# Interfacial Studies on the Surface Modified Aramid Fiber Reinforced Epoxy Composites

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Received 4 December 2005; accepted 6 March 2006
DOI 10.1002/app.24460
Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** In this work, solutions of rare earth modifier (RES) and epoxy chloropropane (ECP) grafting modification method were used for the surface treatment of aramid fiber. The effect of chemical treatment on aramid fiber has been studied in a composite system. The surface characteristics of aramid fibers were characterized by Fourier transform infrared spectroscopy (FTIR). The interfacial properties of aramid/epoxy composites were investigated by means of the single fiber pull-out tests. The mechanical properties of the aramid/epoxy composites were studied by interlaminar shear strength (ILSS). As a result, it was found that RES surface treatment is superior to ECP grafting treatment in promoting the interfacial adhesion between aramid fiber and epoxy matrix, resulting in the improved mechanical properties of the composites. Meanwhile, the tensile strengths of single fibers were almost not affected by RES treatment. This was probably due to the presence of reactive functional groups on the aramid fiber surface, leading to an increment of interfacial binding force between fibers and matrix in a composite system.  J Appl Polym Sci 102: 4165–4170, 2006

**Key words:** chemical treatment; aramid fiber; composites; interfaces; adhesion

## INTRODUCTION

Aramid fiber is a kind of high performance organic fiber since it registers a high specific strength and modulus. Since it came to market in 1972, the availability of aramid fiber has advanced in material science, particularly in the areas of fiber-reinforced composites, rubber goods, ropes and cables, ballistics, pulp-reinforced friction products, gaskets, and so forth.[1] Structures made of aramid-fiber-reinforced (ARF) plastics are widely used in aviation and space engineering due to the low density and high specific strength of aramid fibers and composites based on them, which is important for aircraft industry.[2]

The interfacial adhesion of fiber-reinforced composites plays a very important role in determining the composite mechanical properties. A better fiber/matrix interfacial adhesion/bond will impart better properties such as tensile strength, interlaminar shear strength, delamination resistance, fatigue, and corrosion resistance to a polymeric composite.[3] However, the aramid fiber-reinforced composites show poor interfacial adhesion between the aramid fiber and the matrix resin, due to the low surface energy and chemically inert surface of the fiber.[4]

To improve the interfacial adhesion between aramid fiber and epoxy resin matrix, several fiber surface modification methods have been used, such as chemical treatment (including coupling agent and chemically grafting methods) and plasma treatment used to improve the adhesion with the resin matrix. The mechanism of these surface modification methods is to increase the concentration of reactive functional groups or roughen the surface of the fiber to enlarge the physical interface with the resin matrix.[5–7]

In this work, solutions of rare earth modifier (RES) and epoxy chloropropane (ECP) grafting modification method are used for the surface treatment of F-12 aramid fiber. The purpose of this study was to examine the influence of these two surface treatment methods on the interfacial adhesion and the mechanical properties of aramid/epoxy composites. Also, the damages to the fibers by the surface treatments were investigated.

## EXPERIMENTAL

### Materials

F-12 aramid fiber used in this study was provided by the 46th Institute of The Sixth Academy of CASIC. F-12 fiber is a kind of Apmoc fiber, which is made in Russia.[8] The fiber properties are shown in Table I. Rare earth compound $LaCl_3$ was purchased from Shanghai Yuelong New Materials Co. Ethylenediamine tetraacetic acid (EDTA), ammonium chloride, and hydrogen nitrate were commercially obtained without further puri-

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Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 50275093.

TABLE I
Properties of F-12 Aramid Fibers

| Filaments diameter (μm) | 14–16 |
|---|---|
| Tensile strength (MPa) | 4,200 |
| Tensile modulus (GPa) | 135 |
| Elongatition (%) | 3–4 |
| Density (g/cm$^3$) | 1.45 |

fication. E-51 epoxy resin and 593 curing agent were manufactured by Shanghai Resin Factory Co. E-51 epoxy resin is bisphenol-A liquid epoxy resin (Epoxide Eq. Wt. 184–210). Curing agent (593) is a kind of aliphatic amine which provides room temperature cure.

For the preparation of the RES, $LaCl_3$, EDTA, ammonium chloride, and hydrogen nitrate were added to ethanol. The final pH of solution was 5.

