Influence of the amount of absorbed moisture in nylon fibers on atmospheric pressure plasma processing

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Abstract

During atmospheric pressure plasma treatment, the existence of moisture in the substrate material may have a potential influence on the treatment effect. In this study, nylon 6 fibers with three different moisture regains (1.23, 5.19 and 9.70%) were treated by atmospheric pressure plasma jet were investigated to improve the wettability and dyeing properties of fibers. The scanning electron microscope showed that at 9.70% moisture regain, the surface layer of the fibers was partially peeled off after plasma treatment. X-ray photoelectron spectroscopy analysis indicated that the plasma-treated fibers had higher oxygen concentration than the control fibers. In dynamic contact angle measurement, the advancing contact angles of all three treated groups decreased about 12°, while the groups with 5.19 and 9.70% moisture regains had lower receding contact angles than the group with 1.23% moisture regain. Using acid dye and dispersive dye, respectively, greater dye uptake was observed in treated fibers whereas the dye depths of the two dyes in nylon fibers were not affected by plasma treatment. The dyeability of the treated fibers with 1.23% moisture regain was a little better than that of the other two treated groups. In addition, no significant difference in single fiber tensile strength was found among control and treated fibers.

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Keywords: Atmospheric pressure plasma jet; Nylon fiber; Moisture regain; X-ray photoelectron spectroscopy

1. Introduction

Atmospheric pressure plasma devices have been developed to overcome the drawbacks of low pressure plasma treatment in which a vacuum system is required, limiting its application in certain industries such as textiles. Atmospheric pressure plasma treatments are carried out in open environment, potentially saving significant capital cost and providing higher throughput for some treatment processes [1–5]. It has been reported that atmospheric pressure plasma treatments are effective in surface etching, surface chemical modification, and plasma polymerization [6–10]. Nevertheless, little has been reported about the influence of moisture regain (MR) of hygroscopic fibers on the results of atmospheric pressure plasma treatment. Water molecules in a hygroscopic material can disrupt the inter-molecular forces, swell the material, and participate in the chemical or physical reactions with active species and polymer molecules which could potentially influence the interaction between the plasmas and the material surfaces [11]. In our previous studies, it was found that moisture in air as well as in a polymeric fiber facilitated modification of fiber surfaces for improvement of surface hydrophilicity, although the roughness of the fiber surface was not significantly influenced for the fibers [12,13].

Nylon 6 fiber is one of the most important synthetic fibers used in textile industry due to its excellent mechanical, thermal and chemical properties [14]. However, it has relatively low surface energy and weak hydrophilicity, which could restrict its applications in the fields of anti-electrostatic, handle comfort, adhesion and so on. Nylon 6 fiber also has shortcomings in dyeing process. In general, nylon fiber can be dyed by both anionic and cationic dyes owing to the presence of amide groups in its molecular chain [15]. Acid dyes are most commonly used in dyeing the polyamides whereas poor uniformity has been
reported because of slow dye diffusion into the internal structure of the fibers [16]. Dispersive dyes, on the other hand, are limited to achieve vivid colors although they have excellent migration abilities [16]. With an aim of improving both the wettability and dyeability of nylon fibers, atmospheric pressure plasma was applied in this study to modify the fiber surface.

Surface modification of nylon substrate using atmospheric plasma treatment has been reported in literature [17–24]. Cui et al. [20] used atmospheric pressure air dielectric barrier discharge (DBD) to treat nylon 6,6 films, and found that the surface oxidation occurred in two stages: the creation of the carbons singly bonded to oxygen dominated in the first stage, while in the second stage these carbons were further oxidized into those doubly bonded to oxygen. A remarkable decrease of surface contact angle was observed and considered to be closely related to the oxidation of the film surface. Borcia et al. [21,22] reported the enhancement of the adhesion properties of polyamide-6 fiber using DBD treatment and attributed that to the increase of the surface energy and surface polarity, as well as modified surface morphology. Under atmospheric pressure glow discharge, Pappa et al. [23] found that through the addition of new reactive chemical groups such as –COOH and –OH on the nylon 6 fibers, the wettability of the surfaces were improved. However, little has been reported on the influence of moisture in the environment and the fiber on the plasma treatment of nylon fiber surface.

