Journal of Applied Polymer Science

Surface Modification of Aramid Fibers via Ammonia-Plasma Treatment

Shuang Li, Keqing Han, Huaiping Rong, Xuanzhe Li, Muhuo Yu
State Key Laboratory for Modification of Chemical Fibers and Polymer Materials,
College of Materials Science and Engineering, Donghua University, Shanghai 201620, People's Republic of China
Correspondence to: K. Han (E-mail; hankeqing@dhu.edu.cn) or M. Yu (E-mail; yumuhuo@dhu.edu.cn)

ABSTRACT: In this article, aramid fibers III were surface modified using an ammonia-plasma treatment to improve the adhesive performance and surface wettability. The surface properties of fibers before and after plasma treatment were investigated by X-ray photoelectron spectroscopy, scanning electron microscopy, atomic force microscopy, and water contact angle measurements. The interfacial shear strength of each aramid fibers III-reinforced epoxy composites was studied by micro-debonding test. The ammonia-plasma treatment caused the significant chemical changes of aramid fibers III, introducing nitrogen-containing polar functional groups, such as —C—N— and —CONH—, and improving their surface roughness, which contributed to the improvement of adhesive performance and surface wettability. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40250.

KEYWORDS: fibers; morphology; surfaces and interfaces

Received 12 September 2013; accepted 3 December 2013
DOI: 10.1002/app.40250

INTRODUCTION

Aramid fibers, well known for its high strength, good toughness, low weight, low dielectric constant, and good thermal resistance, have been developed as reinforcement for composite materials. These composites are widely used in aerospace, aviation, protective garment, automobile, and shipbuilding.[1–3] However, the interfacial adhesion between aramid fibers and most matrices is poor because of the fiber's chemical inertness from its high crystallinity and smooth surface, which is the biggest disadvantage of its applying to the composite materials.[4,5] Many studies have focused on improving the interfacial adhesion between aramid fibers and matrices using various surface modification methods, such as plasma technique, ion sputtering, oxidation, and corona discharge.[6–9] Among these techniques, plasma modification is a widely accepted physical method because it is convenient and environmentally friendly, which can be used to modify the uppermost layer of the fiber surface, attaining the desired properties without affecting its bulk properties.[5,9–15]

Compared with conventional techniques, plasma technique not only can induce the selection of desired functional groups onto the fiber surface, but also etch the surface of fiber to enhance the contact area of the fiber with resin, leading to a more significant improvement in the interfacial adhesion between the fiber and the matrix.[16,17] The working gas used for plasma generation is important as it can introduce different functional groups on the fiber surface.[18] Much research in recent years has focused on surface modification by plasma treatment using non-polymerizing gases, such as helium, argon, oxygen, air, and nitrogen.[19–27] Several studies have shown that inert gases predominantly initiate surface activation by generating free radicals on the surface from chain scission. In contrast, reactive gases such as oxygen and ammonia can incorporate oxygen- or nitrogen-containing groups. These surface modifications may lead to changes in properties such as adhesion.[28–30]

The aim of our article was to improve the surface properties of aramid fibers III (aramid fiber III is a new type of aramid fibers manufactured in China in recent years, which is one of the synthetic fibers with high strength and modulus of elasticity fabricated from aromatic polyamides and copolyamides[31]) using ammonia-plasma treatment and obtain the optimum treatment parameters. Moreover, the effects of the significant process parameters, including treatment time, power and discharge pressure, were studied. The interfacial shear strength (IFSS) was used to characterize the interfacial adhesive performance. The elemental compositions of the fiber surfaces were investigated by X-ray photoelectron spectroscopy (XPS). Surface morphology and roughness were analyzed by scanning electron microscopy (SEM), and atomic force microscopy (AFM), respectively. The wettability of the fiber surface was inspected by the contact angle measurements.

© 2013 Wiley Periodicals, Inc.

EXPERIMENTAL

Materials

Aramid fibers used in this study were domestic aramid fibers III supplied by China Blue Star Chengrand Research and Design Institute of Chemical Industry. The average diameter and tensile strength of a single fiber were about 13 μm and 46.8 cN/dtex, respectively. The fibers were washed successively in acetone and distilled water at room temperature to remove surface residuals and then dried at 100°C in a vacuum oven for 24 h prior to the plasma treatment. The matrix used in this paper (Epoxy resin E51) and curing agent were supplied by Shanghai Resin, China.