### Fiber surface treatment and characterization

Aramid fiber must be treated before proceeding surface-modification to eliminate the organic impurity on the fiber surface. The pretreatment is to extract the fibers in a circumfluent extraction apparatus with toluol, acetone, and deioned water for 3 h in sequence. Then, dry it in a vacuum oven at 110°C for 6 h.

Two types of fiber surface treatment have been applied in this research: RES treatment and ECP grafting modification treatment.

For ECP grafting modification treatment, F-12 aramid fibers were immersed in the solution of KOH (0.7%)/alcohol at 30°C for 2 h, then washed and dried. After that, these fibers were grafted in ECP at 90°C for 6 h, then washed with distilled water and dried.

For RES surface treatment, F-12 aramid fibers were immersed in the RES/alcoholic solution at room temperature for 1 h, and dried in a vacuum oven at 110°C for 4 h. The untreated fibers were used for blank experiments.

Infrared spectra of the chemically treated aramid fibers and untreated fibers were measured with Fourier Transform Infrared Spectrometer (Model: EQUINOX55).

### Single fiber pull-out test

The single fiber pull-out specimens were prepared as shown in Figure 1. An acrylic ring was placed on an aluminum plate. A fiber was hanging freely through a hole in the plate and was loaded with weight providing ~ 5 MPa. Epoxy matrix was injected into the acrylic ring. Specimens were cured at room temperature for 8 h. Embedded fiber length measured after pull-out tests ranged from 0.21 to 0.72 mm and free fiber length was kept at about 10 mm.

The single fiber pull-out tests were performed at 25°C using an Instron tester (Model 4302) at a crosshead speed of 0.5 mm/min. A load cell of 1 N was used. The interfacial shear strength (IFSS), τ, was calculated using the relationship:

$$\tau = \frac{F}{\pi d l} \quad (1)$$

where, $F$ is the pull-out force (N), $d$ the diameter of the fiber (m), and $l$ the embedded length of the fiber (m). Each reported IFSS value is the average of more the 10 successful measurements.

### Interlaminar shear strength

F-12 aramid/epoxy unidirectional laminated composites were manufactured using a filament winding technology. Impregnated aramid filament yarns were winded onto a plate up to a certain thickness and cured for 24 h. Then, the composites were machined into specimens. The content of the F-12 aramid fibers was fixed at 60% by volume for all composite specimens.

The interlaminar shear strength (ILSS) of composites was determined using the short-beam-shear (SBS) tests according to ASTM D-2344-76. The specimen dimensions were nominally 16 × 11 × 2 mm$^3$, with a span to thickness ratio of 5. The experiments were performed on

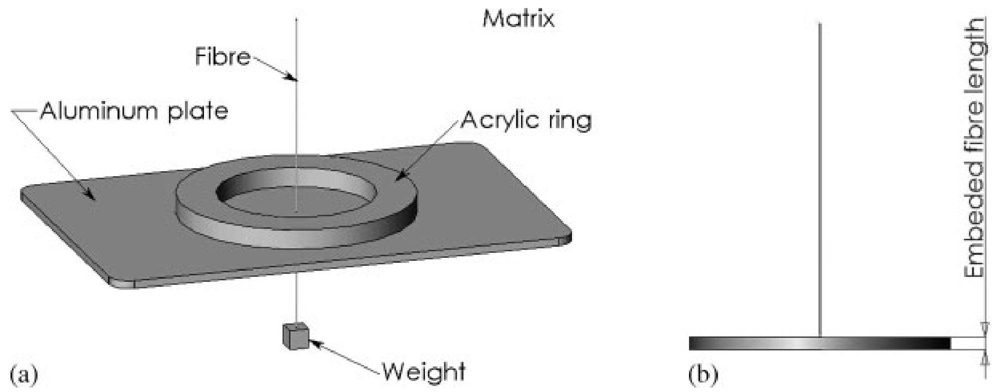


**Figure 1** Single fiber pull-out specimen (a) Specimen preparation. (b) Shape and dimensions of specimen.

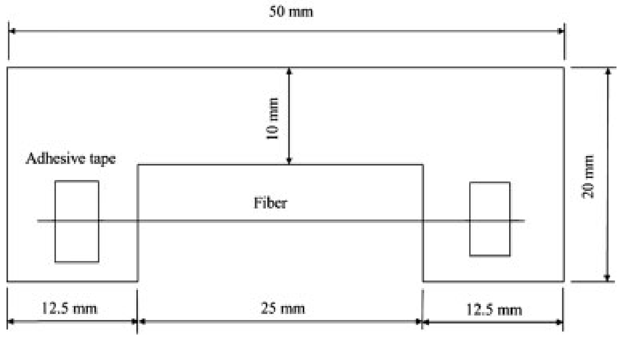


**Figure 2** Single fiber tensile strength test specimen.

a Zwick/Roell Z020 Material Testing Machine, at a cross-head speed of 1 mm/min. The experimental condition was maintained at 25°C and 50% relative humidity.