Since our previous studies found that moisture could significantly influence the outcome of the plasma treatment of polyethylene and aramid fibers [12,13], in this study, nylon 6 fiber is used as a model system to investigate the influence of moisture on surface modification of ordinary polyamide fibers in terms of surface wettability, surface morphology, and dyeability. Three typical moisture regains were selected to treat the fiber corresponding to the relative humidity (RH) of 10, 65, and 100%, respectively, based on the three regimes with different modes of hydrogen bonds breakage in a hygroscopic polymer proposed by Nissan [25]. Scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS) were used to study the changes of surface morphology and chemical composition of the plasma-treated fibers. The tensile strength of the fibers was also measured before and after the plasma treatments to assess the potential damage to the fiber.

2. Experimental

2.1. Sample preparation

Nylon 6 fibers with a filament diameter of about 19 μm and a tensile modulus of 500 MPa were provided by Jiangsu Yizheng Chemical Fiber Textile Limited Company (Jiangsu Province, China). Before plasma treatment, the fibers were cleaned with acetone followed by drying in vacuum oven at 100 °C for 1.5 h. The cleaned fibers were divided into four groups: the nearly dry group stored in a desiccator with 10% RH until the plasma treatment, moisture-saturated group suspended in a container with 100% RH, the intermediate moisture regain group and the control group both balanced in the standard conditions of 20 °C and 65% RH for 24 h.

The moisture regain of the fibers were tested by oven drying method using the following Eq. (1):

\[
\text{MR} = \frac{W_m - W_d}{W_d} \times 100\% \tag{1}
\]

where \(W_d\) is the mass of dried fibers conditioned in the vacuum containers and \(W_m\) is the mass of fibers under three relative humidities (10, 65, and 100%). The moisture regains (MR) for the three groups were calculated as 1.23, 5.19, and 9.70% respectively.

2.2. Plasma treatment

The plasma treatment of samples was conducted on an atmospheric pressure plasma jet (APPJ), with a model Atomflo\textsuperscript{TM}-R, manufactured by Surfx Technologies, USA. It was developed by Schutze et al. in collaboration with Park et al. [26,27]. The APPJ was a small RF plasma jet with a length around 15 cm, consisting of two concentric electrodes with a 1.6 mm gap through which the working gas flows. The gas discharge was ignited by applying a low RF power which enabled the jet to produce a stable discharge and to avoid the arc transition. A detailed schematic illustration of the device was given in our previous paper [28].

In this study, the discharge power and the radio frequency were 10 W and 13.56 MHz, respectively. The distance between the nozzle and the specimen was kept at 2 mm. Helium gas with a purity of 99.99% was introduced into the nozzle at a flow rate of 10 l/min and the nozzle temperature was set at 100 °C. The nozzle temperature was independently controlled by a heater with a thermal couple. The specimens were moved on a conveying belt vertical to the nozzle at a rate of 3 mm/s, which was equivalent to around 3 s stationary treatment time. The specimen went under the nozzle two laps to achieve a homogenous treatment effect. The plasma device was kept in a sealed plastic bag in order to keep a predetermined relative humidity. The almost dry environment with a 10% relative humidity was conditioned by putting desiccants into the plastic environment chamber for several hours. After the plasma treatment under 10% RH condition, the relative humidity was adjusted by removing the desiccants and spraying the water vapor into the small environment. Within half an hour, the relative humidity could be raised to 65% and 100%.

2.3. Surface analysis

The SEM (JSM-5600LV Model, Japan) was employed to analyze the surface morphology of control as well as treated fibers. The magnification of the image was set at 5000×. Before the SEM experiment, the fiber was coated with a vapor-deposited thin layer of gold to induce conductivity.

The analysis of surface chemical composition was evaluated by XPS analysis carried out using VG Multilab 2000 electron
A spectrometer equipped with a single Mg Kα X-ray source (400 W, 13 kV). The take-off angle was 90° and the holding pressure of the XPS chamber was 2×10⁻⁹ Torr. The C1s, O1s and N1s core level spectra were recorded to determine the surface composition changes. With correction algorithms calculated from XPS peak area, the spectra were fitted using Gaussian peak profiles and linear background.

2.4. Measurement of dynamic contact angle

The surface wettability was characterized by the measurement of dynamic contact angles with Thermo Cahn DCA322 system based on Wilhelmy technique [29]. Distilled water was poured in a beaker and placed inside a closed test chamber. Immersion and withdrawal of the specimen were accomplished by moving the beaker stage up and down at a speed of 30 μm/s. An electrobalance recorded the wetting force at the fiber–water interface as a function of immersion depth. Advancing and receding contact angles were calculated using a computer system.

