

# Influence of Moisture Regain of Aramid Fibers on Effects of Atmospheric Pressure Plasma Treatment on Improving Adhesion with Epoxy

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**ABSTRACT:** One difference between a low-pressure plasma treatment and an atmospheric pressure plasma treatment is that in the atmosphere, the substrate material may contain significant quantities of moisture, which could potentially influence the effects of the plasma treatment. To investigate how the existence of moisture affects atmospheric pressure plasma treatment, aramid fibers (Twaron 1000) with three different moisture regains (0.5, 4.5, and 5.5%) were treated by an atmospheric pressure plasma jet for 3 s at a gas flow rate of 8 L/min, a treatment head temperature of 100°C, and a power of 10 W. The scanning electron microscopy analysis showed no observable surface morphology change for the plasma treated samples. X-ray photoelectron spectroscopy analysis showed the oxygen contents of the 0.5 and 4.5% moisture regain groups increased from that of the control, although the opposite was true for the 5.5% moisture regain group. The advancing

contact angles of the treated fibers decreased about 8°–16° whereas their receding contact angles decreased about 17°–27°. The interfacial shear strengths of the treated fibers as measured using microbond pull-out tests were more than doubled when the moisture regain was 4.5 or 5.5%, whereas it increased by 58% when the moisture regain was 0.5%. In addition, no significant difference in single fiber tensile strength was observed among the plasma treated samples and the control sample. Therefore, we concluded that moisture regain promoted the plasma treatment effect in the improvement of the adhesion property of aramid fibers to epoxy. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 242–247, 2006

**Key words:** aramid fibers; atmospheric plasma treatment; interfacial shear; tensile strength; surface analysis

## INTRODUCTION

As nonaqueous surface modification processes, plasma treatments have been widely studied in the laboratory for improving wettability or hydrophilicity.<sup>1–5</sup> However, most of the studies use vacuum systems that require an expensive and complicated vacuum environment.<sup>6,7</sup> In addition, in a vacuum system, the sample has to be completely dried before the degree of vacuum can be reached, which can be difficult and energy consuming for many hygroscopic materials.<sup>8</sup>

Atmospheric pressure plasma treatment does not require the complicated and expensive vacuum system, and there are few restrictions on the treated materials. It can treat materials continuously with much higher activated particle density.<sup>1,2</sup> One of these types of devices is an atmospheric pressure plasma jet (APPJ) that can generate a homogeneous plasma under low temperature and provide large quantities of oxygen atoms and other active species.<sup>9,10</sup> A potential problem for atmospheric pressure plasma treatment is

that the substrate could contain a large quantity of moisture such as hygroscopic materials in textile processes, which may affect the effects of the atmospheric pressure plasma treatment. However, there have been few reports in the literature on the influence of moisture regain on plasma treatment results.

According to Nissan,<sup>11,12</sup> when a hygroscopic material absorbs moisture, it goes through three regimes. In regime 1 or at a low moisture regain, the hydrogen bonds (H bonds) disassociate individually. In regime 2, a number of H bonds break cooperatively or in a cluster. In other words, in that regime one H-bond breakage can trigger a few neighboring bonds to break simultaneously. The cluster size for most polymers is about 4–10. In regime 3, the molecules interact with one another at a much higher number of broken H bonds.<sup>12</sup>

As one type of hygroscopic fiber, aramid fibers such as poly(*p*-phenylene terephthalamide) (PPTA) have a moisture regain as high as 7.5% when the humidity is 100% at a temperature of 30°C and there is a large hysteresis between the absorption and desorption curves.<sup>13</sup> It has been suggested that the absorbed water is mainly located in inter- and intrafibrillar microvoids and in larger core defects.<sup>13,14</sup> The microvoids in

