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ScienceDirect
Composites Science and Technology 67 (2007) 3261–3270
COMPOSITES SCIENCE AND TECHNOLOGY
www.elsevier.com/locate/compscitech

Effect of γ-ray irradiation grafting on the carbon fibers and interfacial adhesion of epoxy composites

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Received 18 November 2006; received in revised form 23 March 2007; accepted 29 March 2007
Available online 19 April 2007

Abstract

A special technique using γ-ray irradiation-induced graft-polymerization was applied to carbon fibers. Epoxy resin and chloroepoxy propane reacted with carbon fibers by a co-irradiation grafting method and acrylic acid was graft-polymerized onto the fiber surface via a pre-irradiation grafting method. The roughness, amount of containing-oxygen functional groups and surface energy were all found to increase significantly after irradiation grafting. Gamma-ray irradiation grafting improved marginally the tensile strength of carbon fibers, which was evaluated by statistical analysis using the Weibull distribution. The interlaminar shear strength of treated carbon fiber/epoxy was enhanced by at least 17.5%, compared with that of untreated carbon fiber/epoxy. The mechanisms of irradiation grafting are proposed by radical reactions. The γ-ray co-irradiation grafting and pre-irradiation grafting are both an effective method for modifying the physicochemical properties of carbon fibers and improving the interfacial adhesion of composites.

Keywords: A. Carbon fiber; A. Polymer–matrix composites; B. Interfacial strength; D. Scanning electron microscopy; E. Irradiation grafting

1. Introduction

The unique combination of physical and chemical properties of polymer composites has led to their widespread application in different fields of industry, machine and sport. The interface between carbon fibers and resin matrix plays a critical role in controlling the overall properties of the composites, such as off-axis strength, fracture toughness and environment stabilities [1–3]. A strong interface increases the structural integrity of the composites and transfers the stress efficiently from fibers to the matrix. However, the smooth and inertness characteristics of carbon fiber surface usually result in inferior wettability and weak adhesion between the fibers and resin [4–6]. As a result, extensive research has been devoted to the surface treatment of carbon fibers in order to improve their bonding to the resin matrix, such as thermal treatment [7,8], wet chemical or electrochemical oxidation [9–11], plasma treatment [12,13], gas-phase oxidation [14,15], ultrasonic bombardment [16] and so on.

At present, the plasma treatment on carbon fibers has been studied as one surface modification method owing to the feasibility of improving the tailored chemical, physical and mechanical properties of composite materials if optimum treatment conditions are offered. However, it has the drawback that it is difficult to use for applications because of its high facilities, high energy consumption, and high maintenance cost, in spite of improved interfacial adhesion force of the final composites [17]. In addition, conventional oxidative carbon fiber modifications lead usually not only to an improved adhesion (at least for epoxy systems), but sometimes also to a significant loss in single fiber strength [18].

In recent years, 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 [19]. An irradiation can induce chemical reactions at any temperature in the solid,

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doi:10.1016/j.compscitech.2007.03.038

liquid and gas phase without any catalyst. It is a safe method that could protect the environment against pollution, reduce maintenance cost and save energy consumption. The large and thick three-dimensional fabrics could be treated by irradiation without consideration of the shape of the samples, which is convenient for industrialization [20].

In the present work, therefore, two different irradiation approaches, i.e. simultaneous method and pre-irradiation method, were applied to treat carbon fibers at various conditions. The effect of γ-ray irradiation grafting of three different monomers onto polyacrylonitrile(PAN)-based carbon fibers on the fiber surface and composite interface is investigated. The chemical composition of treated carbon fiber surface was determined by X-ray photoelectron spectroscopy (XPS). The configurations of fibers and fractography of composites were characterized by using scanning electron microscopy (SEM). Carbon fiber surface energy was determined by dynamic contact analysis. The strength of single carbon fibers is evaluated with Weibull distribution. The fiber/epoxy interfacial adhesion was investigated by interlaminar shear strength (ILSS).

2. Experimental

2.1. Materials

The PAN-based high-strength carbon fibers with kidney-type cross section investigated in current studies were supplied by Institute of Coal Chemistry.CAS (linear mass is 0.0626 g/m). The matrix system used was E-618 epoxy resin system consisting of diglycidyl ether of bisphenol-A (the molecular weight of 350–400 and molecular structure shown in Eq. (1)), curing agent: phthalic anhydride and benzyl dimethylamine at 100, 70 and 1 parts by weight, respectively. 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.

