Preparation of highly active aramid fiber and effect on the interface property of aramid/epoxy composites

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Abstract. The smooth surface and the lack of active groups make para-aramid fiber reinforced composites have poor interfacial adhesion property, which limits their applications in various fields. In this study, aramid fiber was coated with nano-coating solution and functional groups such as epoxy and amino groups were introduced to the surface of aramid fiber to enhance the surface activity of the fiber, thereby improving the adhesion between fiber and resin. The surface composition and roughness of the modified fibers were characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), and scanning electron microscope (SEM), respectively. The effect of functional groups on the interfacial adhesion properties of aramid/epoxy composites was studied by the interfacial shear strength (IFSS) and the flexural strength. After modification, the roughness and the polarity of the fiber were considerably improved. The IFSS reached 45.9 MPa with a significant enhancement by 27.5%; while the flexural strength increased from 240.7 MPa to 302.2 MPa, with a reinforcement of 25.6%, indicating that the study provides an effective method to achieve highly active aramid fiber.

1. Introduction

Due to low density, high strength and high modulus, para-aramid fiber has been widely used in aerospace, transportation, chemistry, electrical, construction, machinery, sports and other fields.[1] However, the inset surface of aramid fiber caused by smooth surface and few active groups make poor interfacial adhesion of fiber and matrix when it is used to reinforce composites, which results in the decrease of the mechanical properties of the composites.

In order to improve the poor interfacial adhesion, many efforts have been taken including plasma treatment[2], γ-ray radiation[3], surface grafting[4]. Although various modification methods can improve the interfacial adhesion, the mechanical properties of the fiber will be damaged. How to achieve non-destructive modification has become the focus of researchers. In recent years, aramid nanofibers (ANF) have attracted widespread attention. High-strength insulating membranes[5] and/or high-strength conductive films[6-7] with conductive fillers such as carbon nanotubes (CNT) and graphene were most reported, while there is less research in the field of fiber modification.

In this work, ANF coatings were prepared by sulfone-functionalized poly(p-phenylene terephthalamide) (SPPTA) in dimethyl sulfoxide (DMSO)/NaH solution. Epichlorohydrin (ECH) and Tris(2-aminoethyl)amine (TAEA) were further added in the coating solution to introduce epoxy and amino groups. The presence of polar functional groups makes a significant contribution to the interfacial adhesion of the composites. The chemical structure of the coating solution was confirmed by Fourier
transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS). The morphology of the coated fiber was observed scanning electron microscope (SEM). And the effect of the coating solution on the interfacial adhesion properties of aramid/epoxy composites was evaluated by the interfacial shear strength (IFSS) and the flexural strength. Experiments showed that this modification method was suitable to improve the interfacial properties of the composites.

2. Experimental Section

2.1. Chemicals
SPPTA was synthesized in the laboratory. DMSO (Shanghai Lingfeng Chemical Reagent Co., Ltd) were dried and stored over 4A molecular sieves. Sodium hydride (NaH) and Tris(2-aminoethyl)amine (TAEA) were supplied by Sigma-Aldrich. Epichlorohydrin (ECH) was purchased from Sinopharm Chemical Reagent Co., Ltd. Epoxy resin (GE-7118A) and curing agent (GE-7114B) were purchased by Wells Advanced Materials (Shanghai) Co., Ltd. Aramid fabric (420g·m⁻²) was supplied by Yantai Taparan Advanced Manufacturing Technology Co., Ltd. The copolymer was synthesized in the laboratory (Scheme 1).

