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Amino-Functionalization of Carbon Fibers Through Electron-Beam Irradiation Technique

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ABSTRACT: Amino-functinonalized carbon fibers were achieved via electron-beam (EB) irradiation in Diethylenetriamine (DETA) solution and triethylene tetramine (TETA) solution at 200 kGy. Different graft monomer concentrations were investigated to find the optimal concentration of each graft monomer. X-ray photoelectron spectroscopy, scanning electron microscopy, and Raman spectroscopy were applied to investigate chemical composition and functional groups, topography and disorder degree of amino-functionalized carbon fibers surface. Meanwhile, adsorption ability and interfacial adhesion between modified carbon fibers and epoxy resin were determined by TGA and interlaminar shear strength (ILSS). It is found that amino-functionalized carbon fibers which had rougher and more active surface performed better adsorption ability on epoxy resin than untreated fibers. The optimal ILSS values of carbon fiber (treated with DETA and TETA) reinforced composites were 21.37 MPa and 18.28 MPa, which were much higher than that of untreated fiber reinforced composites. The comprehensive results demonstrated that in this condition, the optimal grafting concentrations of both DETA and TETA were 1.5 mol/L. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40274.

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INTRODUCTION

Nowadays, the excellent properties of carbon fibers, such as high tensile strength and modulus, thermal stability in the absence of oxygen to over 3000°C, low thermal expansion coefficient and excellent creep resistance and so forth, make carbon fibers maintain their predominance in nonmetal reinforcement materials field. Nevertheless, inert and smooth carbon fibers surface resulting from high fraction of graphitic carbon leads to poor interfacial performance between fibers and matrix. These are of particular concern as the properties of fiber-reinforced composites are, to a large extent, determined by the interface performance between fibers and matrix. Good interfacial properties are the guarantee of efficient load transference from matrix to reinforcements, which conduces to reduce stress concentrations and improves integral mechanical properties of fiber-reinforced composites.[1,2] Therefore, the lifetime of carbon fiber reinforced composites is always confined to an inferior interface between carbon fibers and surrounding polymer matrix.[3–5]

It is generally believed that surface roughness and functional groups can enhance interfacial adhesion between fibers and matrix[6] and then improve the mechanical properties of carbon fiber reinforced composites. According to this, extensive investigations have been studied and as a result, chemical oxidation,[7] electrochemical treatments,[8,9] sizing,[5,10] plasma treatments,[11,12] high energy irradiation,[13,14] and chemical grafting[3,15] have all applied as viable techniques for surface modification of carbon fibers. Among these methods, electron-beam (EB) irradiation modification has been extensively developed in fiber surface modification recently.[16–19] EB irradiation technique has prominent merits, for instance, fast reaction time, low damage of materials, high efficiency and not demanding for reaction conditions.[17,20] Carbon fibers are activated and produce free radicals during EB irradiation modification. Subsequently, molecules are grafted onto carbon fibers, and functional groups on carbon fibers surface increase remarkably.[21,22]

Among precious studies, most of them are emphasis on increasing oxygen functional groups on carbon fibers surface to improve interfacial properties between fibers and matrix while it's generally believed that amino functional groups are more useful than oxygen functional groups when reacting with epoxy resin.[23,24] General way of amino-functionalization of carbon fibers surface must undergo several chemical reactions step by

Table I. Different Concentrations of Graft Monomer in 7 Samples

Sample number	Grafting solution	Concentration (mol/L)
0	Distilled water	0
1	DETA/distilled water	1
2	DETA/distilled water	1.5
3	DETA/distilled water	2
4	TETA/distilled water	1
5	TETA/distilled water	1.5
6	TETA/distilled water	2

step, like Peng et al.[15] do, which is tedious and time consuming. With the emerging of applying EB irradiation to carbon fibers surface modification, it offers another efficient way to graft amino groups onto carbon fibers surface.

In this study, amino functional groups were grafted onto carbon fibers surface via EB irradiation technique. Diethylenetriamine (DETA) and triethylene tetramine (TETA) were applied as graft monomer and their optimal concentrations were investigated. The chemical structure changes on carbon fibers surface were evaluated by X-ray photoelectron spectroscopy (XPS) and the surface topography changes of carbon fibers were investigated by scanning electron microscopy (SEM). The degree of disorder on carbon fibers surface and surface crystallinity were analyzed by Raman spectroscopy. The adsorption ability of carbon fibers on epoxy matrices was characterized by TGA. The interfacial adhesion improvement of carbon fiber/epoxy resin composites was evaluated by interlaminar shear strength (ILSS) and SEM. The results denoted that amino-functionalized carbon fibers surface was rougher and had more amino functional groups than that of untreated fibers. Good compatibility between amino-functionalized carbon fibers and matrix had been achieved. The comprehensive results demonstrated that in this condition, the optimal grafting concentrations of both DETA and TETA were 1.5 mol/L.

