Influence of atmospheric pressure plasma treatment time on penetration depth of surface modification into fabric

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Abstract

In order to determine the relationship between the treatment duration of atmospheric pressure plasma jet (APPJ) and the penetration depth of the surface modification into textile structures, a four-layer stack of polyester woven fabrics was exposed to helium/oxygen APPJ for different treatment durations. The water-absorption time for the top and the bottom sides of each fabric layer was reduced from 200 s to almost 0 s. The capillary flow height for all fabric layers in the stack increased linearly with the treatment duration but the rate of increasing reduced linearly with the fabric layer number. A model for the capillary flow height as a function of treatment duration and the layer number was established based on the experimental data and the maximum penetration depth of the APPJ was predicted for the polyester fabric. The improved wettability of the fabrics was attributed to the enhanced surface roughness due to plasma etching and the surface chemical composition change due to plasma-induced chemical reaction as detected by scanning electron microscopy and X-ray photoelectron spectroscopy, respectively. The surface roughness and the surface chemical composition change diminished as the fabric layer number increased.

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1. Introduction

Plasma treatment of textiles is becoming more and more popular as a surface modification technique. Effects of plasma treatment include the improved wettability [1,2], adhesion [3], dyeability [4] because it can incorporate a large variety of chemically active functional groups as well as roughen the surface of the materials [5–7].

For a nonporous substrate, it is believed that plasma treatments only modify the surface within several nanometers thickness of a material without affecting the bulk properties. Textile fabrics are plasma-treated to improve the wettability and dyeability which requires all the fibers in the fabric to be treated evenly instead of just the fibers in the top layer of the fabric [7]. Therefore the penetration depth of plasma treatment will determine the quality of the plasma treatment of a textile fabric.

The penetration of plasmas into porous materials has been studied. Krentsel et al. [8,9] have demonstrated that the CF4 and C2F4 plasma–surface interaction is not just limited to the outer surfaces of a filter paper directly in contact with a low temperature plasma torch, but extends into the inner layers of a porous substrate. Mukhopadhyay et al. [10] investigated the surface modification of porous filter papers using RF plasma and found that hydrophobic coatings can be deposited on a stack of five porous filter papers and the extent of permeation can be controlled by altering the applied power of the treatment.
Geyter et al. [11] reported that process pressure had an important effect on the penetration of plasma through the textile layers at medium pressure (5.0 kPa).

Most of the published studies were carried out using low or medium pressure plasmas. Atmospheric pressure plasma reactors are considered more suitable for textiles and other porous materials because it can be applied on-line in production. However, little information can be collected from the literature regarding the treatment depth of atmospheric pressure plasmas and how it can be influenced by plasma treatment parameters. Poll et al. [12] treated textiles at various pressures and found no plasma penetration into textile structures at high pressure despite long treatment time. They concluded that the penetration of plasmas into textiles were inversely proportional to the pressure of plasma treatments. However, the device used in that study was not an atmospheric pressure plasma reactor. Vatuna et al. [13] treated layers of textile fabrics with atmospheric pressure plasma and observed penetration only after a treatment time of 20 min which is not practical in many industrial applications.

One of the atmospheric pressure plasma treatment devices available relatively recently is atmospheric pressure plasma jet (APPJ) [14,15] which is significantly milder than a plasma torch but still highly effective at room temperature. APPJ works in an open system in which plasma is produced between capacitively coupled electrodes and then ejected from nozzle onto the substrate. Therefore, only one surface of the substrate is directly bombarded by the plasma jet while in other plasma devices such as dielectric barrier discharge (DBD) systems both surfaces of the substrate are in contact with the plasma. However, little has been reported in the literature about penetration depth of APPJ treatment effects into porous structures such as textile fabrics.

