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Wettability of carbon fibers modified by acrylic acid and interface properties of carbon fiber/epoxy

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Abstract

The oxidation–reduction and pre-irradiation induced methods were employed to study the effect of acrylic acid modification on the wetting and adsorption ability of carbon fiber (CF) in epoxy solution and the interfacial properties of CF/epoxy. Systematic experimental work was conducted to determine the surface topography, surface energy, surface chemical composition, absorbability and tensile strength of carbon fibers and interfacial adhesion of CF/epoxy before and after modification. The roughness, surface energy, amount of containing-oxygen functional groups and wetting ability were all found to increase significantly after modifications. The tensile strength of carbon fibers was improved marginally by γ-ray pre-irradiation while was decreased little by oxidation–reduction modification. Consequently, the surface modifications of carbon fibers via both oxidation–reduction and pre-irradiation led to an improvement (more than 15%) of the interlaminar shear strength of CF/epoxy composites. The mechanisms of interfacial improvement of modified CF/epoxy composites are proposed.
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Keywords: Carbon fibers; Wettability; Interface adhesion; Composites; Pre-irradiation

1. Introduction

Carbon fibers (CF) have a unique combination of outstanding mechanical, physical and chemical properties, such as high strength, high modulus and thermal resistance. Composites reinforced by carbon fibers have been used in aircraft and space structures [1,2]. However, as reinforcements for manufacturing high performance composite materials, carbon fibers have poor wettability and adsorption with most polymers because carbon fiber surface is non-polar and compound of highly crystallized graphitic basal planes with inert structures. As a result, the interfacial bonding strength between the fibers and polymer matrices is low, and good mechanical performance of composites cannot be ensured [3–5]. In a high performance composite material, chemical bond and physical interactions, i.e. van der Waals attraction and hydrogen bond force between the fiber reinforcement and the polymer matrix are required during processing.

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To improve the wettability of carbon fibers and interfacial adhesion of composites, several techniques for surface treatment on carbon fibers have been applied, including plasma [6,7], electrochemical oxidation [8,9], wet chemical [10,11] and thermal treatment [12–14]. These treatments on carbon fibers improved interfacial wetting and adhesion force of the final composites to some extent, but they had the drawbacks of high cost, high energy consumption and significant loss in single fiber strength. It is necessary to develop some convenient and inexpensive methods to increase the interfacial wettability and adhesion without sacrificing the mechanical properties of carbon fibers.

Acrylic acid, which is a vinyl monomer with a polar group, possesses some unique characteristics and the grafting of acrylic acid onto different types of natural polymers is reported to have wide range of application in various fields [15–18]. If the carboxyl functional group is introduced onto carbon fiber surface by grafting of acrylic acid, the polarity of fiber surface and interfacial wetting of CF/epoxy would be enhanced significantly. Irradiation-induced grafting is being extensively investigated as a new technique to alter surface properties of polymeric materials, such as films, fibers, powders and molded objects. An irradiation can induce chemical reactions at any temperature in the solid, liquid and gas phase without any catalyst [19–22]. Besides irradiation, the oxidation–reduction induced grafting is a convenient and environmentally-friendly modification method [23–25]. $KMnO_4$ reacts with H^+ generating MnO_2 which can induce the production of reactive free radicals and create the grafting reaction. The mechanical properties of the fiber are not significantly degraded. Therefore, an attempt has been made to graft acrylic acid onto carbon fiber surface by γ-ray pre-irradiation and oxidation–reduction of $KMnO_4/H_2SO_4$.

In this work, carbon fibers were modified by γ-ray pre-irradiation grafting and oxidation–reduction induced grafting. Basing on measuring and analyzing the scanning electron microscopy (SEM) images, surface energy and thermogravimetry (TG) results, the wetting and adsorption of carbon fibers modified by different methods on the epoxy matrices were characterized, and the composition changes of the fiber surface were analyzed by X-ray photoelectron spectrometry (XPS). The tensile strength of single fiber was investigated by the Weibull distribution. The effectiveness of improving the interfacial adhesion of composites was evaluated by interlaminar shear strength (ILSS) and SEM.