Plasma Treatment

Plasma treatment was carried out in a SY-1 cold plasma processing apparatus. The treatment system was an inductively coupled radio frequency plasma generator, including a cylindrical vacuum chamber, two mass flow controllers, a pumping system, and a radio frequency source. Ammonia gas was used for the plasma treatment, which was fed into the vacuum chamber at a flow rate of about 30–40 sccm. The operating pressure was set at 30 Pa throughout the plasma treatment processes. Aramid fibers III were treated by the ammonia plasma with different experimental conditions. The treated powers of the plasma were 50–200 W and the treated time was at an interval of 5 min from 5 to 20 min. The pressure of ammonia was changed from 20 to 50 Pa. After the treatment, the samples were stored in a vacuum oven for 24 h.

XPS Analysis

The surface chemical compositions of aramid fibers III were analyzed by XPS (PHI-5000C ESCA system, RBD, USA). The XPS spectra were obtained using Mg K radiation ($h = 1253.6$ eV). The base pressure of the analyzer chamber was about 5×10^{-8} Pa. The energy of X-ray source was 250 W at 14.0 KV. The sample was directly pressed to a self-supported disk (10×10 mm^2) and mounted on a sample holder then transferred into the analyzer chamber. The whole spectra (0–1100 [1200] eV) and the narrow spectra of all the elements with much high resolution were both recorded using RBD 147 interface (RBD Enterprises).

SEM Analysis

Surface morphology of aramid fibers III was observed by scanning electron microscope (SEM, S-4800, Hitachi, Japan).

AFM Analysis

Surface roughness and morphologies of aramid fibers III were analyzed by AFM (NanoScope IV, Digital Instrument). The images with a 5×5 μm^2 scan area were obtained under the tapping mode. The roughness of fiber surface was characterized by arithmetic mean roughness (Ra) calculated automatically by the software.

Contact Angle Measurement

The wettability of aramid fiber III was measured by the contact angle system using the sessile drop method (OCA40, Data physics Instrument, Germany). The single fiber was fixed on a frame with a certain amount of tension. The droplet of 30 μL distilled water dropped onto the surface of fiber with a matched syringe, and then water droplet attached to the fiber were recorded as digital images taken by Nikon video camera and then the contact angle was calculated with SAC 20 software.

Interfacial Shear Strength

The IFSS of the aramid fiber III/epoxy composite was measured *via* micro-debonding test. Both ends of the fiber were fixed onto a frame and kept in place horizontally. After mixing the epoxy resin with plasticizer and harder, the epoxy mixture was dropped on the fiber, and epoxy droplets were formed naturally on the single filament, then the prepared samples were placed into a vacuum drying oven and solidified at 40°C for 24 h. The micro-debonding test was carried out at an upper clamp displacement rate of 0.1 mm/min on an XQ-1 fiber tensile testing machine (Shanghai Lipu Research Institute, China). A steady displacement was applied to the free end of the fiber to pull it out of the matrix as described in literature.[32] The IFSS, τ, was calculated using following equation

$$\tau = F_{\max} / \left(\pi \ D_f L_e\right) \quad (1)$$

where $F_{\max}$, D_f, and L_e are the maximum pullout force, the fiber diameter and the fiber embedded length in the matrix resin, respectively. The average values of the samples were acquired through more than 30 times tests.

RESULTS AND DISCUSSION

Effects of Ammonia-Plasma Treatment on the Interfacial Adhesion of Composite

It is well known that the interface is an important factor for stress transferring from the matrix to the reinforcing fibers and good mechanical properties of the composites were largely dominated by the nature of the interface.[33] IFSS is one of the important mechanical properties for signifying composite interfacial adhesion. During the plasma treatment, three important parameters, including the treatment time, power, and discharge pressure dramatically affected the interfacial adhesive performance between the reinforcing fibers and the resin. Figure 1 shows the effects of different treatment conditions on the IFSS of aramid fiber III/epoxy composites. It can be observed that the interfacial adhesion between fiber and epoxy resin was obviously improved after the ammonia-plasma treatment. As shown in Figure 1(a), the IFSS increased firstly and then declined slightly with the increase of treatment time under the treatment power of 100 W and the discharge pressure of 30 Pa, and the optimum treatment time was 15 min. In Figure 1(b), the treated time and power were selected as 15 min and 100 W and when the discharge pressure was 30 Pa, the best value of IFSS was acquired. Figure 1(c) showed that the IFSS reached its maximum value with a 42% increase when the treatment power was 100 W. These results obtained from the above analyses also illustrated that the optimum processing parameters were the treatment time of 15 min, the power of 100 W and ammonia discharge pressure of 30 Pa.

