Surface Modification of Aramid Fibers with New Chemical Method for Improving Interfacial Bonding Strength with Epoxy Resin

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ABSTRACT: Friedel-Crafts reaction was elected as the specific chemical approach to modify Aramid fiber surface in this article. After the surface treatment, the interfacial shear strength value of Aramid fiber/Epoxy composites was enhanced by about 50%. The surface elements of Aramid fibers were determined by X-ray photoelectron spectroscopy, whose results showed that the ratio of Oxygen/Carbon was increased. The crystalline state of Aramid fibers was determined by X-ray diffraction instrument, and the surface morphological of Aramid fibers was analyzed by Scanning electron microscope. The results indicated that this novel surface treatment approach, which is a suitable way of the batch-process for Industrialization, not only can improve the interfacial bonding strength of Aramid fibers reinforced Epoxy resin matrix composites remarkably, but also hardly has any negative influence on the intrinsic tensile strength of Aramid fibers. The wettability degree of the fiber surface was enhanced by this new approach too. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 2541–2552, 2010

Key words: aramid fibers; interfacial properties; surface treatment; Friedel-Crafts reaction

INTRODUCTION

Aramid fibers are characterized by low density, high tenacity and modulus, thus they are widely used as a good reinforcement material for polymer composites in aircraft, aerospace, and missile application.[1–3]

It is well-known that the mechanical properties of the fibers reinforced polymer composites are influenced by the properties of the interface between the fiber and the resin matrix directly, however the surface of Aramid fiber is so chemically inert and smooth, which derives from the high crystallinity of Aramid fiber surface layer and the lack of the polar functional groups in the polymer molecule chain, that the adhesion between Aramid fibers and the resin matrix is very poor.[4–7] Hence, surface modification is essential for Aramid fibers to enhance the interfacial bonding strength. Various approaches of the surface modification for Aramid fibers have been developed, such as chemical, physical treatments, and the coalescence of the two approaches. The physical method is mainly ultrasound treatment.[8–13] The coalescence approach mainly contains ionizing radiation, plasma treatment and graft polymerization.[14–20] Although the latter two modification approaches have been studied for a long time, they are still only fit to be carried out in laboratories due to the low security and operability, the high cost and "degradation effect" of the surface modification results with time, whereas the chemical modification approaches are convenient, stability and suitable ways of the batch-process for industrialization because of forming the stable chemical bonding effect between Aramid fibers and the resin matrix via the chemical reaction.

On the other hand, the conventional chemical modification approaches[21–27] mainly contain: (1) Etching on the fiber surface via the nitration reaction or the sulfonation reaction on Phenyl ring; and (2) introducing the active functional groups into the fiber surface molecule structure via the graft reaction in the active hydrogen atoms of Imide groups. But it is very hard for the former to control the surface treatment depth and degree, and then it is inevitable to decrease the fiber intrinsic strength because of the corrosive and destructive effects of the strong oxidative acids on the fiber surface. The latter has a very poor treatment effect because the hydrogen atoms in Imide group had been inactivated intensively, which

derives from the conjugation effect among Imide group, Carbonyl group and Phenyl ring; as well as the steric hindrance effect of Phenyl ring.

In this article, a novel chemical graft reaction (hereinafter referred to "new approach") based on Friedel-Crafts Reaction, which is a very important electrophilic substitution reaction on Phenyl ring, was carried out to break through the shielding effect and large steric hindrance effect of Phenyl ring, just as the antenna was erected on the top of a mountain. Then the surface characteristics of Aramid fibers were evaluated by X-ray photoelectron spectroscopy (XPS), Scanning electron microscope (SEM), and Fourier infrared spectrum (FTIR). The crystalline state of fibers was determined by X-ray diffraction (XRD) instrument. The Aramid fiber surface wettability was measured too. The Single Fiber Pull-out (SPF) test was carried out to study the interfacial bonding strength.

EXPERIMENTAL

Instruments and equipments

An oil bath (TC-202, Shanghai Canny Precision Instrument, Shanghai, China) was used to control any sudden heat production and keep the reactor temperature at the set-point value. FTIR (Nicolet 8700, Thermo Fisher Scientific), XPS (ESCA PHI 1600, Physical Electronics), XRD (XRD-6000, shimadzu, Japan), and Wettability testing device (C20, Solon technology Science, Shanghai, China) were employed to evaluate the surface characteristics of Aramid fibers and SEM (S-3500H, Quasi-S Pte, Japan) was employed to observe the morphological change of the fibers treated. Wettability of Aramid fiber surface was determined by Dynamic contact angle analysis device (SB213; Keen, Beijing, China).

A single fiber embedding machine (SFP 04, Xi'an Jiao Tong University, China) was employed to prepare the specimens of Single fiber pull-out test. A single fiber pull-out test instrument (SFP 08, Xi'an Jiao Tong University, China) was employed to measure the pull-out force and evaluate the interfacial shear strength (IFSS) of Aramid fiber reinforced Epoxy matrix composites. A Universal materials test machine (Instron-2211, Instron Corporation) was employed to measure the tensile strength of Aramid fiber.

Materials

Aramid fibers used were Twaron fibers (average diameter 14.4 μm, density 1.45 g/cm^{-3}, tensile strength 2.8 GPa, elasticity modulus 140 GPa), which were purchased from Teijin Aramid B.V., Netherlands. The fiber surface modification treatment reagent (Epoxy chloropropane, technical grade), and the catalyst (Anhydrous aluminium chloride, technical grade) were provided by Xi'an organic chemical plant, China. The adhesive (Ethoxyline E-51, technical grade) and the curing agent (Triethylenetetramine, abbreviation "TETA," technical grade) were provided by Shanghai Xing-Guang Chemical Plant, China.

