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Surface modification of aramid fibers with novel chemical approach

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Abstract *Friedel–Crafts Reaction* as a simple and convenient approach to the surface modification of aramid fiber was introduced in this paper. Epoxy chloropropane was chosen as the treatment reagent to modify aramid fibers surface via *Graft reaction*. After the modification, the interfacial properties of aramid/epoxy composites were investigated by the single fiber pull-out test (SFP), and the mechanical properties of aramid fibers were investigated by the tensile strength test. The results showed that the interfacial shear strength (IFSS) value of aramid/epoxy composites was enhanced by about 50%, and the tensile strength of aramid fibers had no obvious damage. The crystalline state of aramid fibers was determined by X-ray diffraction instrument (XRD), and the results showed that there were not any distinct crystal type varieties. The surface elements of aramid fibers were determined by X-ray photoelectron spectroscopy (XPS), the analysis of which showed that the oxygen/carbon ratio of aramid fiber surface increased obviously. The possible changes of the chemical structure of aramid fibers were investigated via Fourier transform infrared spectrum (FTIR), and the analysis of which showed that the epoxy functional groups were grafted into the molecule structure of aramid fibers. The surface morphology of aramid fibers was analyzed by Scanning electron microscope (SEM), and the SEM results showed that the physical structure of aramid fibers was not etched or damaged obviously. The surface energy of aramid fibers was investigated via the dynamic capillary method, and the results showed that the surface energy was enhanced by 31.5%, and then the wettability degree of

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aramid fiber surface was enhanced obviously too. All of the results indicated that this novel chemical modification approach not only can improve the interfacial bonding strength of aramid/epoxy composites remarkably, but also have no negative influence on the intrinsic tensile strength of aramid fibers.

Keywords Aramid fibers · Interfacial properties · Surface treatment · Friedel–Crafts Reaction

Introduction

Aramid fibers are characterized by low density, high heat resistance, high modulus and strength, and so on; thus, they are widely used as an excellent reinforcement material for the advanced polymer composites in aircraft, aerospace, and missile application [1–3].

It is well known that the excellent interfacial bonding strength is one of the necessary conditions to exert the integrated mechanical properties of aramid fiber reinforced composite fully. However, the surface of aramid fiber is so chemically inert and smooth, which derives from the lack of polar functional groups in aramid polymer molecule chain and the high crystallinity of aramid fiber surface, that the interfacial bonding strength between aramid fibers and the resin matrix are very poor [4–7]. Hence, the surface modification is essential to enhance the interfacial bonding strength of aramid fibers/the resin matrix composites. Various approaches of the surface modification for aramid fibers have been developed, such as physical treatments, chemical treatments, and the coalescence of the two approaches. The physical approach is mainly *Ultrasound* treatment, and the coalescence approach mainly contains *Ionizing radiation*, *Plasma* treatment and *Graft polymerization* [8–20]. Although the foregoing two experimentation approaches have been studied for a long time, they are still only fit to be carried out in laboratories due to the low operability, degradation effects, and the high cost. Whereas the chemical treatment approaches are convenient and suitable in batch processes for industrialization, the most important merit is the stability of the treatment effect due to the formation of stable chemical bonding effect between aramid fibers and the resin matrix via the chemical reactions [21–28].

On the other hand, the mechanisms of conventional chemical treatment approaches mainly contain (1) fiber surface etching via the nitration or the sulfonation reaction on *Phenyl ring*, and (2) introducing the active functional groups into the fiber surface molecule structure via the graft reaction. However, it is very hard for the former approach to control the surface etching 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 body. Moreover, the latter approach has a very poor treatment effect, because the so-called active hydrogen atoms of *Imide* groups were elected as the active sites of the graft reaction, but these hydrogen atoms had been inactivated intensively due to the conjugation effect among Imide group, *Carbonyl* group and Phenyl ring; as well as the steric hindrance effect of Phenyl ring.

Just as the antenna was erected on the top of a mountain, a novel chemical graft reaction (hereinafter referred to "the new approach") based on Friedel–Crafts Reaction, which is a very important *Electrophilic Substitution* reaction on Phenyl ring, was carried out to modify aramid fibers and break through the shielding effect and large steric hindrance effect of Phenyl ring in this study. After the modification, the interfacial bonding strength of aramid/epoxy composites were investigated via the single fiber pull-out tests (SFP), and the mechanical properties of aramid fibers were investigated via the tensile strength tests. The crystalline state of aramid fibers was determined by X-ray diffraction instrument (XRD). The surface elements of aramid fibers were determined by X-ray photoelectron spectroscopy (XPS). The possible changes of the chemical structure of aramid fibers were investigated by Fourier transform infrared spectrum (FTIR). The surface morphology of aramid fibers was analyzed by Scanning electron microscope (SEM). The surface energy of aramid fibers was investigated with the dynamic capillary method.

