Penetration depth of atmospheric pressure plasma surface modification into multiple layers of polyester fabrics

C.X. Wang\textsuperscript{a,b,c,d}, Y. Ren\textsuperscript{a,b,c,e}, Y.P. Qiu\textsuperscript{a,b,c,*}

\textsuperscript{a} State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, China
\textsuperscript{b} Key Laboratory of Textile Science and Technology, Ministry of Education, China
\textsuperscript{c} College of Textiles, Donghua University, Shanghai 201620, China
\textsuperscript{d} College of Textiles and Clothing, Yancheng Institute of Technology, Jiangsu 224003, China
\textsuperscript{e} School of Textile and Clothing, Nantong University, Nantong 226007, China

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Abstract

Penetration depth of plasma surface modification of polyester fabrics was investigated. An eight-layer stack of woven polyester fabrics was exposed to a helium/oxygen atmospheric pressure plasma jet. Water-absorption time was used to evaluate surface hydrophilicity on the top and the bottom sides of each fabric layer and water capillary rise height was recorded as a measure of modification effectiveness for each fabric layer. Surface morphology and chemical compositions of each fabric layer in the stack were analyzed by atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). After atmospheric pressure plasma jet treatment, the top side of the polyester fabric became more hydrophilic. The penetration of plasma surface modification into the fabric layers was deeper for fabrics with larger average pore sizes. It was found that helium/oxygen atmospheric pressure plasma jet was able to penetrate 8 layers of polyester fabrics with pore sizes of 200 μm.

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1. Introduction

Plasma surface treatment of various polymeric materials started in 1960s [1] and is recently becoming more and more popular as a surface modification technology. In the textile industry, plasma treatments have many advantages over conventional wet chemical treatments. It does not involve large quantities of chemicals and water and thus is dry and environmentally friendly [2–6].

For a nonporous substrate, plasma surface modification is effective in a depth of several nanometers on one side of the substrate and changes the outermost layer of the material without affecting its bulk properties [7]. However, for porous materials, the picture gets more complicated. Regions of a porous structure that could be exposed to plasma are outer surfaces, interior surfaces and the bulk phase [8]. Especially for porous structured fabrics, there is a difference between the visible surface and the actual inner surface to be modified compared with films or foils. Fabrics are complex structures composed of single fibers and yarns distributed over the total fabric thickness up to several millimeters which have to be treated reasonably homogenously throughout the entire thickness [9]. To ensure a uniform plasma treatment effect on the surfaces of all fibers in a textile structure, the chemically active species must be able to penetrate the textile structure in an acceptable length of treatment time. Good penetration of plasma effects into textile structures is crucial for successful plasma modification of textile materials [2].

There are some reports in literature about the penetration of plasmas into porous materials. It has been suggested that plasma treatments can create a large number of chemically active species (ions or radicals) that permeate through pores [10]. Krentsel and coworkers [11,12] studied the penetration of plasma surface modification into porous media using a low temperature cascade arc torch. It was shown that surface fluorination was detected inside the porous matrix on the surface of
reduce the amount of chemicals used in wet processing of these materials. For atmospheric pressure plasma jet, the nozzle ejects active species on only one side of the substrate and its penetration depth into woven fabrics has not been investigated.

The purpose of this research is to study the penetration depth of atmospheric pressure plasma jet into a stack of woven polyester fabrics with various pore sizes. The surface modification effect of the plasma treatment was characterized by the changes in water-absorption time on the top and bottom sides of each fabric layer and in capillary rise height of each fabric layer in the stack. Atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) were employed to determine the surface morphological and chemical changes after the plasma treatments.

2. Experimental

2.1. Materials

The fabric used in this study was woven polyester fabrics (shown in Fig. 1) with the average pore sizes of 100 μm and 200 μm and a thickness around 0.25 mm. Before the plasma treatments, the polyester fabrics were scoured with acetone for 30 min to clean the fabric and then dried in vacuum at room temperature for 12 h. The cleaned fabrics were cut into 20 mm × 300 mm pieces. Eight layers of woven polyester fabrics were glued together at their periphery with white glue to prevent any plasma penetration through edges and then later placed on the substrate conveyor belt. The fabric layers were labeled as shown in Fig. 2.
2.2. Plasma treatments

Plasma treatments of the stacked samples were carried out in an atmospheric pressure plasma jet apparatus manufactured by Surfx Technologies (California, USA). This device employs a capacitively coupled electrode design and produces a stable discharge at atmospheric pressure with 13.56 MHz radio frequency power. The plasma jet system was equipped with a round nozzle of an active area of 3.14×1 cm² mounted above the conveyor belt (Fig. 2) moving underneath the plasma jet at a speed of 3 mm/s resulting in plasma exposure time of 2.67 s. The distance between the nozzle and the substrate surface was about 2–3 mm. The carrier gas was helium (99.99% purity) with a flow rate of 20 liter/min (LPM) and 0.2 LPM oxygen was added. The power was set at 100 W.