Effects of Ammonia-Plasma Treatment on Surface Wettability

The effects of ammonia-plasma treatment in term of the changing of treatment time, discharge pressure, and treatment power were shown in Figure 2. As seen in Figure 2, the water contact angle of the original fiber was found to be 71.4°, which implied a low surface wettability. After ammonia-plasma treatment, the

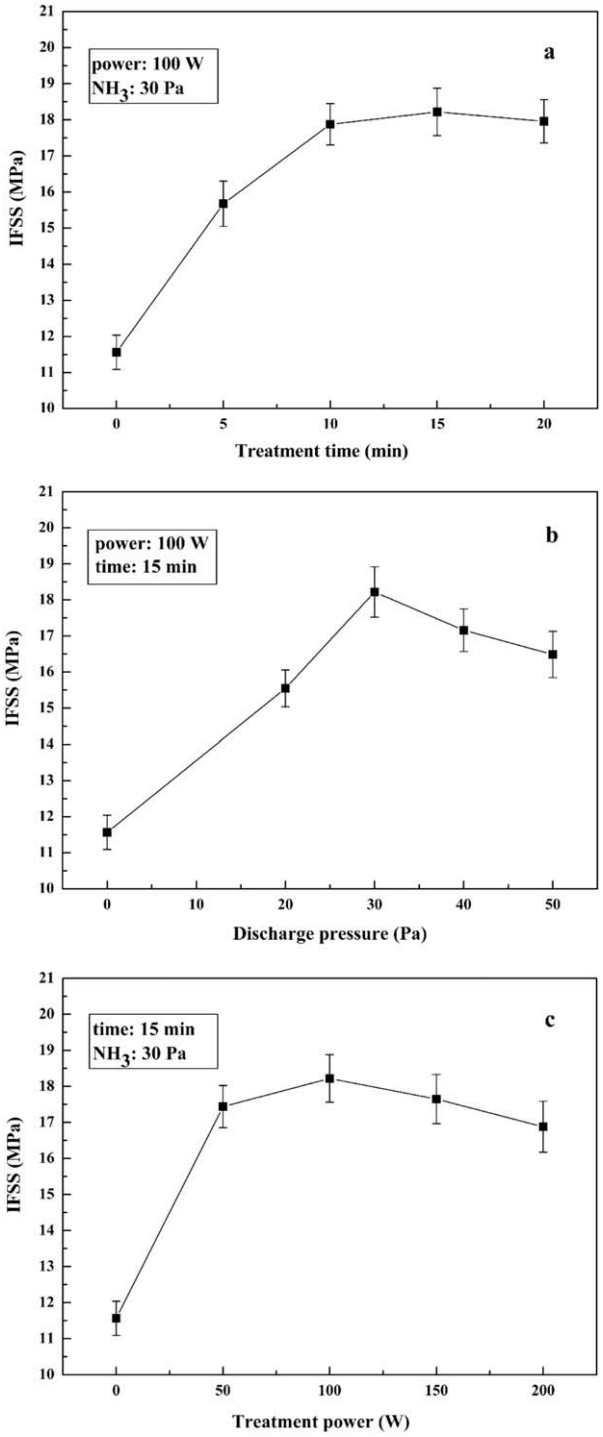

Figure 1. IFSS of aramid fibers III/epoxy composites untreated and treated at different (a) treatment time, (b) discharge pressure, and (c) power.

contact angles decreased rapidly with the increase of treatment time, power, and discharge pressure. This might be due to the increase in surface roughness or the incorporation of some newly formed functional groups onto the fiber surface after the plasma treatment. The minimum contact angle of 47.8° was observed when the fibers were treated under conditions of treatment time 15 min, power 100 W, and the discharge pressure 30 Pa, which corresponded to the results by the IFSS. Conversely, as the increase in the above mentioned parameters the contact angle increased, indicating that the aramid fibers III were excessive treated. The reason was that the excessive treatment of the fibers could reduce the contact area with water; meanwhile, the fiber might ruin the prior produced polar

