A Comparative Study on the Properties of the Different Amino-Functionalized Multiwall Carbon Nanotubes Reinforced Epoxy Resin Composites

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ABSTRACT: Multiwall carbon nanotubes (MWCNTs) were amino-functionalized by 1,2-ethylenediamine (EDA)' triethylenetetramine (TETA), and dodecylamine (DDA), and investigated by fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, and thermogravimetric analysis (TGA). The dispersion of the DDA functionalized MWCNT in DMF is better than that of the MWCNT functionalized by the EDA and the TETA. Carbon nanotubes reinforced epoxy resin composites were prepared, and the effect of the amino-functionalization on the properties of the composites was investigated by differential scanning calorimetry (DSC), dynamical mechanical analysis (DMA), and TGA. The composites reinforced by the MWCNTs demonstrate improvement in various mechanical properties. The increase of T_g of the composites with the addition of amino-functionalized MWCNT compared to the T_g of the composites with the addition of unfunctionalized MWCNT was due to the chemical combination and the physical entanglements between amino group from modified MWNTs and epoxy group from the epoxy resin. The interfacial bonding between the epoxy and the amino group of the EDA and the TETA-modified MWCNT is more important than the well dispersion of DDA-modified MWCNT in the composites for the improvement of the mechanical properties. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 403–411, 2012

Key words: nanocomposites; dispersion; interface; mechanical properties; thermal properties

INTRODUCTION

Carbon nanotubes (CNTs) have attracted many scientists to pay more attention recently because of their remarkable chemical stability and physical properties.[1,2] Because of unique properties, carbon nanotubes are expected to be used as the reinforcement and functional materials for the applications in a variety of fields, such as high-performance composites, biological and chemical sensors, magnetic recording, nanoelectronic devices, tips for scanning probe microscopy, and flat panel displays.[3,4]

Multiwall carbon nanotubes (MWCNTs) have been used as reinforcement to produce MWCNT/epoxy resin composites [5,6]. However, many research reports indicate that MWCNT/epoxy resin composites are weaker or only slightly stronger than the neat epoxy resin. Researches ascribed this to poor MWCNTs dispersion, inadequate alignment, and weak interfacial bonding.[7]

The dispersion of carbon nanotubes in the epoxy resin is one of the most important factors in preparation of carbon nanotube composites,[8–12] which have been found to be critical in reinforcing efficiency because the bonding of nanotubes sliding significantly affects the mechanical properties of the resulting materials.[7] Also, the aggregation of carbon nanotubes and large resin-rich area due to poor dispersion of tubes are harmful to mechanical properties of the resultant nanocomposites. Therefore, the key factor of improving nanotube composites processing techniques is to prevent the nanotubes from aggregating together in the composites. The methods of the improvements included ultrasonic dispersing, high shear mixing, surfactant treatment, chemical modification, physical wrapping with polymer chains, and the combinations of these methods. To graft amino group to the surface of CNTs is an effective method to improve the dispersion and the interfacial bonding owing to the polarity effect and curing behavior of epoxy polymer.[13–16] Clearly, the modification of CNT enhances dispersion and the resulting properties. It is not clear, however, how the modified CNTs react with the epoxy resins and how this affects the final properties. Which are important factors between the dispersion and the
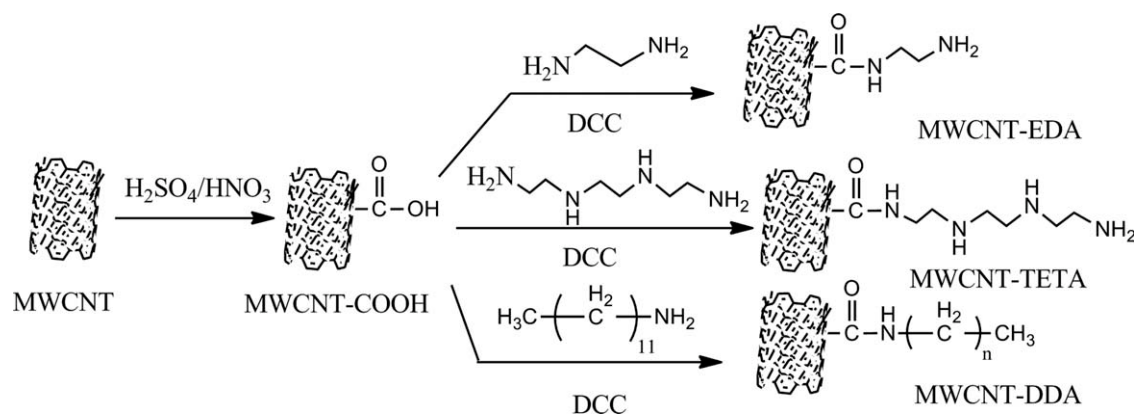
Scheme 1 Reaction of amino-functional MWCNTs.

interfacial bonding for the improvement of the properties of CNT/epoxy composites?

In this study, three types of amino-functionalized MWCNTs were produced after oxidation and amidation with amine, and the MWCNTs/epoxy composites were prepared. The effect of amino-functionalized MWCNTs on the properties of the composites was compared.

