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# Surface and Composite Interface of Carbon Fibre Modified by Pre-irradiation

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Received: 28 December 2008, Accepted: 6 August 2009

## SUMMARY

The  $\gamma$ -ray pre-irradiation induced method was employed to study the effect of chloroepoxypropane modification on the surface of carbon fibre (CF) and the interfacial properties of CF/epoxy. Systematic experimental work was conducted to determine the fibre surface topography, fibre surface energy, fibre tensile strength and interfacial adhesion of CF/epoxy before and after  $\gamma$ -ray pre-irradiation grafting. The roughness and surface energy were all found to increase significantly. The tensile strength of carbon fibres was improved marginally by  $\gamma$ -ray pre-irradiation. The surface modification of carbon fibres led to an improvement (at most 18.2%) of the interlaminar shear strength of CF/epoxy composites. The mechanisms of pre-irradiation of CF are proposed.

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## 1. INTRODUCTION

The unique combination of physical and chemical properties of carbon fibres has led to their widespread application in different fields of industry, machine and sport. Over the last four decades, carbon fibres have emerged as the main reinforcement filler for high performance polymer matrix composites<sup>1</sup>. However, the smoothness and inertness of the carbon fibre surface usually result in inferior wettability and weak adhesion between the fibres and resin, which implies that an effective fibre-matrix adhesion should not be expected. The various methods developed for the surface modification of carbon fibres include thermal treatment<sup>2</sup>, wet chemical or electrochemical oxidation<sup>3,4</sup>, plasma treatment<sup>5</sup>, gas-phase oxidation<sup>1</sup>, laser bombardment<sup>6</sup>, rare earth treatment<sup>7</sup>, coating treatment<sup>8</sup> and so on. However, these methods have the drawback that they are difficult to use for applications because of their higher

facilities requirements, high energy consumption, environmental pollution and high maintenance cost, in spite of the improved interfacial adhesion force of the final composites. It is necessary to develop some convenient and inexpensive methods to increase the interfacial adhesion without sacrificing the mechanical properties of carbon fibres.

In recent years, irradiation-induced grafting is being extensively investigated as a new technique to alter the surface properties of polymeric materials, such as films, fibres, powders and moulded objects<sup>9-11</sup>. Irradiation can induce chemical reactions at any temperature in the solid, 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.

In this work, carbon fibres were modified by  $\gamma$ -ray pre-irradiation

grafting of chloroepoxypropane. The surface topography of the fibre was characterized by scanning electron microscopy (SEM) images and the surface energy and tensile strength of the fibre was analysed. The effectiveness of improving the interfacial adhesion of composites was evaluated by interlaminar shear strength (ILSS).

## 2. EXPERIMENTAL

### 2.1 Materials

The grafting reactant, chloroepoxypropane was obtained from Tianjin Chemical Company and was reagent-grade. The polyacrylonitrile (PAN)-based continuous carbon fibres investigated in current studies were provided by Institute of Coal Chemistry, Chinese Academy of Sciences. The linear mass is 0.0638 g/m, the equivalent diameter of fibre is 7.6  $\mu\text{m}$  and a fibre bundle consists of  $1 \times 10^3$  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

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1 parts by weight, respectively. The irradiation field was provided by Harbin Rui Pu Irradiation Technology Company of China. The intensity of  $\text{Co}^{60}$   $\gamma$ -ray source was  $1.5 \times 10^4$  Ci and the dose rate was  $6.0 \times 10^3$  Gy/h.

Using the carbon fibres and epoxy resin, the prepreg was paid unidirectionally into a mould 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 in a hot-press machine, and specimens with fibre mass fraction of 64 ( $\pm 1.5\%$ ) were obtained.

## 2.2 Pre-irradiation Grafting

The carbon fibres for investigations were extracted with acetone for 12 hours, and then vacuum dried. There are essentially two basic methods of radiation grafting, namely the simultaneous (co-irradiation) method and the pre-irradiation method. In the pre-irradiation technique used in this paper, the carbon fibres are first exposed to  $\gamma$ -ray irradiation under inert atmosphere ( $\text{N}_2$ ) to generate radicals before being exposed to a monomer<sup>12</sup>. Firstly, carbon fibres (50 g) were put in a tight plastic container and the container was filled with nitrogen. This was exposed to  $\gamma$ -ray irradiation at various doses. Then the container was evacuated, and chloroepoxy propane was inhaled into the container under negative pressure. After reaction for 6 h, the treated carbon fibres were dried for 2 h at 120 °C. The grafting yield (degree of grafting) was calculated using equation (1):

$$\text{Degree of grafting (\%)} = \frac{W_g - W_0}{W_0} \times 100 \quad (1)$$

where  $W_0$  denotes the weight of the blank carbon fibre and  $W_g$  presents the weight of the fibre after treatment.