The penetration depth of APPJ may potentially be affected by plasma treatment conditions such as treatment duration, gas flow rate, applied power, nozzle to substrate distance and nozzle temperature as well as substrate pore size or structure [16]. In our previous study, the influence of fabric pore size on penetration depth of APPJ into a stack of fabrics was investigated [17]. It was observed that larger pore sizes (200 μm versus 100 μm) lead to a deeper penetration of the plasmas. In this study, the effect of APPJ treatment time on the penetration depth of the plasma surface modification into a textile structure was studied. Four layers of woven polyester fabrics, a typical hydrophobic material, were stacked together as a model porous system to simulate a textile structure with certain thickness. Penetration of APPJ surface modification effect through the fabric layers was detected by the changes in wettability of both sides of each fabric layer and capillarity flow height of each fabric in the stack were detected by the water-absorption time test and capillary flow height test. Morphological roughness and chemical composition on the surface of each layer were characterized using scanning electron microscopy (SEM) observation and X-ray photoelectron spectroscopy (XPS) analysis, respectively.

2. Experimental

2.1. Materials

The polyester fabrics were supplied by Wujiang Jiutian Textile Company (Jiangsu, China) with an average pore size of about 200 μm and a thickness of about 0.75 mm. Before the plasma treatment, the polyester fabrics were washed in acetone for 30 min to remove the surface contamination, thoroughly rinsed by distilled water and dried in a vacuum oven overnight. Then the cleaned fabrics were cut into strips of 2 cm × 30 cm. Four layers of woven polyester fabrics (labeled as in Fig. 1) were glued together at their periphery with white glue to prevent any plasma penetration through edges and were later placed on the substrate conveying belt fabricated to move the treated samples underneath the plasma jet at a constant speed.

2.2. Plasma treatment

Plasma treatment of stacked samples was carried out in an atmospheric pressure plasma jet apparatus manufactured by Surfx Technologies (CA, USA). This devise employs a capacitively coupled electrode design and produces a stable discharge at atmospheric pressure with 13.56 MHz radio frequency power. A round APPJ nozzle was mounted above the conveying belt which carried the fabric sample moving at a speed of 3 mm/s. The carrier gas was helium with a flow rate of 20 LPM and 0.2 LPM oxygen was added. The power was set at 100 W. Four samples were respectively treated for different number of laps corresponding to stationary treatment durations of 0.67 s, 1.33 s, 2 s and 2.67 s, respectively.

2.3. Wettability measurements

The wettability of the top and the bottom sides of each fabric layer was measured according to 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 [18]. Five measurements were taken for each sample.

In the capillary flow height test, the fabric strips of 2 cm × 30 cm area were suspended vertically with the lower end dipped into a diluted potassium chromate aqueous solution.
(0.5 wt%). Spontaneous wicking occurred due to capillary forces. The capillary flow height as a function of time was recorded and the absorption rate was calculated as cm/min. Height readings measured by a ruler marked in centimeters assembled along the strip were made at time intervals of 1 min in the first 10 min and 5 min afterwards. For each sample, three specimens were measured to obtain the average height value within the measurement error of ±1 mm.

2.4. Surface morphology analysis

The fiber surface morphology was examined using a SEM (model JSM-5600LV). The specimens were inspected at 5,000× magnification at 15 kV to see if there was any obvious change of fiber surface morphology caused by the plasma treatments. All of the samples were gold-coated prior to conducting the SEM observation.

Fig. 2. SEM micrographs of (a) control, (b) Layer 1, (c) Layer 2, (d) Layer 3 and (e) Layer 4 of polyester fabrics treated for 2 s.
2.5. Surface chemical composition studies

The surface chemical compositions of the fabrics were analyzed by XPS measurements on Thermo ESCALAB 250 system, which was equipped with a Mg Kα X-ray source having a pass energy of 1253.6 eV. The analysis was carried out under UHV conditions (10⁻¹⁰ Torr to 10⁻¹¹ Torr). The power was set at 300 W and spectra were taken at a take-off angle of 45°.

