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Functional nanostructures generated by plasma-enhanced modification of polypropylene fibre surfaces

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Polypropylene (PP) fibres have an extensive range of applications, including filtration, composites, biomaterials and electronics. In these applications, the surface properties of the fibres are particularly important. This paper presents examples of the use of gas plasma technology to create functional nanostructures on PP fibre surfaces, which render the surfaces hydrophilic. It is also shown how these treatments can be regulated to produce the desired level of hydrophilicity for a given application. Three principal modifications have been performed, to create functional nanostructures: plasma activation with oxygen gas plasma, grafting of polyacrylic acid following argon gas plasma treatment, and plasma-enhanced deposition of silver. Atomic force microscopy (AFM) and environmental scanning electron microscopy (ESEM) were employed to characterise the morphology, surface structure and composition of the fibres treated by gas plasma.

1. Introduction

It is well known that textile fibre surfaces play a key role in textile processing and application technology. In fibre processing, for example, the surface nature affects the extent of cohesion between fibres during staple yarn production and in the effectiveness of spin finishes in both staple and filament yarn production. Indeed, the nature of the spin finish applied is significantly determined by the surface properties of the fibres. In application, a whole range of performance properties depends on fibre surface characteristics: ease of wetting, frictional properties, abrasion resistance, uptake of dyes, fibre-matrix adhesion in composites and biocompatibility in textiles applied as wound dressings or *in vivo* [1–3].

As with many other types of material, the surface properties of textile fibres can be readily altered by treatment of the textile with a gas plasma, without impairment of their bulk mechanical properties. Gas plasmas are complex mixtures of highly excited atomic, molecular, ionic and free radical species. Although gas plasmas have been recognised for many decades, it is only recently that the technology has become available on a commercial scale. As a result the technology has attracted the interest of a wide variety of industries [4], which perceive environmental advantages of gas plasma treatments over traditional textile coating procedures. Indeed, gas plasma treatment offers great potential for significant improvements in fibre surface properties, based on changes in physical and chemical properties resulting from introducing functional nanostructures [5].

One valuable strength of gas plasma treatments is the ability to alter the hydrophilicity or hydrophobicity of a textile surface. Thus, plasma polymerisation of fluorinated hydrocarbons on fibre surfaces can render them highly hydrophobic, whilst treatment with polar gas plasmas can render the surfaces more hydrophilic.

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However, a further requirement is some means of altering hydrophilicity or hydrophobicity to a desired level in a controlled fashion. In the work described in this paper, we outline the effectiveness of various treatments in rendering polypropylene (PP) fibres hydrophilic, bearing in mind their wide variety of technological applications, such as filtration materials, components in composites, biomaterials and materials for electronic components [6–8]. We also show how these treatments can be regulated to produce the level of hydrophilicity required. In our work, three principal modifications have been performed, which create functional nanostructures on PP fibre surfaces:

plasma activation with oxygen gas plasma;
grafting of polyacrylic acid, following argon gas plasma treatment;
plasma-enhanced deposition of silver.

Atomic force microscopy (AFM) and environmental scanning electron microscopy (ESEM) were employed to characterise the morphology, surface structure and composition of the fibres treated by gas plasma.

2. Experimental

2.1. Materials preparation

2.1.1. PP fibres

The PP fibres used in this study were spun from a melt extrusion machine, supplied by Extrusion Systems Limited (ESL). Details of the extrusion equipment are provided elsewhere [9]. The PP resin used was HF445J B-29037 (kindly supplied by Borealis), with a melt flow index of 19.0 g/10 min. The spinning conditions are outlined in Table I. The as-spun fibres were subsequently drawn at room temperature at a ratio of 2:1.

TABLE I Spinning conditions

Chips	MFI18-HF445
Quenching air speed (%)	50
Hole size of spinneret (mm)	0.4
Barrel 1 temperature (°C)	215
Barrel 2 temperature (°C)	225
Barrel 3 temperature (°C)	230
Spinning temperature (°C)	230
Winding speed (m/min)	100
Metering pump speed (rpm)	3
Spin finish	0

2.1.2. Plasma activation

Plasma activation of the PP fibres was performed in a Europlasma CD 400 M/PC laboratory system. The system consists of 5 modules or functions: vacuum system, power supply, matching network, reactor centre and controller. In this system, the whole process was controlled by a personal computer. The gas used was oxygen, and the conditions for plasma treatment were set for 30 and 60 s at a power of 300 W in a gas flow of 0.3 l·min^{-1}.