Fiber surface modification treatment

Aramid fibers were cleaned successively by Soxhlet extraction with Dichloroethane and Acetone, and then the cleaned fibers were dried at 100°C for 3 h in a vacuum drying oven before being used. Subsequently, the fibers were treated via the two-step graft reaction based on Friedel-Crafts Reaction. The specific modification treatment steps are as follows:

The three-mouth flask, into which Aramid fibers and excessive Epoxy chloropropane were put, was warmed to 115°C (the boiling point of Epoxy chloropropane) for a given time in an oil bath. The reasons, why the reaction temperature was set to such a high level, are that: (1) a stronger reaction condition is required by Friedel-Crafts Reaction occurring in the molecule chain of Aramid polymer[28]; (2) the vibration of the whole reaction system can take the place of the agitation effect at the boiling point of Epoxy chloropropane, otherwise, the fibers will not contact with the modification treatment reagent enough to occur the sufficient reactions because the fibers will entwine the stirrer. At the same time, a condensate reflux device is needed by the flask to avoid Epoxy chloropropane vaporizing too fast to obtain a satisfied treatment result. During the modification treatment, the excess catalyst was added into the flask in batches to avoid reacting too tempestuously. Especially, the fibers and modification treatment reagent must be dried rigorously before being used, because the catalyst will be inactivated even if there is only a small amount of water. Aramid fibers treated were taken out from the flask and cleaned continuously by Soxhlet extraction with Acetone. Then the fibers were put into the sodium hydroxide solution at 80°C for 2 h. At last, Aramid fibers were washed via the distilled water repeatedly and dried at 100°C for 3 h in a vacuum drying oven.

Tensile strength and interfacial bonding strength test

The tensile strengths of Aramid fibers with and without the modification treatment were measured via Universal materials test machine at a constant speed of 10 mm/min, and the strength value (σ_b/MPa) was calculated according to eq. (1):

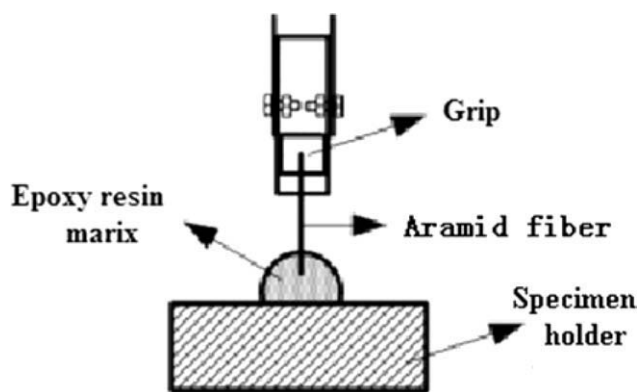$$\sigma_b = \frac{4F_p}{\pi D^2} \tag{1}$$

Figure 1 Single fiber pull-out test model.

where F_p is the maximal tensile fracture force in kilogram; D is the mean diameter of Twaron Aramid fibers in centimeter, and its value is about 14.4×10^{-4} cm. Each experiment is carried out five times, and each data entry was the average of five specimens.

According to ASTM D 3379-75, the interfacial bonding strength of Aramid fibers reinforced Epoxy matrix composites was evaluated via Single fiber pull-out test instrument at a constant speed of 5 mm/min. The specimen for Single fiber pull-out test is a few millimeters long fiber, which is partly embedded at one end in Epoxy resin and is orientated perpendicular to the resin surface (shown in the Fig. 1).

For the preparation of SPF test specimens, the specific procedure is as follows: Firstly, a small amount of Epoxy resin matrix was dropped on a metal board surface. And the resin matrix was made of Epoxy resin E-51 and TETA as the curing agent, which were mixed at the ratio of 100 : 5 by Mass share, respectively. When the matrix droplet forms a steady hemisphere, one end of a single Aramid fiber of a definite length is inserted into the matrix droplet, and the inserted length is about 0.2 cm. Secondly, the fiber is pulled out of the matrix droplet vertically and slowly until the inserted depth reaches the standard required, that is less than 0.1 cm. The whole pull-out procedure is controlled by a special embedding machine with an optical microscope, and the free length of Aramid fiber out of the droplet of Epoxy resin matrix can be measured by a precision scale of the optical microscope. Accordingly the embedded depth of Aramid fiber can be calculated according to eq. (2):

$$L = L_1 - L_2 \qquad (2)$$

where L is the embedded depth of Aramid fiber in the Epoxy resin matrix droplet; L_1 is the raw length of Aramid fiber; L_2 is the free length of Aramid fiber out of the droplet of Epoxy resin matrix.

Finally, SPF test specimens are cured at 30°C for 24 h. It must be emphasized that due to the flow of the matrix droplet caused by its weight and shrinkage of the matrix droplet during cooling and curing respectively, the exact embedded depth ought to be the depth value after the curing procedure has finished.

The common interpretation of such experiment is to calculate the interfacial shear strength (τ) between the fiber and resin matrix according to eq. (3):

$$\tau = \frac{F}{\pi D L} \qquad (3)$$

where F is the maximal pull-out force of Aramid fiber from the resin matrix in kilogram; D is the mean diameter of Twaron Aramid fiber in centimeter, and its value is about 14.4×10^{-4} cm; L is the depth of Aramid fiber embedded in the resin matrix in centimeter, and for all the experiments in this study, the embedded depth of Aramid fiber monofilament must be less than 0.1 cm to pull out the fiber rather than making fiber fracture.[29] Moreover, it is possible for this condition to get a nearly equal stress distribution around the fiber/resin matrix interface. Each data entry was the average of at least 50 or more specimens, and the standard deviation of these data must be less 5%.

XRD test of Aramid fibers

The crystalline states of Aramid fibers surface with and without the modification treatment were determined via XRD instrument. The preparation process of the specimens used for XRD test is as follows:

Aramid fibers with the adequate length were homogeneously laid on the special aluminum plate, and then the two ends of the fibers were fixed on the aluminum frame with the double-faced adhesive tape.

The test condition was that Cu Kα-radiation, graphite crystal as the monochromator, wavelength $\lambda = 1.5418 \times 10^{-10}$ m, tube voltage 40 kV, current 40 mA, sequential scanning counting mode and diffraction angle (2θ) range 10 to 90°. The standards employed were DS 1°, SS 1°, and RS 0.3 mm.

Surface element analysis of Aramid fibers

XPS is a very useful approach to the determination of the chemical composition and functional groups of the fiber surface, and the testing depth is about 5 nm. The surface composition, as measured by XPS, can be understood easily and related to the fibers.