2. Experiments

2.1. Materials

The polyacrylonitrile-based high-strength carbon fibers with kidney-type cross-section investigated in current studies were supplied by Institute of Coal Chemistry.CAS. The linear mass is 0.0638 g/m, the equivalent diameter of fiber is 7.6 μm and a fiber bundle consists of 1×10^3 mono-filaments. The matrix system used was E-618 epoxy resin system consisting of diglycidyl ether of bisphenol-A, curing agent: phthalic anhydride and benzyl dimethylamine at 100, 70 and 1 parts by weight, respectively. The reactants, acrylic acid, sulfuric acid and potassium hypermanganate, obtained from Tianjin Chemical Co. were reagent-grade. The irradiation field was provided by Harbin Rui Pu Irradiation Technology Company of China. The intensity of Co^{60} γ-ray source was 1.5×10^4 Ci and the dose rate was 6.0×10^3 Gy/h.

Epoxy resin, curing agent and accelerating agent were mixed at 50 °C and the mixed epoxy resin was coated onto the unidirectional fiber bundle to manufacture prepreg in the manual way. And then the prepreg was paid unidirectionally into a mold at 60 °C. The mold was closed and operated according to the following technique. The prepreg was pressed and cured under 5 MPa pressure for 2 h at 90 °C, under 10 MPa pressure for 2 h at 120 °C and under 10 MPa pressure for 4 h at 160 °C by hot-press machine and we could obtain composites with fiber mass fraction of 64 (±1.5%).

2.2. Modification of CF and preparation of CF/epoxy specimen

The carbon fibers for pre-irradiation and oxidation–reduction were washed with acetone for 12 h, and then vacuum dried.

There are essentially two basic methods of simultaneous (co-irradiation) method and pre-irradiation method for radiation grafting. It has been shown that the latter is more proper for grafting of acrylic acid onto carbon fibers. In pre-irradiation, the carbon fibers are first exposed to γ-ray irradiation in vacuum or under inert atmosphere to generate radicals before being exposed to a monomer [26]. Firstly, carbon fibers (50 g) were put in plastic container and the container was filled with nitrogen. The tight container containing carbon fibers and nitrogen was exposed to γ-ray irradiation at the dose of 2×10^2 kGy. Then

the container was vacuumized and acrylic acid was inhaled into the container under negative pressure. After the reaction for 6 h, the treated carbon fibers were dried for 2 h at 120 °C.

For oxidation–reduction induced grafting, dry carbon fibers (approximately 50 g) were immersed in mixed solution containing 0.3 wt% of sulfuric acid and 10 wt% of acrylic acid. After the 10 min interval, the reaction was initiated by adding drop-wise 40 ml of $KMnO_4$ 0.118 g/ml at a rate such to keep the solution colourless through the addition. The mixed solution system was then heated at 80 °C for 3 h. The treated carbon fibers were taken out and carefully washed with warm water removing any remaining homopolymer, and subsequently they were vacuum dried at 120 °C for 2 h.

Untreated and modified carbon fibers (approximately 8 mg) were immersed in epoxy/acetone solution containing 10 wt% of epoxy resin for 1 h, respectively. Then the immersed carbon fibers were vacuum dried at 60 °C for 30 min to remove acetone. In result, the CF/epoxy specimens were prepared for differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA).

2.3. Measurements

The morphology of fiber surface and failure of fiber-reinforced composites were inspected by SEM (FEI SIRION 200). ESCA (Lab220i-XL) made in V.G. Scientific Company, UK and equipped with a Al Kα (1.25 keV) radiation source generated at 12 kV and 20 mA, was used to determine composition of fiber surface. DSC and TGA of CF/epoxy specimens were obtained using a STA449C thermal analyzer in an argon atmosphere at a heating rate 10 °C /min.

Carbon fiber surface energy and its dispersive component and polar component were determined by dynamic contact angle analysis. The contact angles of de-ionized water and diiodomethane on carbon fibers were measured by a capillary method using a wettability testing device (SB-312, Keen Co., Beijing, China). Before XPS and surface energy tests, untreated and modified carbon fibers were both extracted with acetone for 48 h in order to wash out impurities on their surface.

2.4. Mechanical testing

The influence of modification on the fiber tensile strength was determined by a single-fiber tensile test.

The fiber's cross-section was measured by an optical microscope. Single filament tensile was performed according to the ASTM standard, D3379–75. A mono-filament was separated from the roving and each end was glued onto a small piece of paper for bet-ter handing. The distance between the papers, i.e. the gauge length, was varied to 10, 15 and 20 mm. The samples were fixed and tested by the Instron at a cross-head speed of 1 mm/min. At least 30 samples were tested for each level of modification method and gauge length.

The ILSS of composites was measured by short-beam bending test according to ASTM D-2344 using an Instron 1125. A span-to-depth ratio of 5:1, a cross-head speed of 2 mm/min, and a sample thickness of 2 mm were used. More than eight specimens were tested for each of the composites studied and the average value was taken in the present work studied.