2.5. Dyeability evaluation

Control and plasma-treated fibers were dyed with commercially available acid dyes (Polar Red 10B) and dispersive dyes (Terasil Blue). Dyeing was performed in a stirred vessel in a thermostatic bath. The acid dye-bath contains 4% o.w.f. (on weight of the fabric) dyes and 2.5% o.w.f. amine sulfate. For dispersive dye-bath, 5% o.w.f. dyes and 2 g/l Glauber’s salt were added. Both dye-baths had a liquor ratio of 1:100 and the pH was adjusted by adding acetic acid. The dye-baths were kept at 90 °C and their exhaustion was determined by extracting certain residual dye liquor at prescribed durations. The absorbance of dye solutions was measured using a 2100 Visible Spectrophotometer (Unico Instrument Company, USA). The percentage of exhaustion (E) at time t was calculated as follows:

\[ E = \frac{A_0 - A_t}{A_0} \times 100\% \]

where \( A_0 \) is the absorbance of dye solution at 0 min, and \( A_t \) is the absorbance of dye solution at t min.

For evaluation of the color depth of the dyed samples, the color reflectance of visible light from 400 to 700 nm was measured at every 10 nm, using a Datacolour 650 Spectrophotometer.

2.6. Fiber tensile test

The bulk mechanical properties of nylon fibers were measured using XQ-1 Fiber Tensile Testing Machine. The tensile strength test was implemented with single fiber specimens at a gauge length of 10 mm and a crosshead speed of 20 mm/min under standard textile testing condition at 20 °C, 65% RH. A Nikon Eclipse E400 Pol optical microscope was
used to record the longitudinal images of fibers under 400× magnification. The diameter of each sample was determined from the digital images using Photoshop 7.0.

2.7. Statistical analysis

The data of contact angles and tensile strengths in different groups were analyzed with one-way analysis of variance (ANOVA) and Tukey pair-wise multiple comparison. A p value (<0.05) was considered significant.

3. Results and discussion

3.1. Morphological study

Fig. 1 shows the SEM results of control and plasma-treated nylon 6 fibers. The surface of control fibers was very smooth while a few micro-pits appear at the surface of plasma-treated samples with 1.23% MR. In comparison, a more roughened surface was observed for 5.19% MR fibers treated. The most aggressive etching takes place at the surface of 9.70% MR samples after plasma treatment. The surface of nylon fibers are partially peeled off and only small fragments remained on the surface. So much material etched off from the surface of a fiber or polymer in such a short time (3 s) under the influence of moisture has not been reported in literature. This is an important finding which could lead to a new method for selective etching of polymer surfaces if a surface of hygroscopic and hydrophilic polymer alloy or block copolymers is etched when the hygroscopic polymer is saturated with water.

3.2. Chemical composition analysis

To gain insight into the interaction between plasma and fiber surface, XPS technique was applied to analyze the surface chemical composition of nylon 6 fibers. Fig. 2 presents the X-ray photoelectron survey spectra for the control and the treated groups. The photoelectron peaks at 532 eV, 400 eV and 285 eV correspond to the O1s, N1s and C1s orbits, respectively. Compared to the control, the intensities of O1s peaks after plasma treatment were raised at the expense of the C1s intensities. The element composition and the atomic ratios of O/C and N/C derived from survey spectra for the four groups are given in Table 1. The results of the element composition of control nylon 6 fibers are in accordance with those

Table 1  

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chemical composition (%)</th>
<th>Atomic ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C1s</td>
<td>O1s</td>
</tr>
<tr>
<td>Control</td>
<td>78.94</td>
<td>14.12</td>
</tr>
<tr>
<td>1.23% MR, treated</td>
<td>73.23</td>
<td>19.75</td>
</tr>
<tr>
<td>5.19% MR, treated</td>
<td>76.22</td>
<td>18.22</td>
</tr>
<tr>
<td>9.70% MR, treated</td>
<td>76.47</td>
<td>15.8</td>
</tr>
</tbody>
</table>
The O/C ratios increased dramatically when the fibers with 1.23 and 5.19% MR were exposed to atmospheric pressure plasma, whereas a slight increase of O/C ratio was found for 9.70% MR fibers after plasma treatment. This finding is consistent with what was reported in literature [19,21,23,31,32]. The reduced chemical composition change for the 9.70% MR group could be a result of severe etching by the plasma which removed the modified surface quickly and thus leaving a relatively fresh fiber surface with a lot less chemical composition alteration. The N/C ratios showed only small fluctuations for different groups after plasma modification.