Scheme 1. The structure of SPPTA copolymer

2.2. Preparation of the coating solution

2.2.1. Synthesis of SPPTA-ECH-x
Preparation of SPPTA-ECH-0.07 was chosen as an example to describe the synthesis procedure (x is the concentration of NaH). Firstly, 0.252g NaH (0.07M) was added into 150mL DMSO under nitrogen atmosphere and stirred to ensure that NaH dissolved completely. Secondly, 2g SPPTA powder was added into the above solution and stirred at 30°C for 2 h, leading to a dark red solution. With 3.915mL ECH adding into the solution and reacting at 30°C for 8 h, the colour of the solution changed from dark-red to yellow. The dark red solution and the yellow solution were mixed with an equal amount of deionized water and sonicated to prepare coating polymers through solvent exchange, which were named SPPTA-ANF and SPPTA-ECH, respectively. The polymers were treated in a soxhlet apparatus to extract for 12 h with anhydrous ethanol, and then dried at 80°C for 24 h.

2.2.2. Synthesis of SPPTA-ECH-TAEA
Overdose of TAEA were added into the 150mL SPPTA-ECH-0.07 reaction solution and reacted at 30°C for 12 h, respectively. Then the coating polymers were obtained by solvent exchange, which were designated SPPTA-ECH-TAEA. The polymers were treated in a soxhlet apparatus to extract for 12 h with anhydrous ethanol, and then dried at 80°C for 24 h. The preparation and structure of coating polymers were presented in Scheme 2.

2.3. Preparation of the coated fiber
The same amount of aramid fibers was immersed in the coating solution for 5 minutes and washed by deionized water and anhydrous ethanol for several times. The modified fibers were marked as AF-ANF, AF-ECH, AF-ECH-TAEA, respectively.

2.4. Sample preparation for micro-bond test
Microbond test was carried out to estimate the interfacial property between fibers and epoxy resins. As shown in Scheme 3, the aramid monofilament was fixed on hollow frame. The epoxy resin droplet (the mixture of epoxy resin and curing agent at the ratio of 10:3 by weight) was placed on the monofilament and cured at 80°C for 3 h.
The interfacial shear stress (IFSS) can be calculated by formula (1):

$$IFSS = \frac{F}{\pi \cdot d_f \cdot d_r}$$

(1)

Where $F$ is the maximum force measured, $d_f$ and $d_r$ is the diameter of aramid fiber and the droplet, respectively. Five samples were tested to take the average value.

2.5. Sample preparation for three-point flexural test
Aramid fiber/epoxy composites were prepared by vacuum assisted resin infusion (VARI). Gas in the aramid fabric was removed in the vacuum state and the aramid fabric was impregnated through the flow and penetration of the epoxy resin into the fabric. Then the composites with the fiber volume content of 60% was manufactured at 80°C for 3 h.

The flexural strength of the composites with a dimension of 40×16×3 mm was tested according to ASTM D7264 and it can be calculated by formula (2):

$$\sigma = \frac{3PL}{2bh^2}$$

(2)

Where $P$ is the maximum force measured, $L$ is the support span, $b$ and $h$ is the width and thickness of the beam, respectively.

2.6. Characterization
The chemical structures of the coating polymers and aramid fiber were characterized by FT-IR spectrometer (Nicolet 8700, Thermo Electron Corporation, America) and X-ray photoelectron spectroscopy (XPS) measurements (Escalab 250 Xi, Thermo Fisher, America). The morphology of the samples was observed by SU8010 scanning electron microscope (SEM, Hitachi Limited, Tokyo, Japan) and transmission electron microscope (TEM, JEM 2100). The surface free energy of the pristine and treated fiber was evaluated using an Automatic video micro contact angle measuring instrument (OCA40 Micro, China). The IFSS of the fiber reinforced composites was measured on YG006E-10 Fiber Electronic Strength Tester with a strain rate of 10 mm·min$^{-1}$ and the flexural strength of the composites was measured on the universal testing machine (MTS C44 104) with a strain rate of 2 mm·min$^{-1}$.