3. Results and discussion

3.1. Surface topography of carbon fibers

The SEM configurations of as-received, pre-irradiation modified and oxidation–reduction modified carbon fibers are given in Fig. 1a–c, respectively. Remarkable differences in micrographs can be observed on untreated and modified carbon fibers. The surface of as-received fiber seemed to be rela-tively smooth. However, the surface of fibers modi-fied by acrylic acid became very rough and many pieces of tiny fragments could be observed on fiber surface, which suggested that the absorbability of modified carbon fibers might be improved to some extent [16,27]. Some striations along the fiber axis could be found on the fiber surface on account of removing the amorphous carbon layer. Moreover, pre-irradiation treatment seemed to be more efficient than the oxidation–reduction induced treatment.

3.2. Surface energy of carbon fibers

To obtain the information about the surface activity of carbon fibers before and after modifica-tions, an analysis of surface free energy was evalu-ated by dynamic contact angle analysis. All the measurements were carried out with a dynamic cap-illary method. The contact angle could be calculated according to Eqs. (1) and (2) [28,29]:
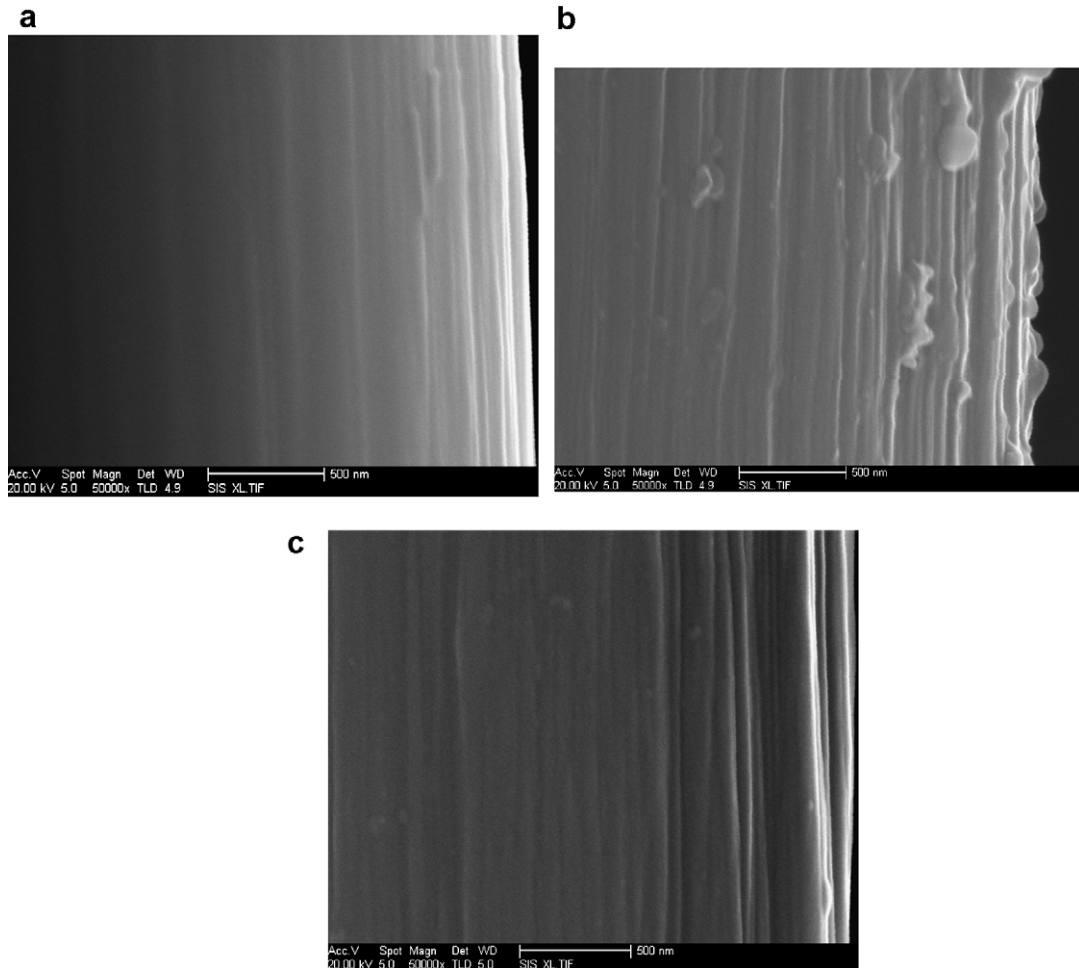
a

b

c

Fig. 1. SEM micrographs of carbon fiber surface (a) as-received; (b) pre-irradiation modified; (c) oxidation-reduction modified.

