, Performance and Protection*, R. Paul ed., Woodhead Publishing Limited, Cambridge, 2015, p.193.
- [151] E. Heine and H. Höcker, *Rev. Prog. Coloration*, 25 (1995) p.57.
- [152] H. El-Sayed, R.R. Hamed, A. Kantouch, E. Heine and H. Höcker, *AATCC Rev.*, 2 (2002) p.25.
- [153] W. Rakowski, *Melliand Berichte*, 10 (1989) p.780.
- [154] W. Rakowski, *J. Soc. Dyers and Colourists*, 113 (1997) p.250.
- [155] B.A. McGregor and A.C. Schlink, *J. Text. Inst.*, 105 (2014) p.927.
- [156] H. Xu, S. Peng, C. Wang, L. Yao, J. Sun, F. Ji and Y. Qiu, *J. Appl. Polym. Sci.*, 113 (2009) p.3687.
- [157] K.M. Byrne, *Machine-washable knitwear – production routes*, in *Chemistry of the Textiles Industry*, C.M. Carr ed., Blackie Academic and Professional, London, 1995, p.187.
- [158] J. Lewis, *Wool Sci. Rev.*, 55 (1978) p.23.
- [159] J.M. Cardamone, J. Yao and A. Nuñez, *Text. Res. J.*, 74 (2004) p.555.
- [160] R.H. Bradley, I. Mathieson and K.M. Byrne, *J. Mater. Chem.*, 7 (1997) p.2477.
- [161] C.W. Kan, K.Chan, C.W.M Yuen and M.H. Miao, *Text. Res. J.*, 69 (1999) p.407.
- [162] N. Chandwani, P. Dave, V. Jain, S. Nema and S. Mukherjee, *J. Phys.: Conf. Ser.*, 823 (2017) 012010 (6 pp).
- [163] Z. Cai and Y. Qui, *J. Appl. Polym. Sci.*, 107 (2008) p.1142.
- [164] S. Shahidi, A. Rashidi, M. Ghoranneviss, A. Anvari and J. Wiener, *Surf. Coatings Technol.*, 205 (2010) p.S349.
- [165] C. Canal, F. Gaboriau, R. Molina, P. Erra and A. Ricard, *Plasma Process. Polym.*, 4 (2007) p.445.
- [166] S.Y. Cheng, C.W.M. Yuen, C.W. Kan, K.K.L. Cheuk, W.A. Daoud, P.L. Lam and W.Y.I. Tsoi, *Vacuum*, 84 (2010) p.1466.
- [167] X.J. Dai, S.M. Hamberger and R.A. Bean, *Aust., J. Phys.*, 48 (1995) p.939.

- [168] X. Dai, (1996). Aust. J. Phys., 49 (1996) p.1169.
- [169] M. Naebe, R. Denning, M. Huson, P.G. Cookson and X. Wang, (2011). J. Text. Inst., 102 (2011) p.1086.
- [170] F. Osenberg, D. Theirich, A. Decker and J. Engeman, Surf. Coatings Technol., 116-119 (1999) p.808.
- [171] <http://www.oceanoptics.com>
- [172] M. Kuzuya, K. Kamiya, Y. Yanagihara and Y. Matsuno, (1993). Plasma Sources Sci. Technol., 2 (1993) p.51.
- [173] W.S. McCulloch and W. Pitts, Bull. Math. Biophys., 5 (1943) p.115.
- [174] R. Chattopadhyay and A. Guha, Text. Prog., 35 (2004) p.1.
- [175] D. Veit, *Neural networks and their application to textile technology*, in *Simulation in Textile Technology: Theory and Applications*, D. Veit ed., Woodhead Publishing Limited, Cambridge, 2012, p.9.
- [176] G. Allan, A. Fotheringham and P. Weedall, AUTEX Res. J., 2 (2002) p.64.
- [177] R.A. Jelil, X. Zeng, L. Koehl and A. Perwuelz, Engineering Applications of Artificial Intelligence, 26 (2013) p.1854.

Table 1. Effects of some gas plasmas on textile surfaces.

Gas plasma	Effect
Argon	Increased surface roughness
Sulfur hexafluoride	Fluorine-containing groups on surface Increased hydrophobicity
Fluorocarbons	Fluoropolymer films on surface Increased hydrophobicity
Oxygen	Oxygen-containing groups on surface Increased hydrophilicity
Nitrogen	Nitrogen-containing groups on surface Increased hydrophilicity

Table 2. Examples of reactions of plasma species in the plasma chamber.

Ionisation	$e + A \rightarrow 2e + A^+$
Dissociation	$e + AB \rightarrow e + A + B$
Dissociation	$AB + M \rightarrow A + B + M$
Electronic excitation	$e + A \rightarrow e + A^*$
Energy transfer	$A^* + B \rightarrow A + B^*$
Relaxation	$A^* + B \rightarrow A + B$
Neutralisation	$A^- + B^+ \rightarrow A + B$
Charge transfer	$A^+ + B \rightarrow A + B^+$
Dissociative charge transfer	$A^+ + BC \rightarrow A + B + C^+$

e represents an electron and \* an electronically excited state.

Table 3. Examples of reactions of plasma species with a surface.