EXPERIMENTAL

Materials

The MWCNTs (diameter was 8–15 nm, and the purity was more than 95 wt %) was supplied by Chengdu Organic, China Academy of Sciences.

Epoxy resin (E-51) was supplied by Shanghai Xinhua Resin Manufacturing Company (China). Sulfuric acid (H_2SO_4) 98 wt %, nitric acid (HNO_3), hydrogen peroxide(H_2O_2) 30 wt %, tetrahydrofuran (THF), N,N-dicyclohexylcarbodiimide (DCC), diamino diphenyl methane (DDM), 1,2-ethylenediamine (EDA), triethylenetetramine (TETA), and dodecylamine (DDA) were purchased by Sinopharm Chemical Reagent (Shanghai).

Amino-functionalization of MWCNTs

Totally, 0.3 g MWCNTs were dispersed in 150-mL mixture with sulfuric acid 98 wt % and nitric acid 68 wt % in ratio 3 : 1 in a 500-mL round bottom flask equipped with a condenser. The dispersion was refluxed at 40°C under ultrasonic vibration for 4 h. After that, the resulting dispersion was diluted in water and filtered, and then the filter residue was dispersed in 25 mL of mixture of sulfuric acid 98 wt % and hydrogen peroxide 30 wt % in ratio 4 : 1, refluxed at 70°C for 2 h. After that the resulting dispersion was diluted in water and filtered. Then the filter residue was washed up to neutral pH, and the

sample was dried in vacuum at 40°C overnight. The MWCNT-carboxyl was obtained for next step.

The mixture of 0.2 g MWCNTs-carboxyl, 30 g EDA or TETA or DDA and 5 g DCC was heated to 120°C and retained for 24 h. Then the reaction system was cooled to room temperature, the insoluble black material was deposited and filtered with a Teflon membrane of 0.45-μm pore size. The product was washed several times with large amounts of ethanol and was dried overnight in a vacuum oven at 60°C. The reaction of amino-functionalized MWCNT was shown in Scheme 1.

Preparation of MWCNTs/epoxy resin composite

Epoxy resin was heated to 60°C for several minutes. Totally, 1.0 g modified MWCNTs was added into the resin, and stirred for 8 h. Ultrasonic vibration was then conducted for 4 h to disperse MWCNTs into the resin. DDM (resin/DDM = 10/2.92) was added into the MWCNTs/epoxy resin mixture and stirred for 30 min at 50°C. A degassing process was then carried out as the mixture was heated to 35°C for 1 h to remove trapped air. The mixture was filled in a mold and cured in an oven at 80°C for 2 h. The samples were postcured at 150°C for another 4 h. Corresponding chemical reactions are shown as Scheme 2.

Characterization

The structure of MWNTs before and after modification was characterized using Fourier Transform Infrared Spectrometer (EQUINOXSS, Bruker Optics Company) and Raman Spectroscopy (LABRAM-1B, HORIBA Jobin Yvon Company). Thermogravimetric analysis (TGA) was performed on a STA 449 C Jupiter thermogravimetric analyzer (NETZSCH) at a heating rate of 20°C/min. Samples were examined under the presence of nitrogen (80 mL/min) over a
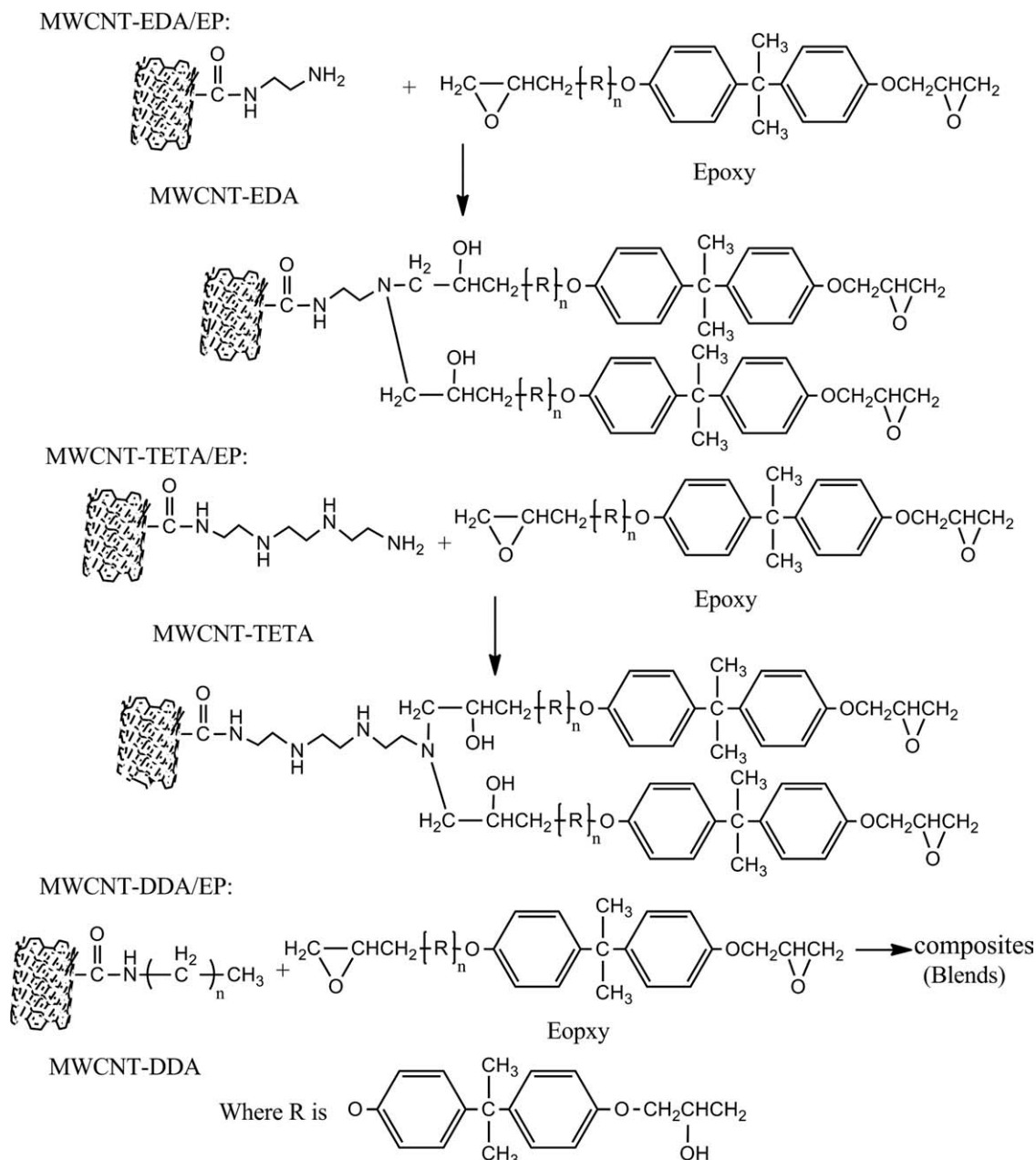
Scheme 2 Preparation of MWCNTs/epoxy composites.