## 2.3 Measurements

The morphology of fibre surface was inspected by SEM (FEI SIRION 200).

Carbon fibre surface energy, dispersive component and polar component were determined by dynamic contact angle analysis. The contact angles of de-ionized water and diiodomethane on carbon fibres were measured by a capillary method using a wettability testing device (SB-312, Keen Co., Beijing, China). Before surface energy tests, untreated and modified carbon fibres were both extracted with acetone for 48 h in order to wash out impurities on their surface. The influence of pre-irradiation on the fibre tensile strength was determined by a single-fibre tensile test. The fibre's cross section was measured by an optical microscope. Single filament tensile was performed according to the ASTM standard, D3379-75. The distance between the papers, i.e., the gauge length was varied to 10, 15 and 20 mm. 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

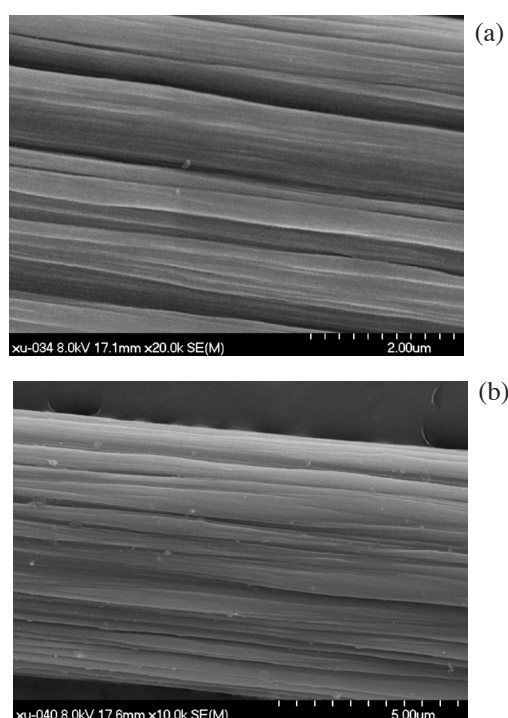
were used. More than eight specimens were tested for each of the composites studied and the average value was taken in the present work studied.

## 3. RESULTS AND DISCUSSION

### 3.1 Surface Topography of Carbon Fibres

The SEM images of untreated and pre-irradiated carbon fibres (at 300 kGy dose) are shown in **Figures 1a** and **b**, respectively. Remarkable differences in the micrographs can be observed for the untreated and treated carbon fibres. It was shown that the surface of untreated carbon fibres seemed to be relatively smooth, having a few narrow grooves or channels that were parallel with, and distributed along the longitudinal direction of fibre. After pre-irradiation grafting, many tiny fragments stuck to the fibre surface, which suggested that the absorbability of treated fibres might be enhanced to some extent. Therefore, interfacial

**Figure 1. SEM micrographs of carbon fibre surface (a) as-received; (b) pre-irradiation grafted**



adhesion between grafted fibres and matrix resin may be enhanced by increasing the surface activity which may provide more effective wetting between the fibre and the matrix.

### 3.2 Surface Energy of Carbon Fibres

To obtain information about the surface activity of carbon fibres before and after modification, analysis of surface free energy was performed by dynamic contact angle analysis. All the measurements were carried out with a dynamic capillary method. The contact angle could be calculated according to equations (2) and (3)<sup>13</sup>:

$$\Delta\gamma = \frac{0.064H^2\rho_f\eta(1-\epsilon)^2m^2}{d_fk^2w_f\rho_l^2\epsilon^3v_Tt} \quad (2)$$

$$\cos\theta = \frac{\Delta\gamma}{\gamma_l} \quad (3)$$

where  $\Delta\gamma$  is the change in fibre surface free energy;  $\gamma_l$  is the surface tension of the immersion liquid;  $\epsilon$  is the volume percent of fibres in the tube ( $\epsilon$  is in the range 48%~52%);  $H$  is the length of fibre bundle (40 mm);  $\rho_f$  and  $\rho_l$  are the densities of fibre and immersion liquid, respectively;  $\eta$  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 fibre bundle;  $d_f$  is the diameter of a single fibre;  $t$  is the time of immersion equilibrium;  $\theta$  is the dynamic contact angle;  $m$  is the amount of adsorption at immersion equilibrium.

The surface free energy ( $\gamma_f^T$ ), dispersive component ( $\gamma_f^d$ ) and polar component ( $\gamma_f^p$ ) of carbon fibres were determined by measuring the dynamic contact angle of two liquids and analyzing the results in accordance with the method proposed by Owens<sup>14</sup> and Kaelble<sup>15</sup>.