The Aramid fibers were cut into a certain length and affixed on a sheet metal for testing. The changes in the proportions of the elements such as C and O

on the surface of Aramid fibers were analyzed according to GB/T 19,500–2004. XPS analysis was performed by ESCA PHI 1600, which was equipped with Mg Kα (1253.6 eV) Mono X-ray source. The test conditions were a pressure range of 10^{-8} to 10^{-9} Torr power of 150 W and electric pressure of 15 kV.

Surface functional groups analysis of Aramid fibers

FTIR was also carried out to analyze and verify whether the anticipant functional groups had been grafted on Aramid fiber surface in this article.

Because of the remnants of the surface modification treatment reagent will disturb us to distinguish the experiment result, Aramid fibers treated must be cleaned continuously by Soxhlet extraction with Acetone before testing. Moreover, owing to the high water absorption of Aramid fibers, the specimens must be dried sufficiently to avoid the disturbance of the wider association belt of Water. On the other hand, the fibers must be finely cut into segments, whose length is less than 1 mm, to avoid the interference and reflection effect of Infrared light wave by the fibers before being mixed with KBr.

Observation of Aramid fiber surface morphology

SEM is usually performed to observe the fiber surface and fiber fracture micromorphology. It is well-known that Aramid fibers possess a poor conductivity,[1–3] thus the specimens were fixed on the aluminum plate via a conducting adhesive and degassed sputter coated with the gold for 5 min to provide the conductivity for the impinging electrons. Subsequently, a thin layer of gold (about 10 nm), was coated at the fibers surface. SEM employed a field emission gun. The typical values of the voltage and operation distance were 20 kV and 7 to 10 mm, respectively. SEM was successfully employed to obtain morphology details of the Aramid fibers up to micron scale resolution in this article.

Surface free energy measurement of Aramid fibers

This investigation was carried out via Dynamic capillary method. A bundle of Aramid fibers was inserted into a polyethylene tube (diameter 2 mm, length 50 mm), and the fiber specimen of 1 mm length was left outside the tube. One end of Aramid fiber bundle was suspended on the hook of a precision balance, and then another end of the Aramid fiber bundle was impregnated into the liquid. As soon as the end of the bundle impregnated the liquid, the wetting mass and time were recorded by the special computer respectively. The testing process went on until the liquid was no longer adsorbed by Aramid fiber bundle. The

TABLE I
Surface Free Energy of the Liquids at Room Temperature

	Surface tension (dyn cm^{-1})		
	γ_l^T	γ_l^d	γ_l^p
Second vaporized water	72.8	21.8	51.0
Normal octane	21.8	21.8	0

second vaporized water and the normal octane were chosen. Then Contact angle between the wetting liquid and Aramid fibers can be calculated according to eqs. (4) and (5)[30]:

$$\Delta\gamma = \frac{0.064 H^2 \rho_f \eta}{DK^2 W_f \rho^2} \times \frac{(1-\varepsilon)^2}{\varepsilon^3} \times \frac{1}{V_T} \times \frac{m^2}{t} \qquad (4)$$

$$\cos\theta = \frac{\Delta\gamma}{\gamma_l} \qquad (5)$$

where $\Delta\gamma$ is the difference of Aramid fiber free energy between the dry and the wet unit surface; H is the height of fiber bundle; ρ_f is the density of Aramid fibers; η is the viscosity of the wetting liquid; ε is the void volume fraction in the tube (between 0.48 and 0.52); m is the mass of the wetting liquid adsorbed by the fibers at the immersion equilibrium point; D is the diameter of Aramid fiber, and its value is about 14.4×10^{-4} cm; K is the hydraulic constant; W_f is the weight of the fiber bundle before immersion; ρ is the density of the wetting liquid; V_T is the total volume of the body system; t is the time of the immersion equilibrium point; θ is Dynamic contact angle between the fibers and the immersion liquid; γ_t is the surface tension of the wetting liquid. Dynamic contact angle is used to calculate the fiber surface free energy according to Kealble eqs. (6) and (7).[31]

$$\gamma_l^T(1 + \cos\theta) = 2\left(\gamma_l^p \gamma_f^p\right)^{1/2} + 2\left(\gamma_l^d \gamma_f^d\right)^{1/2} \qquad (6)$$

$$\gamma_f^T = \gamma_f^d + \gamma_f^p \qquad (7)$$

where γ_f^T, γ_f^d, and γ_f^p are the total surface free energy, dispersive component energy, and polar component energy of the fibers, respectively; γ_l^T, γ_l^d, and γ_l^p are the surface tension of an immersion liquid and its dispersive and polar component, respectively. The surface free energy values of the liquids used in experiments are listed in Table I.[32] The value of test is more than 20 successful measurements.

RESULTS AND DISCUSSION

Surface modification theory

The traditional chemical approach has a good idea, namely it tries to provide the guarantee for the

stability of the modification results via the chemical bonds, which is the strongest interaction force among the molecules or atoms. So the chemical approach is just what we want.

Whereas the traditional chemical approach has a very poor modification result at the same time, because the so-called active hydrogen atoms of Imide groups were elected as the active site of the graft reaction, but these hydrogen atoms had been inactivated intensively due to the conjugation effect among Imide groups, Carbonyl group and Phenyl ring; as well as the steric hindrance effect of Phenyl ring.

In view of the aforementioned reasons, Phenyl rings were elected as the goal and active site of the graft reaction in this work because there is not any strong inactivation here. And then Friedel-Crafts Reaction, which is a very important Electrophilic substitution reaction on Phenyl ring, was elected as the base of the surface modification to break through the shielding effect and large steric hindrance effect

of Phenyl rings, just as the antenna was erected on the top of a mountain.

After a lot of investigations, Epoxy chloropropane was finally elected as the surface modification treatment reagent of Aramid fiber in this work, and an exciting breakthrough was obtained at the aspect of the modification results. Because Epoxy chloropropane only possesses two reaction active sites including the chlorine atom and Epoxy group; moreover, the reaction activity of Phenyl ring between two Carbonyl groups on Aramid polymer molecule chain is very low, so the possible mechanisms under the given reaction condition are as follows:

1. Epoxy lateral chain is directly grafted onto Phenyl rings of the Aramid polymer molecule chain via Friedel-Crafts Reaction under the condition of the catalyst and heating.[33] This mechanism is the most anticipant for us because it is very simple and convenient.