temperature range from ambient to 700°C. Cure behaviors of the epoxy and the composites were analyzed using Q100 DSC thermoanalyzer. The test temperature ranged between 20 and 200°C with heating rate of 10°C/min in nitrogen atmosphere. The tensile and flexural properties of neat epoxy and MWCNTs/epoxy composites were tested according to GB11997 and GB/T 1040-92 by using the mechanical analysis instruments (DXLL-5000, Shanghai D and G Measure Instrument). And the impact strength of neat epoxy and MWCNTs/epoxy composites was determined in accordance with GB 9341-88 by using the instruments (Charpy XCJ-50, Hebei Chengde Measure Instrument). Dynamic me-

chanical analysis (DMA) was performed in three-point bending mode using a Q800 Dynamic Mechanical Analyzer. The samples were cut from the sheets with typical dimensions of $60 \times 13 \times 2.4$ mm^3. The test specimen dimensions were kept as consistent as possible to obtain an accurate comparison.

RESULTS AND DISCUSSION

Analysis of the amino-functionalized MWCNT

Figure 1 shows the Raman spectra of MWCNT and MWCNT modified by different amino, and the data was listed in Table I. In the Raman spectra, the
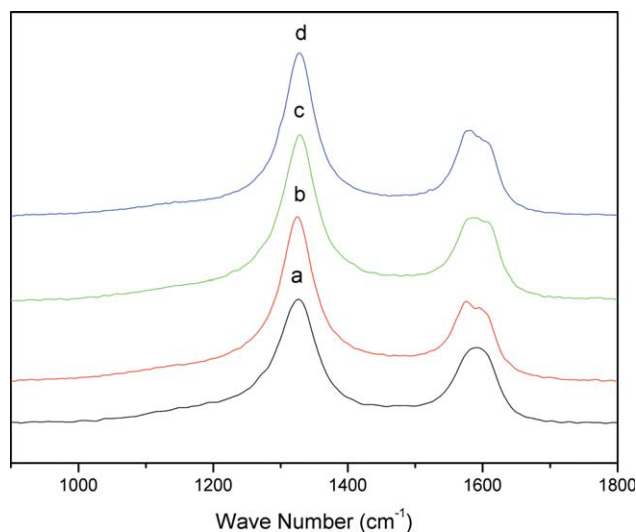
Figure 1 Raman spectra of MWCNT and amino-functionalized MWCNTs (a) MWCNT, (b) EDA-MWCNT, (c) TETA-MWCNT, (d) DDA-MWCNT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 2 FTIR spectra of MWCNT and amino-functionalized MWCNTs (a) MWCNT, (b) EDA-MWCNT, (c) TETA-MWCNT, (d) DDA-MWCNT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

