Influence of ethanol pretreatment on effectiveness of atmospheric pressure plasma treatment of polyethylene fibers

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Abstract

Unlike low pressure plasmas, atmospheric pressure plasmas can treat materials with adsorbed liquids such as organic solvents used as cleaning agents in preparation of material surfaces for plasma treatments. These solvents may interact with the plasma to influence the treatment results. This paper studies the influence of ethanol pretreatment on atmospheric pressure plasma jet (APJ) treatment of ultra-high molecular weight polyethylene (UHMWPE) fibers when a mixture of helium and 1% of oxygen is used as the treatment gas. The fibers had 0.82% and 0.86% weight gain after soaking in ethanol for 12 and 24 h, respectively. Scanning electron microscopy shows that the surface of fibers soaked in ethanol for 12 h or longer before the plasma treatment does not show any morphological change. X-ray photoelectron spectroscopy shows oxygen content doubled for the plasma treated fibers compared with control but a rather small increase in oxygen content on the surface of the ethanol pretreated UHMWPE fibers compared with the plasma treated fibers without pretreatment. Water contact angle of the ethanol pretreated fibers did not change after the plasma treatment compared with the control fiber. Microbond test shows that the interfacial shear strength values (IFSS) of the fibers to epoxy do not change for the ethanol pretreated fibers while that of the plasma directly treated fibers increases significantly. It is likely that ethanol absorbed into the fiber reacts with the plasma, forming a weakly bonded layer of polymers that reduced plasma etching and IFSS.

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1. Introduction

Plasma treatment of materials is a vital technology in many areas such as electronics, aerospace, automotive, textiles [1] and biomedical industries [2], due to its ability to induce various surface modifications, such as etching [3], deposition [4], and polymerization [5]. Currently most plasma treatments are carried out at low pressure or in vacuum, which limits the application scope of the technology [6,7]. In contrast, atmospheric pressure plasma treatments do not require a vacuum system and therefore can greatly expand the current scope of plasma treatments in materials processing [8]. Unlike low pressure plasmas, atmospheric pressure plasma plasmas may treat materials containing adsorbed liquid [9]. Our previous studies have investigated the influence of adsorbed water on atmospheric pressure plasma treatment using helium or helium plus oxygen as the treatment gas and found that higher substrate water content promoted surface wettability and surface chemical composition change of atmospheric pressure plasma treated aramid fibers [9,10]. Water is not the only liquid which could be adsorbed by the substrate in manufacturing processes. Many chemicals such as cleaning and sizing agents are widely used in industry for various purposes. These chemicals may be absorbed into the substrates and potentially interact with plasmas, influencing the effectiveness of the plasma treatments. In many industry applications such as polymer surface cleaning [11], metal surface cleaning [12] and human health care [13], ethanol is one of the most frequently used organic solvents for surface cleaning and various other purposes due to its low cost and low impact on the environment, compared with other cleaning agents such as Trichloroethane (TCA) [14] dimethylsulfoxide (DMS) and N,N-dimethylformamide (DMF) [15]. Therefore the influence of ethanol absorbed into the substrate material on the effectiveness of atmospheric pressure plasma treatments is of great importance to the industries. Dillingham and Oakley accidentally found that the effectiveness of atmospheric pressure plasma treatment diminished when they tried to adhesively bond graphite/epoxy composite panels cleaned with ethanol prior to the plasma treatment [16]. However, how ethanol interferes with the plasma treatment of the composites has not been investigated. Therefore it is necessary to study the influence of ethanol on atmospheric pressure plasma treatment of polymeric materials.
UHMWPE fibers possess high specific tensile modulus and strength but low surface energy and chemically inert surfaces, resulting in poor adhesion to many matrices. Both chemical treatments and vacuum plasma treatments have been used to enhance the surface wettability and adhesion properties of UHMWPE fibers. Compared with the chemically treated filaments, plasma treated samples show greater improvement of adhesion to epoxy resin, due to better penetration of the epoxy resin and enhanced mechanical keying [17]. In this study, UHMWPE fiber is selected as a model system to analyze the influence of ethanol on the outcome of atmospheric pressure plasma treatments. Morphology, wettability, and chemical composition of the fiber surface, and adhesion strength of the fiber to epoxy, with and without ethanol pretreatment were investigated using scanning electron microscopy (SEM), static water contact angle, X-ray photoelectron spectroscopy (XPS), and micro-bond pull-out test, respectively.

