Surface wettability aging behavior of aramid fiber III after oxygen plasma treatment

Lu Guo, Jing Wang*, Song Jia, Mingfei Yang, Fuding Sun and Junyang Wang
School of Materials Science and Engineering & Liaoning Key Laboratory of Advanced Polymer Matrix Composites, Shenyang Aerospace University, Shenyang, China

*Corresponding author e-mail: wally9932@126.com

Abstract. Aramid Fiber III was modified by oxygen plasma treatment. The fiber surface wettability before and after different oxygen plasma treatment pressure, and surface wettability aging behavior were observed by Dynamic Contact Angles Analysis (DCAA), respectively. The results showed that aramid fiber surface wettability were increased after oxygen plasma treatment. The total surface free energy increased from 37.78 mJ/m$^2$ for untreated sample to 69.63 mJ/m$^2$ with 40 Pa plasma treated fiber. The fiber surface wettability decreased slowly with storage time in air. The fiber surface wettability decreased from 67.79 mJ/m$^2$ for 20 Pa plasma-treated sample to 63.85 mJ/m$^2$ after 30 days.

1. Introduction
The aramid fibers have been widely used in the fields of aerospace aviation due to its low density and high strength [1, 2]. Aramid fiber III is a recently developed type of para-aramid fibers manufactured in China, which is spun from poly-(polyamide benzimidazole-co-p-phenylene terephthalamide). Due to its surface smooth and chemical inert fiber surfaces, which lead to poor fiber-matrix compatibility and weak adhesion as reinforcement in composite [3-6]. Plasma treatment was proved an effective method to modify the fiber surface for improving fiber surface wettability properties [7].

The purpose of this work is to investigate the effects of oxygen plasma treatment pressure on aramid fiber III surface wettability and its aging behavior. The fiber surface wettability before and after different oxygen plasma treatment pressure, and surface wettability aging behavior were observed by Dynamic Contact Angles Analysis (DCAA), respectively.

2. Experimental

2.1. Materials and plasma treatment
Aramid fibers III (polyheteroarylene-co-p-phenylenterephthalamide) were supplied by China Bluestar Chengrand Chemical Co. Ltd. The fibers were cleaned successively with acetone and distilled water and then dried in a vacuum oven for 3 h at 110 °C before further analysis. Plasma was excited by an inductive coupling radio frequency generator (13.56 MHz). Oxygen was kept at a flow rate of about 20-30 SCCM. The operation pressure was set at 10Pa, 20Pa, 30 Pa, 40 Pa, 50 Pa, 60 Pa, 70 Pa. The fiber samples were treated for 10 min with plasma treatment power of 200 W. The 20 Pa plasma-treated
samples were kept in air for 5, 10, 15, 30 days. After that, the fiber surface wettability was measured by DCAA.

2.2. Characterization
Surface wettability of DAF III fiber before and after oxygen plasma treatment was characterized by DCAA (Dataphysics, KRüSS). The fiber samples were cut into about 1 cm in length and fixed directly to a cylindrical rods. Four fibers stick to the rods dispersedly at the same time and then immersed into the testing liquid mediums (water and diiodomethane) by raising the elevating stage at a constant speed of 2 mm/min. The contact angles (θ) were calculated using a computer system from eq. (1). The surface free energy was calculated from Owens-Wendt equation (2) and (3). Each sample are tested three times. The final contact angles with water and diiodomethane are the average value.

\[ F = \gamma \cdot p \cdot \cos \theta \]  
\[ \gamma_f(1 + \cos \theta) = 2 \cdot \sqrt{\gamma_s^p \gamma_f^p} + 2 \cdot \sqrt{\gamma_s^d \gamma_f^d} \]  
\[ \gamma_s = \gamma_s^p + \gamma_s^d \]

Where F is the wetting force measured by the microbalance; p is the wetted perimeter; θ is the contact angle between fiber and liquid; \( \gamma_f \) is the surface tension of the testing liquid; \( \gamma_{Total} \) is the surface free energy of the fiber; \( \gamma_s^p \) is the polar component and \( \gamma_s^d \) is the dispersive component.