2.1.3. Plasma-induced polymerisation

Plasma-induced polymerisation of acrylic acid onto the PP fibres was carried out in several steps. The PP fibres were first treated with argon in the plasma chamber, using a gas flow rate of 0.2 l·min^{-1} and a power of 200 W. The plasma treatment time was set for 60 s. After the plasma treatment, the fibres were exposed to atmospheric air for 10 min, in order to allow the formation of peroxides on the fibre surface, to facilitate polymer grafting [10]. The treated fibres were then placed in two beakers containing identical aqueous solutions of acrylic acid. The concentration of the acrylic acid was adjusted to 20% (w/v). The grafting process was carried out at 50°C in a water bath for 1 and 5 h, respectively, and nitrogen was bubbled through the solutions. After the grafting process, the fibres were removed from the beakers and rinsed in boiling deionised water, to remove any monomer and unattached acrylic acid polymer. The fibres were then dried at 50°C for 24 h.

2.1.4. Plasma enhanced deposition

Plasma enhanced deposition was performed in a lab DC sputtering system at room temperature. A high-purity silver target was mounted on the cathode, and argon was used as the bombardment gas. The deposition conditions were set at an argon current of 20 mA and a vacuum chamber pressure of 0.1 Torr (13.3 Pa). The depositions were performed for 1 and 5 min, respectively.

2.2. Surface characterization

2.2.1. AFM characterization

The AFM used in this work was a Topometrix TMX 2000 Explorer (TM Microscopes). Scanning was carried out in contact mode AFM. All images were obtained at ambient conditions. Each fibre sample was mounted onto double-sided tape on magnetic AFM sample stubs.

2.2.2. ESEM observation

In the wetting experiments, the fibre specimens were pre-cooled to approximately 4–6°C in the fridge, and placed onto the Peltier cooling stage using a specimen holder. The Peltier cooling stage was used to control the temperature. The specimen holder was specially designed for fibre materials, as illustrated in Fig. 1. Images were acquired at a temperature of 5°C, as this minimised the risk of accidental freezing [11]. Wet mode was selected from the ESEM controller, and the

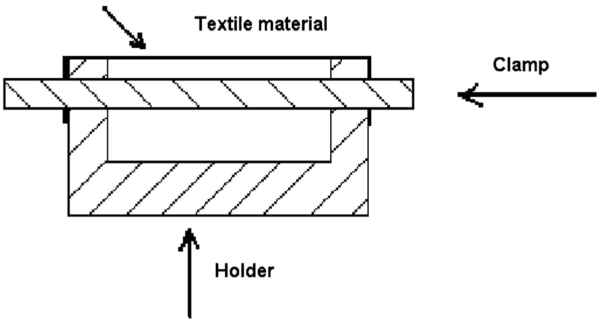


Figure 1 Specimen holder.

chamber was then pumped to 6 Torr. The relative humidity inside the chamber was gradually increased to 100%, through successive increments in pressure of 0.5 Torr, whereupon water condensed onto the surfaces of the fibre samples. Observations of water droplets on fibres could then be made at each point of interest.

2.2.3. Contact angle measurement

Contact angle measurements were made using image analysis [12]. The results were an average of 10 measurements and represented the advancing contact angles of growing droplets.

3. Results and discussion

3.1. Plasma activation

Fig. 2a shows an AFM image of the untreated fibres. The fibre surface reveals nanofibrils, probably induced by fibre drawing. These nanofibrils are oriented in the direction of the fibre axis.

Figs 2b and c show the effects on the PP fibre surface of oxygen plasma treatments for 30 and 60 s, respectively. The treatments have significantly modified the PP fibre surface topography. After treatment for 30 s (Fig. 2b), large aggregates of cross-section 100 nm to over 400 nm are revealed, and other, smaller, aggregates are also clearly visible in the background. The PP fibre surface has been considerably roughened. Oxygen plasma treatment for 60 s results, in addition, in the formation of nanogrooves on the fibre surface (Fig. 2c). The presence of these nanogrooves can be attributed to an etching effect of the plasma treatment.

Oxygen plasma treatment also significantly affects the behaviour of the PP fibre surface towards water, as shown in the ESEM photomicrographs in Fig. 3. On untreated PP fibre surfaces, water droplets are formed in the shape of segments of spheres, as shown in Fig. 3a. The contact angle is ca. 99° [12], and so the fibres are not properly wetted. This results accords with the expected hydrophobic nature of the PP fibre surface.