typical peaks for MWCNTs disorder and tangential mode peaks around 1330 cm^{-1} (Peak D, related to sp^3 hybridization of carbon) and 1580 cm^{-1} (Peak G, related to sp^2 hybridization of carbon) were respectively, observed, which provided a diagnostic indication of the reservation of the structure of MWCNTs and suggested their side wall was functionalized. When amine group is grafted to surface of MWCNT via covalent bond, original sp^2 carbon is transferred to sp^3 carbon, and therefore the percentage of sp^2 relatively decreases while sp^3 carbon increases in quantity, which would result in peak intensity ratios ($R = I_G/I_D$) decreased. As Table I shown, the peak ratio between G and D of the MWCNT-carboxyl was 0.54, which was higher than that of MWCNT modified by different amino group. It showed that the content of sp^3 hybridization increased resulting from the reactions between the carboxyl group on the surface of MWCNT and amino group that destroyed the order mode of the MWCNT.

FTIR spectra of MWCNT and MWCNT modified by different amino were shown in Figure 2. From Figure 2(b–d), the broad peak at 3425 cm^{-1} can be ascribed to N—H stretching vibration, and the absorption peaks at 2916 and 2845 cm^{-1} are present due to stretching vibration of CH$_2$ group. The

absorption peaks around 1638 cm^{-1} are due to the stretching vibration of the C=O bond. The appearance of new peaks in the 1538 cm^{-1} attributed to the N—H bending vibration, and 1439 cm^{-1} attributed to C—H vibration, around 1100 cm^{-1} due to the C—N stretching vibration, these respectively, gave a strong indication of the amino group attachment to the side walls on the MWCNTs.

Figure 3 showed the TGA thermograms of MWCNT and amino-functionalized MWCNT. As shown in Figure 3, the weight loss of MWCNT is 3.68, but that of functionalized MWCNTs are all more than 30%. The weight loss of the functionalized MWCNTs mainly decreased rapidly at 300–450°C, which was due to the decomposed of the amino group. The graft

TABLE I
Data of Raman Spectra of Amino-Functional MWCNTs

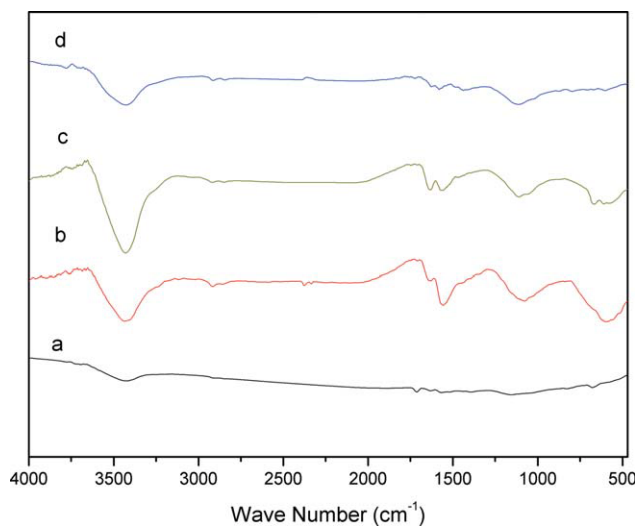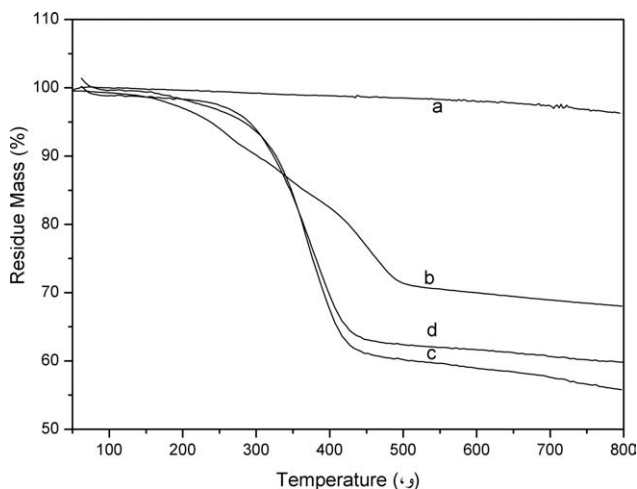|	X_G	X_D	$R = I_G/I_D$
MWCNT	1586.70	1329.75	0.54
MWCNT modified by EDA	1575.33	1325.16	0.49
MWCNT modified by TETA	1588.45	1328.83	0.49
MWCNT modified by DDA	1581.43	1327.89	0.53

Figure 3 TGA curves of MWCNT and amino-functionalized MWCNTs (a) MWCNT, (b) EDA-MWCNT, (c) TETA-MWCNT, (d) DDA-MWCNT.