$$\Delta\gamma = \frac{0.064H^2\rho_f\eta(1-\varepsilon)^2 m^2}{d_f k^2 w_f \rho_l^2 \varepsilon^3 v_T t} \tag{1}$$

$$\cos\theta = \frac{\Delta\gamma}{\gamma_l} \tag{2}$$

where $\Delta\gamma$ is the change in fiber surface free energy; γ_l is the surface tension of immersion liquid; ε is the volume percent of fibers in tube (ε is in the range 48–52%); H is the length of fiber bundle (40 mm); ρ_f and ρ_l are the densities of fiber and immersion liquid, respectively; η is the viscosity of immersion liquid; k is the hydraulic constant; v_T is the total volume of system; w_f is the weight of fiber bundle; d_f is the diameter of a single fiber; t is the time of immersion equilibrium; θ is the dynamic contact angle; m is the amount of adsorption at immersion equilibrium.

The surface free energy consists of two components: a dispersive component of nonpolar interaction and a specific (polar) component (Debye, Keesom of van der Waals, H-bonding, π-bonding, and other small polar effects). The surface free energy (γ_f^T),dispersive component (γ_f^d) and polar component (γ_f^p) of carbon fibers were determined by measuring the dynamic contact angle of two liquids and analyzing the results in accordance with the method proposed by Owens and Wendt [30] and Kaelble [31].

Using two wetting liquids with known surface energy, the dispersive and polar components can easily be determined by solving the following Eq. (3):

$$\gamma_l^T(1 + \cos\theta) = 2(\gamma_l^d\gamma_f^d)^{1/2} + 2(\gamma_l^p\gamma_f^p)^{1/2} \tag{3}$$

where γ_l^T, γ_l^d and γ_l^p are the surface tension of immersion liquid, its dispersive and polar component, respectively.

Table 1
Surface free energy of carbon fibers

	γ_f^d (mJ $\cdot$ m^{-2})	γ_f^p (mJ $\cdot$ m^{-2})	γ_f^T (mJ $\cdot$ m^{-2})
As-received	39.8 ± 1.6	2.4 ± 0.3	42.2 ± 2.0
Pre-irradiation	43.6 ± 2.1	6.9 ± 0.5	50.5 ± 2.3
Oxidation–reduction	42.4 ± 1.5	7.4 ± 0.5	49.8 ± 2.1

In Table 1, the surface free energy, its dispersive component and its polar component of carbon fibers are summarized. It can be seen that both the dispersive and polar components of surface free energy, γ_f^d and γ_f^p, increased after modifications. The increase in the surface free energy γ_f^T was mainly influenced by its polar component. We have found that the acrylic acid modifications of carbon fibers gave an increase in surface functionality in the context of XPS studies, which may take chief responsibility for the improved polar component. The increase in dispersive component was attributed to the possible presence of deep grooves in fiber surface, which were generated by pre-irradiation and oxidation–reduction etching. In general, if the surface energy of a solid is higher than that of a liquid, good wetting and adhesion properties can be obtained. In practice, by increasing the surface energy of a fiber through surface treatments, the wettability of the reinforcement to the matrix can be improved [4].

3.3. Wetting of carbon fibers on epoxy

To investigate the effect of surface treatment on the wetting and adsorption of carbon fibers in epoxy solution, the CF/epoxy specimens were tested in a thermal analyzer. Fig. 2 shows TG and DSC curves of CF/epoxy specimens under argon from 30 °C to 560 °C.
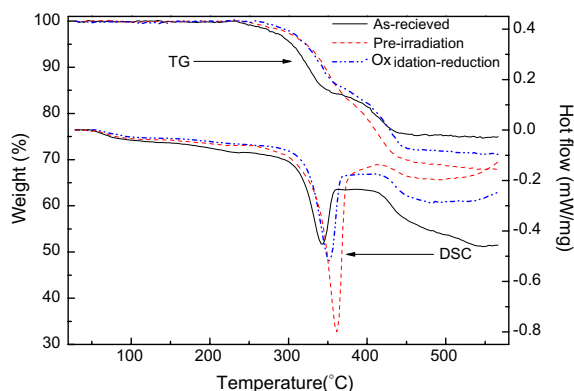

Fig. 2. TG and DSC curves for the CF/epoxy specimens.