Experimental

Instruments and equipments

Oil bath (TC-202, Shanghai Precision Instrument Co., Ltd, Shanghai, China) was used to control any sudden heat production and keep the reactor temperature at set-point value.

Single fiber pull-out test instrument (YG-020A, Changzhou textile instrument corporation, China) was employed to measure the pull-out force and evaluate the interfacial shear strength (IFSS) of aramid/epoxy composites. A universal materials test machine (Instron-2211, Instron Corporation, USA) was employed to measure the tensile strength of aramid fiber. XRD (XRD-6000, shimadzu Ltd., Japan), XPS (ESCA PHI 1600, Physical Electronics, USA), and FTIR (Nicolet 8700, Thermo Fisher Scientific Inc., USA) were employed to evaluate the surface characteristics of aramid fibers. SEM (S-3500H, Quasi-S Pte Ltd., Japan) was employed to observe the morphology difference between the fibers with and without treatment. Aramid fiber surface energy was determined by Dynamic contact angle analysis device (SB213; Keen, Beijing, China).

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 treatment reagent (epoxy chloropropane, technical grade), and the catalyst (anhydrous aluminum chloride, technical grade) were provided by Xi'an organic chemical plant, China. The resin matrix (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 treatment

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

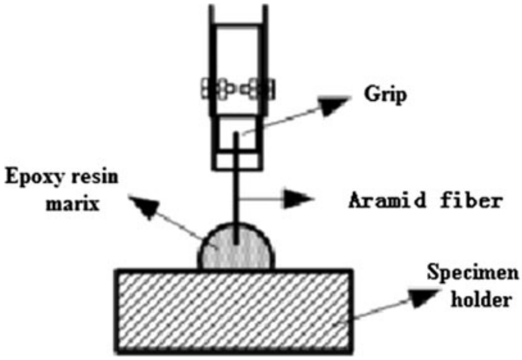
Aramid fibers and excessive epoxy chloropropane were put into a 3-mouth flask, and then the flask was warmed to 115 °C (the boiling point of epoxy chloropropane) in the oil bath. Subsequently, the modification reaction carried out at 115 °C for a given time, such as 20, 40, 60, 80, 100, and 120 min. The reasons, why the dose of epoxy chloropropane was excessive, are that: Friedel–Crafts Reaction is a reversible reaction, thus the excessive reactant is beneficial to the proceeding of the positive reaction. Moreover, the reasons, why the reaction temperature was set to such a high level, are that: (1) a stronger reaction condition is needed by Friedel–Crafts Reaction to break through the binding of the crystal lattice energy and meet the reaction activation energy; (2) the ebullition of the whole reaction system at the boiling point of epoxy chloropropane can produce an ideal vibration to replace the agitation effect, which makes aramid fibers entwine the stirrer and contact with the treatment reagent insufficiently. At the same time, a condensate reflux device is needed by the flask to avoid epoxy chloropropane vaporizing too fast to receive a satisfied modification result. During the modification treatment, the catalyst was added into the flask in batches to prevent the drastic reaction. Especially,the treatment reagent must be dried rigorously before being used, since even a small amount of water will make catalyst inactivation.

Aramid fibers with the first step treatment were taken out from the flask and cleaned continuously by Soxhlet extraction with Acetone, and then the fibers were put into the sodium hydroxide solution at 80 °C for 30 min. At last, Aramid fibers were washed via *Distilled water* repeatedly to remove the unreacted sodium hydroxide until the surface pH value of aramid fibers with treatment was *Neutrality*, and then aramid fibers were dried at 100 °C for 3 h in a vacuum drying oven.

Interfacial bonding strength and tensile strength test

The interfacial bonding strength of aramid/epoxy composites was evaluated via SFP instrument at a constant speed of 5 mm/min. The specimen for SFP was a few centimeters long fiber, whose one end was partly embedded in the resin matrix and orientated perpendicular to the resin surface (shown in the Fig. 1). In this study, the resin matrix was made of epoxy resin E-51 and TETA (curing agent), which were mixed at the ratio of 100:5 by mass share, and the corresponding curing conditions was as follows: 30 °C for 48 h. On a metal surface, a small amount of epoxy resin in the form of a hemisphere carried the vertically positioned fiber which is embedded by a special embedding machine [29]. For all the experiments in this study, the depth of aramid fiber monofilament, which was embedded in epoxy resin matrix, was <1 mm to pull out the fiber rather than make the fiber fracture. Moreover, it is possible for this condition to get a nearly equal stress distribution around the fiber/

Fig. 1 Single fiber pull-out test model



matrix interface [30]. The common interpretation of such experiment is to calculate the IFSS (τ) between the fiber and resin matrix according to Eq. 1:

$$\tau = \frac{F}{\pi DL} \tag{1}$$

where F is the maximal pull-out force of aramid fiber in kilogram; D is the mean diameter of Twaron aramid fiber in centimeter, with its value being about 14.4×10^{-4} cm; L is the depth of aramid fiber embedded in the resin matrix in centimeter, and L must be <1 mm. Each data entry was the average of at least 50 specimens, and the standard deviation of these data must be less than 5%.