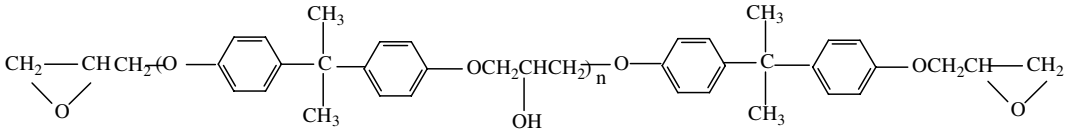
2.2. Irradiation grafting

There are essentially two basic methods of simultaneous (co-irradiation) method and pre-irradiation method for radiation grafting in this study. The former is also sometimes called as mutual method. The carbon fibers are immersed in the monomer, which may be a liquid, vapour or diluted with solvent and then exposed to radiation. This method is more effective for grafting of chloroepoxy propane and epoxy resin. In the latter method (pre-irradiation grafting), 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 [21]. It has been shown that the latter is more proper for grafting of acrylic acid onto carbon fibers.

The epoxy resin used for matrix was employed to obtain 3 wt% epoxy/acetone solution. Carbon fibers (approximately 30 g) used for co-irradiation were put in two plastic containers and vacuumized. The epoxy/acetone solution (400 ml) and chloroepoxy propane (400 ml) were inhaled into the containers under negative pressure and the fibers were wholly immersed, respectively. The mixture of carbon fibers and liquid was irradiated by γ-ray for the dose of 3×10^2 kGy and the treated carbon fibers were dried for 2 h at 120 °C. For the pre-irradiation, carbon fibers (30 g) were put in plastic container and the container was full of nitrogen. The tight container containing carbon fibers and nitrogen was exposed to γ-ray irradiation at the dose of 3×10^2 kGy. Then the container was vacuumized and acrylic acid was inhaled into the container under negative pressure. After the reaction for 6 h, the grafted carbon fibers were dried for 2 h at 120 °C. The grafting yield (degree of grafting) was calculated using the following equation:

$$\text{Degree of grafting } (\%) = [(W_g - W_0)/W_0] \times 100 \qquad (2)$$

where W_0 denotes the weight of the blank carbon fiber and W_g presents the weight of the fiber after treatments.



(1)

Using the carbon fibers and epoxy resin, the prepreg was paid unidirectional into a mold to manufacture composites. 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 specimens with fiber mass fraction of 63 (±1.5%).

2.3. Equipments

The morphology of fiber surface and failure of fiber-reinforced composites were inspected by scanning electron microscopy (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.

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 X-ray photoelectron spectroscopy (XPS) and surface energy tests, untreated and treated 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 irradiation and grafting 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 single fiber was separated from the roving and each end was glued onto a small piece of paper for better 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 treatment 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. Effect of irradiation grafting on fiber surface topography

The SEM images of as-received, epoxy co-irradiation treated, chloroepoxy propane co-irradiation treated and acrylic acid pre-irradiation treated carbon fibers are shown in Fig. 1a–d, respectively. Remarkable differences in micrographs can be observed on untreated and treated carbon