2. Experimental

2.1. Materials

The UHMWPE fibers were provided by Ningbo Dacheng Chemical Fiber Group in the form of a yarn composed of 240 monofilaments with a tensile modulus of 130 GPa and a single fiber diameter around 28 μm. The matrix was epoxy resin prepared with Araldite LY 3600 CL and hardener Aradur 3600-1 CL (Ciba-Geigy, Basel, Switzerland) at a ratio of 7:3 (wt/wt). The ethanol was 99.7% pure provided by Changshu Yangyuan Chemical Company (Jiansu, China).

2.2. Sample preparation and plasma treatment

All the UHMWPE fibers including the control fibers were soaked in acetone in a container for 10 min and then dried at 80 °C for 1 h in a vacuum oven. The fibers were then divided into 3 groups: control or untreated, plasma treated, and ethanol pretreated for 12 h, followed by plasma treatment. The mass change of the fibers was determined by weighing the fibers before and after drying in ambient air for 4 h using an analytical balance. The plasma treatments were carried out using an atmospheric pressure plasma jet (APPJ) system (Model AtomfusTM-R 250, SurfX Company, USA) with the discharge power of 10 W and a frequency of 13.56 MHz. Helium (≥99.99% pure) as the carrier gas was introduced into the rectangular nozzle (2×10 mm) at a flow rate of 10 l/min and 1% of oxygen was added as the treatment gas. For all the groups, the nozzle was heated to 100 °C. The distance between the nozzle and the specimen was 2 mm. The specimens were fixed on a frame and treated under the nozzle (2 mm×10 mm) for one lap on a conveying belt moving at a rate of 2.2 mm/s. The treatment was performed in an environment of 17 °C and 54% relative humidity.

2.3. Wettability measurements

The wettability was determined by measuring the static contact angle between single fibers and water. The sessile drop technique was applied on a JC2000A Stable Contact Angle Analyzer by observing the digital images of the distilled water droplets on the fibers.

2.4. Microbond test

All the single fiber specimens for microbond test were prepared the same way as reported previously [8]. Small epoxy beads were put onto the fibers and then cured at 80 °C for 2 h. The embedded length and the diameter of each bead as well as the diameter of the fiber were measured using an optical microscope.

The microbond test was conducted on a single fiber tensile testing machine (XQ-1) with a microvise. The upper clamp displacement rate was 1 mm/min.

The interfacial shear strength (IFSS), \(\tau_i\), was calculated using the following equation derived from the well-known shear-lag model [18]:

\[
\tau_i = \frac{p_{\text{max}} \coth(nL/r)}{2A}
\]  

where \(p_{\text{max}}\) is the peak load, \(A\) is the cross-sectional area of the fiber, \(L\) is the embedded length, \(r\) is the equivalent fiber radius calculated from the fiber cross-sectional area, and \(n\) is defined as [18]

\[
n = \left[ \frac{E_m}{E_r (1 + \nu_m) \ln(K/r)} \right]^{1/2}
\]

where \(E_m = 2.69 \text{ GPa} [15]\) is the Young’s modulus of the matrix, \(\nu_m = 0.4 [19]\) is the Poisson’s ratio of the matrix. \(E_r = 130 \text{ GPa}\) for the UHMWPE fiber is the fiber tensile modulus, \(R\) is the radius of the epoxy beads, and \(r\) is the same as defined previously.

2.5. XPS

The surface chemical composition of the control and the treated fibers was evaluated by the Thermo ESCALAB 250 X-ray photoelectron spectrometer. The spectra were collected using Mg Kα, (hv = 1253.6 eV) with pass energy of 20 eV. The X-ray source power was 300 W and the take-off angle was 45°. The pressure within the XPS chamber was between 10⁻⁷ and 10⁻⁸ Pa. The C1s and O1s core level spectra were recorded to determine the surface composition of the fibers. In deconvolution analysis of the XPS peaks, the spectra were fitted using Gaussian peak profiles and a linear background.