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aramid fibers appear to be located mainly around the periphery of fibers with lengths of about 24  $\mu\text{m}$ .<sup>14,15</sup> The average ratio of length to width of one microvoid is approximately 4.<sup>16</sup> When the moisture regain of the fiber increases, the width of the microvoids tends to increase and the size of the crystallites tends to decrease.<sup>13</sup>

Aramid fibers are widely used as reinforcing fibers in the manufacture of composite materials because of their high tensile strength, tensile modulus, thermal resistance, and low specific density. However, their adhesion with the matrix is relatively poor because of a lack of morphological, chemical, and physical bonds as well as fibrillar separations within the fiber surface as reported previously.<sup>17</sup> In order to enhance the aramid/matrix adhesion, atmospheric pressure plasma treatments have been applied.<sup>18</sup>

The present study was designed to investigate the influence of moisture regain on the effectiveness of atmospheric plasma treatment on the interfacial shear strength (IFSS) of aramid fibers to epoxy, dynamic contact angle, surface morphology, surface chemical composition, and tensile strength. Microbond tests, dynamic contact angle tests, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and single fiber tensile tests were utilized. Three moisture regains were selected to represent the three regimes described by Nissan.<sup>12</sup>

## EXPERIMENTAL

### Materials

The PPTA fibers used in this study were Twaron 1000 supplied by Teijin Limited Company. The yarn was composed of 1000 monofilaments with a linear density of 110 tex, a single fiber diameter of about 10  $\mu\text{m}$ , and a tensile modulus of 79 GPa as reported by Edmunds and Wadee.<sup>19</sup> The matrix was epoxy resin prepared with DER 311 (bisphenol A type epoxy) and DER 732 (polyglycol diepoxide) and the curing agent was DEH 26, all supplied by Dow Chemical.

### Sample preparation

To eliminate finishes and surface contamination, the aramid fibers were washed with acetone for 5 min and dried in a vacuum oven for 2 h to remove remaining acetone. In order to prepare samples with different moisture regain, all fibers were separated into four groups. Two groups were balanced in standard textile testing conditions (20°C and 65% relative humidity) for 24 h. Another group was heated in the oven for another 2 h at 100°C and then stored in a desiccator after being sealed in a plastic bag as soon as being taken out of the oven. The last group was soaked in distilled water for 24 h to ensure saturation.

### Plasma treatment

After reaching different levels of moisture regains, three groups of samples, (oven dried, standard conditioned, and wet samples) were treated by an APPJ (Atomflo-R, Surfex Company) with pure helium gas at a flow rate of 8 L/min and a gas temperature of 100°C. In order to keep the moisture regain of the samples relatively constant, the dried sample was conditioned for 12 h and then plasma treated on the plasma machine that was sealed in a plastic bag with desiccants such that the relative humidity in the bag was kept at 10%. The standard conditioned sample and the saturated sample were treated at 54% relative humidity. The power for the plasma jet was 10 W and the frequency was 13.56 MHz. The sample was moved on a conveying belt at a rate of 17 cm/min vertically to the jet, which is equivalent to around a 3-s stationary treatment time. All treatments were performed at a room temperature of about 20°C.

### Microbond specimen preparation and test

The epoxy resin was prepared with DER 311 and DER 732 at a ratio of 70:30 with 12 phr DEH 26. After putting the epoxy beads on the fibers, the samples were cured for 2 h at 100°C. The embedded lengths of the beads and the fiber diameters were measured using an optical microscope. The microbond pull-out test was carried out on a tensile testing machine (H5KS) with an upper clamp displacement rate of 1 mm/min and a load cell of 50-cN capacity.