3. Results and Discussion

3.1. Effects of plasma treatment pressure on fiber surface wettability
The results of contact angles with water and diiodomethane before and after oxygen plasma treatment were given in Table 1. For the untreated fiber, the contact angles with water and diiodomethane were 77.47° and 55.02°, respectively. After 10 Pa plasma treatment, the contact angle with water decreased to 32.59° and increased to 65.85°. When the plasma treatment pressure were set between 20 Pa to 60 Pa, the contact angle with water was stable at about 20° and the contact angle with diiodomethane was kept at 67°. The results showed that oxygen plasma treatment can obviously change the fiber surface properties.

| Plasma treatment pressure(Pa) | Water (θ) ± s.d. (°) | Diiodomethane (θ) ± s.d. (°) |
|-------------------------------|----------------------|-------------------------------|
| Untreated                     | 77.47 (1.31)         | 55.02 (0.78)                  |
| 10                            | 32.59 (1.56)         | 65.85 (2.00)                  |
| 20                            | 22.46 (1.13)         | 65.31 (1.13)                  |
| 30                            | 19.20 (0.46)         | 67.70 (0.83)                  |
| 40                            | 17.15 (1.10)         | 70.73 (0.86)                  |
| 50                            | 19.66 (0.33)         | 65.48 (2.07)                  |
| 60                            | 21.07 (1.08)         | 67.54 (1.46)                  |
| 70                            | 34.25 (0.99)         | 67.53 (0.51)                  |

s.d.: standard deviation
According to the equation (1), (2) and (3), we can calculate the fiber surface total free energy, the polar component and dispersive component. Figure 1 showed the results of surface free energy of Aramid fiber III via oxygen plasma treatment pressure. The total surface free energy increased from 37.78 mJ/m$^2$ for untreated sample to 69.63 mJ/m$^2$ with 40 Pa plasma treated fiber. The fiber surface wettability was improved greatly with oxygen plasma treatment.

3.2. Fiber surface aging behaviors

Table 2. Contact angles with water and diiodomethane after oxygen plasma treatment with aging time

| Aging days | Water (θ) ± s.d. (°) | Diiodomethane (θ) ± s.d. (°) |
|------------|----------------------|-------------------------------|
| 0          | 22.46 (1.13)         | 65.31 (1.13)                  |
| 5          | 21.33 (1.52)         | 65.19 (3.53)                  |
| 10         | 25.33 (0.53)         | 63.97 (1.00)                  |
| 15         | 26.96 (2.47)         | 64.07 (2.01)                  |
| 30         | 31.72 (1.63)         | 59.38 (1.38)                  |

s.d.: standard deviation

The results of contact angles with water and diiodomethane after oxygen plasma treatment with aging time were given in Table 2. The results of surface free energy of Aramid fiber III after oxygen plasma treatment via aging time was shown in Figure 2. For the fresh plasma-treated fiber, the contact angles with water and diiodomethane were 22.46° and 65.31°, respectively. After storage in air for 5 days, the contact angle with water decreased to 21.33°. There is a little slight decrease for short time storage in air. It may be due to the surface chemical structure adjustment after plasma treatment. With the storage time extended to 10 days or longer, the contact angle with water increased slowly. Meantime, the contact angle with diiodomethane decreased. The results showed that oxygen plasma treatment has aging behavior for organic fiber surface. As seen from Figure 2, the fiber surface wettability decreased slowly with storage time in air. The fiber surface wettability decreased from 67.79 mJ/m2 for 20 Pa plasma-treated sample to 63.85 mJ/m2 after 30 days.
Figure 2. Surface free energy of Aramid fiber III after oxygen plasma treatment via aging time

4. Conclusion
The dynamic contact angles analysis results showed that oxygen plasma treatment can improve aramid fiber III surface wettablity. The total surface free energy increased from 37.78 mJ/m² for untreated sample to 69.63 mJ/m² with 40 Pa plasma treated fiber. The fiber surface wettablity decreased slowly with storage time in air. The fiber surface wettablity decreased from 67.79 mJ/m² for 20 Pa plasma-treated sample to 63.85 mJ/m² after 30 days.

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