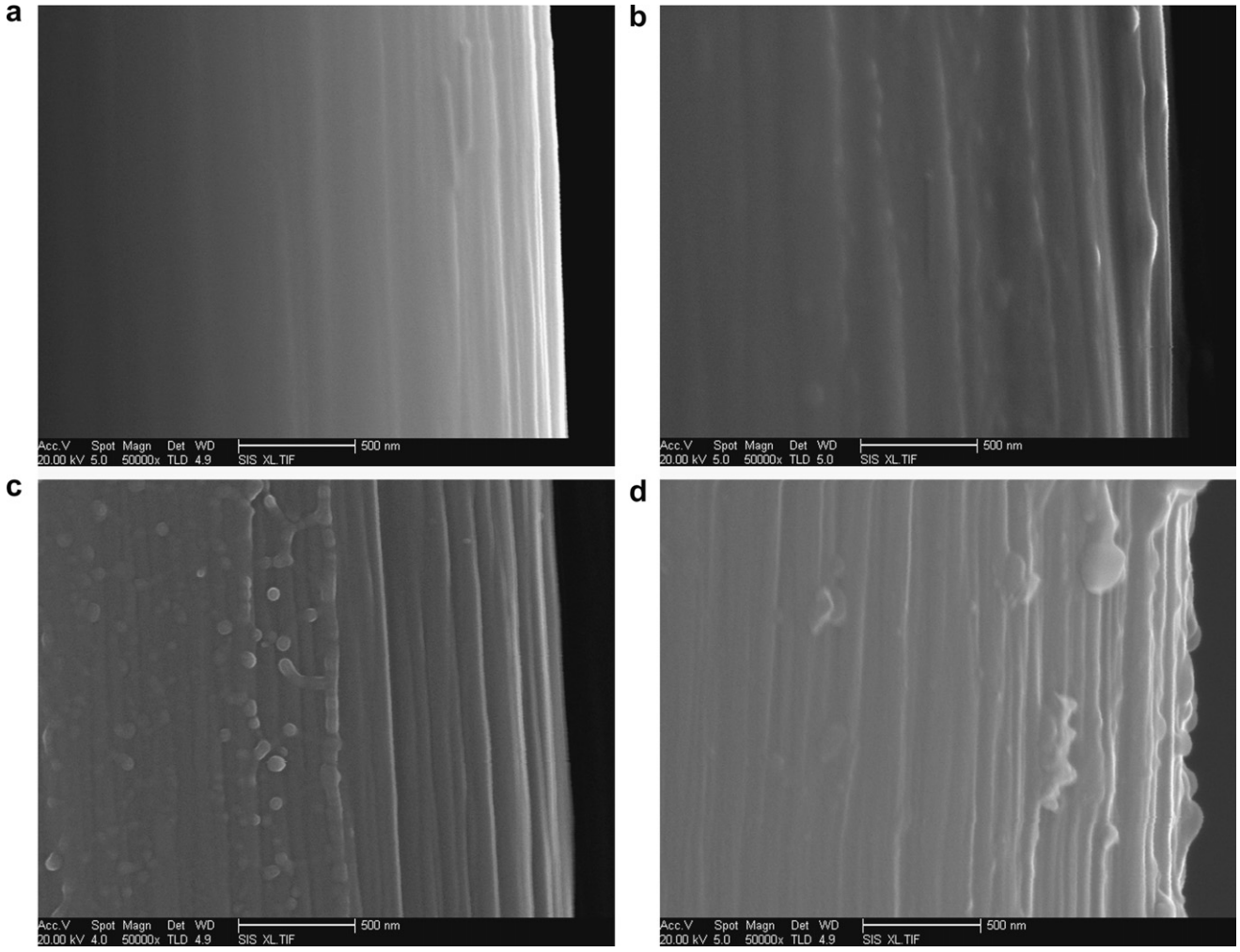


Fig. 1. SEM micrographs of carbon fiber surface: (a) as-received; (b) epoxy co-irradiation treated; (c) chloroepoxy propane co-irradiation treated; (d) acrylic acid pre-irradiation treated.

fibers. It was shown that the surface of untreated carbon fiber seemed to be relatively smooth and a few narrow grooves or channels that parallel distributed along with the longitudinal direction of fiber, due to the structure of carbon fibers were characteristic of the fiber surface [3]. Compared with the original carbon fiber, the treated carbon fiber surface was rougher and the grooves of fiber surface became wider and deeper. It could be interpreted by γ photons etching process on carbon fiber surface. After irradiation and grafting, more pieces of tiny fragments stuck to the fiber surface, which suggested that the absorbability of treated fibers might be enhanced to some extent. Moreover, the carbon fibers treated by co-irradiation method showed a more distinct increase in roughening and depth of grooves than those treated by pre-irradiation method. Therefore, interfacial adhesion between grafted fibers and matrix resin may be enhanced by increasing the surface area (increasing roughness) which may provide more points of contact between the fiber and the matrix.

3.2. Effect of irradiation grafting on fiber surface composition

XPS is a very useful technique in the determination of chemical composition and functional groups of fiber surface and the maximal XPS sampling depth is ~6 nm. Wide scan spectra in the binding energy range 0–1350 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. The surface composition of untreated and treated carbon fibers was determined by XPS and the results are given in Table 1.

The grafting yield of epoxy, chloroepoxy propane and acrylic acid onto the carbon fibers was 1.8%, 0.8% and 1.2%, respectively. These results may be attributed to the grafting of monomers and the removal of weak surface layer on fiber surface. Moreover, after the irradiated and grafted carbon fibers were sputtered by X-ray for 10 min 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 after the treated fibers were extracted by acetone.

As shown in Table 1, the amount of surface oxygen was increased and the amount of surface carbon was decreased after irradiation and grafting. An about two-fold increase in oxygen content occurred after irradiation grafting. The large variation of oxygen groups may be attributed to the grafting of monomers onto carbon fiber surface and the oxidation of carbon fibers by γ-ray irradiation.

Table 1
Variation of surface composition of the carbon fibers before and after treatment

	C (%)	O (%)	Cl (%)	O/C
As-received	87.39	12.61	0	0.14
Epoxy co-irradiation	72.47	27.53	0	0.38
Chloroepoxy propane co-irradiation	69.29	30.12	0.59	0.43
Acrylic acid pre-irradiation treated	72.75	27.25	0	0.37

Fig. 2a–d presents C_{1s} envelopes for the virgin, epoxy co-irradiation treated, chloroepoxy propane co-irradiation treated and acrylic acid pre-irradiation treated fibers, respectively. It can be noticed that the total fraction of the C_{1s} envelope associated with oxygen environments (shoulders located on the high energy side of the main peak at 284.8 eV) is greater for the samples processed by irradiation grafting. However, XPS is not capable of resolving the individual contributions of functionalities such as hydroxyl-ester, carbonyl, carboxyl, anhydrides or lactose. Following previous work in the literature, a semi-quantitative description of the differences was attempted using a curve-fitting deconvolution procedure [22].