![Scheme 2. The preparation and the structure of coating polymers](image-url)
3. Results and discussion

3.1. Coating polymers

3.1.1. The chemical structure of the coating polymers

The chemical structure of the coating polymers was detected by FT-IR spectra and XPS analysis. The infrared spectra of the coatings were illustrated in figure 1(a). There were peaks at 3311, 1650, 1590, 1399, 1302 and 1105 cm$^{-1}$ appeared in all polymers, which were corresponding to N-H stretching vibration, amide I (C=O tensile vibration), II (N-H in-plane bending vibration), III (C-N tensile vibration) and antisymmetric and symmetric telescopic vibration of-SO$_2$- groups. In the spectra of SPPTA-ECH, the appearance of epoxy groups (950cm$^{-1}$) and-CH$_2$- (2927cm$^{-1}$) proved that ECH was successfully introduced into the structure of the polymer. The structure of polymers changed when the functional groups reacted with epoxy groups. The absorption peak at 1590 cm$^{-1}$ observed in the spectra of SPPTA-ECH-TAEA was obviously strengthened, indicating the successful introduction of a large number of nitrogen-containing functional groups.

The amount of epoxy groups was limited by the concentration of amide bond. The appropriate amount of ECH was discussed and the result was presented in figure 1(b,c). The value of $I_{953}/I_{1650}$ was used to describe the degree of epoxidation of the polymer. When the NaH concentration was lower than 0.07M, the ratio of $I_{950}/I_{1650}$ increased with the increase of NaH concentration; while the concentration was higher than 0.07M, due to electrostatic repulsion, the metallized amide bond caused the molecular chain to curl or entangle, so that the unreacted amide bonds encapsulated in the interior and could not exposed to the reactants. Therefore, 0.07M was determined to be an optimal NaH concentration.

The structural changes of the coating polymers were further confirmed by XPS. The signals of oxygen and carbon of the polymers were different before and after modification. As shown in figure 2, for SPPTA, oxygen had only two forms of existence, the amide bond (531.4 eV) and the sulfone group (532.3 eV) on the backbone, while the signals of carbon were presented in four forms: C-N (285.6 eV, amide bond), C=O (288.0 eV, amide bond), C=C (284.8 eV, benzene ring) and C=S (286.1 eV, polymer chain). For the SPPTA-ECH sample, there were new peaks in the spectrum, such as the peak at 532.2 eV in the O 1s spectrum and the peak at 286.4 in the C 1s, which were corresponding to the epoxy groups. The appearance of peaks demonstrated that epoxy groups had been successfully introduced into the polymer structure. For the SPPTA-ECH-TAEA sample, oxygen atom existed in a variety of forms, which was due to the oxidation of amino groups.

The chemical composition of the coating polymers was listed in Table 1. When the epoxy groups were introduced to aramid fiber, the content of carbon increased while the oxygen decreased slightly. The content of nitrogen of SPPTA-ECH-TAEA increased from 5.53% to 10.58% due to the abundant amino groups. It is worth noting that the content of oxygen of SPPTA-ECH-TAEA reached 18.09%. It could be explained that the -NH$_2$ was converted to -NO$_2$ caused by the oxidation of air. This result was further confirmed by the O 1s spectra of SPPTA-ECH-TAEA.

| Sample | Atom% | Atom ratio |
|--------|-------|------------|

![Scheme 3. Preparation process and the micro-bond test of the specimen](image)
3.1.2. The morphology of the coating polymers

The morphology of the coating polymers was observed by TEM. Through the deprotonation of the NaH/DMSO system, the amide bond was broken, which greatly weakened the intermolecular hydrogen bond of polyamide, achieving aramid nanofibers (ANFs). As shown in figure 3a, the diameter of ANFs ranged from 15nm to 30nm. When the oxygen groups were aramid fiber onto the amide bond, due to the charge repulsion, epoxy groups agglomerated around ANFs and finally formed a stable nanosphere with a diameter of 150nm. When -NH2 was further aramid fiber, the coating solution still exhibited spherical properties, but the size of the nanosphere was slightly different due to the molecular weight of the aramid fiber agent.