According to ASTM D 3379-75, the tensile strengths of aramid fibers with and without the treatment were measured using the universal testing machine for materials at a constant speed of 10 mm/min, and the strength value (σ_b/MPa) was calculated according to Eq. 2:

$$\sigma_{\mathrm{b}} = \frac{4F_{\mathrm{p}}}{\pi D^2} \tag{2}$$

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

XRD test of aramid fibers

The surface crystalline states of aramid fibers with and without the treatment were determined by XRD instrument. The preparation process of the specimens used for XRD test is as follows: the adequate length aramid fibers were homogeneously laid on the special aluminum plate, and then the two ends of aramid fibers were fixed on the frame of the specific circle cavity with the double-faced adhesive tape.

The test conditions were Cu K_α-radiation, graphite crystal used 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°–90°. The standards employed were DS 1°, SS 1°, and RS 0.3 mm.

Surface element analysis of aramid fibers

X-ray photoelectron spectroscopy is a very useful approach 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.

Aramid fibers were cut into a certain length and affixed on a sheet metal for testing. The changes in the proportions of C and O on the surface of aramid fibers were analyzed according to GB/T 19500-2004. XPS analysis was performed by ESCA PHI 1600, which was equipped with Mg K_α (1253.6 eV) Mono X-Ray Source. The test conditions were a pressure range of 10^{-8}–10^{-9} Torr, power of 150 W, and electric pressure of 15 kV.

Surface functional groups analysis of aramid fibers

Fourier transform infrared spectrum (FTIR) was also carried out to analyze whether the anticipant functional groups had been grafted onto aramid fibers surface in this study. Owing to the high water absorption of aramid fibers, the specimens must be dried sufficiently to avoid the disturbance of water. Moreover, the fibers must be finely cut into segments (length is <1 mm) via a special cutting machine before being mixed with KBr, because it is so easy for *Infrared light wave* to be reflected by long fibers that the analysis sensitivity and precision will be decreased enormously.

Observations of fiber surface morphology

Scanning electron microscope was successfully employed to observe the micro-morphology details of aramid fiber surface and the epoxy resin coat on aramid fiber in this study. The specimens used for observing the surface wettability of aramid fibers were manufactured according to the following steps:

Aramid fibers with and without treatment were sufficiently impregnated into the epoxy resin for 5 min and taken out. Subsequently, aramid fibers resin-impregnated were cured at 30 °C for 48 h.

On the other hand, it is well known that aramid fibers possess a poor conductivity; therefore, the specimens were fixed on the aluminum plate via a conducting adhesive and degassed sputter coated with 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 surface of aramid fibers. SEM employed a field emission gun. The typical values of voltage and working distance range of operation were 20 kV and 7–10 mm, respectively.

Surface free energy measurement of aramid fibers

This investigation was carried out using the dynamic capillary method. A bundle of aramid fibers was inserted into a polyethylene tube (diameter 2 mm, length 50 mm), and the fibers of 1-mm length was left outside the tube. Aramid fibers bundle was suspended on the hook of a precision balance, and then the left end outside the polyethylene tube was impregnated into the liquid. As soon as the end of aramid fibers bundle impregnated the liquid, the wetting mass and time were recorded by the special computer. The testing process went on until the liquid was no longer adsorbed by aramid fibers bundle. The second vaporized water and normal octane were chosen. Then, the contact angle between wetting liquid and Aramid fibers can be calculated according to Eqs. 3 and 4 [31]:

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

$$\cos\theta = \frac{\Delta\gamma}{\gamma_l} \tag{4}$$

where $\Delta\gamma$ is the difference of aramid fiber free energy between dry and 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 point of immersion equilibrium; D is the diameter of Twaron fiber, with its value being 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 the dynamic contact angle between the fibers and the immersion liquid; and γ_l is the surface tension of the wetting liquid. The dynamic contact angle is used to calculate the fiber surface free energy according to *Kealble equations* 5 and 6 [32].

$$\gamma_l^T(1+\cos\theta) = 2\left(\gamma_l^p\gamma_f^p\right)^{1/2} + 2\left(\gamma_l^d\gamma_f^d\right)^{1/2} \tag{5}$$

$$\gamma_f^T = \gamma_f^d + \gamma_f^p \tag{6}$$

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 tensions 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 1 [33]. The value of test is based on more than 20 successful measurements.