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 [23,24].

The narrow scan spectra of the C_{1s} region deconvoluted into surface functional group contributions are shown in Fig. 2a–d for the untreated, epoxy co-irradiation treated, chloroepoxy propane co-irradiation treated and acrylic acid pre-irradiation treated fibers, respectively. The percent contribution of each curve fit photopeak was estimated from these curve fit C_{1s} photopeaks and is listed in Table 2. Deconvolution of the C_{1s} spectra of carbon fibers gave four peaks designated as peak A (at 284.7–284.9 eV assigned to graphitic carbon), peak B (at 285.5–285.8 eV, carbon bonded phenolic or alcoholic hydroxyls or ether oxygens), peak C (at 286.5–286.8 eV, carbonyl carbon in ketones and quinines) and peak D (at 288.5–288.9 eV, carboxyl functions or ester groups) [25–27].

From these results, it is clear that the carbonyl carbon in ketones and quinines (C═O) and carboxyl or ester (COOH/COOR) functional groups increased, and the graphitic carbon (C—C) and carbon bonded phenolic or alcoholic hydroxyl or ether oxygen (C—OH/C—O—C) functional groups decreased after treatment. Furthermore, the carboxyl or ester functional group percentage of carbon fibers treated by acrylic acid is greater than that of carbon fibers treated by epoxy and chloroepoxy propane. These results may be attributed to the γ-ray irradiation inducing free radical reaction between carbon fiber surface and monomers [28].

3.3. Effect of irradiation grafting on fiber surface energy

To obtain the information about the surface activity of carbon fibers before and after treatments, an analysis of

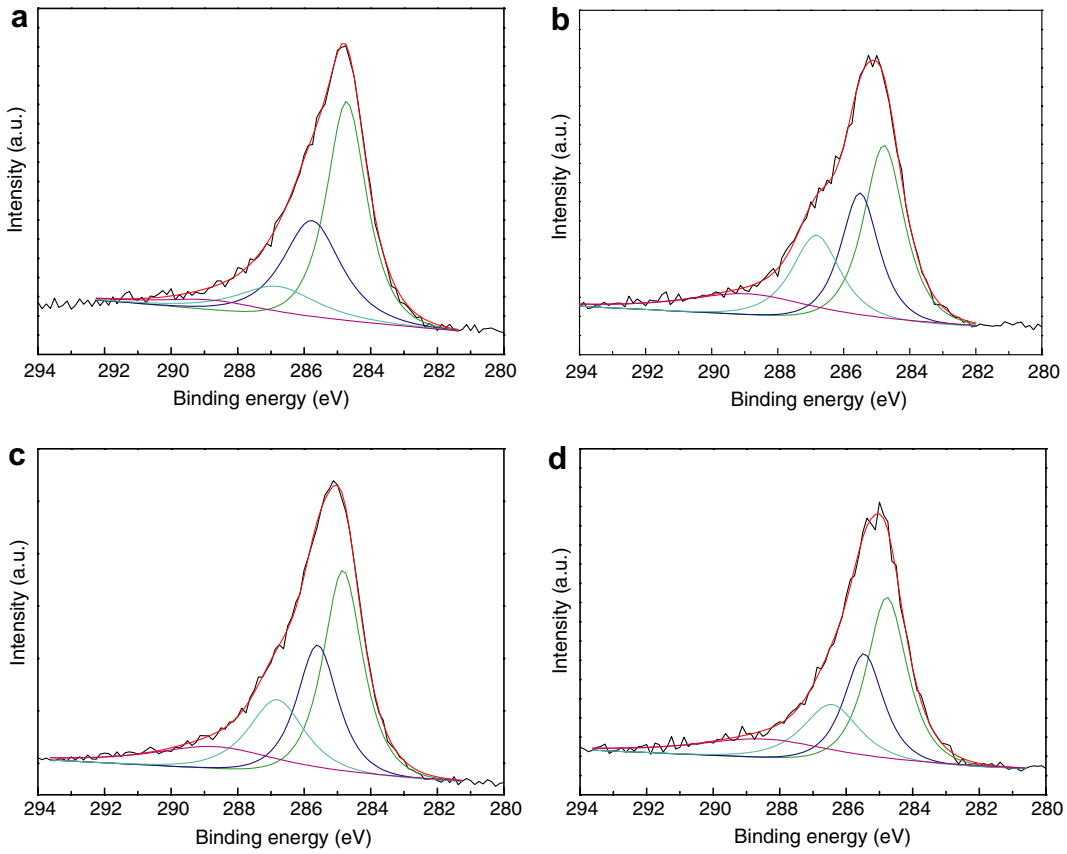


Fig. 2. C_{1s} XPS spectra of carbon fibers untreated and treated: (a) untreated; (b) epoxy co-irradiation treated; (c) chloroepoxy propane co-irradiation treated; (d) acrylic acid pre-irradiation treated.