### Analysis of surface morphology

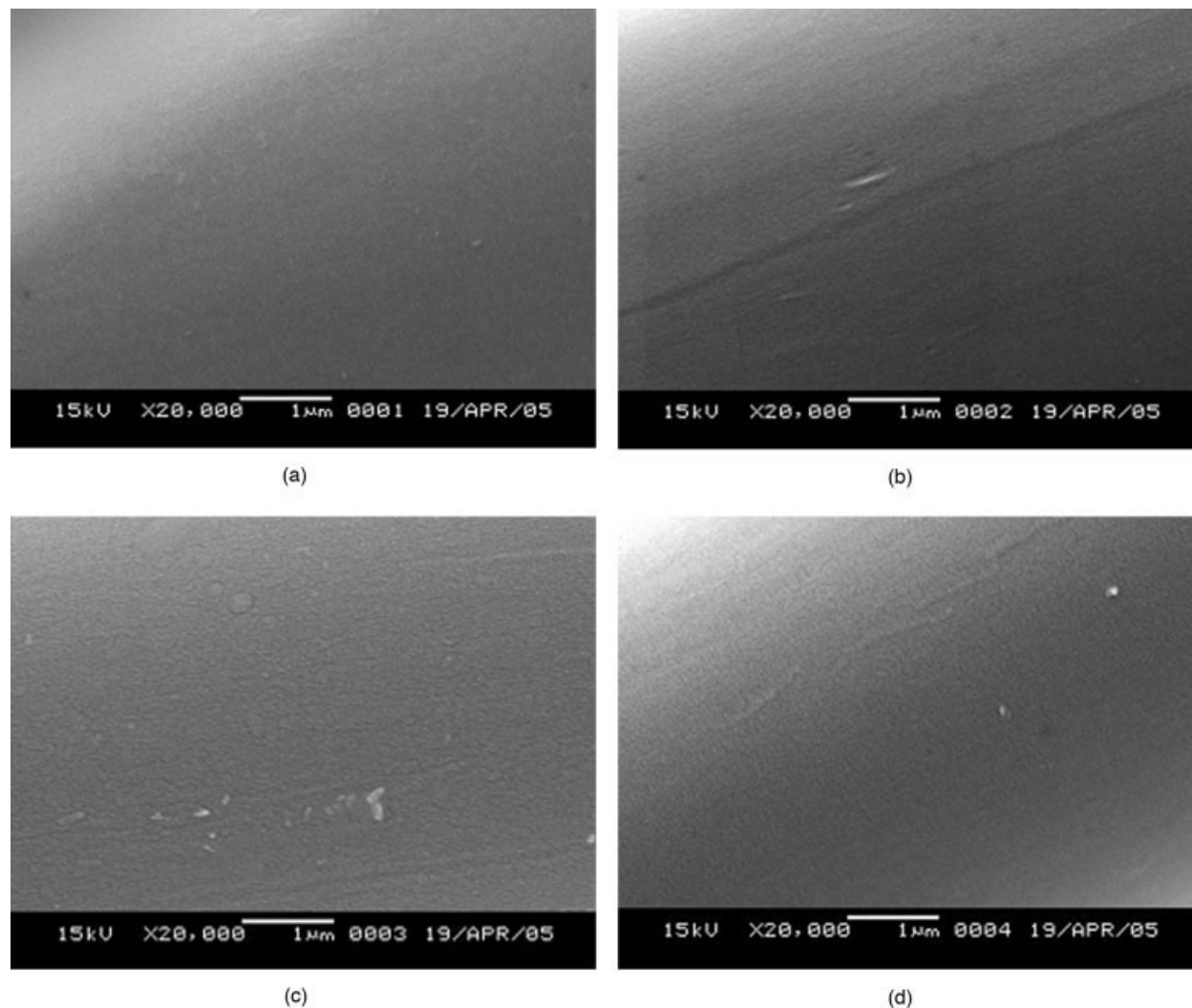
The surface morphology changes of the treated and untreated fibers were observed using a scanning electron microscope (JSM-5600LV) at a magnification of 20,000 $\times$  and 15 kV. The fibers were gold coated before being inspected.

### Analysis of surface chemical composition

XPS was used for the analysis of the chemical composition of the surface. The spectra were collected using a Mg K $\alpha$  ( $h\nu = \text{eV}$ ) X-ray source operated at 300 W with a 13-kV voltage and 20-mA current. The beam angle was 90° and the pressure was  $2 \times 10^{-9}$  MPa.