After oxygen plasma treatment, however, the profiles of the water droplets are markedly altered (Figs 3b and c). The shapes of the droplets have lost their regularity, and this loss of regularity can be attributed to the uneven surface properties resulting from the plasma treatment. Moreover, the drops are flattened along the curvature of the fibre surface at rightangles to the fibre axis. The contact angles are considerably reduced: ca. 54° on the PP fibres plasma treated for 30 s and as low as ca. 46° for those treated for 60 s [12]. Oxygen plasma treatment thus confers on the PP fibre surface a considerable degree of hydrophilicity.

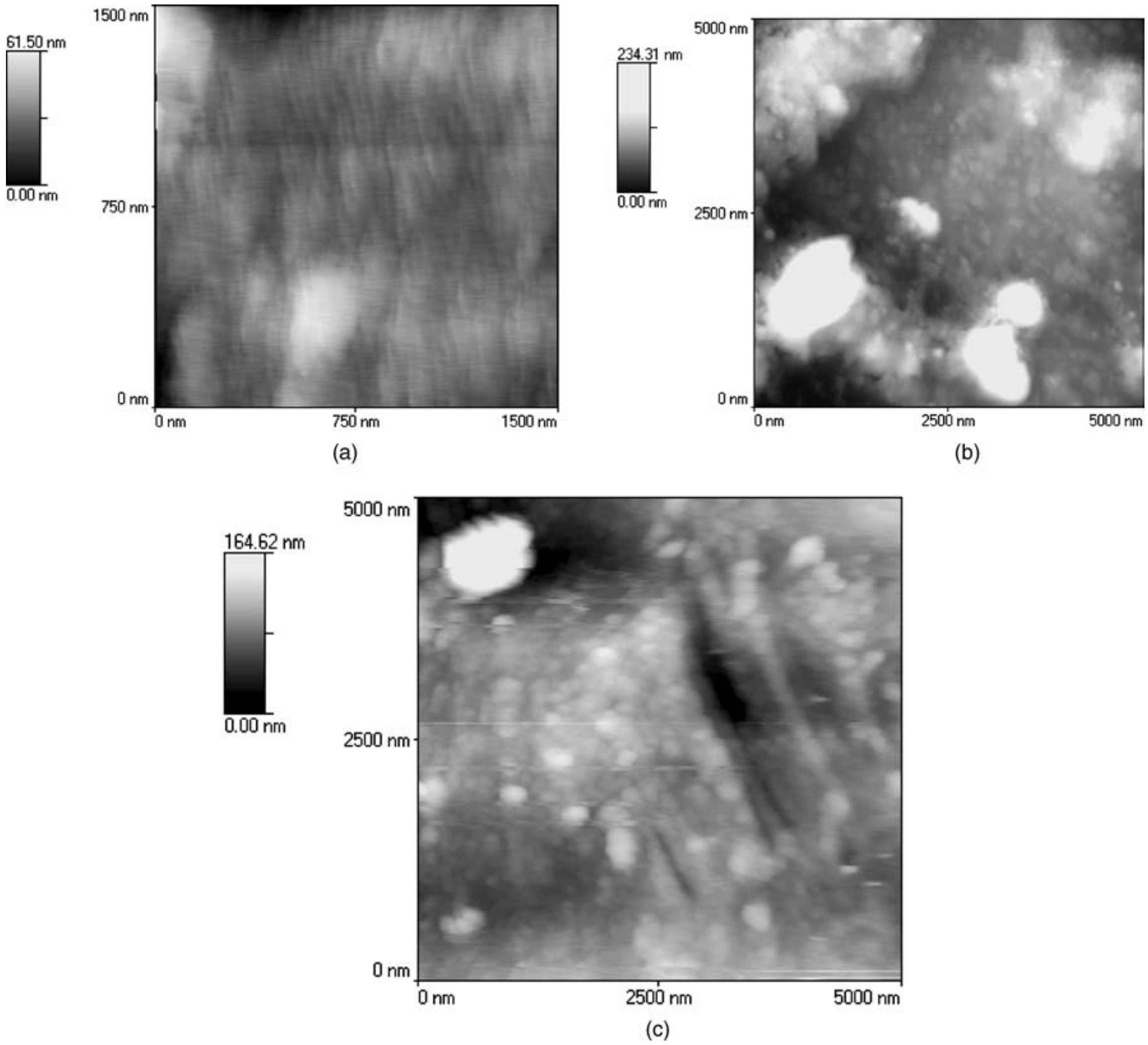
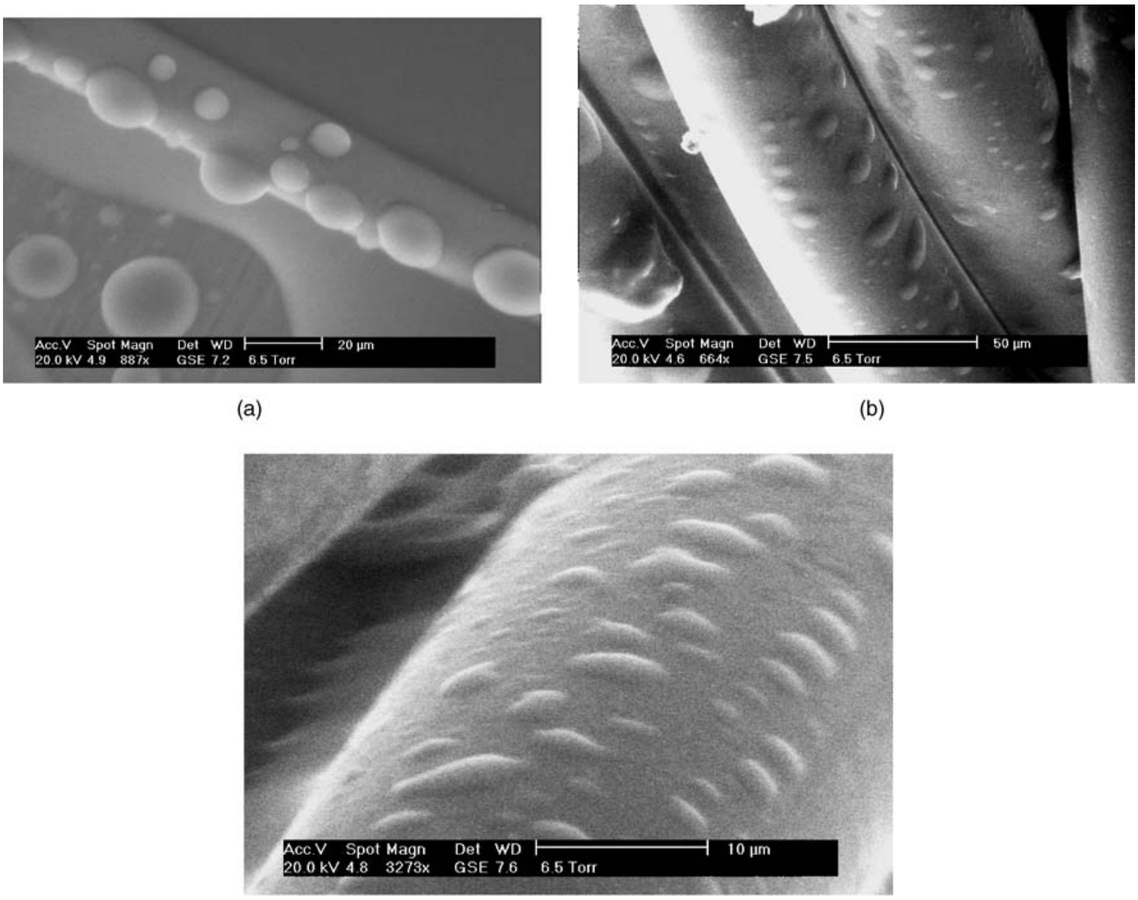