Table 2
Relative content of functional groups in C_{1s} spectra from XPS

	C—C (%)	C—OH/ C—O—C (%)	C=O (%)	COOR/ COOH (%)
	284.7–284.9	285.5–285.8	286.5–286.8	288.5–288.9
As-received	49.7	31.9	12.9	5.5
Epoxy co-irradiation	38.4	26.0	21.4	14.1
Chloroepoxy propane co-irradiation	40.2	26.2	20.1	13.5
Acrylic acid pre-irradiation	40.3	25.6	19.1	15.0

surface free energy was evaluated by dynamic contact angle analysis (DCAA). All the measurements were carried out with a dynamic capillary method [28,29].

The surface free energy was divided by 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 [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 equation:

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

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

In Table 3, 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 treatments.

In previous studies, we have found that the irradiation treatments 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 pos-

Table 3
Surface free energy of carbon fibers

	γ_f^d (mJ m^{-2})	γ_f^p (mJ m^{-2})	γ_f^T (mJ m^{-2})
As-received	39.8 ± 1.6	2.4 ± 0.3	42.2 ± 2.0
Epoxy co-irradiation	44.6 ± 1.9	6.2 ± 0.5	50.8 ± 2.3
Chloroepoxy propane co-irradiation	46.8 ± 2.4	7.8 ± 0.6	54.6 ± 2.6
Acrylic acid pre-irradiation	45.1 ± 2.5	8.4 ± 0.5	53.5 ± 2.1

sible presence of deep grooves in fiber surface, which were generated by pre-irradiation and co-irradiation etching.

3.4. Effect of irradiation grafting on fiber tensile strength

Single filament tensile test results of brittle materials, such as carbon fibers, are difficult to analyze due to the high scatter observed. Thus, the tensile strength data must be statistically analyzed. For the same fiber, the variation of length is mainly responsible for the changes observed in fiber strength [32].

The Weibull distribution function is normally used to describe strength data. 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. The Weibull cumulative distribution function $F(\sigma;\sigma_0,m)$, and the corresponding mean Weibull strength ($\overline{\sigma}$), now functions of L, can thus be written as:

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

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

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. When a two-parameter Weibull distribution is used to characterize fiber strength over a range of gauge lengths, the average strength at any length may be obtained by using Eq. (5) [17,32,33]. We take double logarithms on both sides of Eq. (4), i.e.

$$\ln\ln[1/(1-F(\sigma,\sigma_0,m))]=m\ln\sigma+\ln L-m\ln\sigma_0 \tag{6}$$

Based on Eq. (6), 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. The parameter estimate for the two-parameter Weibull distribution is made for the strength data obtained at all gauge lengths simultaneously. In this work, the maximum likelihood theory is used to determine the Weibull parameters. The results of the parameter estimation and the average tensile strength for all gauge lengths are presented in Table 4.

As previously mentioned, the tensile strength is expected to decrease with gauge length. As can be seen in Table 4, the results of the present study tend to obey this trend. In previous work, it was shown that γ-ray irradiation grafting had an important effect on the surface characteristics of the fibers. The tensile strength results obtained in the present work do suggest slight effect of the irradiation treatment. It seemed that the tensile strength of fibers was improved by the γ-ray irradiation and grafting process, regardless of the treatment method. The shape parameter, m was increased after irradiation grafting at each gauge length. These results are 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.

Table 4
Weibull distribution parameters for the carbon fibers

Fiber	Gauge length, L (mm)	Average tensile strength, σ (GPa)	Shape parameter, m
As-received	10	3.55	5.30
	15	3.38	5.48
	20	3.16	5.56
Epoxy co-irradiation	10	3.81	6.23
	15	3.67	6.18
	20	3.39	6.38
Chloroepoxy propane co-irradiation	10	3.79	6.37
	15	3.66	6.22
	20	3.40	6.40
Acrylic acid pre-irradiation	10	3.76	5.94
	15	3.67	5.72
	20	3.34	5.96

3.5. Effect of irradiation grafting on ILSS of composites

The ILSS results of composites reinforced by carbon fibers treated in different methods are shown in Fig. 3. After irradiation grafting, the ILSS of treated samples increased significantly. A maximum ILSS value can be found after epoxy co-irradiation grafting, i.e. 94.1 MPa, about 21.8% improvement compared with that of untreated one. The chloroepoxy propane co-irradiation and acrylic acid pre-irradiation grafting carbon fiber/epoxy composites per-