(Minor)   (Majority)
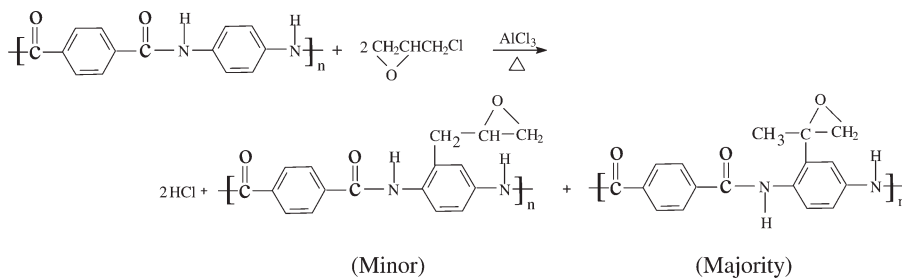
2. The lateral chain of β-halogenated alcohol is grafted onto Phenyl rings of Aramid polymer
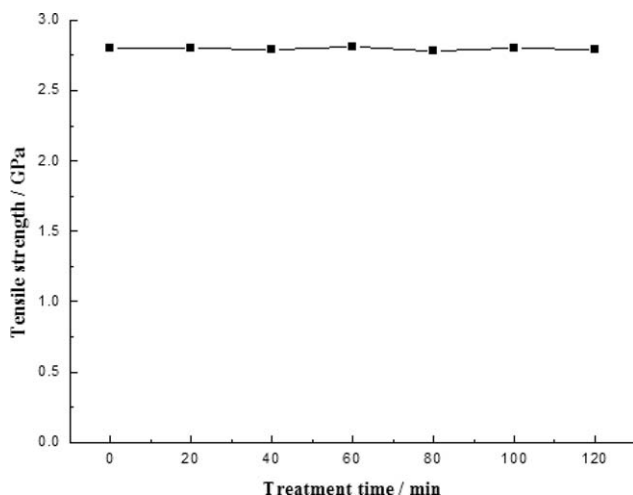
molecule chain via Friedel-Crafts Reaction under the condition of the catalyst and heating.[34]
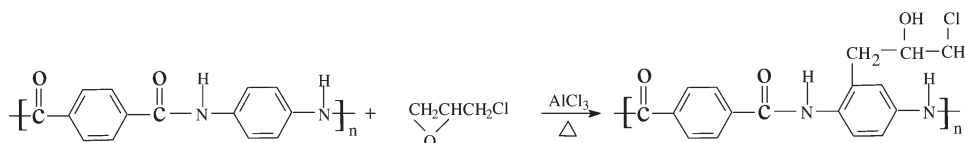
In such a case, Epoxidation can take place on the lateral chain of the β-halogenated alcohol on Aramid

polymer molecule chain under the condition of the sodium hydroxide solution.[35]
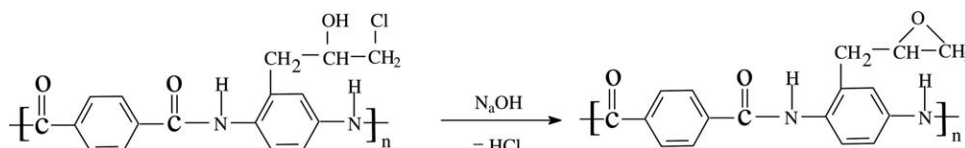
Figure 2 Tensile strength of Aramid single fiber at various treatment time.

Specially, it is worth being mentioned that no matter which kinds of possible mechanism, (1) Aramid fiber surface wettability can be enhanced remarkably via introducing the oxygen containing functional groups; (2) because both the resin and Aramid fiber surfaces possess the same Epoxy group, it is very easy for Epoxy resin matrix to impregnate Aramid fibers sufficiently according to Similar Compatibility principle[36]; (3) Friedel-Crafts Reaction will occur at multipoints on Phenyl ring one after the other. Although this characteristic was always criticized previously by the person engaged in the organic synthesis because the single substitution products can not be obtained easily, it is just what we want because the more substitution reaction points Phenyl ring possesses, the more Epoxy groups the fiber surface possesses. Thus this characteristic is just the most outstanding advantage of the new approach.

Single fiber tensile strength analysis

The change tendency of Aramid single fiber tensile strength with the increasing modification treatment time was investigated and recorded in Figure 2. The result shows that any obvious reduction in tensile strength was not observed at the treatment time range of less than or equal to 2 h. In fact the decreasing value can be neglected because it is wholly within the range of the experiment error. It is obvious that the new approach hardly have any negative influence, such as corrosion, on the tensile strength of the single fiber and does not badly impair the tensile property of Aramid fibers in substance, or the damage degree of the new approach is very low. It is the optimal result anticipated. Accordingly, this result offers the best supporting to Aramid fibers surface modification with Friedel-Crafts Reaction.
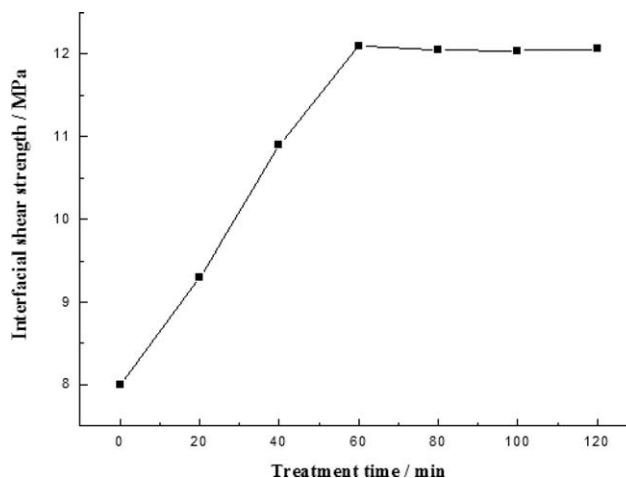
Interfacial property of Aramid/Epoxy composites

The effect of the new approach on the interfacial property of Aramid/Epoxy composites was investigated via SFP test. The effect of the modification treatment time on the interfacial shear strength of Aramid single fiber/Epoxy composites is shown in Figure 3. The result shows that all the interfacial shear strengths of the composites, whose fibers were treated by the new approach, were improved to some extent. The effect tendency of the treatment time on the interfacial shear strength is that the value was rising at first and then keeping invariant on the whole. In fact, the decreasing value can be neglected because it is wholly within the range of the experiment error. This indicates that the new approach is a very efficient modification treatment method in improving fibers/matrix bonding strength. The value of the interfacial shear strength reached the maximum at 1 h, namely, the value are 12.1 MPa, and there are 50% improvement compared with the untreated specimen, whose interfacial shear strength value was 8.0 MPa. So the most optimal treatment time was 1 h, and all possible reaction active sites on Phenyl ring had almost been grafted under this reaction condition.

