Effect of Amino-Functionalization of Multi-walled Carbon Nanotubes on the Dispersion with Epoxy Resin Matrix

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ABSTRACT: Amino-functionalization of multiwalled carbon nanotubes (MWCNTs) was carried out by grafting triethylenetetramine (TETA) on the surfaces of MWCNTs through the acid–thionyl chloride way. The amino-functionalized MWCNTs show improved compatibility with epoxy resin and, as a result, more homogenous dispersion in the matrix. The mechanical, optical, and thermal properties of the amino-functionalized MWCNT/epoxy composites were also investigated. It was found that introducing the amino-functionalized MWCNTs into epoxy resin greatly increased the charpy impact strength, glass transition temperature, and initial decomposing temperature of cured epoxy resin. In addition, introducing unfunctionalized MWCNTs into epoxy resin was found greatly depressing the light transmission properties, which would affirmatively confine the application of the MWCNTs/epoxy composites in the future, while much higher light transmittance than that of unfunctionalized MWCNTs/epoxy composites was found for amino-functionalized MWCNTs/epoxy composites. SEM of the impact cross section and TEM of ultrathin film of the amino-functionalized MWCNTs/epoxy composites showed that the amino-functionalized MWCNTs were wetted well by epoxy matrix. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 97–104, 2006

Key words: MWCNTs; epoxy resin; functionalization; dispersions; composites

INTRODUCTION

Since the first observation of carbon nanotubes (CNTs) in 1991 by Iijima[1] and the awareness of their novel mechanical and electrical properties,[2–3] extensive researches in the field of CNTs/polymer nanocomposites have been done. Many studies showed that introducing CNTs as a structure element in nanocomposites is able to improve the material's properties. Besides improving the material's electrical and thermal conductivities,[4–8] in view of their high axial Young´s modulus and high aspect ratio, CNTs, single-walled carbon nanotubes (SWCNTs) or multi-walled carbon (MWCNTs), are potentially excellent mechanical reinforcing fillers in polymer composites.[9–11] However, how to disperse CNTs in polymer matrix homogenously and achieve a strong interfacial interaction between CNTs and polymer matrix, is the biggest challenge in developing high performance CNTs/polymer composites.