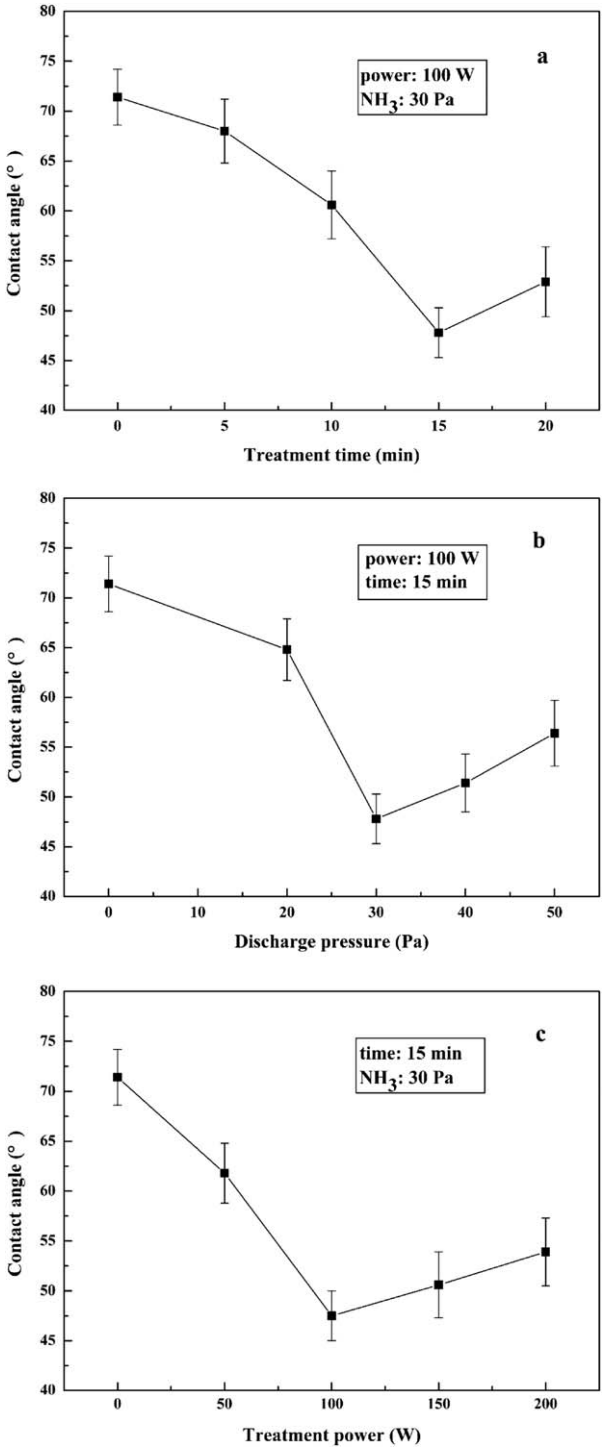

Figure 2. Water contact angle measurement for untreated and treated aramid fibers III at different (a) treatment time, (b) discharge pressure, and (c) power.

Table I. Surface Composition of Aramid Fibers III Before and After Plasma Treatment Measured by XPS

	Chemical composition (at %)			Atomic ratio (%)	
Samples	C1	O1	N1	O/C	N/C
Untreated	77.7	20.6	1.7	0.26	0.02
Treated for 100 W, 15 min, 30 Pa	73.9	13.1	10.1	0.18	0.14

functional groups, and thus resulting in the increase of contact angle.

Effects of the Ammonia-Plasma Treatment on the Surface Chemical Composition

XPS is the leading analytical technique for characterizing various chemical/physical forms of elements in surface structures, and was applied to analyze the surface compositions and introduction of additional functional groups both original and treated aramid fibers quantitatively.[34,35] Table I lists the surface composition of aramid fibers III which were treated under the optimum processing parameters. It can be found from Table I that the untreated fibers had high contents of O and C atoms and a low amount of N atoms. After ammonia-plasma treatment, C and O atoms content decreased to 73.9% and 13.1%, respectively, while N atoms content increased to 10.1%. The atomic ratio of O/C decreased from 0.26 to 0.18, while the ratio of N/C increased obviously from 0.02 to 0.14 after ammonia-plasma treatment. The results[36,37] indicated that the nitrogen atoms were incorporated into the fiber surfaces during ammonia-plasma process.