	MWCNT	MWCNT modified by EDA	MWCNT modified by TETA	MWCNT modified by DDA
Weight loss /%	3.68	31.96	44.21	40.17
Graft ratio /%	/	9.39	6.51	4.36

ratio of amino group could be calculated according to the graft ratio formation:

$$R = \frac{x/M_a}{(1-x)/M_c} \times 100\%$$

Where x was the weight loss of the composite, and M_c and M_a denotes the atomic weight of carbon and the molecular weight of the amino-compound (EDA, TETA, or DDA). The graft ratios were shown in the Table II. From Table II, the graft ratio of MWCNT-EDA (9.39 EDA molecule in every 100 carbon atoms) was higher than that of MWCNT-TETA (6.51 TETA molecule in every 100 carbon atoms) and MWCNT-DDA (4.36 DDA molecule in every 100 carbon atoms), which indicated that the reactivity of monoamine is lower than that of diamine and the reactivity of the short molecular chain compound is higher than that of the long chain compound.

Before being mixed with epoxy, the MWCNTs were dispersed in DMF through bath sonication for 1 h and remained for 1 week, which was shown in Figure 4. The dispersion of the DDA functionalized MWCNT in DMF is better than that of the MWCNT functionalized by the EDA and the TETA. The DMF solution with the DDA functionalized MWCNT is a nearly opaque black suspension and remains stable one week with minimal precipitation formed. However, the EDA functionalized MWCNT and the TETA functionalized MWCNT are agglomerated. The monoamine groups were successfully attached to the MWCNT and play a positive role on the solubility of the DDA functionalized MWCNT in DMF. Both the EDA functionalized MWCNT and the TETA functionalized MWCNT show appearance of the agglomerates in DMF, which maybe attributed to an diamine reaction that occurs on not only one nanotube, that is, one amine group may be linking between different MWCNT together to make big indispersible aggregates.[16]

Analysis of the MWCNTs/epoxy composites

To study the effect of MWCNT and functionalized-MWCNT on the composites, the cure behavior of epoxy without or with MWCNT was investigated by DSC. Figure 5 showed the cure curve of the composites. All curves present one exothermic reaction peak, and the peak shifted to the lower temperature with the addition of the MWCNT, which indicated MWCNT could accelerate the cure reaction. It resulted from the increased surface area contributed to the higher thermal conductivity. Cure onset temperature of the composites containing the amino-functional MWCNT was further lower which was due to the better dispersion by amino-functional reaction. DDA-MWCNT/epoxy composite has a lowest onset temperature of curing than others resulting from the long molecular chain of DDA can make the MWCNT get the best dispersion in epoxy resin.
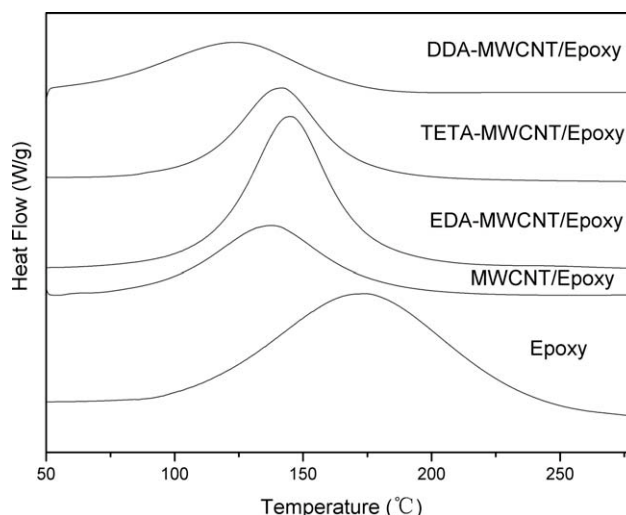

Figure 4 Photos of the MWCNTs in DMF, respectively, (1 mg for each kind of nanotube dispersed in 15 mL of DMF). (a) unfunctionalized MWCNT, (b) DDA-MWCNT, (c) EDA-MWCNT, (d) TETA-MWCNT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5 DSC curing curve of neat epoxy and amino-functionalized MWCNTs/epoxy composites (0.5 wt % MWCNTs).
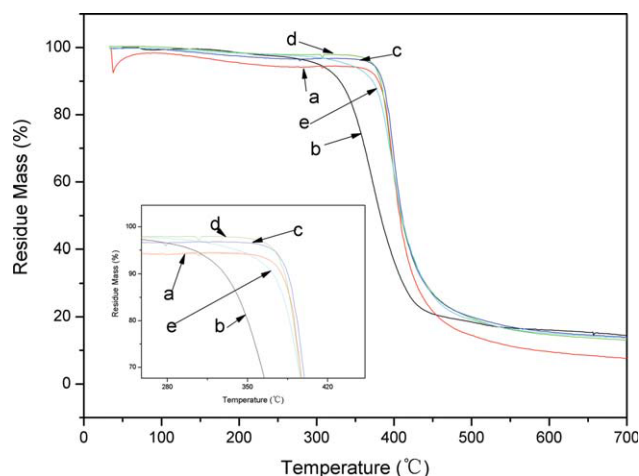
Figure 6 TG curve of neat epoxy and amino-functionalized MWCNTs/epoxy composites (0.5 wt % MWCNTs). (a) neat epoxy, (b) MWCNT/epoxy, (c) EDA-MWCNT/epoxy, (d) TETA-MWCNT/epoxy, (e) DDA-MWCNT/epoxy. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6 showed the weight loss curve for unfiller cured epoxy and the MWCNT/epoxy composites. It can be observed that the decomposition was occurred at 250–450°C. Compare with the unfiller cured epoxy, the onset temperature of decomposition of the unmodified MWCNT/epoxy composite decreased, which was assigned to the poor bonding force between noncovalent filler and matrix[17] resulting in vacancies or voids increasing in the composite. However, when the amino-modified MWCNTs was added, the onset temperature of decomposition of the composites was improved, which indicates the thermal stability improvement of the composite. The reason may be attributed to the fact that amino-modified MWCNTs have a better bonding to the polymer matrix than unmodified MWCNTs.