Table 1 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

Results and discussion

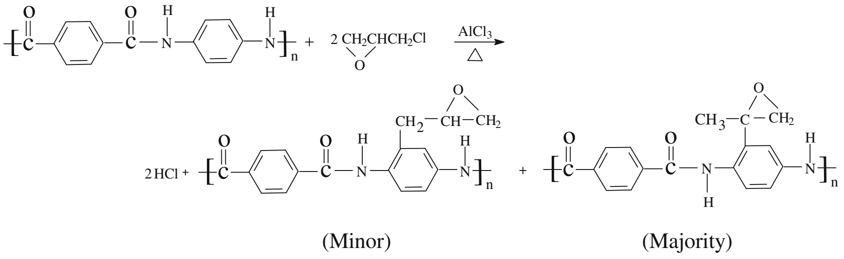
Surface treatment theory

The traditional chemical approach has a good idea, namely that it tries to provide the guarantee for the stability of the surface modification effect via the chemical bonds, which is the strongest interaction force among the molecules or atoms. Whereas the traditional chemical approach has a very poor modification result too, because the so-called active hydrogen atoms of Imide group were elected as the active sites of graft reaction, these hydrogen atoms had been inactivated intensively due to the conjugation effect among Imide group, Carbonyl group, and Phenyl ring—as well as the steric hindrance effect of Phenyl ring.

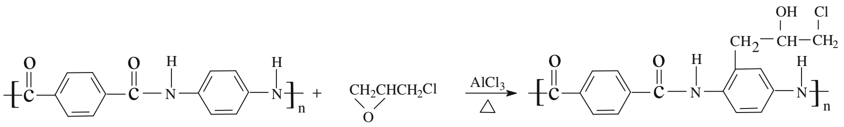
In view of the aforementioned reasons, Phenyl ring was elected as the active site of graft reaction in this study, because there is not any strong inactivation groups here, and then Friedel–Crafts Reaction was elected as the base of the surface modification to break through the shielding effect and large steric hindrance effect of Phenyl ring.

On the other hand, there are two reaction active sites including *Chlorine* atom and epoxy group in the molecule structure of epoxy chloropropane, and so the possible reaction mechanisms are as follows:

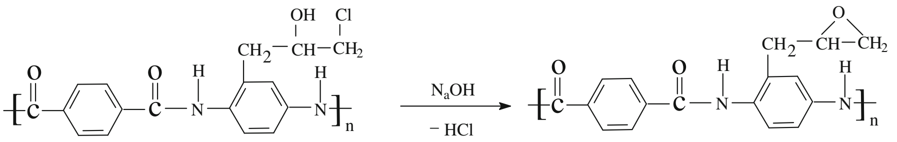
1. Epoxy lateral chain is directly grafted onto Phenyl ring of aramid polymer molecule chain via Friedel–Crafts Reaction under the condition of the catalyst and heating [34].



2. The lateral chain of β-halogenated alcohol is grafted onto Phenyl ring of the aramid polymer molecule chain via Friedel–Crafts Reaction under the condition of the catalyst and heating [35].



In such a case, the epoxidation can take place on the β-halogenated alcohol lateral chain of aramid polymer molecule under the condition of the sodium hydroxide solution.



Specially, it is worth mentioning that irrespective of the kind of possible mechanism, Friedel–Crafts Reaction will occur at multi points 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 cannot be obtained easily, it is just what we want because the more the substitution graft reaction points that Phenyl ring possesses, the more the epoxy groups that the aramid fiber surface possesses. Thus, this characteristic is just the most outstanding advantage of the new approach too.

Interfacial property of aramid/epoxy composites

The modification effect of the new approach on the interfacial bonding strength of aramid/epoxy composites was investigated via SFP test. Here, the IFSS of aramid single fiber/epoxy composites was employed to express the interfacial bonding strength, and the treatment time effect on the IFSS is shown in Fig. 2.