Furthermore, the deconvolution analysis of C1s peaks was performed to study the changes of various functional groups quantitatively. As shown in Figure 3, the C1s spectra contained four peaks with binding energy of 284.8, 286.3, 287.7, and 289.0 eV, which may be attributed to —C—C—, —C—N—/—C—O—, —CONH—, and —COO—. The spectrum intensity and peak areas of the untreated and the ammonia-plasma treated fibers surfaces in the C1s spectra were markedly different. The contents of functional groups, which can be calculated from the related peak areas in XPS C1s spectra, are shown in Table II. The —C—C— content sharply decreased from 77.9% for untreated fiber to 66.7% after ammonia-plasma treatment, while the contents of the polar functional groups such as —C—N—/—C—O— and —CONH— had an increase from 10.6% and 7.9% to 18.8% and 10.1%, respectively. In addition, the functional groups containing oxygen such as —C═O and —COO— decreased slightly after plasma treatment. It is suggested that ammonia-plasma treatment could introduce some nitrogen-containing polar functional groups such as —C—N— and —CONH— onto the surface of the fibers, which could improve the wettability and the adhesive property between fibers and epoxy matrix. The reason could be explained that there were lots of active particles under sputtering of the ammonia plasma process, and the energies were transferred by those particles to the fiber surface, activating the surface layer by making the bombardment of ions, electrons, free radicals, and UV radiations and introducing polar functional groups on the surface of fiber. The introduction of polar functional groups on the fiber surface could form chemical bonding between the fibers and the matrix, and thus resulting in improvement of IFSS.

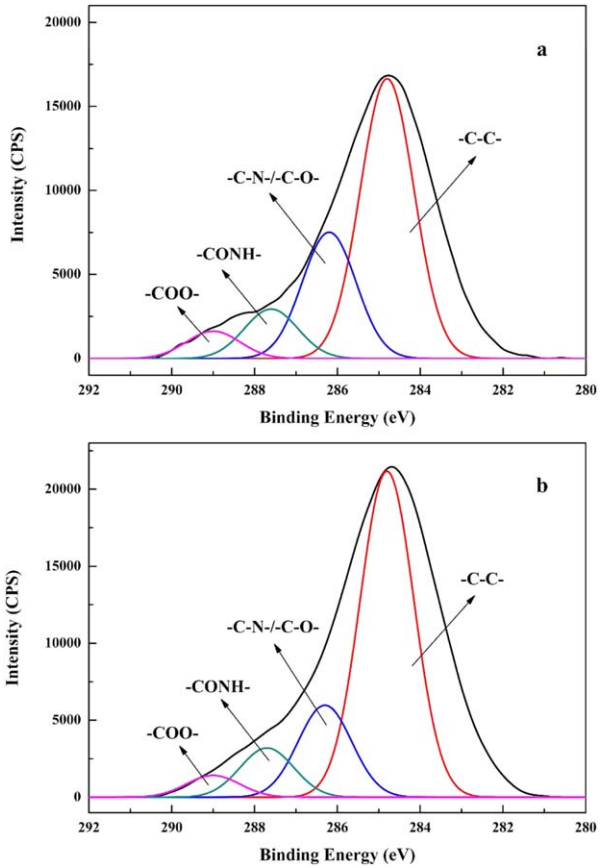

Figure 3. C1s spectra of aramid fibers III: (a) untreated and (b) ammonia-plasma treated with 100 W, 15 min, 30 Pa. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Deconvolution Analysis of C1s Peaks of Untreated and Ammonia-Plasma-Treated Aramid Fibers III

	Content of functional group (at %)			
Sample	—C—C—	—C—N—/—C—O—	—CONH—	—COO—
Untreated	77.9	10.6	7.9	3.6
Treated for 100 W, 15 min, 30 Pa	66.7	18.8	10.1	4.4