2.6. Scanning electron microscopy

The UHMWPE fibers prepared for the SEM tests were divided into five groups, namely control or untreated, plasma directly treated, ethanol pretreated for 1 h, 12 h, and 36 h, respectively and then plasma treated.

A JSM-5600LV Scanning Electron Microscopy (SEM) system was employed to observe the surface morphology of the fibers. The fibers were gold coated prior to being loaded into the SEM chamber.

2.7. Statistical analysis

The water contact angles and IFSS data were analyzed using one-way analysis of variance (ANOVA) and Tukey’s pair-wise multiple comparison [20]. A P-value smaller than 0.05 was considered statistically significant.

3. Results and discussion

3.1. Surface morphology

Fig. 1 exhibits the surface morphology of the untreated and treated UHMWPE fibers. All samples have longitudinal straits which inherently exist as a result of gel spinning process for manufacturing UHMWPE fibers. From the comparison of Fig. 1(A) and (B), surface cracks resulting from the plasma treatment are easily observable. Similar results were observed in our previous studies [21] in which UHMWPE fibers were treated by He/O₂ atmospheric pressure plasma on a dielectric barrier discharge (DBD) devise. Micro-cracks were also detected though they were smaller than those found here. In another study [22], pure He gas was used in the plasma treatment and there were no micro-cracks generated. It seems that O₂ could enhance the etching effect.

However, where the fibers were pre-soaked in ethanol, the etching effect was quenched as shown in Fig. 1(C)-(E), and the quenching
efficiency seemed to be related to the soaking time. When the fibers were soaked in the ethanol for 1 h, certain degree of roughness was still visible on the surface. However, after 12 h and 36 h soaking in ethanol, no microscopically visible morphological change can be observed on the fiber surfaces at 10,000× magnification. This could be due to the increased amount of ethanol molecules absorbed into the fiber bulk for longer soaking time which could result in deeper penetration of ethanol into the fibers and thus allow more ethanol release during the plasma treatments. Indeed, the mass gains for the fibers soaked in ethanol for 12 h and 24 h were 0.82% and 0.86%, respectively. The existence of the absorbed ethanol may produce ethanol/helium/oxygen plasma which could deposit a weakly bonded layer of polymeric material onto the surface of the fibers. The energy of the plasma was thus consumed, minimizing the etching effect of the plasma.

3.2. Surface chemical composition

The element composition and the atomic ratios of O/C derived from survey spectra for the control and the treated groups are given in Table 1. The O/C ratios increased when the fibers were treated with

<table>
<thead>
<tr>
<th>Group</th>
<th>Chemical composition (%)</th>
<th>Atomic ratio (O/C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>93.4  6.6</td>
<td>0.07</td>
</tr>
<tr>
<td>Plasma treated only</td>
<td>88.2  11.8</td>
<td>0.13</td>
</tr>
<tr>
<td>Plasma treated with ethanol pretreatment</td>
<td>84.3  15.7</td>
<td>0.19</td>
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</table>

Fig. 1. The SEM photographs (10000× magnification) of the APPJ treated UHMWPE fibers: (A) control; (B) plasma treated with no pretreatment; (C) ethanol treated for 1 h followed by plasma treatment; (D) ethanol treated for 12 h followed by plasma treatment; (E) ethanol treated for 36 h followed by plasma treatment.
atmospheric pressure plasma. The deconvolution analyses of the C1s peaks were performed as shown in Fig. 2 and Table 2. The C1s peaks were deconvoluted into five peaks corresponding to C–C (285 eV), C–O (286.5 eV), C=O (288.1 eV), COOR (289.6 eV), and β-COOR peak (285.4 eV) equal in area to that of the COOR peak similar to those illustrated by Briggs and his coworkers [23,24]. The chemical shifts used in the current analysis are determined by observing the locations of the peaks in the original spectra as well as comparing with the values used by others in literature. For each sample, these component peaks have a constant full width at half-maximum (FWHM) [23,24]. The control PE C1s peak has a FWHM of 1.1 eV, while the two plasma treated samples have the FWHM of 1.25 eV.