Figure 2 AFM image of PP fibres: (a) untreated; (b) oxygen plasma treated for 30 s, and (c) oxygen plasma treated for 60 s.



(a) (b)

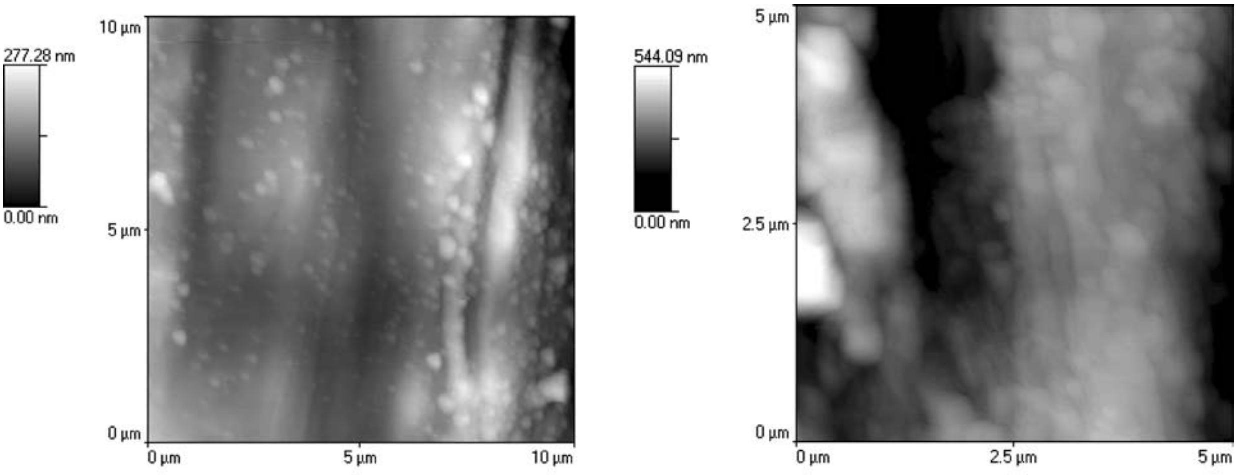
(c)

Figure 3 Wetting of PP fibres in ESEM: (a) untreated; (b) oxygen plasma treated for 30 s, and (c) oxygen plasma treated for 60 s.

3.2. Grafting of polyacrylic acid

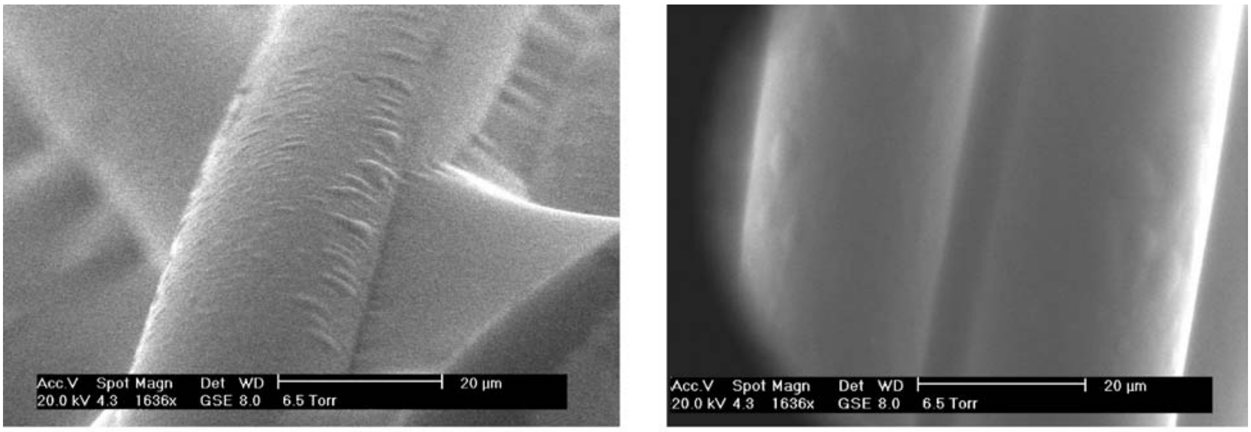
Fig. 4 shows AFM images of the surface characteristics resulting from the grafting of polyacrylic acid on the argon plasma treated PP fibre surface. In Fig. 4, it can be seen that nanosize clusters of the grafted polyacrylic aggregates are formed on the PP fibre surface after grafting for 1 h. The underlying nanofibrils are still visible. After grafting for 5 h, however, the grafted layers cover the fibre surface, as illustrated in Fig. 4b.

Water was also condensed onto these fibre surfaces. Grafting for 1 h improves the wetting of the fibre surface considerably (Fig. 5a). The irregularity of the shapes of the droplets renders it difficult to determine the contact angles. As with oxygen plasma treatment, the droplets have irregular shapes and are flattened along the curvature of the fibre surface. Indeed, some droplets are absorbed by the grafted aggregates. In Fig. 5b, which shows the PP fibre surface after 5 h of the grafting process, it can be seen that no water