Accordingly, except the special declaration, all modification treatment time of Aramid fibers in the subsequent experiments are 1 h, because the modification result of Aramid fibers with 1 h treatment is the best.

XRD analysis

The Aramid fibers with and without the modification treatment were elected to analyze the effect of the new approach on the crystal properties of the fiber surface via XRD instrument.

Figure 3 Interfacial shear strength of Aramid single fiber/epoxy composites untreated and treated with various time.
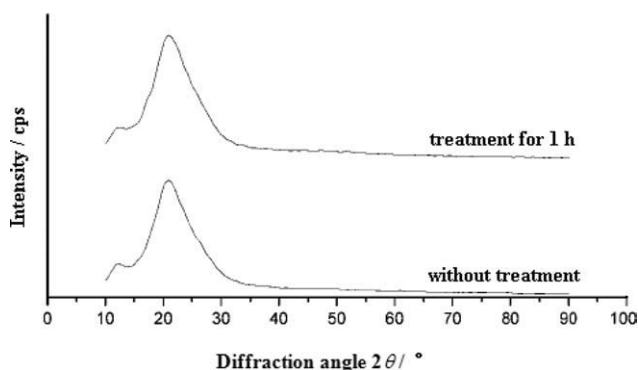
Figure 4 XRD spectra of Aramid fibers with and without treatment.

Figure 4 shows that there is no distinct variety from XRD spectra, which illuminated the new approach did not change the crystal type.

Figure 5 shows the crystallinity of the Aramid fibers before and after the modification treatment. It illustrated that the crystallinity of Aramid fibers after the treatment was decreased slightly, and the reason is that the graft reaction occurred on the lateral chain of Aramid polymer molecule, thus the crystal structure regularity of Aramid fiber surface was destroyed slightly, accordingly, the crystallinity changed correspondingly. These results offered another credible experiment proof for the occurrence of the graft reaction based on Friedel-Crafts Reaction.
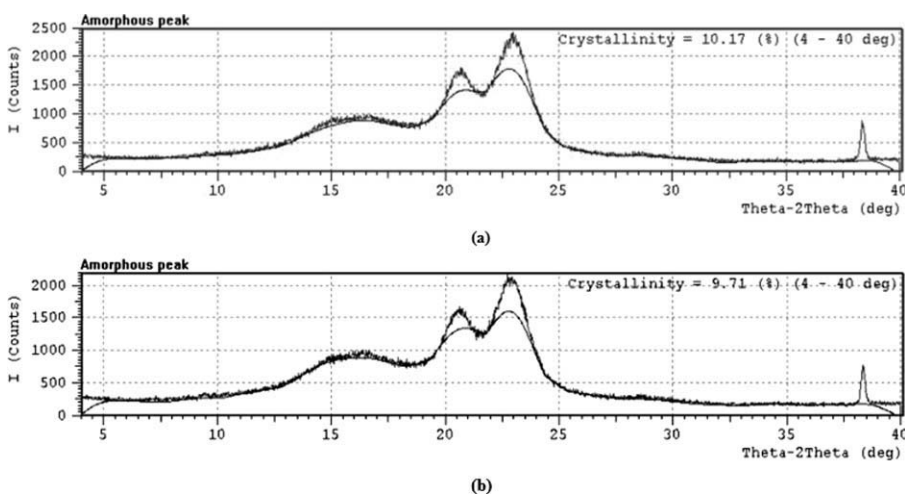
SEM analysis

The surface SEM images of Aramid fiber untreated and treated are showed in Figure 6, which shows that some changes in the roughness have been observed on the surface of Aramid fibers after the modification treatment, but these changes appeared as the tiny bulge rather than obvious groove which

derives from etching effect. So these changes can not be regarded as the result of etching absolutely, because this morphology is distinct from that of Aramid fibers treated by traditional chemical methods.[37] Moreover, the intrinsic strength of Aramid fiber did not decrease (according to the results from the tensile strength of Aramid single fiber section). This result indicates that the new approach would not etch the physical structure of Aramid fiber surface as strongly as other traditional chemical modification treatments. On the other hand, the rougher surface of Aramid fibers is beneficial to improve the adhesion between the fiber and matrix, and improve the mechanical performance of the fiber/matrix composites. It is well known that the adhesion of the treated fibers to other materials is improved with the increases in the surface roughness, surface area for bonding and mechanical interlocking.[38]

The SEM images of the interface layer between various Aramid fibers and Epoxy resin are shown in Figure 7.

Figure 7(a) shows that the wettability between the fiber surface and the resin matrix was so bad that a homogeneous interface layer could not be formed between the untreated fiber and resin matrix. This phenomenon derives from the surface chemical inertness of the untreated fibers, relative smoothness and lack of the polar functional groups in the repeat units of Aramid polymer molecule chain. On the contrary, Figure 7(b) shows that a homogeneous interface layer might be formed between the treated fiber surface and the epoxy resin.

All these results indicate that some polar functional groups were introduced into the treated fiber surface, which could enhance the bond property between the fiber and resin matrix, and made the treated fibers combine with the resin matrix tightly.