The mechanical properties of MWCNT/epoxy resin composites depend on the dispersion of MWCNT and the interfacial strength between MWCNT and epoxy. The results of tensile test were shown in Figure 7(a–c). For the neat resin, the average tensile strength and elongation at break were found to be 48.8 MPa and 2.7%. The tensile strength and elongation have improvement with the addition of MWCNT. Furthermore, the composites containing amino-functionalized MWCNT exhibited an increase in tensile strength and modulus compared with the composites containing raw MWCNT at the same MWCNT content, which was due to the better dispersion and the enhancement of interfacial bonding resulting from amino-functionalization. It is also noticed that the elongation at break of the composites containing the amino-functionalized MWCNT is higher than that of the composites containing MWCNT, suggesting that the bonding between MWCNT and epoxy resin improve load

transfer at the interface, and the chemical bonding at the molecular level with crosslinked polymer chains, the unique flexibility and geometric features of the nanotubes will contribute to continuous absorption of energy and result in increased elongation in the epoxy.[13]
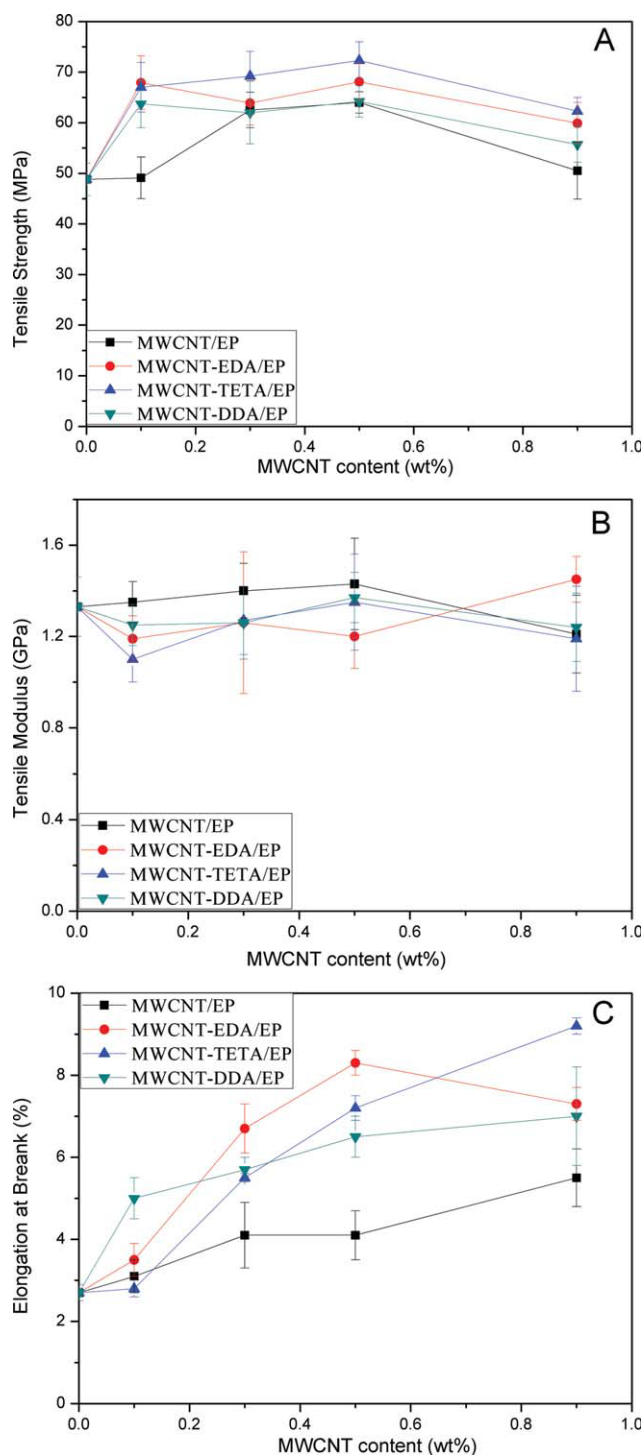