The ILSS for the SBS test is calculated by the expression:

$$\text{ILSS} = \frac{3P}{4Bh} \tag{2}$$

where, $P$ is the maximum load (N), $B$ the width of specimen (m), and $h$ the thickness of specimen (m). An average value was obtained of five specimens tested for each experimental data.

The fracture surfaces of the ILSS specimens were coated with gold then observed using a scanning electron microscope (SEM) (Model: CSM950, made by OPTON Co., Germany).

### Single fiber tensile strength

Single aramid fiber tensile specimens were prepared by attaching a single fiber to a paper frame according to ASTM D3379 as shown in Figure 2. The single fiber tensile strength tests were also conducted using the same Instron tester at a crosshead speed of 1 mm/min. At least five specimens were tested for each group. The average fiber fracture load was obtained and the fiber tensile strength was calculated.

## RESULTS AND DISCUSSION

### Fiber surface properties

The FTIR transmittance spectra of aramid fiber before and after chemical treatments are shown in Figure 3. ECP grafted fiber has the epoxy peak at 2990 $cm^{-1}$, yet untreated fiber and RES treated fiber do not have this peak. This means that the epoxy chloropropane was successfully grafted onto the fiber surface.

RES treated fiber does show a —COOH peak at 1750 $cm^{-1}$. That is, the —COOH groups can be introduced on the surface of aramid fibers by RES treatment.

Rare earth elements have the chemical activity, which depends on their special electron structure ($\ldots 4f^{0-14}$). The rare earth compounds are capable of coordinating and ionic combination reacting with some functional groups. According to the chemical bonding theory, it is suggested that rare earth compounds are adsorbed onto the aramid fiber surface through chemical bonding and continue to coordinate with the reactive functional groups (—COOH, etc.) owing to their large coordination numbers, which increases the concentration of reactive functional groups of fiber surface. These reactive functional groups can improve the compatibility between aramid fiber and epoxy matrix and form a chemical combination between the aramid fiber and epoxy matrix.[9]

### Micromechanical characterization

Figure 4 shows the relationship between embedded fiber length and maximum load of the load-displacement curves (debonding load or fiber fracture load). Strictly speaking, the relationship between debonding load and embedded fiber length cannot be described by a linear function.[10,11] However, experimental results had some scatter band because of difficulties of preparation of specimens and other factors. Therefore, linear relationship was used in Figure 4 as an approximation. The average of the fiber fracture load was plotted for each set of results. The maximum embedded fiber length is a value calculated from the intersection of the two straight lines of the linear regression line for the debonding load and the average fiber fracture load. The slope of the linear regression line for the debonding load is considered to be related to the interfacial strength, and therefore, this value will be used as a measure of the interfacial strength. It can be seen