Figure 5 Crystallinity of Aramid fibers before and after treatment: (a) Untreated Aramid fibers, (b) treated Aramid fibers.
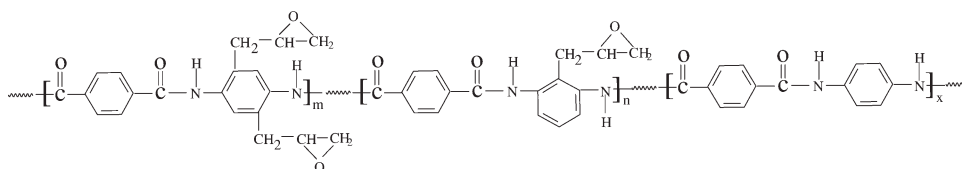
FTIR analysis

To investigate the possible change in the chemical structure of Aramid fibers treated via the new approach, FTIR spectroscopy measurements in the mid infrared region (4000–400 cm^{-1}) were performed, and the spectrum is given in Figure 8.

Figure 8(a) shows that after Aramid fibers had only been treated with Friedel-Crafts Reaction, the anticipated absorption peak of Epoxy group didn't appear, while the flexural vibration peaks of C—H on Phenyl ring appeared at 870 cm^{-1} clearly, which is the typical characteristic of 1,2,4,5-four substitutions on Phenyl ring; and the flexural vibration peaks of C—H on Phenyl ring appeared at 770 and 720 cm^{-1} clearly, which is the typical characteristic of 1,2,3-three substitutions on Phenyl ring. This result indicates the molecule structure of Twaron Aramid fiber is not as simple as the theory,[1–3] on the contrary, it ought to be as follows:
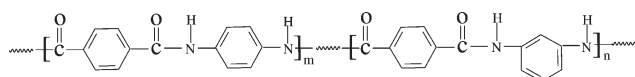
And the electrophilic substitution reaction did occur at on Phenyl rings of Aramid fiber molecule chains, and occurred at multi points on Phenyl ring one after the other.

Moreover, the absorption peak of the hydroxyl group appeared at 3440 cm^{-1}, which ought to derive from the graft reaction of Epoxy chloropropane. These results indicate that the Friedel-Crafts Reaction didn't carry out according to the mechanism (1).

Figure 8(b) shows that after the second step modification treatment with sodium hydroxide solution, the two new absorption belts appeared at 1241 cm^{-1} and 1004 cm^{-1}, which is the typical characteristic of Epoxy functional group. These results indicate further that Friedel-Crafts Reaction just carried out according to the mechanism (2), thus Epoxy functional groups could be introduced into the molecule structure of Aramid fibers via Epoxidation on the β-halogenated alcohol lateral chain.

From the results obtained above, it can be concluded that there ought to be not only 1,2,3-three substitutions structure, but also 1,2,4,5-four substitutions structure and nonsubstitution structure on Aramid fiber molecule chain. Thus the molecule structure of Twaron Aramid fibers treated via the new approach is about as follows:

But it is a pity that the more exact molecule chain structure of Twaron Aramid can not be obtained up to the present time, because the procurement of the exact structure needs a base of the precision characterization via other delicate tool, for example Nuclear Magnetic Resonance (NMR). Whereas, it is very difficult for Aramid fibers to be characterized accurately, because as a polymer, the molecule structure of Aramid fiber is not as simple as that of the micromolecule organic compound, but complicated and polydispersity. Moreover, it is very difficult for Aramid fibers to be characterized via NMR, because as a solid material, Aramid fiber possesses the special physical structure and shape, and the characterization result is certain to be disturbed badly. So further and deeper work is needed to investigate the exact structure, for example the exact amount of Epoxy group introduced on Aramid polymer, and so on.

XPS analysis

XPS is a very useful technique in the determination of the chemical composition and functional groups of the fiber surface, and the testing depth is about 5 nm. The surface composition, as measured by XPS, can be understood easily and related to the fibers.

For Aramid fiber with 1 h treatment, a general survey of the surface atomic distribution of the interested elements for the specimens is given in Figure 9, which shows that the surface content of Carbon decreases after the surface modification treatment via the new approach, whereas the surface content of Oxygen was increased to 20.18%.