Carbon fibers are inert below 1000 °C in argon atmosphere. The residual weight ratio of CF/epoxy specimen is affected entirely by the epoxy resin [32]. Therefore, it can be inferred that at the region from 230 °C to 550 °C, the weight loss is assigned to the decomposition and carbonization of epoxy in CF/epoxy specimens and the main peak in DSC curves between 280 and 380 °C is associated with the decomposition of epoxy [32,33]. By comparing the weight loss at 560 °C for untreated and modified CF/epoxy specimens, a reduction of around 25%, 28% and 32% for untreated, oxidation–reduction and pre-irradiation CF/epoxy specimens can be observed, respectively. The area of peak in DSC curves was also increased after modification. For the modified CF/epoxy specimen, the increase of loss weight is possibly related to the improved wetting ability of carbon fibers for epoxy that could give rise to the ratio of epoxy in CF/epoxy specimen, thus increasing the loss weight of specimen.

The lowest residual weight ratio observed in the case of pre-irradiation is due to the largest amount of epoxy resin absorbed onto carbon fiber surface. The highest residual weight ratio observed in the as-received CF/epoxy system is because the virgin carbon fibers with weak surface energy adsorbed the smallest amount of epoxy resin. The ratio of epoxy in CF/epoxy specimen is increased after surface modification. It is indicated that the pre-irradiation and oxidation–reduction modifications improved the adsorption ability of carbon fibers. In addition, the peak temperature of DSC was increased in order of untreated, oxidation–reduction modified and pre-irradiated CF/epoxy specimens. This fact was possibly because more polar functional groups were grafted on the modified fiber surface and more chemical bond, van der Waals attraction and hydrogen force between modified fiber and epoxy were produced.

3.4. Surface composition of carbon fibers

Wide scan spectra in the binding energy range 0–1400 eV were obtained to identify the surface elements present and carry out a quantitative analysis. The XPS spectra show distinct carbon and oxygen peaks, representing the major constituents of the carbon fibers investigated. Due to the surface modifications, the percentage of oxygen was increased and percentage of carbon was decreased, as listed in Table 2. As can be seen, an about twofold increase in the O_{1s}/C_{1s} composition ratios of modified carbon

Table 2
Variation of surface composition and functional group of the carbon fibers

	C (%)	O (%)	O/C	Peak I C–C	Peak II C–OH/C–O–C	Peak III C=O	Peak IV COOH
As-received	87.4	12.6	0.14	49.7	31.9	12.9	5.5
Pre-irradiation	73.4	26.6	0.36	41.2	26.7	19.5	12.6
Oxidation–reduction	70.9	29.1	0.41	39.1	25.4	21.4	14.1

fibers occurred, compared with untreated fibers due to the deposition of more active forms on the inactive carbon.

Following previous work in the literature, a semi-quantitative description of the differences was attempted using a curve-fitting deconvolution procedure [34]. The carbon peaks, which were observed in the binding energy range from 280 to 295 eV, can be attributed to several carbon-based surface functional groups that have different binding energies. The C_{1s} peak of each carbon fiber sample was analyzed using a peak synthesis procedure, which combines Gaussian and Lorentzian functions. The intensity contribution of each functional component peak was estimated by a computer simulation [3]. Deconvolution of the C_{1s} spectra of carbon fibers gave four peaks designated as peak I (at 284.7–284.9 eV assigned to graphitic carbon), peak II (at 285.5–285.8 eV, carbon bonded phenolic or alcoholic hydroxyls or ether oxygens), peak III (at 286.6–286.8 eV, carbonyl carbon in ketones and quinines) and peak IV (at 288.6–288.9 eV, carboxyl functions or ester groups) [3,35]. The results are shown in Table 2.

From these results, it was clear that the carbonyl carbon in ketones and quinines (C=O) and carboxyl functions or ester groups (COOH/COOR) functional groups increased, and the graphitic carbon (C–C) and carbon bonded phenolic or alcoholic hydroxyls or ether oxygen (C–OH/C–O–C) functional groups decreased after modifications. Furthermore, the oxygen functional group percentage of carbon fibers modified by oxidation–reduction was greater than that of carbon fibers modified by pre-irradiation. The large variation of oxygen groups may be attributed to the introduction of carboxyl onto fiber surface. It is deduced that interfacial adhesion between the carbon fibers and matrix is improved when the carbon fiber is modified with acrylic acid, which results in the promotion of interface properties.