### Measurement of surface energy

The dynamic contact angle was measured by a Thermo Cahn DCA322 system using the Wilhelmy technique.<sup>20</sup> The testing length of each specimen was about 2 cm, and distilled water was used as the testing liquid.



**Figure 1** Micrographs of Twaron 1000 fiber surfaces: (a) control fiber and (b) about 0, (c) 4.5, and (d) 5.5% moisture regains.

### Fiber tensile test

In order to determine if the plasma treatment could have any adverse effect on the bulk property of the fibers, their tenacity was tested. An XD-1 Vibrate Linear Instrument was employed to measure the linear density of the fibers. The tensile strength was tested using an XQ-1 Fiber Tensile Testing Machine at a gauge length of 20 mm and a cross-head speed of 5 mm/min under standard textile testing conditions.

### Statistical analysis

A one-way analysis of variance with Tukey's pairwise multiple comparison was employed to analyze the data. A  $p$  value smaller than 0.05 was considered significant.

## RESULTS AND DISCUSSION

### Microscopy examination

The SEM photos of control and treated fiber surfaces are shown in Figure 1, which shows no observable change of the surface morphology after plasma treatments for all moisture regain levels. That could be due to the high crystallinity structure of the aramid fiber and short plasma exposure time, as well as the low temperature and inert carrier gas that had limited etching and oxidation power. This result is consistent with previous reports on atmospheric pressure plasma treatment of aramid fibers.<sup>18</sup> However, we are not saying that there was no change of the surface morphology at any level. It is still possible that surface etching occurred at a lower level than the SEM could detect. The microvoids reported in the literature were not observable at this magnification.

**TABLE I**  
Relative Chemical Composition and Atomic Ratios Determined by XPS for Aramid Fibers Untreated and Treated with Atmospheric Pressure Plasmas

Treatment	Chemical composition (%)			Atomic ratio (%)		
	C1s	O1s	N1s	O/C	N/C	(O + N)/C
Control	73.89	17.67	8.45	23.9	11.4	35.3
0.5% MR	70.34	20.29	9.37	28.8	13.3	42.1
4.5% MR	70.89	18.90	10.21	26.7	14.4	41.1
5.5% MR	76.16	15.70	8.26	20.6	10.8	31.4

### XPS analysis

Table I provides the XPS analysis results on the chemical composition change on the aramid fiber surface. After the plasma treatments, the O/C and N/O ratios were increased for the fibers with 0.5 and 4.5% moisture regain but were decreased for the fiber with 5.5% moisture regain. In order to examine the change of functional side groups during the plasma treatment, the deconvolution analyses of C1s and O1s peaks were performed (Tables II, III). The aramid fiber surface after treatments has five potential carbon-containing components with binding energies of 285.0 (—C—C—), 286.3 (—C—C—N/—C—O—), 287.8 (—CONH—), and 289.1 eV (—COO—) as reported in the literature.<sup>21–23</sup> In addition, four potential oxygen-containing components exist in the aramid molecule with binding energies of 531.6 (—CONH—), 532.8 (—C=O/O=C—OH), 533.7 (—C—OH), and 534.3 eV (—COO—).<sup>21,22</sup>

Table II presents the results of the C1s peak deconvolution analysis, which show a distinct change of functional groups on the aramid fiber surface after plasma treatment. The peak areas of —C—C—C— and —CONH— all decreased after plasma treatment whereas those of —C—C—N/—C—O— and —COO— all increased. The fiber with 5.5% moisture regain had the lowest amount of —C—C—, but its compositions of —CONH— and —COO— were the highest among all samples. In the O1s peak deconvolution analysis (Ta-

**TABLE II**  
Results of Deconvolution of C1s Peaks for Aramid Fibers Untreated and Treated with Atmospheric Pressure Plasmas