3.2. Coated fibers

3.2.1. The morphology of the coated fibers

The morphology of the pristine and modified fiber was observed by SEM (presented in Figure 4). The untreated fiber surface was smooth with slight gully while the coated fiber became rougher. After treatment with the nanofiber solution, the surface was uniformly covered with nanofibers. When the fiber was coated by SPPTA-ECH and SPPTA-ECH-TAEA solution, particulate matter was deposited onto the surface of the fiber, which might be the result of the agglomeration of the nanosphere, leading to the increase of the polarity of the fiber surface.

![Figure 1: The Infrared spectra of the coating polymers](image)

Figure 1: The Infrared spectra of the coating polymers
Figure 2. XPS full spectrum and high resolution spectra of C 1S and O 1s of all coating polymers

Figure 3. TEM pictures of the coating polymers

Figure 4. The morphology of the untreated and treated fiber (a: AF, b: AF-ANF, c: AF-ECH, d: AF-ECH-TAEA)

3.2.2. The surface free energy of the coated fibers

The surface free energy of the coated fibers could be obtained by the contact angle test. Deionized water and glycerin were used as test liquids to calculate the surface free energy and the results were shown in Table 2. The surface free energy of sized fiber was higher than that of the untreated aramid fiber. We know that the surface free energy consists of two parts: polarity and dispersion. The dispersion contribution of the modified fiber decreased while the polarity contribution increased, which was
primarily due to the introduction of the functional groups that greatly improve the polarity of the fiber. It is worth noting that the contribution of nitrogen to polarity may be more obvious than that of oxygen.

Table 2. The surface free energy of the treated and untreated fiber.

| Sample         | Contact angle |  |  |  |  |  |
|----------------|---------------|---|---|---|---|---|
|                | With H2O(θ1)  | With glycerol(θ2) | γ_d (mJ/m^2) | γ_p (mJ/m^2) | γ_s (mJ/m^2) |
| AF             | 67.0          | 60.9                        | 16.1          | 19.9          | 36.0          |
| AF-ECH         | 62.2          | 66.2                        | 5.1           | 34.4          | 39.5          |
| AFr-ECH-TAEA   | 49.0          | 53.6                        | 4.5           | 49.8          | 54.3          |

3.3. The interfacial adhesion properties of the aramid fiber/epoxy composites

The IFSS and flexural strength can be used to measure the interfacial adhesion properties of the fiber-reinforced epoxy composites. It can be seen from figure 5 that the IFSS and flexural strength of the aramid fiber/epoxy composites were 36.0 MPa and 240.7 MPa, respectively. When ECH was coated onto the surface of the fiber, the IFSS value increased from 36.0MPa to 43.3MPa; while the flexural strength increased from 240.7MPa to 273.4MPa. This was due to the introduction of epoxy groups and the roughness of the fiber surface, and the compatibility between fiber and epoxy resin became better with the introduction of epoxy group. When the functional groups were aramid fiber onto the fiber surface, the IFSS value increased from 36.0 MPa to 45.9 MPa, while the flexural strength increased from 240.7 MPa to about 302.2 MPa, which was the joint contribution of the surface roughness and the polarity. Polar groups could form more covalent bonds in the curing of epoxy resin and curing agent, thereby improving the interfacial adhesion of the composites. In addition, due to the introduction of organic solvents, this modification method was still unable to avoid the problem of reduced mechanical properties of the fiber monofilament.

![Figure 5](image)

Figure 5. The mechanical property of aramid fiber and the IFSS, flexural strength of the aramid fiber/epoxy composites

4. Conclusion

In summary, functional aramid fabric with much polarity was prepared by aramid fiber modifiers. Robust aramid/epoxy composites were achieved using the modified fabric with rough surface and polarity. The IFSS value of aramid fiber reinforced composites increases by 27.5% compared with that of untreated sample; while the flexural strength increases from 240.7MPa to 302.2MPa, with an enhancement of 25.6%, indicating that the study provides an effective method to achieve high active aramid fiber and high strength fiber reinforced composites.
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