The result shows that all IFSSs of the composites were improved to some extent after the modification. The change tendency of the shear strength with the treatment time is that the shear strength value was rising at first and then remaining invariant on the whole. In fact, the decreasing value can be neglected because it is wholly within the range of experiment error. This result indicates that the new approach is a very efficient modification method in improving fiber–resin bonding strength. Moreover, the value of shear strength reached the maximum at 1 h, namely, 12.1 MPa, and

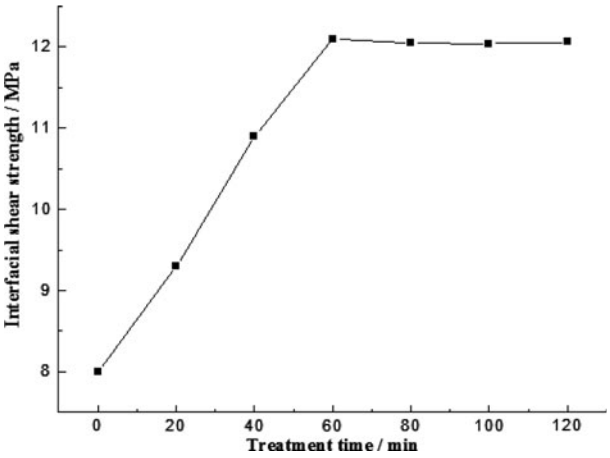


Fig. 2 Interfacial shear strength of aramid single fiber/epoxy composites after different treatment time. *Remark*: 0 min is referred to the untreated fibers in this paper

there is an improvement of about 50% compared with the specimen untreated, whose shear strength value was 8.0 MPa. Therefore, the optimal treatment time was 1 h. The results reveal that under this reaction condition, all possible reaction active sites on Phenyl ring had been utilized; thus, the optima interface bonding strength of aramid/epoxy composites could be obtained at 1-h treatment time.

The main reasons, why the bonding strength between the epoxy resin matrix and aramid fibers can be enhanced remarkably via this new approach, are that (1) it is very easy for the stable chemical bonding effects to be erected among the epoxy resin matrix, curing reagent and active epoxy groups on the lateral chain of aramid polymer molecule, so that aramid fibers are tightly linked with the epoxy resin matrix by the bridge role of the curing reagent; (2) aramid fiber surface wettability can be enhanced remarkably via grafting the oxygen-containing functional groups; (3) with both the resin matrix and aramid fibers possessing the same epoxy group, it is beneficial for the epoxy resin to impregnate aramid fibers sufficiently according to *Similar Compatibility principle*.

Single fiber tensile strength analysis

The change tendency of aramid single fiber tensile strength with the treatment time was investigated and recorded in Fig. 3.

The result shows that any obvious reduction in the tensile strength was not observed at the treatment time range of $\leq$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 had any negative influence, such as corrosion, on aramid fibers, and the tensile property of aramid fibers has not been impaired badly, or the damage degree of the new approach is very low. This result offers the best advantage in terms of aramid fibers' surface modification as a result of this new approach.

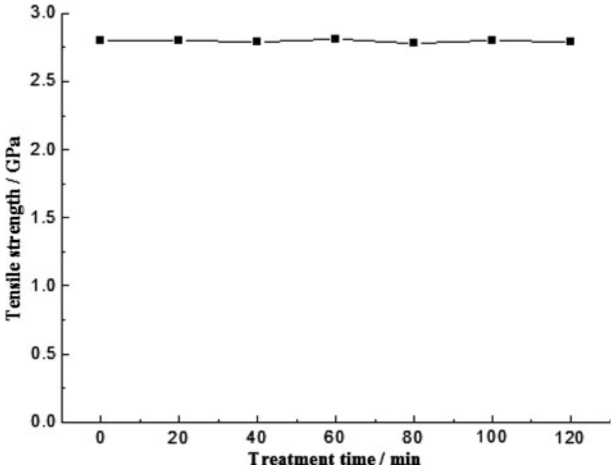


Fig. 3 Tensile strength of aramid single fiber after different treatment time. *Remarks*: (1) 0 min is referred to the untreated fibers in this paper, (2) the untreated aramid fiber had the tensile strength of 2.8 GPa

XRD analysis

Aramid fibers with and without treatment for 1 h (according to the results from the interfacial properties of aramid/epoxy composites section) were chosen to analyze the new approach effect on aramid fiber surface crystal properties via XRD instrument.

Figure 4 is XRD spectra of aramid fibers. It was shown that there is no distinct variety from among the XRD spectra, which illuminated the fact that the new approach did not change the crystal type. Because the special crystal structure is one of the main influence factors of aramid fibers intrinsic mechanical properties, this result offered another theoretic proof that the new approach did not destroy the material base of aramid fibers intrinsic mechanical properties, and then the intrinsic tensile strength of aramid fibers was not been impaired badly.

XPS analysis

X-ray photoelectron spectroscopy 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. A general survey of the surface atom distribution of the interested elements for the aramid fiber specimens is given in Fig. 5.