Treatment	Relative area corresponding to different chemical bonds (%)			
	—C—C—	—C—C—N/—C—O—	—CONH—	—COO—
Control	66.2	28.5	5.3	0
0.5% MR	47.18	24.2	12.6	1.5
4.5% MR	50.4	25.9	11.8	2.2
5.5% MR	43.0	24.4	13.7	4.1

**TABLE III**  
Results of Deconvolution of O1s Peaks for Aramid Fibers Untreated and Treated with Atmospheric Pressure Plasmas

Treatment	Relative area corresponding to different chemical bonds (%)			
	—CONH—	—C=O/O=C—OH	—C—OH	—COO—
Control	52.8	44.2	0	3.0
0.5% MR	51.3	24.9	10.6	13.2
4.5% MR	50.1	25.3	18.5	6.1
5.5% MR	40.6	22.3	17.7	19.5

ble III), the peak areas of —C—OH and —COO— all increased whereas that of O=C—OH and —CONH— decreased after plasma treatments. The amount of —C—OH was the largest for the fiber with 4.5% moisture regain and the amount of —COO— was the largest for the fiber with 5.5% moisture regain. The fibers with 4.5 or 5.5% moisture regains have more hydroxyl groups than the fibers with 0.5% moisture regain.

According to the molecular structure, the free radicals could be generated by photons and chain scission and radical formation could be induced simultaneously.<sup>18</sup> The higher composition of hydroxyl groups for fibers with 4.5 or 5.5% moisture regain may be caused by the enhanced interaction between the plasma and the water molecules preexisting in the fibers during the treatments.

### Dynamic contact angle test

Table IV lists the mean and standard deviation of advancing and receding contact angles. For the advancing contact angle, a significant difference (8°–16°) was detected among the treated fibers and control fibers ( $p < 0.05$ ). Among the treated groups, the 0.5% moisture regain group has the lowest advancing contact angle than the other two plasma treated groups ( $p < 0.05$ ) whereas no significant difference was observed between the 4.5 and 5.5% moisture regain groups ( $p > 0.05$ ). The receding contact angles of the

**TABLE IV**  
Dynamic Contact Angles for Different Treatment Groups

Sample	Advancing contact angle		Receding contact angle	
	Mean	SD	Mean	SD
Control	52.07 <sub>a</sub>	3.90	33.65 <sub>a</sub>	4.44
0.5% MR treated	35.36 <sub>c</sub>	7.61	16.80 <sub>b</sub>	11.71
4.5% MR treated	43.74 <sub>b</sub>	8.19	8.51 <sub>c</sub>	11.09
5.5% MR treated	43.46 <sub>b</sub>	11.94	7.07 <sub>c</sub>	10.77

Means with different subscript letters are statistically significantly different at  $p < 0.05$ .

**TABLE V**  
**Interfacial Shear Strengths (IFSS) of Atmospheric Pressure Plasma Treated Aramid/Epoxy Interface Determined by Microbond Pull-Out Test**

Treatment	No. of specimens	IFSS (MPa)	
		Mean	SD
Control	29	19.55 <sub>a</sub>	8.10
Moisture regain			
0.5%	49	30.82 <sub>b</sub>	14.74
4.5%	27	40.73 <sub>c</sub>	16.19
5.5%	23	40.00 <sub>c</sub>	12.87

Means with different subscript letters are statistically significantly different at  $p < 0.05$ .

three plasma treated groups decreased about 17°–27° from that of the control fibers ( $p < 0.05$ ). Among the three plasma treated groups, the receding contact angle of fibers with 0.5% moisture regain decreased less than the other two plasma treated groups ( $p < 0.05$ ).