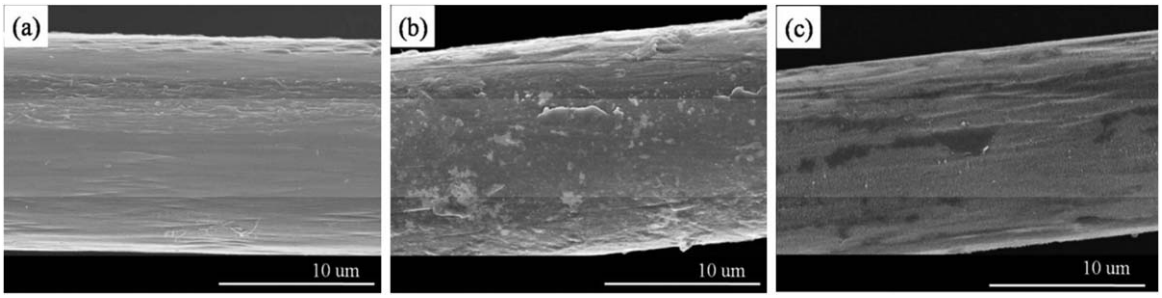

Figure 4. Surface morphology of aramid fibers III: (a) untreated, (b) ammonia-plasma treated with 100 W, 15 min, 30 Pa, and (c) ammonia-plasma treated with 200 W, 15 min, 30 Pa.

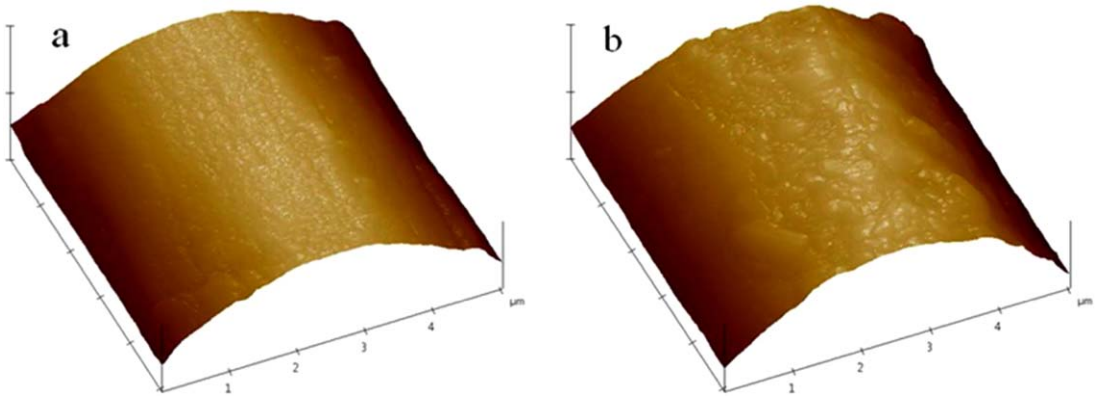

Figure 5. AFM images of aramid fibers III: (a) untreated and (b) ammonia-plasma treated with 100 W, 15 min, 30 Pa. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Effects of the Ammonia-Plasma Treatment on the Morphologies

SEM observation was conducted to investigate the influence of the ammonia-plasma treatment on the surface morphology of aramid fibers III. A comparison of SEM images of the untreated and the ammonia-plasma treated fibers is shown in Figure 4. It can be obviously found that the surface of untreated fiber was relative clean and smooth, and there are some small grooves on the surface [Figure 4(a)]. The fiber treated with ammonia-plasma exhibited rougher surface [Figure 4(b)]. A lot of apparent bulges, granules, and fragments were generated on the fiber surface due to strong etching effect of plasma. This could be explained by following: under sputtering of the plasma, the surface polymer chains would be cutoff and then some atoms, and low molecular weight moieties would be ejected from the fiber surface, leaving the notches; but the degradation products might be initiated by active species in the plasma to polymerize and deposited onto the fiber surface, generating the bulges, and fragments.[38–41] However, with excessive ammonia-plasma treatment (too high treatment power or longer time), the etching effect is so strong that the rough surface of the fiber was stripped, and then subsurface became the "fresh" surface[2], as a consequence, a relatively smooth surface could be observed in Figure 4(c). Besides, the comparative observation of the three-dimensional AFM images (Figure 5) for untreated and treated fibers also confirmed above statement.