3. Results and discussion

3.1. SEM analysis

Significant changes in morphology of the fabric surfaces were observed after the plasma treatments. As shown in Fig. 2(a), the untreated sample showed a smooth surface while for the plasma-treated samples, micro-pits were formed on the

Fig. 3. Deconvolution of XPS core level C 1s spectra of fiber: (a) Control, (b) Layer 1, (c) Layer 2, (d) Layer 3 and (e) Layer 4 of polyester fabrics treated for 2 s.
fabric surface as shown in Fig. 2(b)–(f). As expected, much more micro-pits were formed on Layer 1 indicating that the top layer of the fabrics was bombarded by much more active species from the plasma jet. It was interesting to note that even for Layer 4 of the treated samples there still existed small number of micro-pits indicating the diffusion of chemically active species through the fabric layers. SEM images of treated fabrics showed that APPJ treatment created micro-pits whose density, depth and size decrease with the increasing number of fabric layers. The formation of micro-pits on the treated fabric surfaces were caused by the etching reactions, in which some degradation reactions occurred due to the bombardment of the ions and the electrons as well as the oxidative reactions with atomic oxygen. Therefore the surfaces of plasma-treated polyester fiber were roughed resulting in change of the fabric surface properties [3,19].

3.2. XPS analysis

Detailed XPS studies of all surfaces in the stack were performed to reveal the surface chemical changes. Table 1 shows the atomic concentration for control and the plasma-treated fabrics. The O/C photoelectron peak ratio is an important indicator for the degree of surface chemical modification. The decrease of the content of C1s and the increase of the content O1s suggested that oxygen was incorporated onto the surfaces of all layers of the stacked fabrics exposed to helium/oxygen APPJ. The O/C ratio of Layer 1 surface was doubled compared with that of the untreated fabric surface. Even for Layer 4, the O/C ratio reached 150% of that of the control.

In order to investigate what chemical functional groups are introduced to the surface of each layer after APPJ treatment, the concentration of each chemical component with C1s was calculated by deconvolution analyses using XPSPEAK software as shown in Fig. 3(a)–(e) and the detailed data are shown in Table 2. As well documented in literatures [3,20], the C1s peak for untreated polyester contains three distinct sub-peaks corresponding to C–C/C–H (284.6 eV), C–O (286.1 eV) and O–C–O (288.7 eV). Two new peaks at 286.7 eV and 288.1 eV are presented in the XPS spectra of the treated polyester fabrics, which can be attributed to the existence of C–OH and –C=O [1,19]. The percent of C–C component decreased significantly after the plasma treatment, while most of the oxygen-containing polar groups such as C=O, C–OH and C–OOH increased on the surface of the treated fabrics (Table 2). The result indicates that some of the C–C bonds in polymer surface could be broken by the plasma treatments. Then the carbon radicals, formed by the abstraction of hydrogen atoms from the polymer chains, may combine with the oxygen atoms generated in plasma jet or in the air by the electron impact dissociation [19,21] resulting in the formation of the oxygen-containing polar groups on the fabric surface. It can be seen that the helium/oxygen APPJ mainly modified CH2 rather than ester groups in the polyester polymer chains to form C–OH and C=O groups. The introduction of oxygen-containing polar groups on the fabric surfaces led to the surface change from hydrophobicity to hydrophilicity as reported in literatures [22–24].

3.3. Wettability measurements

The water-absorption time for the top and bottom sides of each fabric layer in the stacked samples was decreased from 200 s to almost 0 s, even for those treated for only 0.67 s. It indicates the effectiveness of APPJ treatment not only on the top sides but also on the other bottom sides due to penetration of the APPJ treatment through the pores in the fabric. Fig. 4 shows capillary flow height versus wicking time for polyester fabrics before and after plasma treatment. Evidently the wettability is greatly enhanced by plasma treatment. At the beginning of capillary flow height test, the capillary rising rate increased as the fabric layer number decreased. After the first

<table>
<thead>
<tr>
<th>Sample</th>
<th>Relative area of different chemical bonds (%)</th>
<th>C–C</th>
<th>C–O</th>
<th>C–OH</th>
<th>C=O</th>
<th>O–C=O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer 1</td>
<td>40.36</td>
<td>17.39</td>
<td>13.35</td>
<td>10.72</td>
<td>18.18</td>
<td></td>
</tr>
<tr>
<td>Layer 2</td>
<td>42.08</td>
<td>19.24</td>
<td>10.81</td>
<td>8.88</td>
<td>18.99</td>
<td></td>
</tr>
<tr>
<td>Layer 3</td>
<td>45.65</td>
<td>20.21</td>
<td>7.42</td>
<td>6.77</td>
<td>19.95</td>
<td></td>
</tr>
<tr>
<td>Layer 4</td>
<td>53.39</td>
<td>20.51</td>
<td>6.97</td>
<td>19.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Control</td>
<td>60.72</td>
<td>20.20</td>
<td>0</td>
<td>0</td>
<td>19.07</td>
<td></td>
</tr>
</tbody>
</table>