Epoxy resin is one of the most commonly used thermosetting polymers in composites productions. Many researchers believe introducing CNTs into epoxy resin will produce the next generation of high performance polymer composites. To improve the interfacial interaction of CNTs with epoxy matrix, many processing methods have been applied,[10,12] among which attaching chemical functional groups to the surface of nanotube is the most commonly used one by far. Through chemical functionalization, various reactive groups are grafted on the CNTs, which can coherent with polymer matrix via chemical bonds. Y. Breton et al.[13] oxidized two types of MWCNTs in sodium hypochlorite and found that the entanglement of the MWCNTs network had influence on mechanical properties of the composites. H. Miyagawa et al.[14] reinforced epoxy resin with fluorinated SWCNTs (FSWCNTs), and found great improvement of the modulus of cured epoxy resin with extremely small loading of FSWCNTs. But, the Izod impact strength of the composites was found decreased when the amount of the FSWCNTs was increased to 0.3 wt %. F. H. Gojny et al.[15] refluxed oxidized MWCNTs in multifunctional amines directly, and gained animografted MWCNTs. They found that the dispersion of MWCNTs was improved and the interfacial interaction was strengthened. L. Valentini et al.[16] grafted diethylene-triamine on SWCNTs and found the functionalized SWCNTs could affect crosslinking reaction of the epoxy resin.
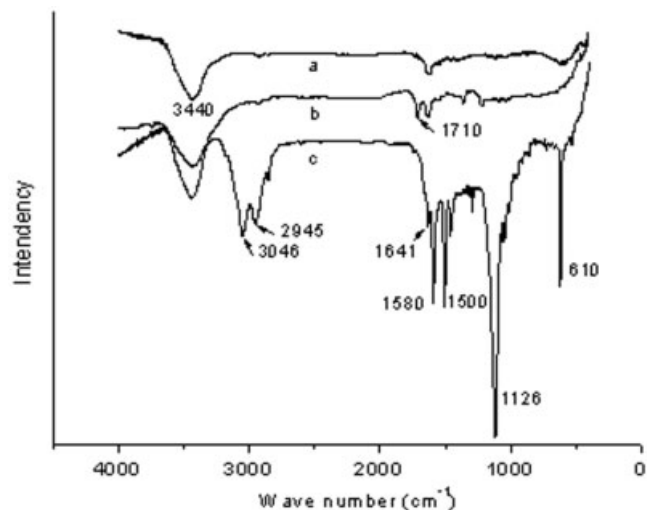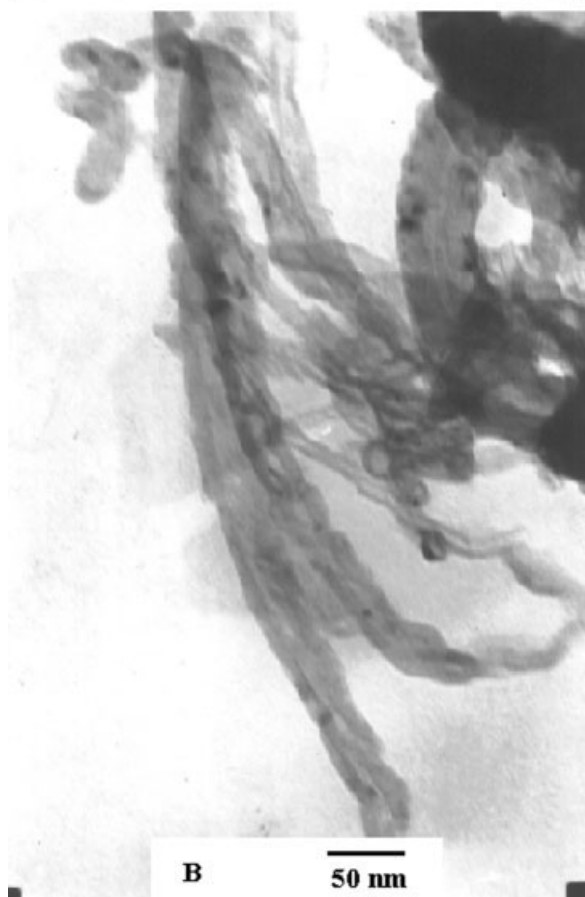
Figure 2 FTIR spectra of (A) p-MWCNTs; (B) a-MWCNTs, and (C) f-MWCNTs.

In this study, the amino-functionalized MWCNTs were prepared using acid–thionyl chloride route. FTIR spectra showed that triethylenetetramine was grafted on MWCNTs effectively with this method. To evaluate the dispersion of the amino-functionalized MWCNTs in the epoxy resin matrix, SEM, TEM, DMA, TGA, and charpy impact tests were performed. In addition, introducing unfunctionalized MWCNTs into epoxy resin greatly depressed the light transmittance of the neat epoxy resin as a result of the poor dispersion of the MWCNTs, which will affirmatively confine the application of the MWCNTs/epoxy composites in the future. For the reason mentioned above, the light transmittance of the amino-functionalized MWCNTs/ epoxy composites was also tested.

EXPERIMENTAL

Materials and equipments

The matrix was prepared by mixing 100 parts by weight of epoxy resin (bisphenol A-epichlorohydrin epoxy resin, E-44) with 10 parts of hardener (Triethanolamine). Triethanolamine is a positive ionic catalytic hardener to initiate the crosslinking reaction of epoxy resin.