The deconvolution analyses of C1s peaks are performed as expressed in Fig. 3. The C1s spectra of control specimen are fitted to four parts: an adventitious carbon (C_{adv}) appeared at a binding energy of 282.4 eV, a major peak at 284.6 eV assigned to aliphatic carbon atoms, a peak at 285.5 eV corresponding to the carbon atoms in C–N bonds and a peak at 287.5 eV arising from the carbon atoms in amide group (–CONH–). The advent of C_{adv} should be induced by sample charging and therefore in principle the C_{adv} can be regarded as the chemical shift of aliphatic carbon atoms [33,34]. The C_{adv} was greatly reduced after the plasma treatments which could result from the increase of the surface electrical conductivity due to more polar groups that were introduced onto the fiber surface. Table 2 gives the corresponding contributions of the different carbon-containing chemical bonds. Relative to the repeating unit of nylon 6 molecules, theoretically the ratio of carbon atoms in C–C, C–N and CONH is approximately equivalent to 4:1:1. From the experimental results, on the other hand, calculated ratio of (C_{adv}+C–C), C–N and CONH in control samples is 6.6:1.5:1, in contrast to the theoretical one. It provides evidence that a surface layer of a polymer displays a different property from the bulk.

After plasma treatment, it can be seen that the newly oxidized carbon functional groups are imparted to the fiber

<table>
<thead>
<tr>
<th>Sample</th>
<th>Relative area corresponding to different chemical bonds (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C_{adv} (282.4 eV)</td>
</tr>
<tr>
<td>Control</td>
<td>14.04</td>
</tr>
<tr>
<td>1.23% MR, treated</td>
<td>3.94</td>
</tr>
<tr>
<td>5.19% MR, treated</td>
<td>4.55</td>
</tr>
<tr>
<td>9.70% MR, treated</td>
<td>3.82</td>
</tr>
</tbody>
</table>
surface. They are primarily assigned to the C–O bonds (286.5 eV) and carboxyl groups (288.5 eV) referring to the most likely formed oxidized groups in plasma treatment [35,36]. From the results shown in Table 2, for the treated groups, the amount of carbon atoms bonded to oxygen (C–O) in the fibers with 5.19 and 9.70% MR were larger than that in the samples with 1.23% MR. This means that probably more hydroxyl groups are present in these two groups. The deconvolution analysis of O1s (Fig. 4) and the relative area corresponding to different oxygen chemical bonds (Table 3) also indicated that after plasma treatment, the oxygen concentration in O = C–NH and O = C–OH, was decreased while the amount of oxygen singly bonded to carbon atoms, including the oxygen atoms in O = C–OH, C–C–OH, was increased remarkably. The higher concentration of hydroxyl groups in the 5.19 and 9.70% MR fibers may be attributed to the enhanced interaction between the active particles and the water molecules pre-existing in the fibers during the plasma treatment.

3.3. Wetting

As shown in Table 4, after plasma treatment, the advancing contact angles of fibers decreased significantly from 66° to around 54° (p<0.05). Among the three different treatment groups, no statistically significant difference was observed (p>0.05) for the advancing contact angles. A significant decrease about 9–19° of the receding contact angles was achieved in plasma-treated samples (p<0.05), while that for the 1.23% MR group was lowered less than the other two treated groups (p<0.05). The statistical analysis showed that the

Table 3
Data of deconvolution of O1s peaks for nylon 6 fibers untreated and treated with atmospheric pressure plasma

<table>
<thead>
<tr>
<th>Sample</th>
<th>Relative area corresponding to different chemical bonds (%)</th>
<th>Binding energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C==O (531.6 eV)</td>
<td>530 to 535</td>
</tr>
<tr>
<td></td>
<td>C–O (533.2 eV)</td>
<td>536 to 538</td>
</tr>
<tr>
<td>Control</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>1.23% MR, treated</td>
<td>86.96</td>
<td>530 to 535</td>
</tr>
<tr>
<td>5.19% MR, treated</td>
<td>79.37</td>
<td>530 to 535</td>
</tr>
<tr>
<td>9.70% MR, treated</td>
<td>74.63</td>
<td>530 to 535</td>
</tr>
</tbody>
</table>

Table 4
Advancing contact angles ($\theta_a$) and receding contact angles ($\theta_r$) for control and plasma-treated nylon 6 fibers with different moisture regains

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\theta_a$ (°)</th>
<th>$\theta_r$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>SD</td>
</tr>
<tr>
<td>Control</td>
<td>65.98*</td>
<td>3.54</td>
</tr>
<tr>
<td>1.23% MR, treated</td>
<td>53.54b</td>
<td>2.16</td>
</tr>
<tr>
<td>5.19% MR, treated</td>
<td>54.77b</td>
<td>3.16</td>
</tr>
<tr>
<td>9.70% MR, treated</td>
<td>54.16b</td>
<td>2.46</td>
</tr>
</tbody>
</table>

*Means with different letters are statistically significantly different at p<0.05. SD = standard deviation.
receding contact angles of the treated fibers with 5.19 and 9.70% MR were not significantly different ($p > 0.05$).