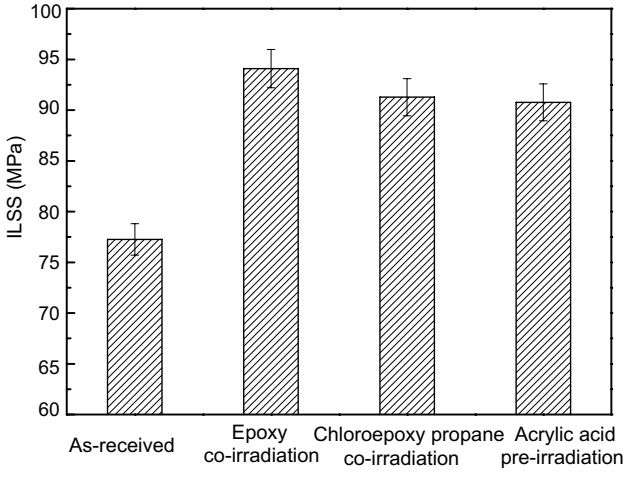


Fig. 3. Effect of γ-ray irradiation grafting on ILSS of carbon fiber/epoxy composites.

formed marginally better (18.1% and 17.5%) than those manufactured using untreated carbon fiber/epoxy composites, respectively.

The improvement on ILSS of carbon fiber/epoxy composites could be attributed to the enhancement of the interfacial adhesion strength of the fiber and matrix after irradiation grafting. There are several mechanisms for the fiber–matrix bonding, which involve mechanical interlocking, chemical bonding, adsorption interaction and diffusion of polymer chain segments [15,34]. As far as irradiation-treated samples are concerned, it can be inferred that surface roughening and polar functionality, both factors generated by irradiation grafting, mainly contribute to the interfacial adhesion. As shown in Table 1, after irradiation grafting the oxygen-containing functional groups increased and the increasing of amounts of oxygen-containing functional groups on the fibers played an important role in improving the degree of adhesion at interfaces (hereby, keesom's attraction of van der Waals force, hydrogen bonding, and the other small polar effects) between fibers and the matrix, and the ILSS of the resulting composites. However, the relative roles of mechanical interlocking due to surface roughness and surface chemical bonding in fiber/matrix adhesion are difficult to separate. The enhancement of the surface roughness was beneficial for the wettability between fiber and matrix, resulting in mechanical anchor and chemical bonds.

Moreover, it should be noted that the enhancement of the interfacial bonding is concerned with the grafting reagent. Interlaminar shear testing has indicated that the epoxy co-irradiation carbon fiber/epoxy composites perform marginally better than those manufactured using chloroepoxy propane co-irradiation carbon fiber/epoxy composites. This result can be attributed to the fact that the grafting coating of the former is the same as matrix resin and thus the functional groups on fiber surface react with the matrix resin easily. However, the mean ILSS was nearly the same for the chloroepoxy propane co-irradiation and acrylic acid pre-irradiation composite systems.

It is indicated that γ-ray irradiation grafting treatment is not only convenient and environment-friendly but high efficient in modification of carbon fibers. It is expected to be employed in the industrialized treatment.

3.6. Fracture topographic features of composites

Fig. 4a–d corresponded to the fracture micrographs of untreated, epoxy co-irradiation, chloroepoxy propane co-irradiation and acrylic acid pre-irradiation fiber/epoxy composites, respectively, as obtained by SEM. There was a marked difference in fracture surface topography between untreated and treated fiber composites. It was easily recognized in Fig. 4a that untreated carbon fibers performed very poor interface bonding with epoxy matrix. The fibers had a relatively smooth surface. Interfacial debonding was obviously observed and no resin matrix adhered on the fiber surface. However, after irradiation grafting treatment shown in Fig. 4(b), (c) and (d), the interfacial bonding of composites appeared to have been obviously improved and strong interlocking of fiber–matrix bonding could be observed, which was termed as "mechanical anchor" by Kalantar and Drzal [34]. The fibers were engulfed by matrix, which allowed the matrix to secure more bonds and better adhesive force between two phases, which can effectively transfer the load applied to the fiber-reinforced composite system. The fracture model of composites was changed from pure interfacial failure to the combination failures of interface and resin interlayer. It was proved that irradiation grafting was an effective method for modification of composite interface.

Contrasting Fig. 4b–d, the epoxy co-irradiation grafting carbon fiber/epoxy composites outperformed marginally those employing the chloroepoxy propane co-irradiation and acrylic acid pre-irradiation grafting carbon fibers. This result is in accordance with the ILSS values of composites. Since epoxy resin is epoxide polymer that has a long chain and can polymerize and crosslink with the catalyzing agent, the diffusion of polymer chain segments can be responsible for these results to some extent.

3.7. Mechanisms of γ-ray irradiation grafting

The irradiation-induced free radical reaction on polymers and physiological compounds is a recent subject of study because of the growing interest of irradiation treatments in technological and medical applications [35].