Table 1

Relative chemical composition and atomic ratios determined by XPS for polyester fabrics untreated and treated with APPJ

Table 2

Results of deconvolution of C 1s peaks for polyester fabric untreated and treated with APPJ
10 min, all four layers had pretty much the same capillary rising rate. These findings were in good agreement with the analysis of SEM and XPS which indicated that as the layer number increased the change of surface roughness and chemical composition diminished.

Longer plasma treatment duration resulted in a deeper penetration of hydrophilisation effect into the fabric layers. It can be assumed that the active species in plasma jet were able to penetrate through all four layers of the fabrics. However, as the layer number increased the treatment dose decreased due to decreased number of active species that could penetrate through the layers. For each additional layer, the treatment time has to be increased substantially in order to obtain the same treatment results. For example, in this study, one lap or 0.67 s had to be added for Layer 4 to have the same results as Layer 3.

Fig. 5 presents the dependence of the plasma penetration effect represented by capillary flow height in 30 min of wicking on the plasma treatment time for each fabric layer. Longer treatment time resulted in a greater capillary flow height and thus a greater hydrophilicity for all four fabric layers. With the increasing layer number, the degree of wettability improvement was decreased. It was interesting to find that the capillary flow height increased linearly with the increasing treatment time but the slope of increasing trend decreased as the layer number increased. A general equation may be written for this trend, that is

\[ H = H_0 + KT \]  

where \( H \) and \( H_0 \) are the capillary flow height for the treated and the control group, respectively, \( K \) is the slope of the line and \( T \) is the treatment duration. If we plot the slopes of the curves versus the layer number (Fig. 6), it can be seen that the slope has a negative linear relation with the layer number, \( N \), namely:

\[ K = C_0 + C_1N = 15.39 - 2.338N \]  

where \( C_1 \) is the slope of the line and \( C_0 \) is the interception of the line on \( Y \) axis. By replacing \( K \) in Eqs. (1) and (2), we have

\[ H = H_0 + (C_0 + C_1N)T \]  

It is obvious that when \( K = 0, H \) will not change as treatment time increases. In the current experimental setup, when \( K = 0 \),

\[ N = -\frac{C_0}{C_1} = 6.58 \]  

This means that for Layer 7, there will be almost no improvement in capillary flow height regardless the plasma treatment time. This relationship of the capillary flow height as a function of the treatment duration and the layer number may be used to determine the maximum penetration depth for a certain set of fabrics and treatment conditions such as gas flow rate, type of gases, applied plasma power, nozzle to substrate distance and nozzle temperature. In addition, one may also conclude that capillary flow height is a relatively stable parameter to characterize the wettability change at various plasma treatment conditions. Of course, capillary flow height is also a function of all the treatment parameters mentioned above and fabric structural parameters which will be studied systematically in our future research.

4. Conclusions

The APPJ treatment was effective in improving the wettability of polyester fabrics due to surface etching and chemical composition change detected by SEM and XPS. The water-absorption time of the top and the bottom sides of each fabric layer was reduced from 200 s to almost 0 s indicating no difference in wettability improvement between the two sides of each fabric layer after APPJ treatment, which demonstrated that interaction of chemically active species generated in plasma jet with the substrate surface was not only on the surface directly in contact with the plasma jet but also observed on surfaces which were not facing the plasma jet. As the layer number increased, the effectiveness of the APPJ treatment gradually reduced. There was a linear relationship between the capillary flow height and the treatment time and the rate of the capillary flow height increasing with the treatment time decreased linearly as the layer number increased. An empirical model constructed using the experimental data predicted that the maximum
penetration depth was six layers of fabrics with reasonable treatment duration as adopted in the current study. Future studies are warranted to explore the relationship between the penetration depth and the processing parameters.

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