In combination with the analysis of surface morphology and chemical composition of nylon 6 fibers, atmospheric pressure plasma treatment resulted in considerable changes on fiber surface, such as increased roughness and more functional groups. It can be seen from XPS analysis that part of the hydrophobic groups in nylon fiber, such as C–C and C–N bonds, are transformed to hydrophilic groups after plasma treatment (Table 2). The increased polar functional groups are responsible for the improvement of the wettability of the fibers. In addition, the greater hysteresis between advancing and receding contact angle observed in the treated fibers with higher moisture regain suggests an increased surface roughness [37], in agreement with the SEM photography shown in Fig. 1.

3.4. Dyeing properties

Fig. 5 shows the rate of exhaustion as a function of dyeing time for control and plasma-treated fibers. Compared to the control specimens using acid dye, the treated fibers had overall higher rate of exhaustion. Furthermore, dyeing of treated fibers needed less time to reach equilibrium. Active species in plasma are known to be capable of breaking primary chemical bonds and induce chain scission [38]. The increased amount of amine end-groups induced by plasma treatment may play an important role in enhancing the formation of ionic linkage with acid dyes for plasma-treated nylon fibers, which speeded up the dye adsorption and the greater rate of dye exhaustion at equilibrium. In contrast to the 5.19 and 9.70% MR groups, it is obvious that the 1.23% MR group had a higher final rate of exhaustion.

In the case of dispersive group, both the rate of exhaustion and the total amount of dye adsorption are increased after plasma treatment, as shown in Fig. 5 (b). The curves for three treated groups have almost no difference, although the exhaustion for the 1.23% MR group is slightly higher. The increased surface energy for treated fibers may be responsible for the improved main linkages (hydrogen bonds and van der Waal forces) between the dye and polyamide fibers in the surface layer [15]. In addition, it is possible that the rougher surface resulting from plasma etching provided a pathway for both acid and dispersive dyes to diffuse into the fiber structure more conveniently [39].

Fig. 6 presents the curves of spectral reflectance of both acid and dispersive dyes. These curves are almost the same for the control and the treated fibers. This looks contrary to the results obtained in Fig. 5 since higher amount of total dye uptake should produce darker color. Nevertheless, it should be noted that as a surface modification technique, plasma treatment has a penetration depth of normally less than 500 Å if no plasma ablation occurs on polymer surface [40]. The available dyesites may be increased primarily on the fiber surface while the
3.5. Single fiber tensile strength

No significant difference ($p>0.05$) in single fiber tensile strength was detected among the four groups, as shown in Table 5. It validated that atmospheric pressure plasma had no damage on the bulk mechanical properties of nylon 6 fibers as reported in literature [6,9]. However, the SEM photos in Fig. 1 showed that significant etching occurred on the surface of the 9.70% MR group which could lead to a reduction in fiber tensile strength. However, the removal of a thin surface layer could reduce the cross-section of the fiber only by less than 1% which would not make a detectable reduction of the fiber strength since coefficients of variation for the tensile strengths were 4–5%. In addition, the elimination of weak points by surface etching may make a contribution to optimize the fiber structure and balance the negative effect on the fiber tensile strength due to loss of material on the surface of the fibers [6,9].

4. Discussion

From the above experiments, it is found that the moisture regain of nylon 6 fibers had a significant influence on the modification effect of atmospheric pressure plasma treatment.

First, the macromolecular structure of a polymer is affected when it absorbs moisture. As a rule, during the processes of spinning and drawing, polymer molecules build three distinguished regions, namely, crystalline parts with dense packed arrangement, semi-crystalline parts with partial arrangement and amorphous parts composed of tie molecules, loose chain loops and ends of macromolecules. Water molecules almost diffuse exclusively into the amorphous regions. The small angle X-ray scattering (SAXS) data in the study of Murthy et al. showed that the lamellar spacing of nylon 6 fibers expanded to 1.3 Å as the relative humidity was increased from 0 to 98% [43]. The diffusion of water into interlamellar region (fold and tie molecules) swells the amorphous region and strains are placed on the tie molecules [43]. With the bombardment of high energy species in plasma, the tie molecules in amorphous domain are likely to be first degraded and then removed from the polymer surface [44]. This could cause a smaller increase of the amine end-groups in the fibers with higher moisture regain, accounting for the higher total absorption of acid dye in the treated 1.23% MR group than the other two treated groups.