Carbon fibers were grafted with various monomers at 300 kGy dose of γ-ray irradiation. The photon beam with high energy hits the surface of carbon fibers and the chain molecules of epoxy resin and chloroepoxy propane to produce active sites and radicals, which initiate the reaction of graft-polymerization. These radicals should be primarily formed either by hydrogen abstraction or by cleavage of a covalent bond followed by other degradation processes. In such reactions the covalent chemical bond is cleaved either symmetrically or asymmetrically ($A{:}B \rightarrow A^{\cdot} + B^{\cdot}$). The created free radicals are usually very reactive because of the strong tendency of their unpaired electrons to interact with other electrons and reform chemical bonds.

Irradiating carbon fiber in solution and nitrogen will also give rise to peroxide groups by oxygen in solution and nitrogen, which on decomposition at occurrence of active monomer will also produce radicals [36]. Peroxide formation is demonstrated by the following reaction mechanisms, where M is the carbon fiber substrate

$$MH \rightarrow M^{\cdot} + H^{\cdot} \quad (7)$$

$$M^{\cdot} + O_2 \rightarrow MO_2^{\cdot} \quad (8)$$

$$MO_2^{\cdot} + H^{\cdot} \rightarrow MO^{\cdot} + HO^{\cdot} \quad (9)$$

For co-irradiation, the use of single-step procedure via γ-ray irradiation on carbon fiber samples impregnated with the solution of epoxy resin and chloroepoxy propane was attempted, respectively [37]. The epoxy ring of epoxy resin and chloroepoxy propane is split by γ-ray irradiation and

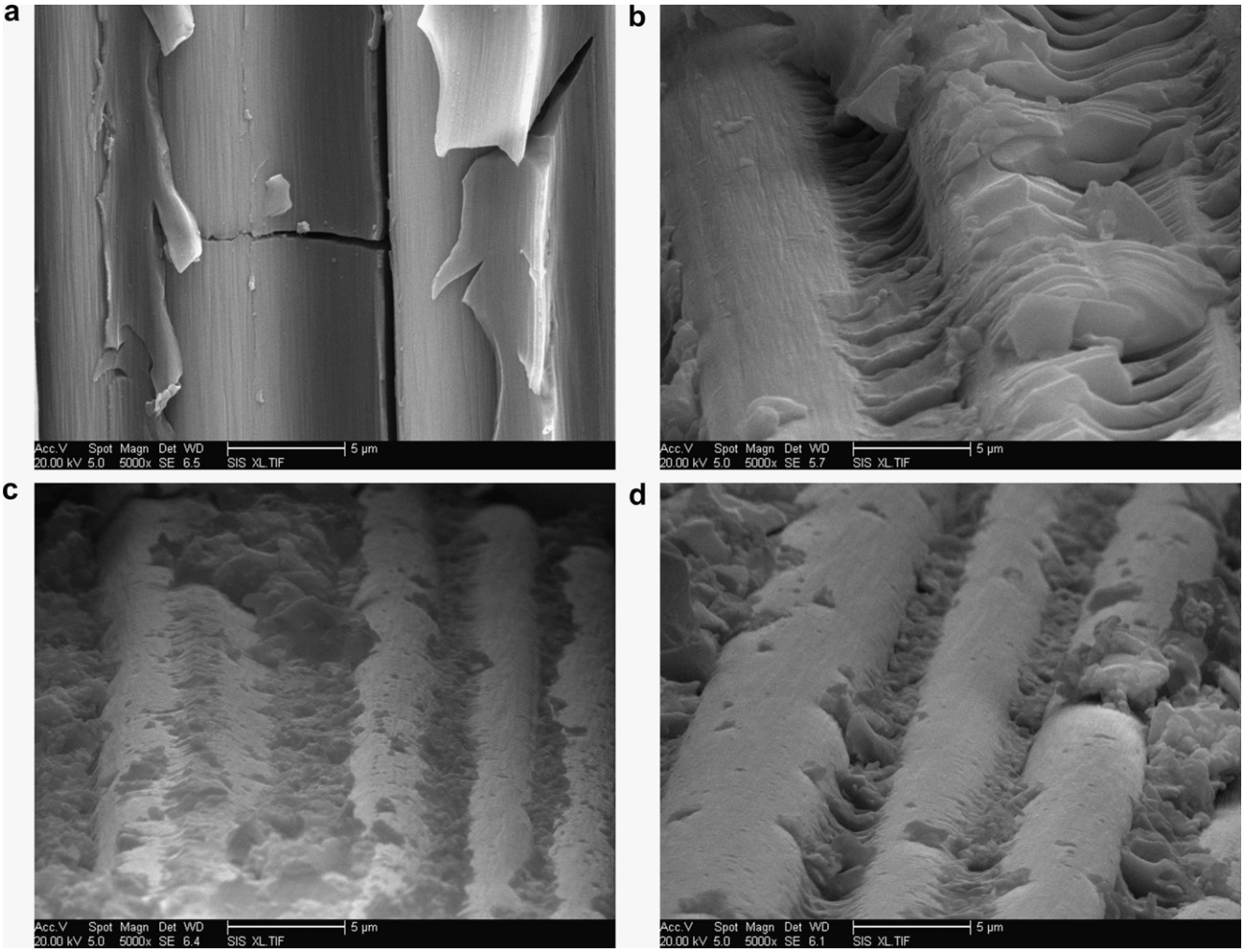
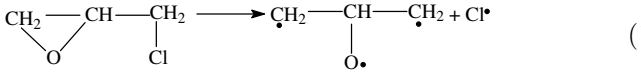