After the modified carbon fibers were sputtered by X-ray to remove the surface layer with about 6 nm, XPS spectra showed that the percentage of carbon on fiber surface gave rise to more than 94%, which was similar to carbon percentage of fiber bulk. It is indicated that the grafted layer is not thicker than the sampling limit of XPS and XPS analysis can determine the surface composition.

3.5. Tensile strength of carbon fibers

The tensile strength of carbon fibers was assessed by single-filament tensile test. The experimental data generated by this test have high scatter, mainly due to the presence of flaws along the fibers. Thus, the interpretation of the data must be done statistically. Several statistical distributions have been used to describe tensile data, and the most flexible is the Weibull distribution so far [36].

This distribution function is adapted to account for fiber length dependency through the weakest link approximation. This approximation assumes that the fiber is formed by L independent links of arbitrary unit length, each link failing or surviving at a given stress level. It also assumes that the strength distribution for each link is described by a two-parameter Weibull function, characterized by identical parameters. Thus, the fiber's probability of survival is equal to the product of the probability of survival of each link [37]. The Weibull cumulative distribution function $F(\sigma, \sigma_0, m)$, and the corresponding mean Weibull strength ($\bar{\sigma}$), adapted to account for the gauge length dependence of the fibers (L), may be described by the equations

$$F(\sigma, \sigma_0, m) = 1 - \exp\left(-L\left(\frac{\sigma}{\sigma_0}\right)^m\right) \qquad (4)$$

$$\bar{\sigma} = \sigma_0 L^{-(1/m)} \Gamma\left(1 + \frac{1}{m}\right) \qquad (5)$$

In the above equation, σ is the fracture tensile strength, L is the tested fiber length, σ_0 and m are the scale and shape parameters and Γ is the gamma function.

The estimate of the tensile strength at any gauge length is performed simply by substituting the

calculated parameters into Eq. (5), for the specified fiber length. Also, σ and L taken as part of σ_0 are redefined with the unit of stress such that the Weibull distribution function is simplified in Eq. (6)

$$P = 1 - \exp[-(\sigma/\sigma_0)^m] \tag{6}$$

We take double logarithms on both sides of Eq. (6), i.e.

$$\ln\ln[1/(1-P)] = m\ln\sigma - m\ln\sigma_0 \tag{7}$$

Based on Eq. (7), the stress/strain curve of fiber filament can be written to a straight line in logarithm coordinate system, and m and σ_0 can be determined according to the slope and intercept of the straight line [19]. Therefore, we can assign a failure probability P_i to each value of σ_i after ranking all the measured values in ascending order (i taking values from 1 to n which corresponds to the number of measurements of the sample tested) according to one of the principal probabilities used:

$$P = i/(n+1). \tag{8}$$

Fig. 3 presents the ultimate fiber tensile strength of untreated and modified carbon fibers. The tensile strength of single carbon fiber was increased after pre-irradiation grafting, whereas the tensile strength of fiber was decreased marginally after oxidation–reduction induced grafting. This result was probably attributed to the reduction of flaws and decrease of interlayer spacing by γ-ray irradiation. Furthermore, the irradiation grafting coating can inhibit failure initiated at fiber surface flaws, resulting in the increase of fiber tensile strength. The strength of all the carbon fibers fell down with increasing gauge length of the specimens.
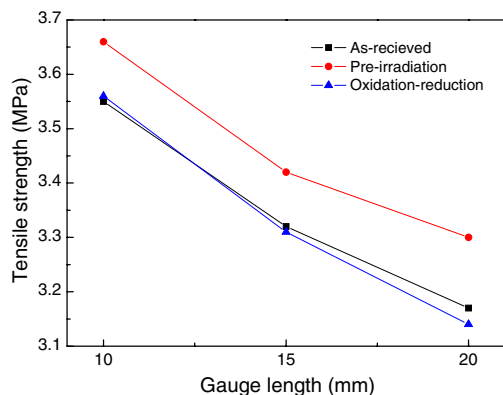
3.6. Interface properties of CF/epoxy composites

The effect of acrylic acid modifications on ILSS for the CF/epoxy composites is given in Fig. 4. The ILSS value was increased with increasing wettability of fibers by the degree of adhesion at interfaces due to surface modification, resulting from increasing polarity and oxygen functional groups of fiber surface [38]. The increasing surface energy of carbon fibers benefited the increase of surface energy difference between carbon fiber and epoxy and thus improved the wettability of fiber with epoxy. As a result, the interface adhesion of CF/epoxy composite was strengthened and ILSS was increased. ILSS of modified CF/epoxy composites increased more than 15%, compared with that for untreated CF/epoxy composites. And the pre-irradiated CF/epoxy composite outperformed the oxidation–reduction grafted CF/epoxy composite in the strength value of ILSS.