Effects of Ammonia Plasma-Treatment on Surface Roughness

The surface roughness of fibers was analyzed by average roughness Ra based on AFM images results. Table III summarizes typical values of calculated surface roughness. It can be seen that the Ra of untreated fibers was 119 nm while the Ra reached 158 nm after ammonia plasma treatment, revealing that the surface roughness increased owing to the ammonia-plasma treatment. This result is corroborated with SEM observation. Note that the increased surface roughness of treated fibers is attractive for reinforcing polymers, because the rougher surfaces bring stronger mechanical interlocking (physical bonding) between the fibers and the matrix, and thus lead to improved composites interfacial properties.[42]

CONCLUSION

In this article, the effects of ammonia-plasma treatment time, discharge pressure and treatment power on the surface adhesive

Table III. Surface Roughness of Untreated and Ammonia-Plasma-Treated Aramid Fibers III

Sample	Ra (nm)
Untreated	119
Treated for 100 W, 15 min, 30 Pa	158

performance and wettability of aramid fibers III were investigated. The results showed that the surface performance of aramid fibers III treated under the appropriated conditions was improved obviously. The contents of nitrogen-containing functional groups on the surface of fibers increased, and the surface of fibers became much rougher after the ammonia-plasma treatment, resulting in the significant improvement in IFSS and wettability.

ACKNOWLEDGMENTS

This work was financially supported by the National Basic Research Program (Grant No. 2011CB606101) of the China 973 Program.