EXPERIMENTAL

Materials

The Chemical Reagents used in this Research were all Analytical Grade. The polyacrylonitrile-based carbon fibers (3×10^3 single filaments per tow) used as reinforcement were supplied by Jilin Petrochemical Company of China. The E-51 epoxy resin applied as matrix was manufactured by Wuxi Resin Factory of China and its curing agent was TETA. DETA and TETA applied as graft monomers were obtained from Changlian Chemical Reagent Factory of Chengdu. Acetone was purchased from Kelon Chemical Reagent Factory of Chengdu. Electrostatic Election Accelerator model JJ-2 which was supplied by Leshan Dongfeng Motor Factory of China was used as irradiation source. The conditions of the irradiation were: electron-current 32 mA, energy 1.7 MeV and overall dose of 200 kGy at the rate of 10 kGy/s.

Methods

Carbon fibers were first extracted in acetone with a Soxhlet extractor for 24 h to remove surface contamination, and then the fibers were vacuum dried at 60°C prior to use. The fibers were placed in six glass containers filled with 1, 1.5, 2 mol/L DETA/de-ionized water solution or TETA/de-ionized water solution, respectively. Another glass container filled with only the fibers and de-ionized water was set as blank comparison. The total seven glass containers were all filled with argon instead of air under negative pressure, and then they were exposed to EB irradiation at 200 kGy. After the treatment, the modified fibers were washed in de-ionized water with a Soxhlet extractor for 12 h to remove residues of reactant on their surfaces and then vacuum dried at 80°C. Table I shows the 7 samples' conditions.

Characterization

X-ray Photoelectron Spectroscopy. The chemical composition and functional groups on carbon fibers surface were analyzed by AXIS Ultra^{DLD}, SHIMADZU Corporation. The data were deconvolution by Gaussian-Lorentzian function. The positions used for peak fitting are according to the components suggested by Biniak[25] and Lee.[26]

Scanning Electron Microscopy Imaging. SEM studies on virgin and treated fibers were done by FEI INSPECT F to characterize the topographical changes on carbon fibers surface. Carbon fibers were first coated with a Au layer of several nanometer thick, and then imaged with the SEM machine. The acceleration voltage was 20 kV.

Raman Spectroscopy of Fibers. HORIBA Lab RAM HR Raman spectroscope with 532.17 nm Nd-Yag laser was used to get Raman spectra of virgin and treated fibers. The fibers were fixed on a microscope slide. The intensity ratio between the D bands (1360 cm^{-1}) and G bands (1593 cm^{-1}) of the Raman spectra fitted by Lorentzian function was employed to evaluate the degree of structural disorder of carbon fibers and the size of the crystalline surface of carbon fibers.

Adsorption Ability of Carbon Fibers on Epoxy Resin. The adsorption ability of carbon fibers was analyzed by NETZSCH TG 209F1 Iris 220-12-0049-L from room temperature to 500°C at a heating rate of 10°C/min. Carbon fibers (approximately 8 mg) were first dipped in epoxy/acetone solution containing 10 wt % of epoxy resin for 1 h, and then vacuum dried at 60°C prior to use.

Interlaminar Shear Strength. The ILSS values of carbon fiber/epoxy resin composites were determined by JC/T773-2010 test method. An electronic universal material testing machine (AG-10TA) was applied to evaluate the ILSS of carbon fiber/epoxy resin composites. The termination samples with span to thickness ratio of 5 : 1 and the thickness of 2 mm were tested at a strain rate of 0.008/s. In order to eliminate the experiment error, ten specimens were respectively tested for each kind of composites, and the average value was adopted in the present studied.