SEM photographs showed that the modified carbon fiber surface was rougher and the grooves of fiber surface became wider and deeper, compared with the original carbon fiber surface. From XPS analysis results, the carbonyl and carboxyl functional groups on fiber surface increased after modification. This result of interface adhesion is in good agreement with surface analyses of the carbon fibers studied.

Fig. 5 demonstrates the interlaminar shear damage morphology along the cross-section in the CF/epoxy composites. As seen in Fig. 5a, the main failure mechanism of untreated CF/epoxy composites was the fiber debonding. After pre-irradiation and oxidation–reduction modifications shown in Fig. 5b and c, strong interlocking of fiber–matrix bonding could be observed. Although some carbon fibers were separated from matrix, the strong inter-

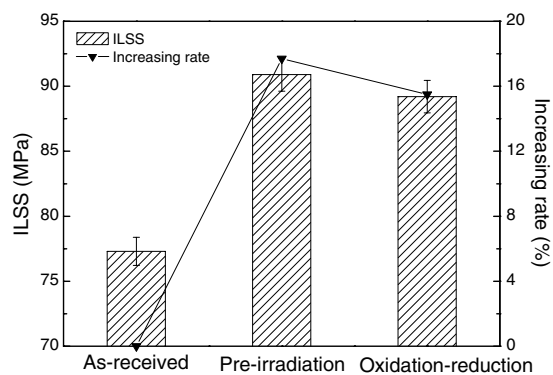Fig. 3. Variation of tensile strength of the carbon fibers before and after modification.

Fig. 4. Effect of surface modification on ILSS of CF/epoxy composites.
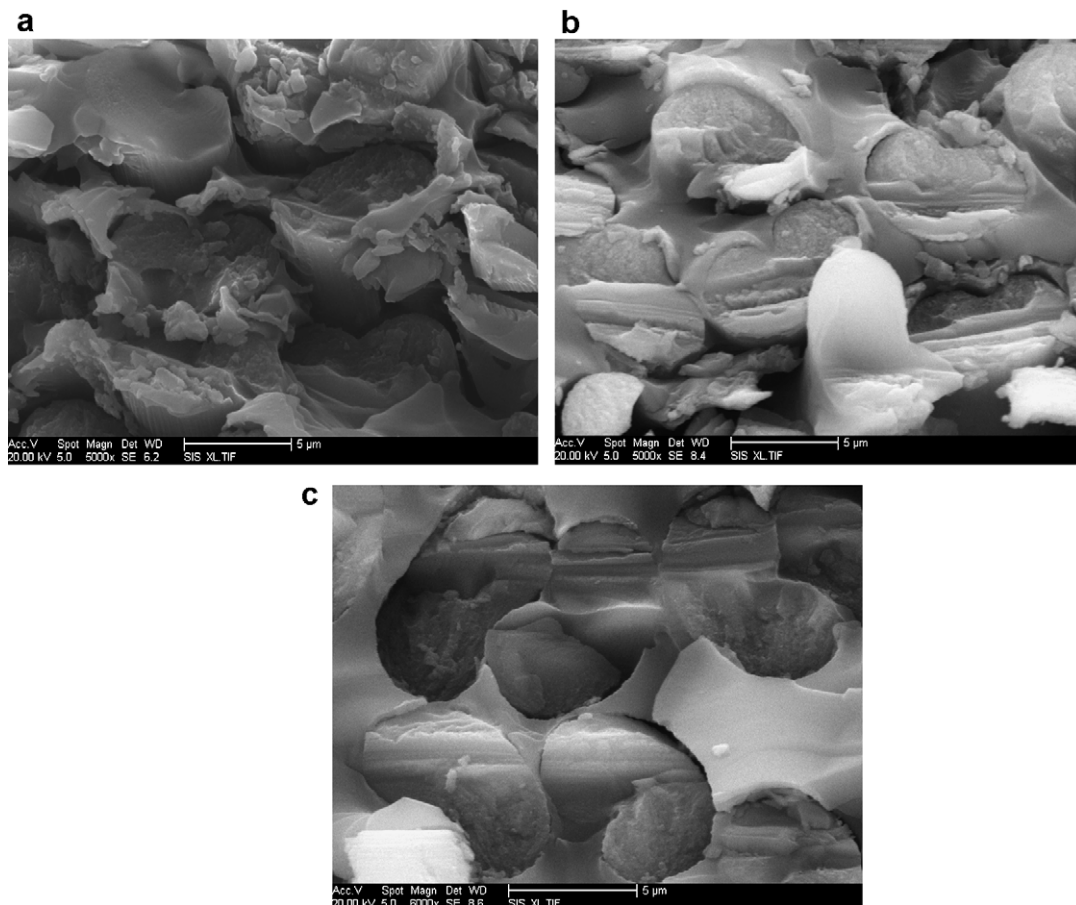
Fig. 5. SEM micrographs of fracture surface of composites (a) untreated CF/epoxy composites; (b) pre-irradiated CF/epoxy composites; (c) oxidation–reduction modified CF/epoxy composites.
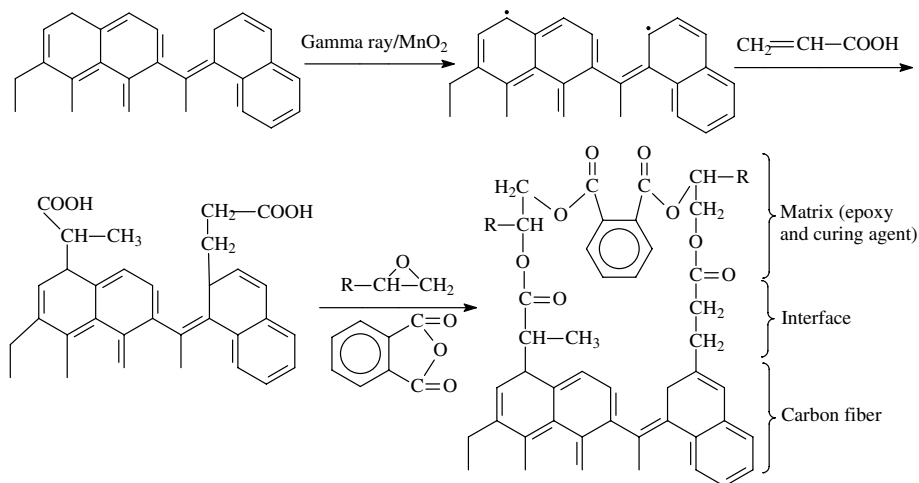