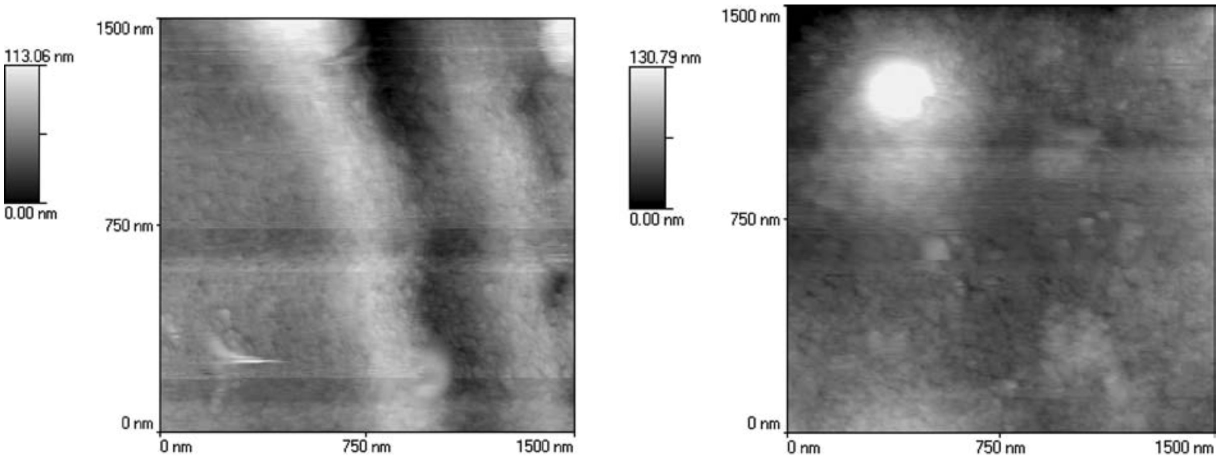
(a) (b)

Figure 4 AFM image of plasma-induced grafted PP fibres: (a) grafting for 1 h, and (b) grafting for 5 h.



(a) (b)

Figure 5 Wetting of plasma-induced grafted PP fibres in ESEM: (a) grafting for 1 h, and (b) grafting for 5 h.



(a) (b)

Figure 6 AFM image of plasma-enhanced coated PP fibres: (a) coating for 1 min, and (b) coating for 5 min.

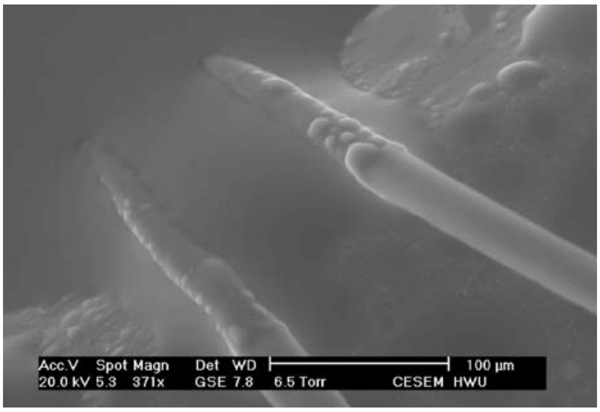


Figure 7 Wetting of plasma-enhanced PP fibres in ESEM (coating for 1 h).

droplets are visible at all. The grafted layer has swollen after condensation of water on it.

3.3. Plasma enhanced deposition of silver

Sputter coating with silver confers a different nanostructure on the PP fibre surface, as illustrated in Fig. 6. The AFM image in Fig. 6a clearly shows the nanocluster of silver after sputter coating for 1 min, although the fibril structure is still visible. Fig. 6b shows, however, that after sputter coating for 5 min, the crystals of silver mask the fibre surface, and the fibril structure is now not visible.

The behaviour of the sputter-coated fibres towards water was also investigated by ESEM. Fig. 7 shows the wetting of PP fibres that had been sputter-coated for 1 min. The contact angle of the water droplets is considerably reduced. The contact angles are in the range, 56–63°. However, in contrast to the effects noted after the oxygen plasma treatment and the 1 h polyacrylic acid grafting treatment, the shape of the droplets is much less distorted by sputter coating.

4. Conclusions

This study illustrates the use of gas plasma technology to generate functional nanostructures on PP fibre surfaces. In particular, it has been shown that the PP fibre surface can be readily rendered hydrophilic by a variety of gas plasma treatments. However, the extent of hydrophilicity conferred, as assessed from the measurement of contact angles of water droplets, varies according to the treatment given. The range of treatments discussed in this paper provide scope for a wide range of levels of hydrophilicity, extending from water contact angles of 90° down to virtually zero. Nevertheless, it has also been observed that the regularity of the condensed water droplets on the fibre surfaces may also vary according to the plasma treatment given, an aspect attributable to the different topographies developed on the PP fibre surface.

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