RESULTS AND DISCUSSION

XPS Analysis

Functional groups on carbon fibers surface were characterized by XPS because of its high sensitivity to the chemical

Table II. The Atomic Concentrations of Carbon Fibers

Sample number	C %	N %	O %	(O+N)/C %
0	73.77	1.41	24.82	35.56
1	72.90	2.66	24.44	37.17
2	70.78	5.45	23.77	41.28
3	73.08	2.56	24.36	36.84
4	73.00	2.77	24.23	36.99
5	71.99	3.75	24.27	38.92
6	72.73	3.07	24.20	37.29

composition of the near surface (up to 6 nm).[27,28] Table II shows atomic concentrations of the seven samples after EB irradiation treatment. The results indicated that treated carbon fibers surface was composed of carbon, nitrogen and oxygen elements. Contrasting with the blank sample, it was shown that nitrogen concentration increased; carbon and oxygen concentrations decreased in all other samples, and the ratio value of (O+N)/C increased as well. A peak in nitrogen concentration was shown in each kind of graft monomers which was 5.45% in no. 2 sample and 3.75% in no. 5 sample, respectively. This phenomenon indicated that the higher concentration of graft monomer, the higher grafting reaction happened, but too high concentration, such as 2 mol/L, would induce monomer to coupling termination rather than grafting reaction. Nitrogen concentration of no. 2 sample was higher than that of no. 5 sample, which was because that TETA monomer had more active hydrogen than that of DETA monomer which could easier to coupling termination rather than grafting reaction.

Deconvolutions of the C 1s peak region for no. 0, no. 2, no. 5 samples and the N 1s peak region for no. 2 sample by Gaussian-Lorentzian function are shown in Figure 1. The positions used for peak fitting are detailed in Table III, together with the relative content of each functional group. The narrow scan spectra of the C 1s peak region of the blank sample gave four peaks assigned as C—C, C—O, C═O and COOH/COOR. However, a shoulder peak associated with C—NHx at about 286 eV in other 6 samples' C 1s response emerged,[29–31] which denoted the existence of amino groups on carbon fibers surface. Examination of the N 1s response also confirmed the existence of C—NHx which was at about 400 eV.[25] Clearly, a significant decline in the relative content of C—C group along with an increase in that of C—NHx group occurred as grafting reaction happened. For no. 2 and no. 5 samples, they had the least amount of C—C group and the most amount of C—NHx group. The relative content of oxygen functional groups, such as C—O, C═O and COOH/COOR, all slightly decreased with different degrees. In conclusion, the total amount of functional groups increased extensively, especially no. 2 and no. 5 samples of which graft monomer concentrations were both 1.5 mol/L, which could improve interfacial adhesion of carbon fiber/epoxy