Fig. 6. The schematic model for chemical reactions between carbon fiber and matrix.

facial bonding may contribute the improvements on ILSS of composites. The fracture model was changed from pure interfacial failure to the combination failures of interface and resin interlayer. These results proved that both pre-irradiation induced grafting and oxidation–reduction induced grafting

were an effective method for improving interfacial adhesion of composites.

There are several mechanisms for the fiber-matrix bonding, which involve mechanical interlocking, adsorption interaction, chemical interaction and hydrogen bond action [27,39]. Generally these mechanisms influence the interfacial adhesion of composites simultaneously. As discussed above, the enhancement of the surface roughness reduces the contact angle between fibers and matrix and hence increases the wettability as well. The introduction of polar functional groups onto fiber surface improves the physical adsorption and polar bond between the fiber and resin.

Fig. 6 shows a schematic reactive process and model of possible chemical reactions among the carbon fiber, acrylic acid and epoxy matrix (including curing agent). The chemical bonding, interdiffusion and hydrogen bond in interface between carbon fiber and matrix may contribute to the improvement of the interfacial adhesion.

4. Conclusion

To make the surface of inert carbon fibers interactive and enhance the interfacial property between a carbon fiber and epoxy matrix, carbon fibers were modified by acrylic acid with the aid of physical energy from γ-ray irradiation and oxidation–reduction reaction.

Compared with the original carbon fiber, the surface of the modified fiber became rougher and more pieces of tiny fragments stuck to the fiber surface. Following treatment there was an increase of oxygen content on fiber surface, of the surface energy and of the number of the carbonyl, carboxyl or ester functional groups. The wetting and adsorption ability of carbon fibers in epoxy solution was enhanced. The tensile strength of carbon fibers was improved marginally by γ-ray pre-irradiation while was decreased little by oxidation–reduction modification. After modifications, the strong interlocking of fiber–matrix bonding could be observed and the ILSS values of composites were increased significantly.

Both pre-irradiation and oxidation–reduction are to be considered promising methods for the modification of carbon fibers.

Acknowledgment

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