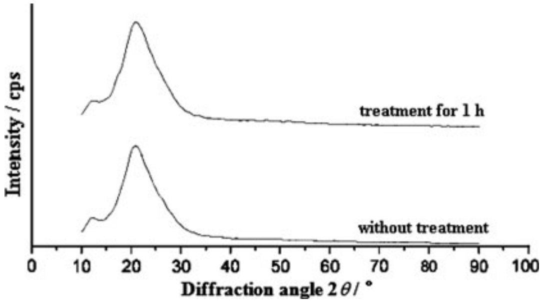
It was shown that the surface carbon content decreases after the surface modification, whereas the surface oxygen content was increased to 20.18%. It is well known that the surface oxygen content has been reported to be crucial for good wetting and bonding of resin [4–7]. Thus, aramid fibers with treatment offered such a good wetting and bonding of resin that the interfacial bonding strength between aramid fibers and the epoxy resin matrix was improved remarkably.

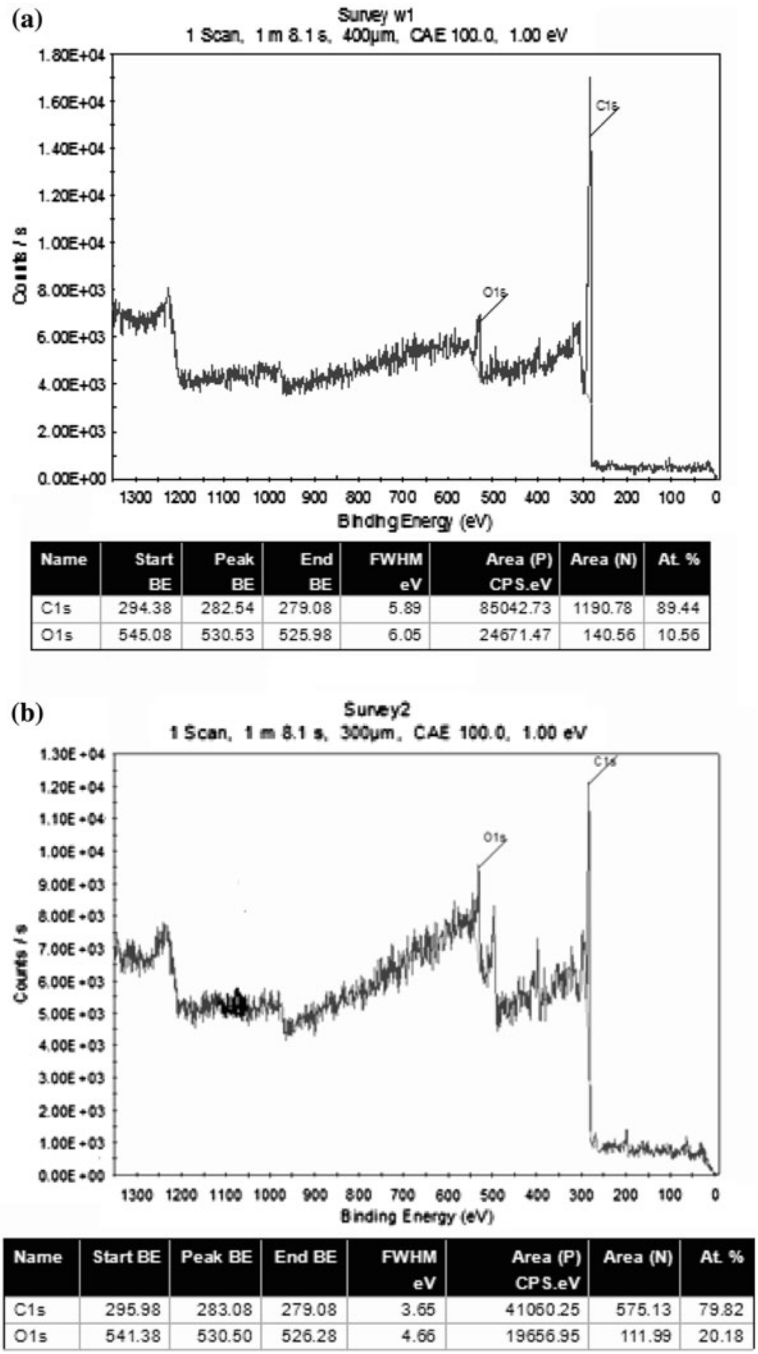
FTIR analysis

In order to investigate the possible change of the chemical structure of aramid fibers with treatment via the new approach, FTIR spectroscopy measurements in the mid infrared region (4,000–400 cm^{-1}) were performed in this study, and the results are given in Fig. 6.