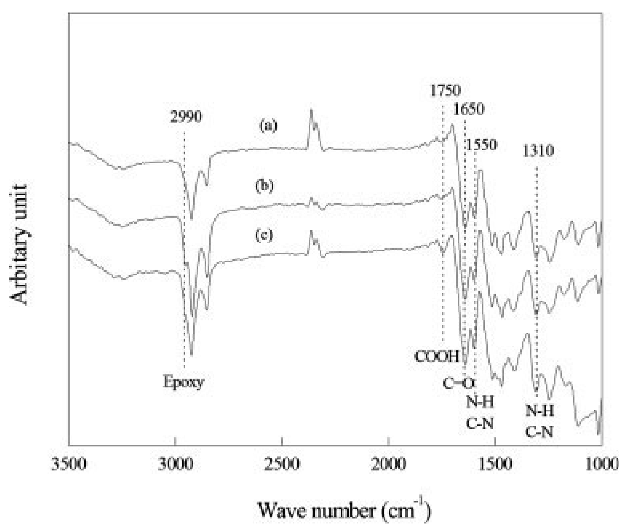


**Figure 3** FT-IR transmittance spectra of aramid fibers (a) original; (b) ECP grafted; (c) RES treated.

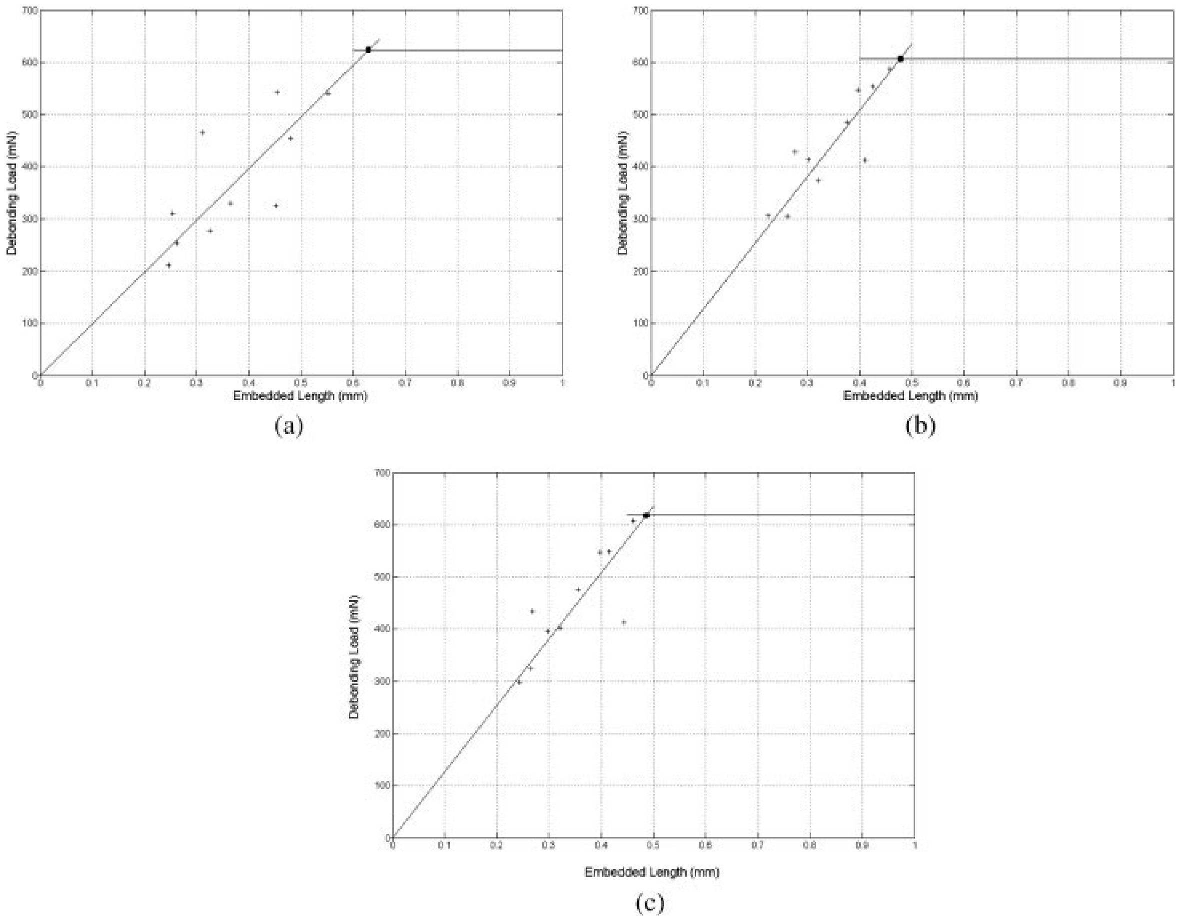


**Figure 4** Relationship between embedded fiber length and maximum load (debonding load or fiber fracture load) (a) untreated; (b) ECP grafted; (c) RES treated.

that the maximum slope was obtained by the RES treatment.

The summarized results are shown in Table II. The IFSS value for the aramid/epoxy composite is determined from eq. (1). The results show that both these two methods can improve the interfacial adhesion. RES surface treatment is superior to ECP grafting treatment in promoting interfacial adhesion between aramid fiber and epoxy matrix. Meanwhile, the tensile strengths of single fibers were almost not affected by RES treatment.