REFERENCES

1. Guo, F.; Zhang, Z. Z.; Liu, W. M.; Su, F. H.; Zhang, H. *J. Tribol. Int.* **2009**, *42*, 243.
2. Su, M.; Gu, A. J.; Guo, Z. L.; Li, Y. *Appl. Surf. Sci.* **2011**, *257*, 3158.
3. Morent, R.; Geyter, N. D.; Verschuren, J.; Clerck, K. D.; Kiekens, P.; Leys, C. *Surf. Coat. Technol.* **2008**, *202*, 3427.
4. De Lange, P. J.; Mader, E.; Mai, K.; Young, R. J.; Ahmad, I. *Compos. Part A: Appl. Sci. Manuf.* **2001**, *32*, 331.
5. Park, J. M.; Kim, D. S.; Kim, S. R. *J. Colloid. Interf. Sci.* **2003**, *264*, 431.
6. Gulati, D.; Sain, M. *Polym. Eng. Sci.* **2006**, *46*, 269.
7. Mader, E.; Melcher, S.; Liu, J. W.; Gao, S. L.; Bianch, A. D.; Zherlitsyn, S.; Wosnitza, J. *J. Mater. Sci.* **2007**, *42*, 8047.
8. Lei, Z. K.; Wang, Q.; Kang, Y. L.; Qiu, W.; Pan, X. M. *Opt. Laser Eng.* **2010**, *48*, 1089.
9. Liu, D. D.; Hu, J.; Zhao, Y. M.; Zhou, X. S.; Ning, P.; Wang, Y. *J. Appl. Polym. Sci.* **2006**, *102*, 1428.
10. Song, B.; Meng, L. H.; Huang, Y. D. *Mater. Lett.* **2012**, *83*, 118.
11. Xi, M.; Li, Y. L.; Shang, S. Y.; Li, D. H.; Yin, Y. X.; Dai, X. Y. *Surf. Coat. Technol.* **2008**, *202*, 6029.
12. Jia, C. X.; Chen, P.; Liu, W.; Li, B.; Wang, Q. *Appl. Surf. Sci.* **2011**, *257*, 4165.
13. Sun, J.; Yao, L.; Sun, S. Y.; Qiu, Y. P. *Surf. Coat. Technol.* **2011**, *205*, 5312.
14. Sun, D. M.; Chen, X. G. *Text. Res. J.* **2012**, *82*, 1928.
15. Jia, C. X.; Chen, P.; Wang, Q.; Li, B.; Chen, M. X. *Appl. Surf. Sci.* **2011**, *258*, 388.
16. Geyter, N. D.; Morent, R.; Leys, C. *Surf. Coat. Technol.* **2006**, *201*, 2460.
17. Swait, T. J.; Whittle, T.; Soutis, C.; Jones, F. R. *Compos. Part A: Appl. Sci. Manuf.* **2010**, *41*, 1047.
18. Marais, S.; Gouanve, F.; Bonnesoeur, A.; Grenet, J.; Poncin-Epaillard, F.; Morvan, C.; Metayera, M. *Compos. Part A: Appl. Sci. Manuf.* **2005**, *36*, 975.
19. Yu, H.; Cheng, D.; Williams, T. S.; Severino, J.; De Rosa, I. M.; Carlson, L.; Hicks, R. F. *Carbon* **2013**, *57*, 11.
20. Li, Y.; Moyo, S.; Ding, Z. Y.; Shan, Z. D.; Qiu, Y. P. *Ind. Crop Prod.* **2013**, *51*, 299.
21. Liu, D.; Chen, P.; Chen, M. X.; Liu, Z. *Surf. Coat. Technol.* **2012**, *206*, 3534.
22. Liu, D.; Chen, P.; Chen, M. X.; Yu, Q.; Lu, C. *Appl. Surf. Sci.* **2011**, *257*, 10239.
23. Chen, P.; Wang, J.; Wang, B. C.; Li, W.; Zhang, C. S.; Li, H.; Sun, B. L. *Surf. Interf. Anal.* **2008**, *41*, 38.
24. Wang, J.; Chen, P.; Li, H.; L., W.; Wang, B. C.; Zhang, C. S.; Ni, R. *Surf. Interf. Anal.* **2008**, *40*, 1299.
25. Zhang, H. J.; Zhang, Z. Z.; Guo, F. *J. Appl. Polym. Sci.* **2009**, *114*, 3980.
26. Vu, N. K.; Zille, A.; Oliveira, F. R.; Carneiro, N.; Souto, A. P. *Plasma Process. Polym.* **2013**, *10*, 285.
27. Huang, H. C.; Ye, D. Q.; Huang, B. C. *Surf. Coat. Technol.* **2007**, *201*, 9533.
28. Seki, Y.; Sarikanat, M.; Sever, K.; Erden, S.; Gulec, H. A. *Fiber. Polym.* **2010**, *11*, 1159.
29. Kale, K. H.; Desai, A. N. *Indian J. Fibre Text. Res.* **2011**, *36*, 289.
30. Demir, A.; Seki, Y.; Bozaci, E.; Sarikanat, M.; Erden, S.; Sever, K.; Ozdogan, E. *J. Appl. Polym. Sci.* **2011**, *121*, 634.
31. Zhang, S. H.; He, G. Q.; Liang, G. Z.; Cui, H.; Zhang, W.; Wang, B. *Appl. Surf. Sci.* **2010**, *256*, 2104.
32. Nishikawa, M.; Okabe, T.; Hemmi, K.; Takeda, N. *Int. J. Solids Struct.* **2008**, *45*, 4098.
33. Zhang, X. Y.; Chen, P.; Kang, X. T.; Chen, M. X.; Wang, Q. *J. Appl. Polym. Sci.* **2012**, *123*, 2945.
34. Ertas, G.; Demirok, U. K.; Suzer, S. *Appl. Surf. Sci.* **2005**, *249*, 12.
35. Suzer, S.; Abelev, E.; Bernase, S. L. *Appl. Surf. Sci.* **2009**, *256*, 1296.
36. Wu, S. R.; Sheu, G. S.; Shyu, S. S. *J. Appl. Polym. Sci.* **1996**, *62*, 1347.
37. Wen, H. C.; Yang, K.; Ou, K. L.; Wu, W. F.; Chou, C. P.; Luo, R. C.; Chang, Y. M. *Surf. Coat. Technol.* **2006**, *200*, 3166.
38. Hu, F. Z. East China University of Science and Technology, Shanghai, *Mater. Surf. Interf.* **2008**, 102.
39. Cioffi, M. O. H.; Voorwald, H. J. C.; Hein, L. R. O.; Ambrosio, L. *Compos. Part A* **2005**, *36*, 615.
40. Wang, C.; Chen, J. R.; Li, R. *Appl. Surf. Sci.* **2008**, *254*, 2882.
41. Liu, D.; Chen, P.; Chen, M. X.; Liu, Z. *Mater. Sci. Eng. A* **2012**, *532*, 78.
42. Wang, J.; Chen, P.; Lu, C.; Chen, H.; Li, H.; Sun, B. L. *Surf. Coat. Technol.* **2009**, *203*, 3722.