It can be shown that if aramid fibers had only been treated with Friedel–Crafts Reaction, then the anticipated absorption peak of the epoxy group didn't appear, while

Fig. 4 XRD spectra of aramid fibers with and without treatment





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

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

Fig. 5 X-ray photoelectron spectra. **a** Untreated fibers and **b** treated fibers

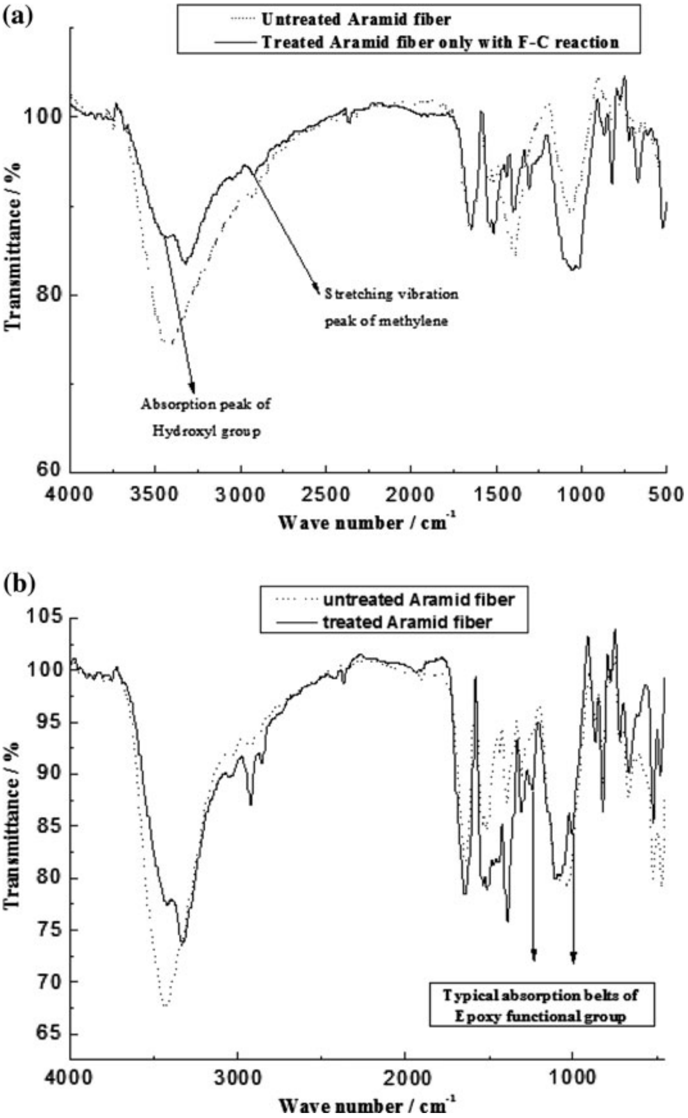


Fig. 6 FTIR spectrum of aramid fibers untreated and treated. **a** After treatment only with Friedel–Crafts Reaction and **b** after the second-step treatment with sodium hydroxide solution

the absorption peak of the hydroxyl group appeared at 3,440 cm^{-1}, and the stretching vibration peak of the methylene appeared at the range of 2,850–2,950 cm^{-1}, which ought to derive from the graft reaction of the epoxy chloropropane. These results indicate that the Friedel–Crafts Reaction did take place on the surface of aramid fiber, but the reaction did not carry out according to the aforementioned mechanism 1.

Moreover, after the second-step treatment with sodium hydroxide solution, the two new absorption belts appeared at 1,241 and 1,004 cm^{-1}, which depict the typical characteristic of the epoxy functional group. These results further indicate that Friedel–Crafts Reaction carried out according to the mechanism 2, thus the epoxy functional groups could be introduced into the molecule structure of aramid fibers via the epoxidation on the *β*-halogenated alcohol lateral chain.

SEM analysis

The surface morphologies of aramid fibers with and without treatment were analyzed by SEM, and SEM images are showed in Fig. 7.

It can be shown that any obvious etching groove didn't appear on the surface of aramid fibers with treatment. This result indicates that the new approach would not etch the physical structure of aramid fiber as strongly as other traditional chemical methods.

The wetting behavior of the epoxy resin on aramid fibers was also investigated via SEM in this study, and the result is shown in Fig. 8.

It can be shown that the epoxy resin coat shrank and fractured under its own interfacial tension due to the wettability was so bad that the surface of aramid fibers without treatment could not be covered with the epoxy resin evenly (Fig. 8a). This phenomenon derives from the surface chemical inertness of aramid fibers without