Fig. 4. SEM micrographs of fracture surface of composites: (a) untreated fiber composites; (b) epoxy co-irradiation treated fiber composites; (c) chloroepoxy propane co-irradiation treated fiber composites; (d) acrylic acid pre-irradiation treated fiber composites.

the ether and carbon chain radicals are produced [36]. The possible grafting reactions of chloroepoxy propane and carbon fibers are only introduced because of the similar functional structure between chloroepoxy propane and epoxy resin.



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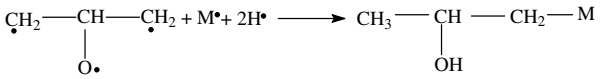

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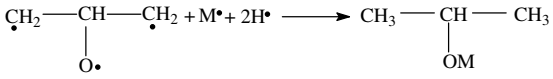
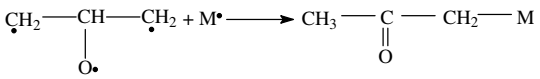
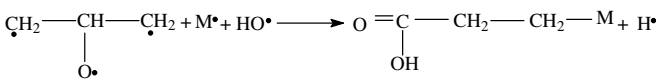


(12)



(13)



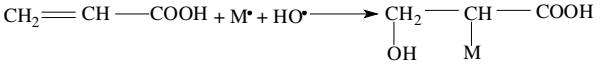
(14)

$$H^{\cdot} + Cl^{\cdot} \rightarrow HCl \tag{15}$$

However, for pre-irradiation grafting procedure, the process is divided into two steps, whereby free radicals are formed on the fiber surface via γ-ray irradiation, and then react with acrylic acid. According to this procedure, carbon fiber surface is activated and functionalized on a preparative scale by γ-ray irradiation in given dose. A goal of this step approach is the generation of carbon radicals enough reactive to be selectively quenched by acrylic acid. The double bond of acrylic acid is destroyed under the induction of carbon, hydroxyl and ether radicals. The grafting reactions are

$$CH_2{=}CH{-}COOH + M^{\cdot} + H^{\cdot} \rightarrow M{-}CH_2{-}CH_2{-}COOH \tag{16}$$

$$CH_2{=}CH{-}COOH + MO^{\cdot} + H^{\cdot} \rightarrow CH_3{-}CH_2{-}OM + CO_2 \tag{17}$$



(18)

If we compare co-irradiation and pre-irradiation procedures, we can argue that in the latter case radicals are formed on carbon fiber surface. When the irradiated fibers are dipped in a solution of acrylic acid, many of these

radicals are trapped. On the other hand, for the co-irradiation process it would appear that radicals are generated both on carbon fiber surface and on grafting monomers, after following irradiation of grafting monomers (epoxy resin and chloroepoxy propane) impregnated fibers. As a result, the covalent bonds are formed between fibers and grafting reagents and there is a physical interaction between grafting reagents and the fiber.

4. Conclusions

To make the surface of inert carbon fibers interactive and enhance the interfacial property between a carbon fiber and epoxy matrix, three kinds of monomers were graft-polymerized onto carbon fiber surface with the aid of physical energy from γ-ray irradiation.

Compared with the original carbon fiber, the surface of treated fiber became rougher and more pieces of tiny fragments stuck to the fiber surface. The increase in oxygen content on fiber surface and surface energy occurred and the carbonyl carbon and carboxyl or ester functional groups increased after irradiation grafting. The tensile strength of fibers was improved by the γ-ray irradiation and grafting process. After treatment, the strong interlocking of fiber–matrix bonding could be observed and the ILSS values of composites were enhanced significantly. The irradiation grafting is proposed to be completed by radical reactions.

Being high efficient, convenient and environment-friendly, γ-ray irradiation grafting is expected to be a promising method for the industrialized modification of carbon fibers.

Acknowledgements

The authors thank Dr. Ying Wang in Institute of Chemistry Chinese Academy of Sciences for help in experiments and suggestion in this paper. The research was supported by the National Natural Science Foundation (50333030).

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