In **Table 1**, the surface free energy, its dispersive component and its polar component of carbon fibres are summarized. It can be seen that both the dispersive and polar components of

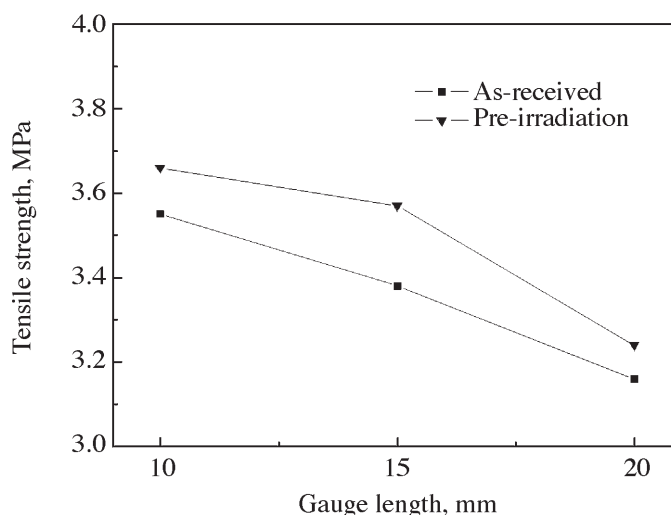
surface free energy,  $\gamma_f^d$  and  $\gamma_f^p$ , increased after modification. The increase in the surface free energy  $\gamma_f^T$  was mainly influenced by its polar component. The chloroepoxy propane modification of carbon fibres gave an increase in surface functionality, which may take chief responsibility for the improved polar component. The increased dispersive component was attributed to the fibre surface physics change, generated by pre-irradiation 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 fibre through surface treatments, the wettability of the reinforcement to the matrix can be improved<sup>16</sup>. The grafting yield of chloroepoxypropane onto the carbon fibres was 0.6 wt.%. These results may be attributed to the grafting of monomers and the removal of a weak surface layer on fibre surface.

### 3.3 Tensile Strength of Carbon Fibres

The tensile strength of carbon fibres 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 fibres. Thus, the interpretation of the data must be done statistically. The Weibull distribution has been used to describe tensile data.

**Figure 2** presents the ultimate fibre tensile strength of untreated and pre-irradiated carbon fibres (at 300 kGy dose). The tensile strength of single carbon fibre increased after pre-irradiation grafting. This result was probably attributable to the reduction of flaws and decrease of interlayer spacing by  $\gamma$ -ray irradiation. Furthermore, the irradiation grafting coating can inhibit failure initiated at fibre surface flaws, resulting in the increase of fibre tensile

**Figure 2. Variation of tensile strength of the carbon fibres before and after irradiation**



**Table 1. Surface free energy of carbon fibres**

	$\gamma_f^d$ (mJ•m <sup>-2</sup> )	$\gamma_f^p$ (mJ•m <sup>-2</sup> )	$\gamma_f^T$ (mJ•m <sup>-2</sup> )
As-received	39.8±1.6	2.4±0.3	42.2±2.0
Pre-irradiated (300 kGy)	42.3±2.0	7.2±0.4	49.5±2.2

strength<sup>17,18</sup>. The strength of all the carbon fibres decreased with increasing gauge length of the specimens.

### 3.4 Interface Properties of Carbon Fibre/Epoxy Composites

The ILSS results of composites reinforced by carbon fibres treated in different dose are shown in **Figure 3**. After pre-irradiation grafting, the ILSS values of composites were enhanced by 6.9% (at 60 kGy dose), 14.7% (at 200 kGy dose), 18.2% (at 300 kGy dose) and 12.2% (at 500 kGy dose) respectively, compared with the untreated carbon fibre composites. The chemical bonding and mechanical interlocking between carbon fibres and matrix resin may be responsible for these results. However, pre-irradiation at 500 kGy dose caused a 6% decrease of ILSS value; this may be due to the fact that excessive irradiation decreased the carbon radical concentration on the fibre surface and did harm to the grafting reaction between chloroepoxypropane and radicals on the fibre surface. It appears that chloroepoxypropane pre-irradiation treatment at the proper dose is beneficial for improving the interfacial adhesion of carbon fibre/epoxy composites, but that excessive irradiation treatment would not achieve a good interface between the carbon fibre and the matrix.

Gamma rays are photons of high energy and can be produced when a nucleus decays from its excited state to a lower or ground state. <sup>60</sup>Co emits two gamma rays, one at 1.173 MeV and the other at 1.332 MeV. Carbon is the dominant element in carbon fibre and has a low atomic number. Therefore, it is concluded that the Compton scattering effect is mostly responsible for the interaction of gamma ray with carbon fibre.