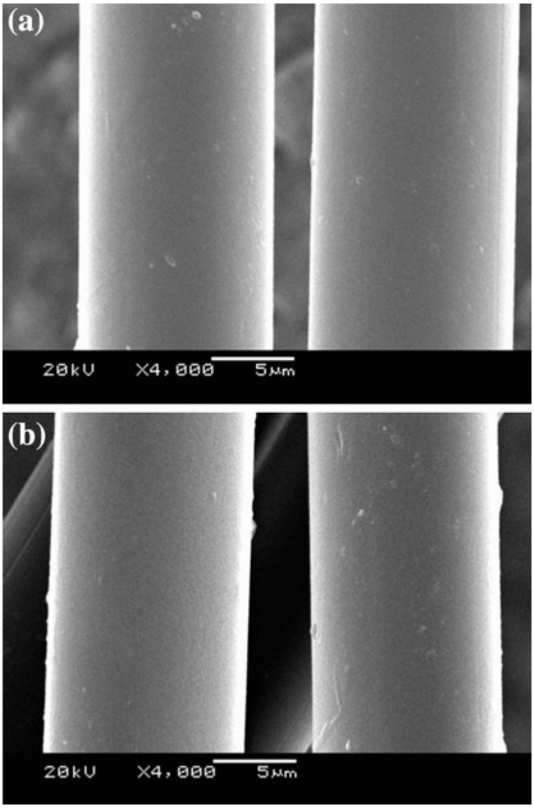


Fig. 7 Surface SEM images of aramid fiber. **a** Untreated fibers and **b** treated fibers

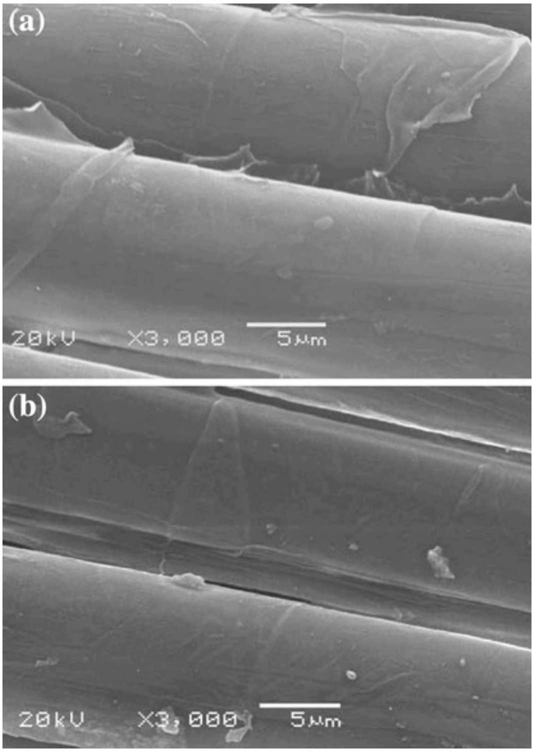


Fig. 8 SEM images of the epoxy resin coat on aramid fibers. **a** Untreated fibers and **b** treated fibers

treatment and lack of the polar functional groups in aramid polymer repeat units. On the contrary, aramid fibers with treatment did form a homogeneous epoxy resin coat (Fig. 8b). All these results indicate that some anticipate polar functional groups were introduced into the surface of aramid fiber with treatment, and the oxygen-containing content of aramid fibers surface was enhanced. Thus, the wettability of aramid fiber was improved, which can make aramid fibers treated combine with the epoxy resin matrix tightly.

Fiber surface free energy

The surface energies of aramid fibers with and without treatment were measured respectively, and the results obtained for the dispersive and polar components of the surface energy are shown in Table 2.

It can be found that the total surface free energy of the fibers and the polar component were increased after the modification, and the total surface energy of aramid fibers was enhanced by 31.5%, and the polar component was increased from 12.051 to 17.530 by 45.5%, which ought to derive from the increase of the surface polar group content for aramid fibers with treatment. At the same time, the dispersive component of the surface energy kept invariant on the whole after the modification, because no obvious change of aramid fiber surface roughness did take

Table 2 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	5.329	12.051
Treated fibers	22.86	5.330	17.530

place. This result offered another theoretic proof that the wettability of aramid fibers was improved from another study angle.

Conclusion

The effects of the new approach on aramid fiber surface have been studied by means of several characterization techniques in this article. As a consequence, the important conclusions obtained from the above investigation are summarized as follows:

(1) The oxygen-containing functional groups on the surface of aramid fibers increased after the modification; thus, the new approach further enhanced the wettability of aramid fibers. Moreover, the interfacial bonding strength of treated aramid fiber/epoxy resin matrix composites exceeded that of untreated aramid fiber/epoxy resin matrix composites by up to 50%. This result was ascribed to the formation of the stable chemical bonding effects between the curing reagent and active epoxy groups on the lateral chain of aramid polymer molecule.

(2) Aramid fibers intrinsic tensile strength kept steady on the whole, because the new approach did not damage the crystal structure of aramid fibers essentially, or the damage degree could be actually ignored. Moreover, the new approach would not etch the physical structure of aramid fiber surface as strongly as other traditional chemical treatment methods.

In a word, the conclusion can be drawn from the experimental results that the new approach based on Friedel–Crafts Reaction is an effective approach to aramid fiber surface modification.

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