## Mechanical interfacial properties

It is generally accepted that the mechanical properties of composites depend strongly on the degree of interfacial adhesion between fibers and matrix.[12] Figure 5 shows a comparison between untreated, ECP-grafted, and RES-treated F-12 aramid fibers and their composites. It is seen that both the ECP grafting method and the RES treatment can improve the ILSS of aramid/epoxy composite, but the RES-treated aramid fibers yielded better results. The ILSS of the RES-treated aramid/epoxy composite increased by about 12.5% compared with that of the untreated composite. A 7.7% improvement was achieved by the ECP grafting method. The tensile strength of the ECP-grafted F-12 aramid single fibers decreased by about 4.7% compared with that of untreated aramid fibers, which is in accordance with the results obtained in Ref. 13. We should note that, during the ECP treatment, the aramid fibers were also treated with a KOH/alcohol solution to create —COOK groups as grafting initiators on the surface of

**TABLE II**
**Experimental Data of Single Fiber Pull-Out Test with Different Surface Treatments**

| Surface modification | Slope of linear regression line for debonding load (mN/mm) | Critical embedded length $L_c$ (mm) | Fiber average fracture load (mN) | IFSS (MPa) | Number of pull-out specimens |
|---|---|---|---|---|---|
| Untreated | 991.5 | 0.64 | 623.1 | 22.6 ± 5.1 | 10 |
| ECP grafted | 1271.9 | 0.48 | 606.2 | 28.9 ± 4.2 | 10 |
| RES treated | 1326.6 | 0.49 | 618.5 | 30.2 ± 3.8 | 10 |

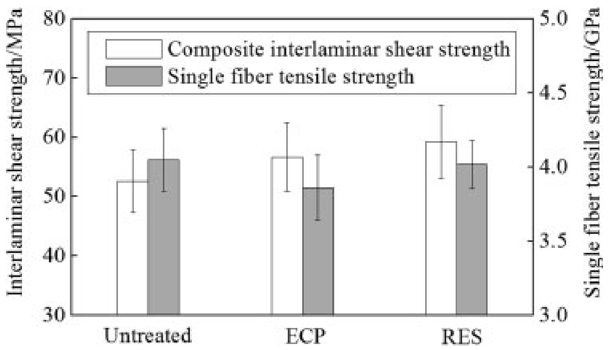


**Figure 5** Effect of surface treatments on ILSS of composites and single fiber tensile strength.

aramid fibers, which may lead to the hydrolyzation of aramid fiber surface molecules. Excess hydrolyzation may cause damage to the fibers and, as a result, affect the tensile strength of composites. The tensile properties of RES-treated aramid fibers did not change greatly.

Compared with the IFSS, the ILSS do not show significant improvement due to the fiber surface treatment. The reason is that the ILSS is determined not only by the interfacial adhesion, but also by the transverse tensile strength of the fiber which cannot be improved by surface treatment.

The SEM micrographs of fracture surfaces of the untreated, ECP-grafted, and RES-treated F-12/epoxy composites are shown in Figure 6. As is seen, the sur-