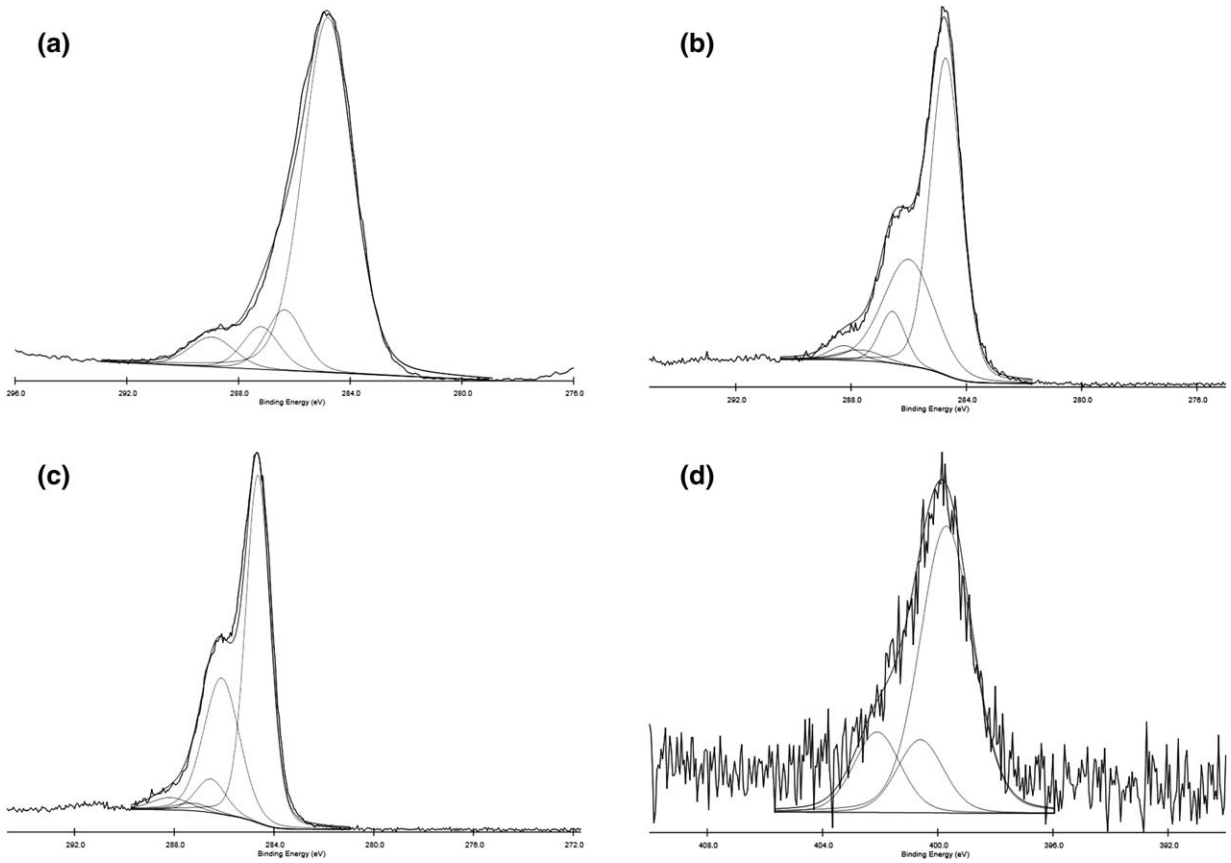

Figure 1. Deconvolution of the C 1s peak region for (a) no. 0 sample, (b) no. 2 sample, (c) no. 5 sample, and N 1s peak region for (d) no. 2 sample.

Table III. Relative Content of Each Functional Group in the Fitting of C 1s Peak of Carbon Fibers

Sample number	C—C (284.7-285.0 eV)	C—NHx (285.4-286.8 eV)	C—O (286.0-286.5 eV)	C=O (287.2-287.6 eV)	COOH/COOR (288.3-289.0 eV)
0	77.37	—	9.93	6.85	5.84
1	58.74	26.18	5.72	5.32	4.05
2	56.47	30.90	7.52	2.65	2.45
3	59.28	22.97	6.42	5.94	5.39
4	59.16	21.27	7.58	5.38	6.59
5	57.30	29.41	8.54	1.69	3.06
6	58.39	26.10	5.59	4.93	4.98

resin composites. This inference would be confirmed by later characterization.

Surface Topography Analysis

Figure 2 shows the SEM photographs of virgin fibers as received, no. 0, no. 2, and no. 5 samples. The images showed that the surfaces of no. 2 and no. 5 samples were much rougher than that of the blank sample. As each sample were extracted in de-ionized water with a Soxhlet extractor for 12 h to remove residues of reactant after treatment, the particles which were still on carbon fibers surface clearly indicated that molecules of DETA or TETA were not adsorbed but strongly chemically bound onto carbon fibers surface. Besides the particles, surface grooves after treatment were wider and deeper than that of virgin carbon fibers owing to etching. The rougher carbon fibers surface would promote mechanical interlocking effection which