Figure 7 Tensile properties of MWCNTs/epoxy composites: (a) Tensile strength; (b) Tensile modulus; (c) Elongation at break. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
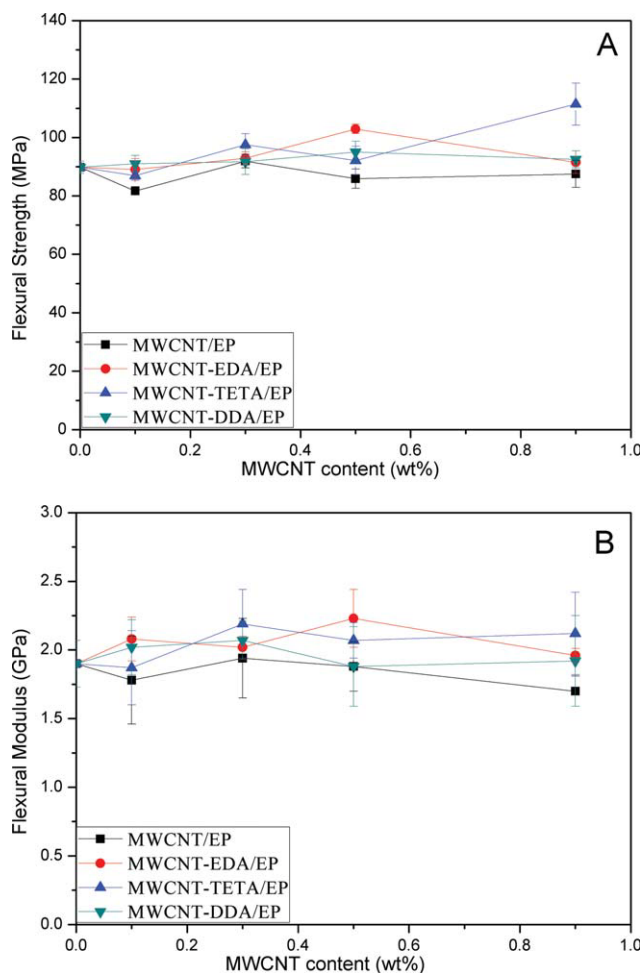
Figure 9 Impact properties of MWCNTs/epoxy composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The impact strength results for the tested materials are shown in Figure 9. The general tendency of the impact strength is similar with that of the tensile strength and the flexural strength. The impact strength of the composites containing amino-functionalized MWCNT is higher than that of the composites containing unmodified MWCNT. It could be explained that the chemical bonding between EDA-MWCNT and TETA-MWCNT with epoxy resins and the physical entanglements between DDA-MWCNT and epoxy resins resulted in the enhancement of the interfacial strength between the MWCNT and the resin matrix.

The DMA data shows how exposure of the composites to elevated temperatures would affect the

Figure 8 Flexural properties of MWCNTs/epoxy composites: (a) Flexural strength; (b) Flexural modulus. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The flexural properties test was performed and the results were shown in Figure 8(a,b). Compared with pure resin, the flexural strength and modulus of the composites containing MWCNT and MWCNT functionalized by DDA have a little enhancement or even a bit decline, however, that of the composites containing MWCNT functionalized by EDA and TETA have obvious improvement. It is believed that MWCNTs functionalized by EDA and TETA as curing agent added into the polymer matrix can increase the fracture energy because the amino-functionalized MWCNTs can be integrated easily into the matrix structure. The new strong covalent bonds between the amino groups and the epoxy matrix can provide strong interfacial shear stress and thus improve the mechanical properties of the composites.[12,18] And the interfacial bonding between the epoxy and the amino group of the EDA and the TETA is more important than the well dispersion for the improvement the mechanical properties.
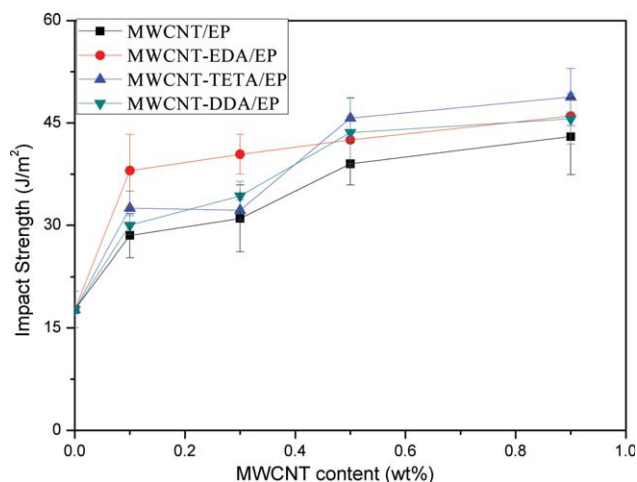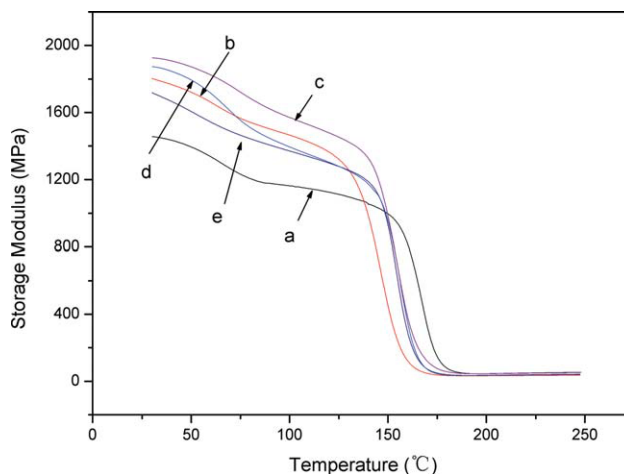