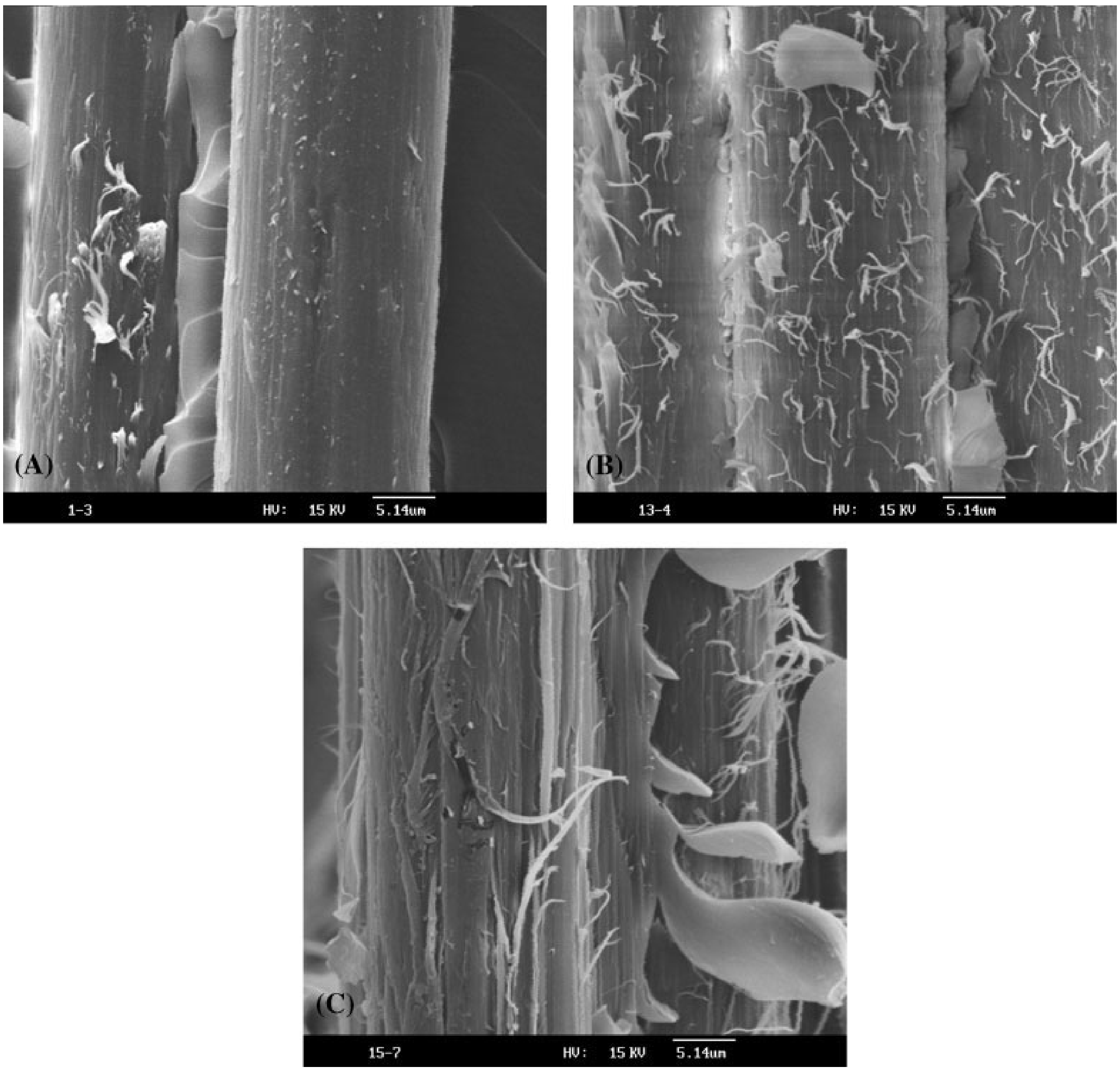


**Figure 6** SEM micrographs of the interlaminar shear fracture surface of F-12/epoxy composites versus surface modification (A) untreated, (B) ECP grafted, (C) RES treated.

face of untreated fibers are rather smooth, with little epoxy matrix adhered to their surface, as shown in Figure 6(A). This means that the interfacial adhesion between the untreated fibers and the epoxy resin is rather poor, and the interface is more likely to undergo the debonding damage. The interfacial adhesion was improved by ECP grafting treatment. An amount of filamentous epoxy resins were adhered to the fiber surface, as shown in Figure 6(B). This means a number of active centers were formed on the fiber surface when treated by RES grafting method. Moreover, the interfacial adhesion became stronger with RES treatment. A large amount of epoxy resin adhered to the fiber surface and formed a thick layer, as shown in Figure 6(C). The abovementioned results are consistent with the ILSS experimental data. All the results indicate that RES treatment is superior to ECP grafting treatment in promoting the interfacial adhesion between F-12 fiber and epoxy matrix; thus, the mechanical properties of the F-12/epoxy composites can be improved considerably.

## CONCLUSIONS

In this study, we investigated the effect of ECP grafting treatment and RES treatment on interfacial and mechanical properties of aramid fiber-reinforced epoxy composites. As a result, the IFSS and ILSS of the composites were improved by ECP grafting treatment and RES treatment. RES treatment is superior to ECP grafting treatment in promoting interfacial adhesion between the F-12 aramid fiber and epoxy matrix due to the presence of reactive functional groups on fiber surfaces, and RES treatment does not cause significant fiber damage.

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