In general, the advancing contact angle indicates the wetting property of fibers and the receding contact angle reflects the liquid sorption/retention of polymeric materials.<sup>24</sup> The lower receding angle of the fibers with 4.5 and 5.5% moisture regain indicated better liquid sorption and retention ability, which was likely to result in better bonding between the fibers and matrix. The reason the receding contact angle of the fibers with 4.5 and 5.5% moisture regain decreased more than the fibers with 0.5% moisture regain could be because the absorbed water may make the microvoids larger, which appear mainly around the periphery of the aramid fibers with a length of about 24  $\mu\text{m}$  and a width of about 6  $\mu\text{m}$ .<sup>14,16,25</sup> During the plasma treatment, new polar side groups can be created in the microvoids. Once the treatment was finished, the side groups on the molecular chains could likely make the intermicrofibril space relatively large and thus leave more surface area or more bonding sites for water molecules. The plasma treated microvoids could be penetrated by and bonded to the matrix better.

### Microbond test

The IFSS values for all treatment groups are shown in Table V. The IFSS or debonding shear stress ( $\tau_i$ ) was calculated using the equation derived from the shear-lag model:

$$\tau_i = \frac{np_{\max}\coth(nL/r)}{2A} \quad (1)$$

where  $P_{\max}$  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-section area, and  $n$  is defined as

$$n = \left[ \frac{E_m}{E_f(1 + \nu_m)\ln(R/r)} \right]^{1.2} \quad (2)$$

where  $E_m$  is the Young's modulus of the matrix (1.4 GPa),  $\nu$  is the Poisson ratio of the matrix (0.4),<sup>26</sup>  $E_f$  is the tensile modulus of the fiber (79 GPa),<sup>19</sup>  $R$  is the radius of the epoxy beads observed under microscope, and  $r$  is the apparent radius of the fiber calculated from images of the fibers under a microscope.

The IFSS values of all treated samples were significantly higher than that of the control group, indicating improvement of fiber–matrix adhesion ( $p < 0.05$ ). The IFSS was not affected by the existence of moisture in the fiber. Conversely, it was enhanced with the increasing content of humidity in the material. The IFSS of the 0.5% moisture regain group was increased by 58%, whereas those of the other two plasma treated groups were more than doubled. This result agrees with the receding contact angle result, which reveals that the receding contact angle can better reflect the adhesion property.

### Single fiber tensile strength

Table VI shows the tensile test results of single fibers for all four groups. No statistically significant difference was observed among all groups ( $p > 0.05$ ), which proved that there was no significant damage after this atmospheric pressure plasma treatment, although the tensile strengths of the treated fibers tended to be somewhat lower. In general, the fiber tensile strength might have been reduced because of ablation or the etching effect of plasma treatments. However, no significant etching was observed among the plasma treated groups and therefore no such negative effect on the fiber tensile strength should be expected here.

## CONCLUSIONS

An APPJ using helium gas lowered the advancing contact angle and the receding contact angle of aramid fibers with various moisture regains. As the moisture regain of the fiber increased, the advancing contact angle decreased less while the receding contact angle decreased more. No observable surface morphological

**TABLE VI**  
**Comparison of Tensile Strength of Three Groups**

Sample	No. of specimens	Tensile strength (GPa)		P Value versus control
		Mean	SD	
Control	50	3434	232	—
0.5% MR	50	3305	367	0.077
4.5% MR	50	3284	256	0.783
5.5% MR	50	3275	286	0.494

change was detected for the plasma jet treated fibers at a 12,000 $\times$  magnification. A chemical composition change was detected for the plasma treated fibers. At 0.5 and 4.5% moisture regain the oxygen contents increased from that of the control, whereas the opposite was true for the 5.5% moisture regain group. The IFSS of all treated aramid fibers increased, but the fibers with 4.5 and 5.5% moisture regain increased twice as much as the 0.5% moisture regain group. The single fiber tensile strength was not affected by the plasma treatments. Therefore, we concluded that the moisture regain of the PPTA fibers during atmospheric pressure plasma treatment enhanced the treatment results.

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