After the APPJ treatment, C–C was reduced significantly, which could result from the in-plasma or post-plasma surface oxidization. Meanwhile, more C–O components were generated as indicated in Table 2. The control group has no C=O and COOR component while the two plasma treated groups have substantial amount of C=O and COOR components. Compared with the plasma treated only group, C–O and C=O groups were raised about 30% and 15% due to the pretreatment of ethanol, which could be partially attributed to the existence of residual ethanol as well as the deposit of a layer of weakly bonded polymer on the surface of the fiber which were oxidized during and after the plasma treatment.

3.3. Wettability of fibers

The wettability of the fibers was determined by measuring static water contact angles as shown in Table 3. It is obvious that the water contact angles for the ethanol pretreated fibers are close to that of the control while the plasma treated fiber has a significantly lower water contact angle than the other two groups. What is more interesting is that when the ethanol pretreated fibers were washed in water after the plasma treatment, the water contact angle decreased significantly although it is still higher than the plasma treated group without ethanol pretreatment. This indicates that there indeed exists a weakly bonded layer of polymer on the surface of the ethanol pretreated fibers.

3.4. Interfacial shear strength

As shown in Table 4, without ethanol pretreatment, the IFSS values for the fiber were significantly increased by APPJ treatment, due to the roughening and the activation of the surfaces. This result is in a good agreement with our previous studies [9,25] in which APPJ plasma

| Table 2 | Deconvolution of C1s peaks for the control and treated UHMPE fibers |
|---------|-------------------------|--------|--------|--------|--------|
| Group   | Relative area under C1s envelop (%) |
|         | C–C  | β-COOR | C–O  | C=O  | COOR  |
| Control | 96.3 | 0      | 3.7  | 0    | 0     |
| Plasma treated only | 81.8 | 2.0    | 10.9 | 2.6  | 2.7   |
| Plasma treated with ethanol pretreatment | 76.8 | 3.1    | 14.1 | 3.0  | 3.0   |

| Table 3 | Static water contact angles for fibers untreated and plasma treated fibers |
|---------|-------------------------|--------|--------|
| Treatment | Sample size | Contact angle (degree) |
|          |             | Mean   | Standard deviation |
| Control  | 30          | 109.5° | 10.4    |
| Plasma treated only | 30          | 74.1°  | 9.7     |
| Plasma treated with ethanol pretreatment | 30          | 107.3° | 13.2    |
| Plasma treated with ethanol pretreatment washed with water | 30          | 89.7°  | 15.6    |

Means with different letters are statistically different at p<0.05.
treatment significantly enhanced the adhesion of aramid and UHMWPE fibers to epoxy matrices. However, with the ethanol pretreatment, the mean IFSS value was similar to that of the control. The effect of plasma seemed to be hindered by the pretreatment of ethanol. The reason for this effect could be again due to the existence of the weakly bonded polymer layer which behaves like a lubricant instead of a coupling layer in addition to retarded plasma etching to the fiber surface. This finding is very important because ethanol is one of the most widely used cleaning agents in industry and laboratories. If the surface of a material has to be cleaned before plasma treatments, one should either avoid using ethanol or dry the material in oven completely before the plasma treatments. Otherwise, the result could become unpredictable.

4. Conclusions

The atmospheric pressure APPJ plasma treatment enhanced the adhesion of UHMWPE fibers with epoxy resin, through roughening the surface and introducing polar groups. However, the fibers pretreated with ethanol showed an IFSS similar to that of the control fibers, which means that ethanol could neutralize the effect of the plasma treatment. This is mainly due to the deposition of a weakly bonded polymer layer on fiber surface and the energy consumption for the ethanol/helium/oxygen plasma polymerization process that greatly reduced plasma etching of the fiber surface.

Acknowledgements

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References


Table 4

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Sample Size</th>
<th>IFSS (MPa)</th>
<th>Mean</th>
<th>Standard deviation</th>
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</thead>
<tbody>
<tr>
<td>Control</td>
<td>35</td>
<td>4.52&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.65</td>
<td></td>
</tr>
<tr>
<td>Plasma treated only</td>
<td>23</td>
<td>19.48&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.62</td>
<td></td>
</tr>
<tr>
<td>Plasma treated with ethanol pretreatment</td>
<td>47</td>
<td>3.92&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.99</td>
<td></td>
</tr>
</tbody>
</table>

Means with different letters are statistically different at p<0.05.