Unlike the interlamellar region that has a ∼ 30 Å gap between the folded chain interfaces of a stacked pair of crystalline lamellae, the interfibrillar domain in nylon fibers may have additional microvoids surrounding fibrils with a diameter of ∼50 Å [45]. Upon exposure of the fiber to atmosphere, water molecules outside the fibrils enter the longitudinal channels embedded in the interfibrillar amorphous domain or reside at the surface irregularities along the length of fibrils [45]. In the extensive work of Murthy et al., it was reported that microvoid and free volume were increased in the wet-heat-set nylon 6 fibers [46]. The partial hydrolysis of molecular chains in the presence of moisture could result in the increased microvoid content. In the same way, for the treated fibers with higher moisture regain, the greater percentage of hydroxyl groups shown in XPS experiment suggests that hydrolysis could also take place in the interaction between plasma and the polymer molecules. It is possible that both factors, namely, the increase of microvoid dimension resulting from hydrolysis as well as surface roughness, enhanced the liquid retention properties of treated nylon 6 fibers with 5.19 and 9.70% MR reflected by their lower receding contact angles (Table 3). As shown in structure I, the molecular chains in nylon 6 fibers are linked together by hydrogen bonds between C=O and N–H groups that contribute to the intermolecular force of 14.6–21.7 kJ/mol [47]. When a water molecule enters into fiber structure, the original hydrogen bond will break up in favor of the water molecule hydrogen bonded with C=O group, i.e. structure II.

\[
\overset{\infty}{\text{CO}} \cdots \overset{\text{HN}}{\text{H}} \overset{\infty}{\cdots} + \overset{\text{H}_2\text{O}}{\text{H}} \rightarrow \overset{\infty}{\text{CO}} \cdots \overset{\text{H}\cdots \text{O} + \text{HN}}{\text{H}} \overset{\infty}{\cdots}
\]

\text{Structure I} \quad \text{Structure II}

According to the mechanism of hydrogen bond dissociation proposed by Nissan, both in regime 1 (at low moisture regain) and regime 2 (larger than the critical moisture regain), one hydrogen bond breakage will trigger a few neighboring bonds to break simultaneously in spite of a significant difference between the two regimes [25]. In regime 1, due to lack of water molecules, the hydrogen bonds between C=O and H–N groups that have been triggered to break could not be kept broken and would rather be quickly “re-made”. In contrast, when the moisture absorption reaches a certain level, the water molecules available provide further active sites for new hydrogen bonds and then the cooperative dissociation of those H–N groups have opportunity to remain broken. Therefore, the intervention of water molecules and the following breakage of hydrogen bond linkages result in a structure of greater flexibility where molecule chains have more freedom to move away from each other without constraints. The van der Waal force, about 2–8 kJ/mol, becomes the new intermolecular force dominating in nylon 6 fibers. The fact that the intermolecular force is weakened by water molecule could enhance the aggressive etching effect illustrated by SEM photos. Meanwhile, when the moisture regain is raised, the plasma created active dye sites might be
etched away by plasma. A new surface with less active dye sites emerged in Fig. 1(d) could cause the slower dye diffusion into the treated 9.70% MR fibers.

5. Conclusions

Atmospheric pressure plasma treatment improved the surface roughness, the hydrophilicity and dyeing properties of nylon 6 fibers. However, what was most interesting was that the plasma etching was able to remove a layer of nylon in merely a few seconds at the presence of 9.70% MR. The results of the XPS indicated that treated fibers had higher oxygen contents than the control group. Among the three treated groups, the advancing contact angles were lowered to the same extent while the receding contact angle lowered more for the 5.19 and 9.70% MR groups. Compared with the control fibers, higher rates of exhaustion and greater dye uptakes were manifested for the treated samples using both acid dye and dispersive dye, whereas the total amount of acid dye absorption of the treated fibers with 1.23% MR was more than those of the other two treated groups. Single fiber tensile strength was not affected significantly by the plasma treatment. In conclusion, the moisture regain of nylon 6 fibers played an important role in surface etching and chemical modification of the fiber by atmospheric pressure plasma treatment.

Acknowledgements

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