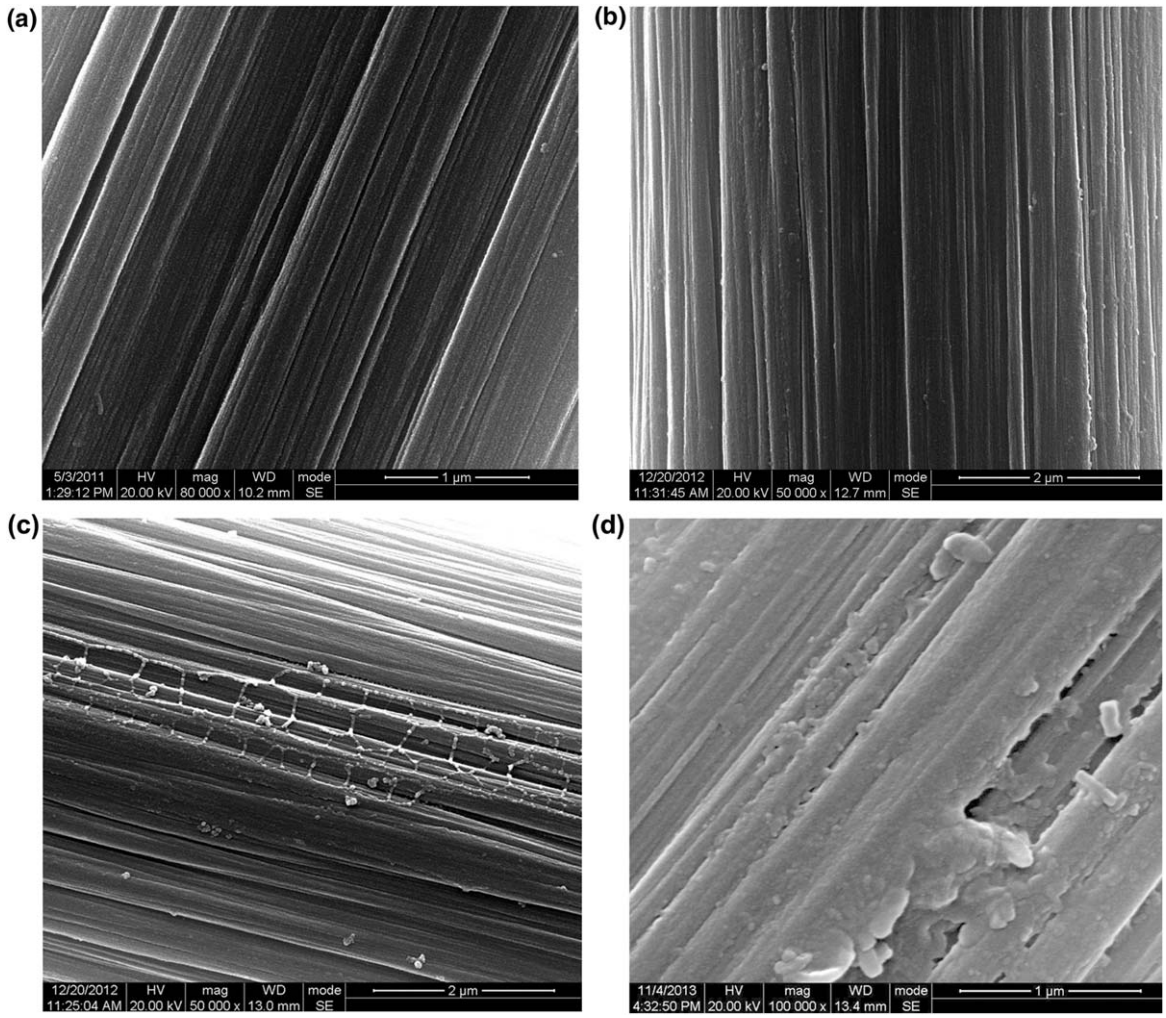

Figure 2. SEM images of surface of (a) virgin carbon fiber, (b) blank sample, (c) no. 5 sample, and (d) no. 2 sample with higher multiples.