Figure 10 Storage Modulus of neat epoxy and amino-functionalized MWCNTs/epoxy composites (0.5 wt % MWCNTs). (a) neat epoxy, (b) MWCNT/epoxy, (c) EDA-MWCNT/epoxy, (d) TETA-MWCNT/epoxy, (e) DDA-MWCNT/epoxy. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 11 tan δ of neat epoxy and amino-functionalized MWCNTs/epoxy composites (0.5 wt % MWCNTs) (a) neat epoxy, (b) MWCNT/epoxy, (c) EDA-MWCNT/epoxy, (d) TETA-MWCNT/epoxy, (e) DDA-MWCNT/epoxy. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
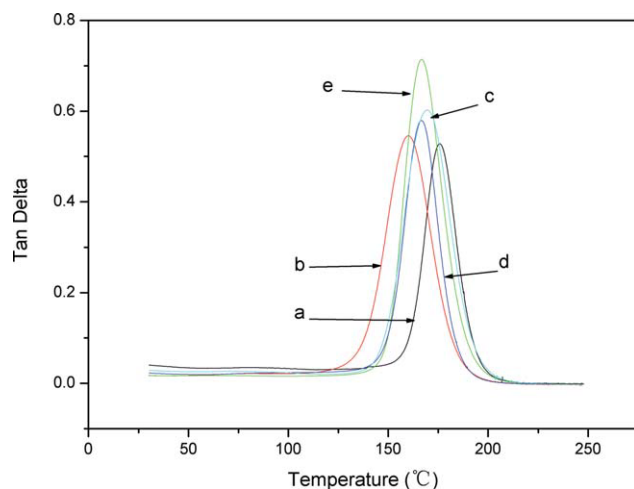
stiffness of the composite material. The dynamic properties reflect the amount of the energy in the composite stored as elastic energy and the amount of energy dissipated during the strain process. These properties are highly dependent on the existence of fillers: dispersion within the matrix, volume fraction, geometrical characteristics, and load transfer from the filler to the matrix. The storage modulus is closely related to the load bearing capacity of the material. Figure 10 showed the storage modulus of the neat epoxy and the MWCNTs/epoxy composites. The storage modulus of the composites at room temperature has lightly increased with the presence of MWCNTs. It was also observed the storage modulus of the composites containing MWCNTs functionalized by EDA and TETA improved compared with that of the composite containing unmodified MWCNTs and neat epoxy, which was attributed to the improvement of the interfacial bonding between MWCNT and epoxy resulting from the interfacial interactions between the amino group and epoxy group.

The glass-transition temperature (T_g) defined as the temperature at which maximum tan δ is reached. T_g is an indicator of the degree of crosslinking in the nanotube-epoxy composite. The higher the glass-transition temperature reflects a higher crosslinking density.[18] As shown in Figure 11, the T_g for the neat expoy is highest, followed by the MWCNT functionalized by EDA-, TETA-, and DDA-filled samples; the lowest one is that of the composite containing unfunctionalized MWCNT. The decrease of T_g with the addition of the unfunctionalized MWCNT was attribute to the fact that the small conglomerations

and matrix holes existing in the network may perform as defects, which make the macromolecules to move easily and the T_g of the matrix is decreased.[19] However, the increase of T_g with the amino-functional reaction compared with that of the composites with the addition of unfunctionalized MWCNT was due to the fact that the amino-functionalized MWCNTs promoted the crosslinking reactions of epoxy and curing agent, effectively discouraging the movement of molecular chains. The other fact is the covalent bonds between the amino-MWCNTs and epoxy enhanced the efficiency of load transfer from matrix to fillers, resulting in an increase in loss modulus due to more energy loss and dissipation in composites. These results confirmed the improved interfacial interactions between the functionalized MWCNTs and polymer matrix, and the EDA is best, followed by TETA and DDA.

CONCLUSIONS

Three types of amino-functionalized MWCNTs were prepared by using EDA, TETA, and DDA, and investigated by FTIR, Raman spectroscopy, and TGA. The graft ratio of amino group on the MWCNTs was calculated. The dispersion of the DDA functionalized MWCNT in DMF is better than that of the MWCNT functionalized by the EDA and the TETA. The MWCNTs/epoxy composites were prepared, and the effect of amino-functionalized MWCNTs on the properties of the composites was studied. It was found that the introduction of amino-functionalized MWCNTs to the epoxy resin could increase the mechanical properties, T_g and initial decomposing temperature of the composites, compared with that of unfunctionalized MWCNT. It was due to the chemical combination and the physical entanglements between amino group from modified MWNTs and epoxy group from the epoxy resin. And the results of the mechanical properties of the composites showed that the interfacial bonding between the epoxy and the amino group of the EDA and the TETA is more important than the well dispersion for the improvement the mechanical properties.

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