Adsorption	$A + (s) \rightarrow A(s)$
Desorption	$A(s) \rightarrow A + (s)$
Reaction at surface	$A + B(s) \rightarrow AB(s)$
Reaction on surface	$A(s) + B(s) \rightarrow AB(s) + (s)$
Sputtering	$A^+ + e + B(b) \rightarrow A + B$
Electron emission	$A^+ + (s) \rightarrow A(s) + e$

e represents an electron, (s) an open surface site, A(s) a species A bound to the surface, B(s) a species B bound to the surface and B(b) a species B in the bulk phase.

Table 4. Contact angles of water on PP before,  $\theta_i$ , and after,  $\theta_f$ , oxygen plasma treatment.

Reference	$\theta_i$	$\theta_f$	Nature of PP substrate
Akischev <i>et al</i> [133]	105°	36°	Film
Carrino <i>et al</i> [137]	86°	69°	Unclear
Denes <i>et al</i> [127]	116°	14°	Unclear
Morent <i>et al</i> [136]	95°	60°	Film
Pandiyaraj <i>et al</i> [134]	98°	46°	Film
Wei <i>et al</i> [23]	99°	46°	Fibre

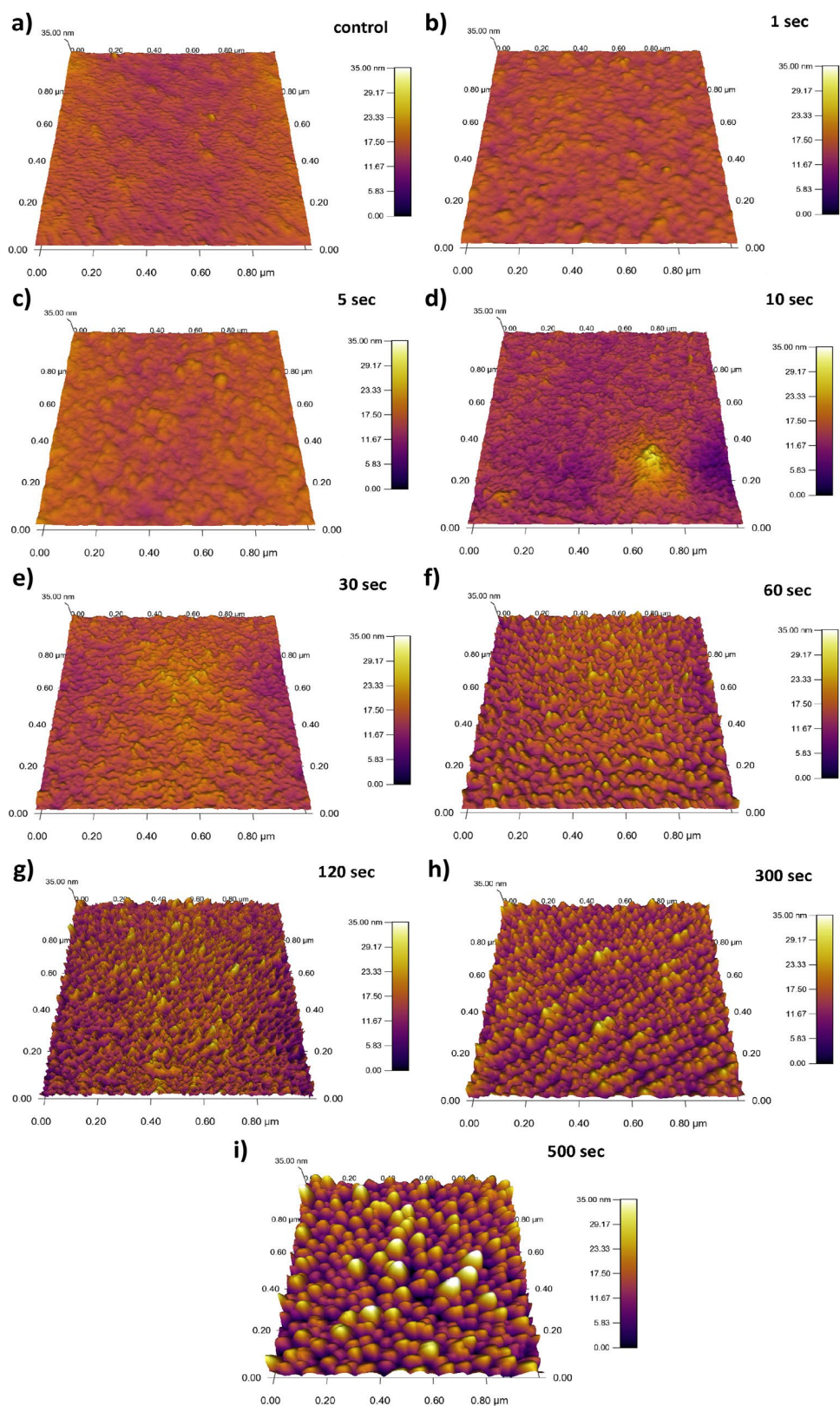


Figure 1. AFM scans of PET thin films before and after oxygen plasma treatments. Treatment times are also shown.

This figure was published in 'Materials Chemistry and Physics', 143, T. Mehmood *et al.*, 668-675, Copyright Elsevier 2014.