To make this work more solid, Oxygen contents of Aramid fibers surface at various treatment times are shown in Table II. It can be found that the effect tendency of the treatment time is that Oxygen content value was rising at first and then keeping invariant on the whole. This result indicates that the new
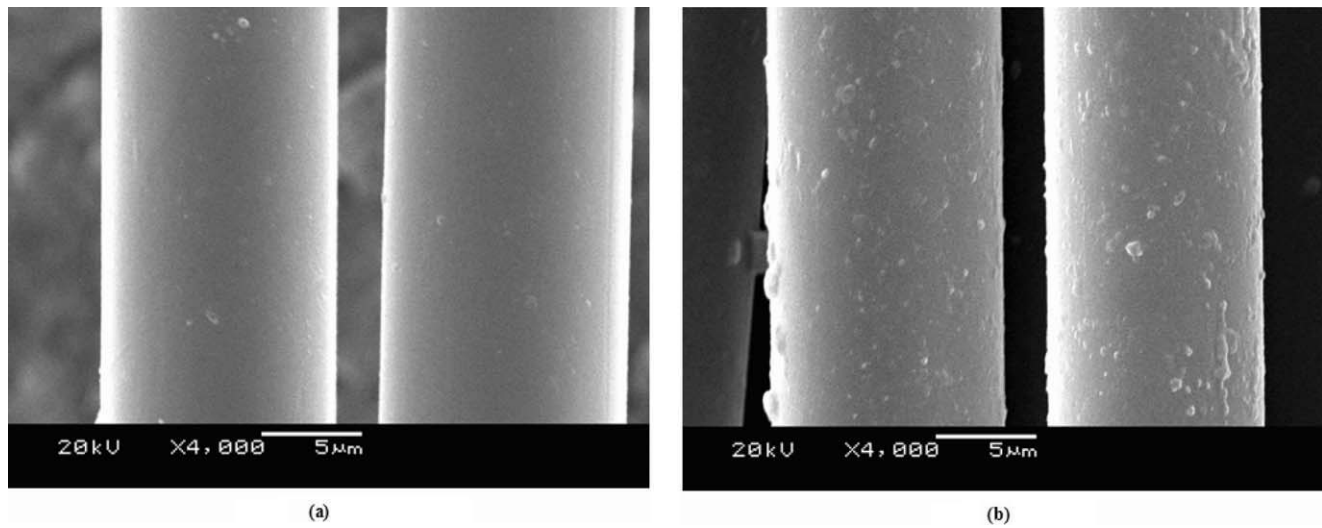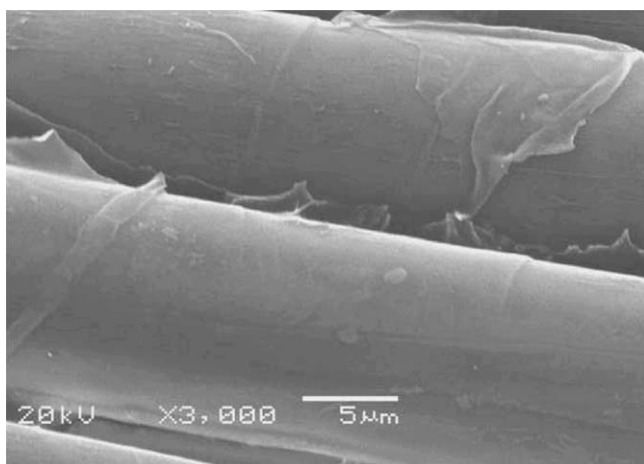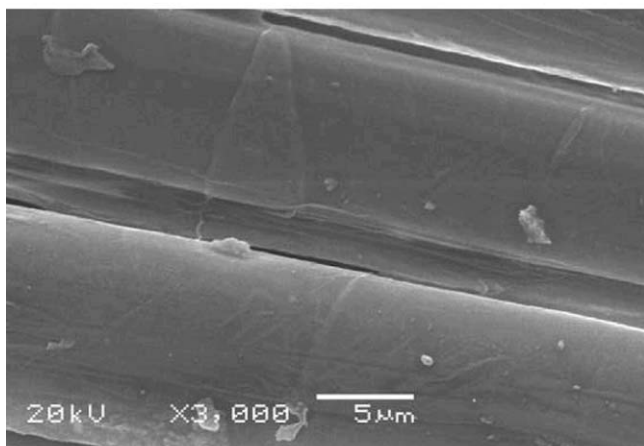
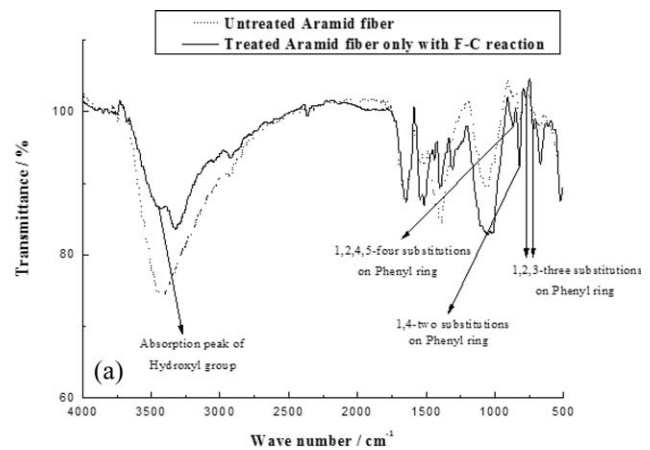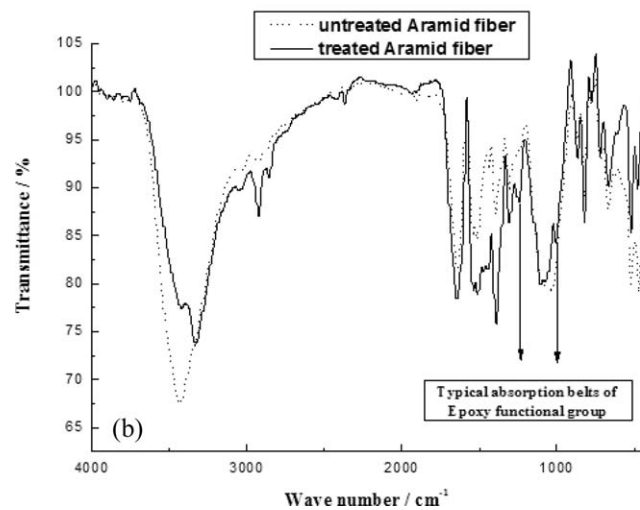**Figure 6** Surface SEM images of Aramid fiber untreated and treated: (a) Untreated fibers, (b) treated fibers.

Figure 7 The SEM images of the interface layer between different Aramid fibers and epoxy resin: (a) Untreated fibers, (b) treated fibers.

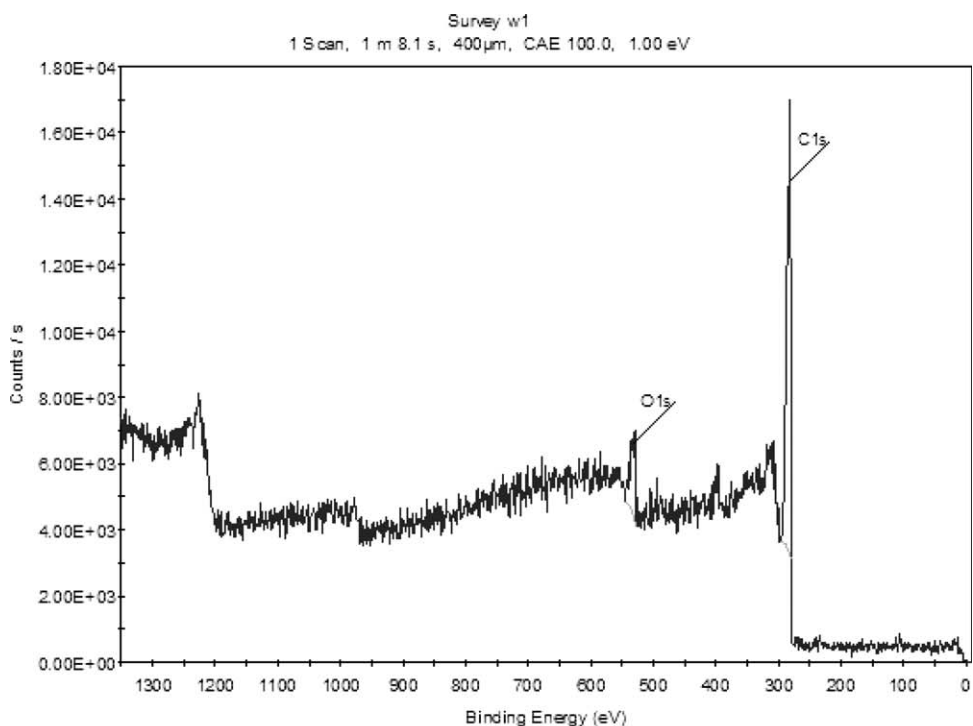**Figure 8** FTIR spectrum of Aramid fibers untreated and treated. (a) After treatment only with Friedel-Crafts Reaction. (b) After the second step treatment with sodium hydroxide solution.