In Compton scattering, charged particles such as electrons and protons interact with atoms primarily by Rutherford (Coulomb) scattering, and cause ionization and atomic displacements. Then carbon free radicals are created by anion or cation radical mechanisms<sup>17,18</sup>. A goal of this approach is the generation of carbon radicals reactive enough to be selectively quenched by chloroepoxypropane. The epoxy ring of chloroepoxypropane is destroyed under the induction of carbon, hydroxyl and ether radicals. As a result, covalent bonds are formed between the fibres and the grafting reagent.

### 4. CONCLUSIONS

Compared with the original carbon fibre, the surface of the modified fibre became rougher, with pieces

of tiny fragments adhering to the fibre surface. Following treatment, there was an increase in the surface energy. The tensile strength of carbon fibres was improved marginally by  $\gamma$ -ray pre-irradiation. ILSS of the composites containing carbon fibres irradiated at 300 kGy dose, showed an 18.2% improvement compared with that of composites employing untreated carbon fibres. However, excessive irradiation decreased the interfacial adhesion of the composites. The pre-irradiation grafting of chloroepoxypropane onto the carbon fibre surface induced by  $\gamma$ -ray was found to be a promising and efficient method for modifying the physicochemical properties of carbon fibres and improving the interfacial adhesion of their composites.

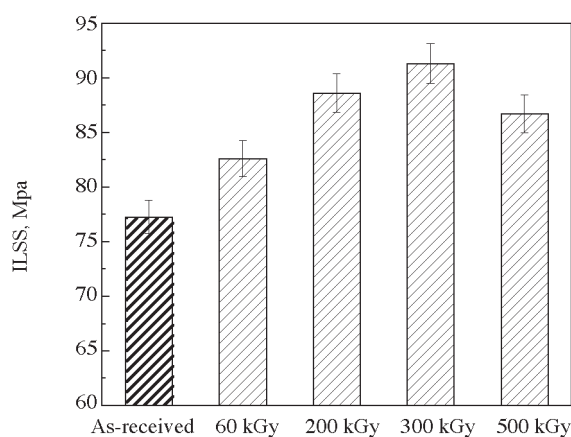
### ACKNOWLEDGMENTS

We acknowledge the Tianjin Natural Science Foundation (Grant no. 08JCZDJC24500) for financial support.

### REFERENCES

1. Zhang H., Zhang Z., and Breidt C., *Compos. Sci. Technol.*, **64**(13-14) (2004) 2021-2029.
2. Bismarck A., Wuertz C., and Springer J., *Carbon*, **37**(7) (1999) 1019-1027.
3. Fukunaga A. and Ueda S., *Compos. Sci. Technol.*, **60**(2) (2000) 249-254.
4. Xu Z.W., Wu X.Q., Sun Y., et al., *J. Appl. Polym. Sci.*, **108**(3) (2008) 1887-1892.
5. Yamada K., Haraguchi T., and Kajiyama T., *J. Appl. Polym. Sci.*, **75**(2) (2000) 284-290.
6. Nematollahzadeh A., Mousavi S.A., Tilaki R.M., et al., *Polym. Polym. Compos.*, **14**(6) (2006) 585-589.
7. Xu Z.W., Huang Y.D., Zhang C.H., et al., *Mater. Sci. Eng. A-Struct.*, **444**(1-2) (2007) 170-177.
8. Zhang X.Z., Huang Y.D., Wang T.Y., et al., *Polym. Polym. Compos.*, **15**(1) (2007) 35-42.
9. Clough R.L., *Nucl. Instrum. Meth. B*, **185** (2001) 8-33.

**Figure 3.** Effect of pre-irradiation dose on ILSS of carbon fibre/epoxy composites



10. Madani A., *Polym. Polym. Compos.*, **12**(6) (2004) 525-534.
11. Deng S.S., Ran Q.P., Wu S.S., et al., *Polym. Polym. Compos.*, **16**(6) (2008) 375-378.
12. Nasef M.M. and Hegazy E.S.A., *Prog. Polym. Sci.*, **29**(6) (2004) 499-561.
13. Huang Y.D., Qiu J.H., Liu L.X., et al., *J. Mater. Sci.*, **38**(4) (2003) 759-766.
14. Owens D.K. and Wendt R.C., *J. Appl. Polym. Sci.*, **13** (8) (1969) 1741-1748.
15. Kaelble D.H., *J. Adhesion*, **2**(2) (1970) 66-81.
16. Lin SP, Han JL, Yeh JT, et al., *Eur. Polym. J.*, **43**(3) (2007) 996-1008.
17. Ercin D, Eken M, Aktas Z, et al., *Radiat. Phys. Chem.*, **73**(5) (2005) 263-271.
18. Khan F, Ahmad SR, Kronfli E., *Biomacromolecules*, **7**(8) (2006) 2303-2309.

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