2.3. Wettability measurements

The wettability of the top and the bottom sides of each fabric layer was measured according to the BS4554: 1970. A microliter syringe was used to place a distilled water droplet of 3 μl on the fabric surface. The time for the droplets to be completely absorbed into the fabric was taken as the water-absorption time [15]. Five measurements were taken for each sample.

The capillary rise method was employed to evaluate the wettability improvement for each fabric layer [21,22], as these porous fabrics were made of textured yarns that could absorb the liquid droplet too quickly and were not compact and flat enough to allow a realistic contact angle measurement. The fabric strip was suspended vertically with the lower end dipped

![Fig. 3. AFM 3-D profiles of (a) Layer 1, (b) Layer 2 and (c) Layer 8 of the stacked fabrics with the pore size of 200 μm and (d) Control.](image)

![Fig. 4. AFM analysis of surface roughness for the control and each treated fabric layer.](image)
into a 0.5% potassium chromate aqueous solution. Spontaneous wicking occurred due to capillary forces. The yellow coloration of chromate solution on the white fabric clearly indicated the capillary rise height and a ruler marked in mm assembled along the strip was used to make the height measurements. The capillary rise height readings were made after 30 min. The heights of three specimens for each sample were recorded to calculate the average height value within the measurement error (±1 mm).

2.4. Surface morphology analysis

The topographical studies of the fiber surfaces were carried out using an Ultra-high Vacuum Scanning Tunneling Microscope (Omicron, Germany). Tapping mode was used to prevent significant deterioration of the fiber surfaces. Each AFM image was analyzed in terms of surface average roughness ($R_a$) and root mean square roughness ($R_{rms}$) of 0.25×0.25 μm² area on the surface of the samples [23].

2.5. Surface chemical composition analysis

The surface chemical composition of the fabrics was analyzed by XPS measurements on a Thermo ESCALAB 250 system equipped with a Mg Ka X-ray source with a pass energy of 1253.6 eV. The analysis was carried out under ultra high vacuum conditions (10⁻⁹–10⁻¹⁰ Torr). The power was set at 300 W and the spectra were taken at 90°.

3. Results and discussion

3.1. AFM analysis

The AFM images of 10×10 μm² area on the fiber surfaces in the control and each treated fabric layer in the stacked samples are presented in Fig. 3. The control fiber has a relatively smooth surface as shown in Fig. 3(d). However, after atmospheric pressure plasma jet treatment, an increased number of micro-pits were formed on the fabric surfaces in different layers as showed in Fig. 3(a–c). Much more micro-pits were formed on the first several layers (Layers 1 to 5) indicating that the active species mainly reacted with the substrate surfaces in the first few layers. It is interesting to note that even for several layers away from the top layer (Layers 6 to 8), some small micro-pits were still present, indicating deep penetration of chemically active species into the fabric layers. AFM images of the treated fabrics showed that atmospheric pressure plasma jet treatment...
created micro-pits whose density, depth and size decreased with increasing fabric layers as shown quantitatively in Fig. 4, similar to what has been reported by others [24].

The formation of micro-pits on the treated fabric surface was caused by the etching reactions, which resulted in polymer degradation through ion and electron bombardment and the oxidative reactions with activated oxygen atoms as well as free radicals. The penetration depths of different activated species are different due to the difference in energy and lifetime of these species. In general, activated particles with short lifetime such as ions, electrons, and atomic oxygen could hardly reach deep into the fabric layers while long lasting free radicals could. Therefore the top few fabric layers had more surface etching while the bottom few layers had little etching but mainly surface chemical modification. In addition UV radiation may also play an important role as helium was used as the plasma gas due to the strong emission in the UV region. The surface of plasma-treated polyester fiber became rougher resulting in improved wettability [25,26].

3.2. XPS analysis

Detailed XPS analysis revealed the surface chemistry changes for top sides of the control and the treated fabric in the stack. Table 1 shows the atomic concentration for the control and the treated fabrics. The O/C photoelectron peak ratio may imply the surface modification extent. The carbon content decreased while the content of O1s increased suggesting that oxidation occurred on the surfaces of all layers of the stacked fabrics.

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Relative area of different chemical bonds (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C=C</td>
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<tr>
<td>Layer 1</td>
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<tr>
<td>Layer 2</td>
<td>50.1</td>
</tr>
<tr>
<td>Layer 3</td>
<td>55.6</td>
</tr>
<tr>
<td>Layer 4</td>
<td>60.1</td>
</tr>
<tr>
<td>Layer 5</td>
<td>65.3</td>
</tr>
<tr>
<td>Layer 6</td>
<td>66.6</td>
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<tr>
<td>Layer 7</td>
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<tr>
<td>Layer 8</td>
<td>67.6</td>
</tr>
<tr>
<td>Control</td>
<td>70.9</td>
</tr>
</tbody>
</table>

![Fig. 6. Water-absorption times for the control and the two sides of each treated fabric layer in the stacked fabrics with the pore size of (a) 100 μm and (b) 200 μm.](image)

![Fig. 7. Capillary rise heights of control and each treated fabric layer in the stacked fabrics with the pore size of (a) 100 μm and (b) 200 μm.](image)
fabrics exposed to the helium/oxygen atmospheric pressure plasma jet [27,28]. The O/C ratio on the surface of Layer 1 was doubled compared to the untreated surface. The O/C ratio of each fabric layer decreased sequentially from Layer 1 to Layer 8. However, even for Layer 8 the O/C ratio was a little larger than that of the control indicating that the surface modification of atmospheric pressure plasma jet could penetrate as deep as the eighth layer of the fabric with the pore size of 200 μm.