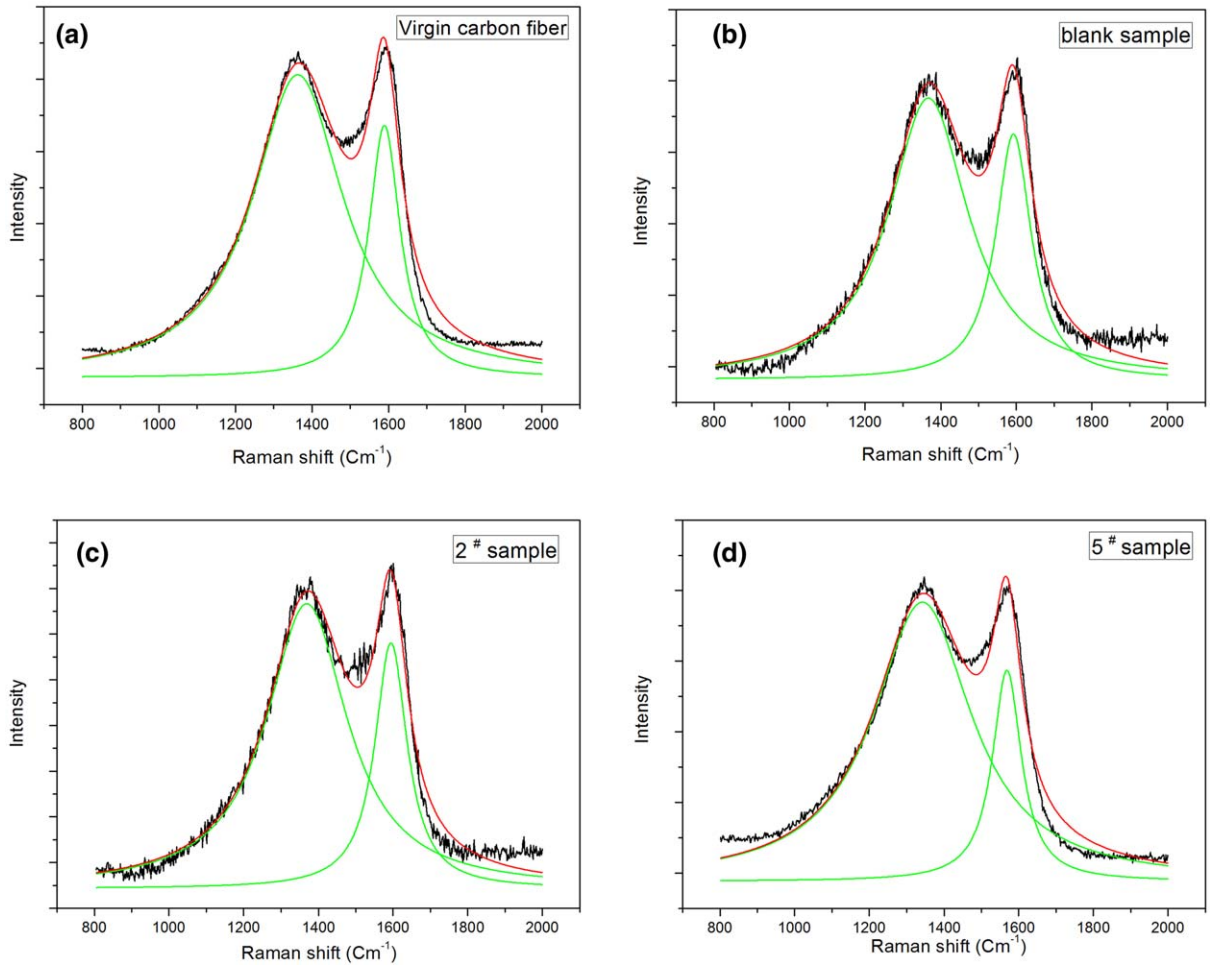

Figure 3. Raman spectra of (a) virgin carbon fiber, (b) blank sample, (c) no. 2 sample, and (d) no. 5 sample. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

could improve interfacial adhesion between carbon fibers and epoxy resin.

Raman Spectroscopy Analysis

Raman spectroscopy was chosen to characterize the degree of structural perturbation of the fibers due to its high sensitivity to the crystallinity of the near surface (up to 10 nm).[21,32] Figure 3 shows Raman spectra of virgin carbon fibers, no. 0, no. 2, and no. 5 samples. Table IV shows (I_D/I_G) ratio and surface crystalline size (La) of carbon fibers which was calculated by the following equation:

$$La = \frac{C}{I_D/I_G} \quad (1)$$

where La referred to the surface crystalline size and C is equal to 44Å.

The results manifested that (I_D/I_G) ratio of no. 0 sample decreased comparing with virgin carbon fibers, which suggested the decrease in the degree of disorder resulted from removing the weak layer of carbon fibers by EB irradiation. However, a rise in (I_D/I_G) ratio was shown in all other samples, which denoted that the increase in the degree of disorder was probably generated by grafting reaction. Removing the weak layer could enhance the mechanical property of carbon fibers and eliminate surface defects and weak link between carbon fibers and epoxy resin. Meanwhile, grafting DETA or TETA onto carbon fibers surface would enhance the roughness of carbon fibers surface which could improve mechanical interlocking effection.

Adsorption Ability

Carbon fibers are noble in the absence of oxygen to over 3000°C. Thus, in TGA system under nitrogen atmosphere, epoxy resin is the only reason that generates residual weight ratio of carbon fiber/epoxy resin specimen.[32] With the aid of thermal analyzer, adsorption ability of carbon fibers on epoxy

Table IV. I_D/I_G Ratio and La of Carbon Fibers

Sample number	I_D/I_G	La(Å)
Virgin carbon fiber	3.47	12.68
0	2.55	17.25
2	2.90	15.17
5	3.29	13.37