Survey w1
1 Scan, 1 m 8.1 s, 400µm, CAE 100.0, 1.00 eV

Name	Start BE	Peak BE	End BE	FWHM eV	Area (P) CPS.eV	Area (N)	At. %
C1s	294.38	282.54	279.08	5.89	85042.73	1190.78	89.44
O1s	545.08	530.53	525.98	6.05	24671.47	140.56	10.56

(a)

Survey2
1 Scan, 1 m 8.1 s, 300µm, CAE 100.0, 1.00 eV
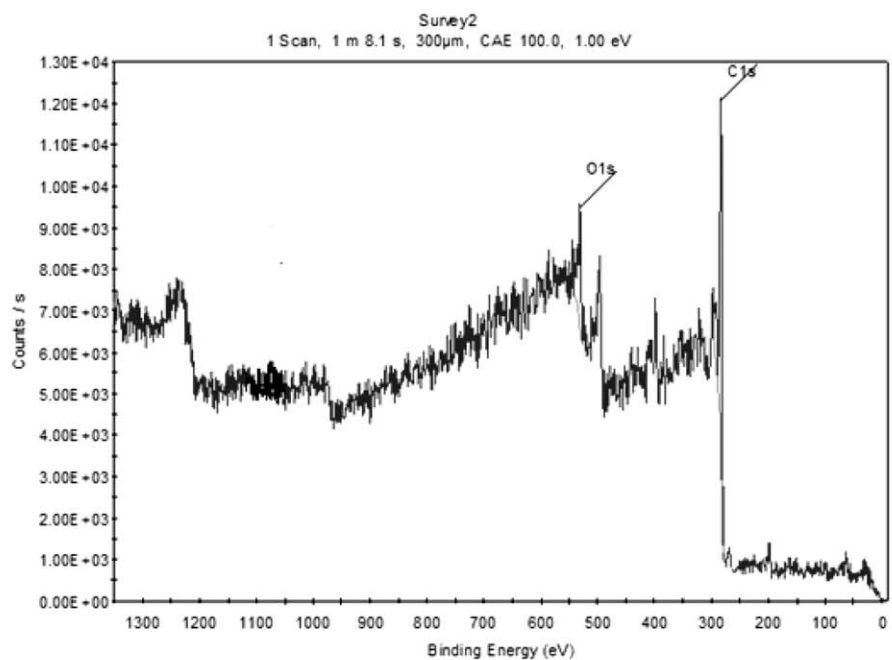
Name	Start BE	Peak BE	End BE	FWHM eV	Area (P) CPS.eV	Area (N)	At. %
C1s	295.98	283.08	279.08	3.65	41060.25	575.13	79.82
O1s	541.38	530.50	526.28	4.66	19656.95	111.99	20.18

(b)

Figure 9 X-ray photoelectron spectra. (a) Untreated fibers, (b) treated fibers.

TABLE II
Surface Elements Content of Aramid Fibers at Various Treatment Times

Treatment time (min)	Atomic distribution (%)	
	C	O
0	89.44	10.56
20	86.28	13.72
40	82.13	17.87
60	79.82	20.18
80	79.83	20.17
100	79.81	20.19
120	79.82	20.18

approach is a very efficient modification treatment method in improving Oxygen content on Aramid fiber surface, and the value of Oxygen content reached the maximum at 1 h.

It has been reported that the surface Oxygen content is crucial for the good wetting and bonding of resin.[39] The fibers treated via the new approach offered so better wetting and bonding of resin that the interfacial mechanical properties between fibers and the resin matrix were improved remarkably.

Fiber surface free energy

Contact angles of the fibers untreated and treated were measured. The results for the two liquids (the second vaporized water and normal octane) were determined by Dynamic contact angle analysis of Aramid fibers. The results obtained for the dispersive and polar components of the surface energy are shown in Table III. It can be found that the total surface energy of Aramid fibers after the modification treatment was enhanced by 31.5%, compared with the untreated fibers. Moreover, the dispersive component of the surface energy after the modification treatment was raised slightly due to the improvement of the fiber surface roughness, and the polar component after the modification treatment was increased from 12.05 to 16.99 by 41% due to introducing of the polar groups on Aramid fiber surface. Therefore, the wettability of the Aramid fibers was improved, and the contact angle of the fibers was decreased.

CONCLUSION

The effects of the new approach on Aramid fiber surface have been studied by means of several char-

TABLE III
Surface Free Energy of Aramid Fibers

	Surface free energy (mJ m^{-2})		
	γ_f^T	γ_f^d	γ_f^p
Untreated fiber	17.38	5.33	12.05
Treated fibers	22.86	5.87	16.99

acterization techniques. And then, the important conclusions obtained from the above investigation are summarized as follows:

1. The interfacial bonding strength of Aramid fiber reinforced Epoxy matrix composites excels that of those composites, which employed Aramid fibers untreated, up to 50%. This result is ascribed to the increasing of Epoxy-containing functional groups and rougher surface obtained by the surface modification. Thus, the new approach can further enhance the resin matrix wettability to the fibers and improve the surface free energy.
2. The intrinsic tensile strength of Aramid fiber keeps steady on the whole. The tensile strength of Aramid fiber decreased hardly. The reason is that the new approach does not essentially damage the mechanical strength of Aramid fibers, or the damage degree can be actually ignored. The new approach will not etch the physical structure of Aramid fiber surface as strongly as other traditional chemical treatment methods.

Briefly, the conclusion can be drawn from these experimental results that the new chemical treatment method based on Friedel-Crafts Reaction is an effective approach to Aramid fiber surface modification.

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