Atmospheric pressure plasmas can generate a wide range of active species including atomic oxygen, ozone, neutral and metastable molecules, radicals and UV radiation [9]. Oxygen-containing plasmas increase the surface energy of materials by introducing oxygen-containing polar groups onto the material surface [29–33]. In order to identify what were the chemical functional groups introduced to the surface of each fabric layer after atmospheric pressure plasma jet treatment, deconvolution analyses were performed to C1s spectra using XPSPEAK software as shown in Fig. 5(a–d) and the results are shown in Table 2. As well documented in literature [25,26,34,35], the C1s peak for untreated polyester mainly contains three distinct sub-peaks corresponding to C–C–C–H (285 eV), C–O (286.1 eV) and C==O (288.6 eV). After plasma treatment, it is evident that the sub-peak at 285 eV decreased markedly and the sub-peak at 286.1 eV drastically increased due to increased methylene carbons singly bonded to oxygen. Some of the C–C bonds in polymer surface may be scissioned by the plasma treatments. The carbon radicals, formed by the abstraction of hydrogen atoms from the polymer chains will recombine with oxygen atoms generated in plasma jet and air by the electron impact dissociation [21,26], resulting in formation of the oxygen-containing polar groups on the fabric surface. In addition, there is a small peak at 291.4 eV due to the π–π shake up satellite in phenyl groups [9]. It almost disappeared after the plasma treatments indicating the breakage of benzene rings resulted from the impact of active species in the plasmas.

It can be seen that the helium/oxygen atmospheric pressure plasma jet mainly modified CH2 or phenyl rings in the polyester polymer chains to form C–O and C==O groups. The introduction of oxygen-containing polar groups on fabric surface leads to increased hydrophilicity as reported in literature [36–38].

3.3. Wettability improvements

Fig. 6 shows the water-absorption times for the control and each treated fabric layer with different pore sizes. Fig. 7 presents the capillary rise height of each treated fabric layer with different pore sizes. After plasma treatment, the water-absorption time for both sides of the fabrics was reduced and the capillary rise height of each fabric layer was increased. It indicates that the atmospheric pressure plasma jet treatment is effective not only on the first layer but also on several layers below the surface. In general the bottom side of each fabric layer had a longer water-absorption time and the fabric in the deeper layer had a lower capillary rise height. The decrease of water-absorption time and the increase of capillary rise height can be attributed to the increased roughness of the fiber surfaces due to plasma etching and the introduction of more polar groups due to plasma chemical modification. This is consistent with the results of AFM and XPS which showed that the first several layers (Layers 1 to 5) had the increased surface roughness and increased number of polar groups while the other three layers (Layers 6 to 8) had mainly surface functionalization.

Increasing pore size results in improved hydrophilicity of the treated fabric layers and a deeper penetration of hydrophilisation. It can be assumed that the active species in the plasma jets hit the surface of the fibers and reacted with polyester molecules, making the fabrics more wettable. Obviously, larger pore sizes make the reactive species less likely to collide with the fibers before they can penetrate through layers of fabrics.

Decreased water-absorption time on both sides of each plasma-treated fabric layer and increased capillary flow heights confirmed that the atmospheric pressure plasma jet treatment took place not only on the top fabric sides facing the plasma jet, but also more or less on bottom sides of the fabric layers [36].

4. Conclusion

Penetration of surface modification of multiple layers of fabrics exposed to helium/oxygen atmospheric pressure plasma jet was possible. The pore size of the fabric affected plasma treatment effect on each fabric layer and its penetration depth into the textile structure. After atmospheric pressure plasma jet treatment, the top side of the first fabric layer of the stacked polyester samples was substantially more wettable than the control fabric. The plasma treatment effect on the fabric surface was gradually reduced as the fabric layer got deeper since the extent of plasma modification of other layers was dependent on the degree of penetration of chemically active species in the plasma jet, which in turn depended on the average pore size of the treated fabric. For fabrics with the larger pores, it should be less likely for the active species to collide with the fabric and more likely for them to move through the pores and to reach subsequent fabric layers. The surface modification of atmospheric pressure plasma jet could penetrate into at least eight layers of fabrics with an average pore size of 200 μm and the thickness of 0.25 mm while it was only able to diffuse through six layers of the fabrics with an average pore size of 100 μm.

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