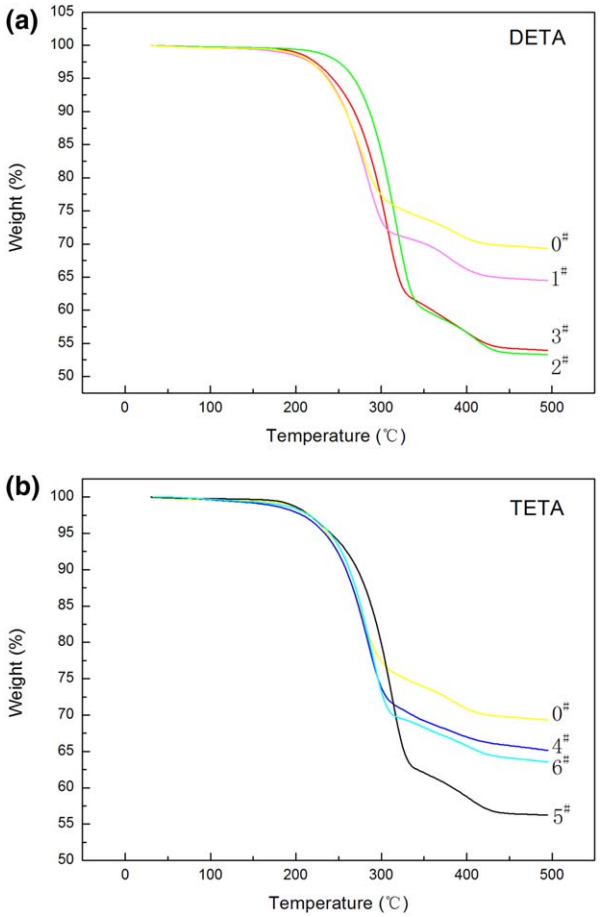

Figure 4. The TG curves of the carbon fiber/epoxy resin specimens. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

resin was studied. Figure 4 shows the TG curves of carbon fiber/epoxy resin specimens under nitrogen atmosphere. It is obvious that decomposition and carbonization of epoxy resin contribute to the weight loss between 250 and 450°C in this system.[33] As seen in Figure 4, no. 2 and no. 5 samples had the biggest weight loss comparing with the others respectively, while the blank sample had the lowest weight loss. The increase in weight loss ratio was possibly due to the improved adsorption ability of carbon fibers on epoxy resin which could give rise to ascend the epoxy proportion as well as reduce the residual weight in carbon fiber/epoxy resin specimen.[20] Therefore, it demonstrated that amino-functionalizetion of carbon fibers surface via EB irradiation grafting could improve adsorption ability of carbon fibers and the best graft monomer concentration of both DETA and TETA were 1.5 mol/L.

ILSS Studies of Composites

The ILSS results of fiber-reinforced composites shown in Figure 5 were calculated by the following equation:

$$ILSS = \frac{3P_b}{4bh} \quad (2)$$

where P_b denoted the load at the break; b and h stand for the width and thickness of the specimen, respectively.

It was clear that the ILSS value increased with different degrees after treatment. Maximum ILSS value of each graft monomer could be found in no. 2 and no. 5 samples which were 21.37 MPa and 18.28 MPa, respectively. They were about 63.12% and 39.54% higher than that of the blank sample. These results were corresponding to the former studies, such as XPS analysis, Raman analysis and thermal analysis.

There are several mechanisms for fiber-matrix bonding, which involve mechanical interlocking, chemical bonding and adsorption interaction.[29,34] It was certainly that not only more functional groups could be generated by amino-functionalization of carbon fibers surface via EB irradiation grafting as shown in the XPS analysis, but also carbon fibers surface became rougher as shown in the SEM photography and Raman spectroscopy. As a result, covalent bonding, mechanical interlocking and adsorption interaction between carbon fibers and matrix could be promoted as shown in the thermal analysis. The three factors generated by amino-functionalization via EB irradiation grafting mainly attributed to the improvement of interfacial adhesion which lead to the significant increase in ILSS values of treated carbon fiber/epoxy resin composites.[13]

Moreover, the interlaminar shear fracture morphology along the cross section of carbon fiber/epoxy resin composites presented in Figure 6 also revealed that amino-functionalization via EB irradiation grafting could improve interfacial adhesion between matrix and fibers. As was seen in Figure 6(a), carbon fibers seemed to be separated from matrix. There was few resin matrix adhered on carbon fibers surfaces and the carbon fibers were pulling out of the composites. The blank sample manifested very poor interface adhesion with epoxy resin.[29] While in Figure 6(b), it was clear that fibers and matrix were in combination with each other tightly. The fracture surface was more neatly than the blank sample which the carbon fibers were engulfed by matrix. These results were probably due to better interfacial bonding between carbon fibers and epoxy resin caused by EB irradiation grafting, which contributed to the improvements of composites' ILSS values.

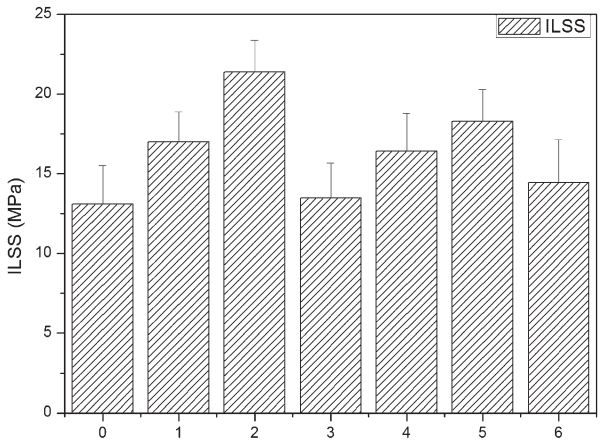

Figure 5. Interfacial shear strength of carbon fiber/epoxy resin composites.

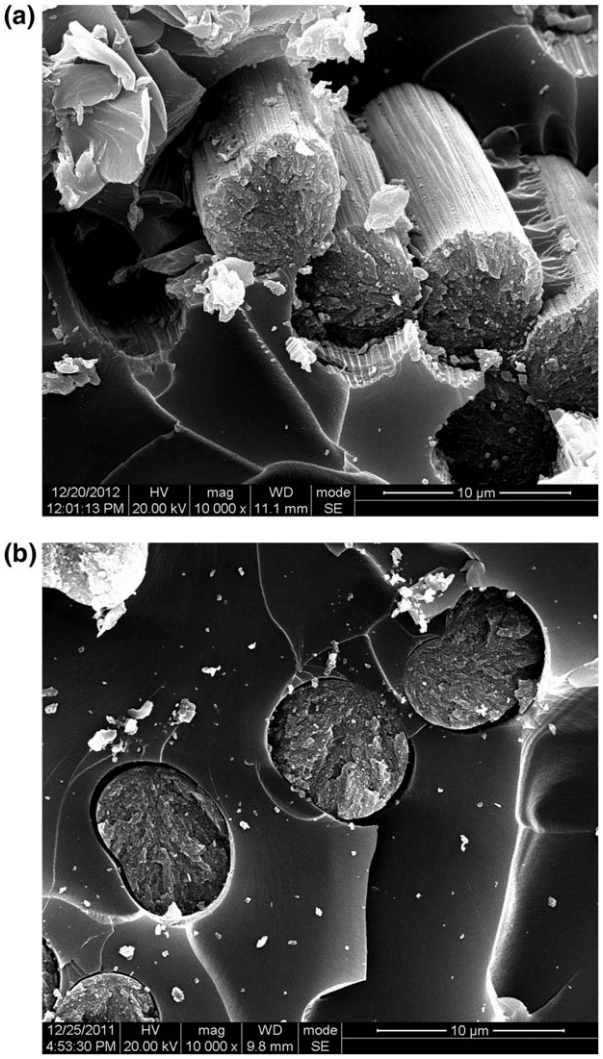

Figure 6. SEM images of fracture surfaces of (a) blank sample and (b) no. 2 sample reinforced composites.

CONCLUSIONS

Amino functional groups were grafted directly onto carbon fibers surface via EB irradiation in this research without undergoing several chemical reactions one step at a time, which is simpler, more effective and environmentally friendly. The comprehensive results manifested that amino-functionalized carbon fibers performed better surface and interfacial properties of carbon fiber composites. The optimal concentrations of the two graft monomers (DETA and TETA) were both 1.5 mol/L. The amino- functionalized carbon fibers surface had more amino functional groups as shown in XPS results, which confirmed the success of grafting amino groups onto carbon fibers surface and also meant the fibers were more active when reacting with epoxy resin. Carbon fibers surface became rougher as shown in SEM photography and Raman spectroscopy. As a result, adsorption ability between carbon fibers and matrix could be promoted as shown in the thermal analysis. The maximum weight loss appeared in no. 2 and no. 5 samples. The ILSS values of no. 2 and no. 5 samples reinforced composites were 21.37 MPa and 18.28 MPa which were 63.12% and 39.54% higher than that of the blank sample. That is to say, amino-functionalized carbon fibers via EB irradiation can remarkably promote their surface functional groups, roughness, adsorption ability and ILSS.

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