The multiwalled carbon nanotubes (MWCNTs) used in this study were synthesized by the catalytic pyrolysis of ethylene and purified by washing with nitric acid. The purified MWCNTs were designed as p-MWCNTs. The CNTs used were MWCNTs, with diameters in the range of 20–80 nm, and average
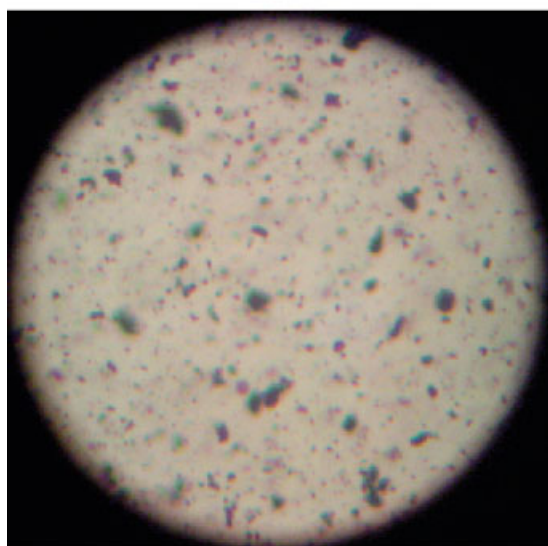
Figure 1 TEM images of (A) p-MWCNTs and (B) f-MWC-NTs.
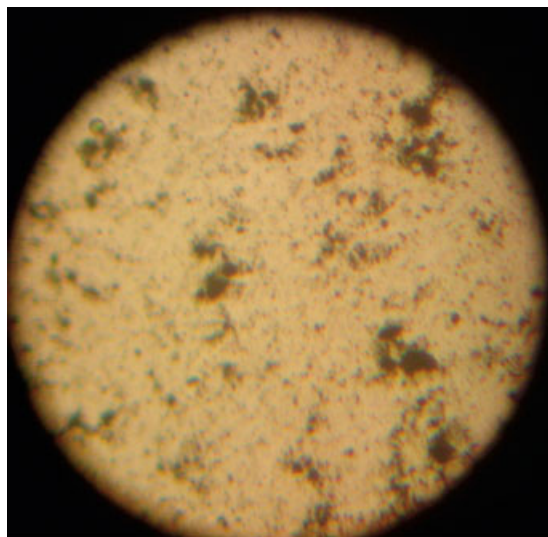
(a)
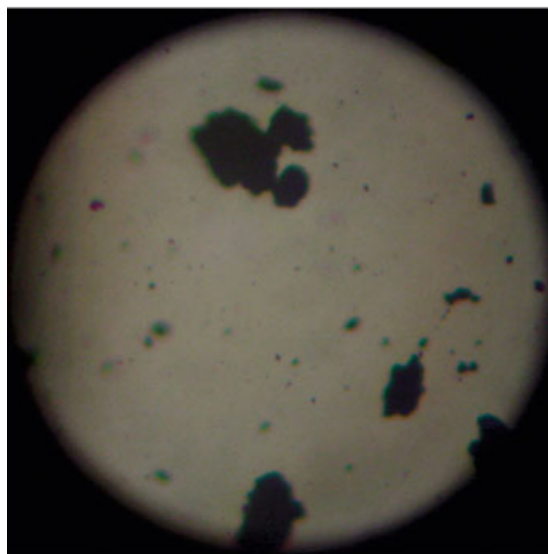
(b)

(c)

length a few hundred microns. There were some catalyst particles, amorphous carbon and anions as impurities in the network of MWCNTs. The MWCNTs are entangled and conglomerated partly [Fig. 1(A)].

Amino-functionalization of MWCNTs

The p-MWCNTs were sonicated in a mixture of sulfuric (98%) and nitric (68%) acids at 40°C for 7 h. The obtained acid-treated MWCNTs (a-MWCNTs) (400 mg) were then refluxed in a mixture of $SOCl_2$ (80 mL) and DMF (4 mL) at 70°C for 24 h. By distillation, the remained $SOCl_2$ was removed. The remained black solid was dried in a vacuum oven at room temperature. The gained solid reacted with excess TETA (120 mL) at 120°C for 96 h. The excess TETA was removed by washing the MWCNTs with anhydrous ethanol, and then black, amino-functionalized MWCNTs, designated as f-MWCNTs, were obtained finally.

Composites preparation

The MWCNTs were added to melt epoxy resin directly. The mixture was agitated under magnetic agitation at 80°C for 20 min to disperse the MWCNTs primarily. After that, the suspension of MWCNTs in epoxy resin was sonicated at 80°C for 2 h. Then the obtained black mixture was added with triethanolamine (hardener) and agitated for 3 min. After degassed in a vacuum oven, the mixture was injected into a mold and cured at 100°C for 2 h followed by postcuring at 120°C for 16 h. Before mechanical and DMA measurements, the surfaces of the specimens were mechanically polished to minimize the influence of surface flaws.

Characterization

Transmission electron microscopy (TEM) observation was carried out with a JEM 1230 operated at 80 kV acceleration voltage to examine the morphology of amino-functionalized MWCNTs and the amino-functionalized MWCNTs/epoxy composites. TEM samples of amino-functionalized MWCNTs were prepared by allowing a drop of amino-functionalized MWCNTs solution in ethanol to dry onto carbon film. Ultra thin films (30–100 nm) of the amino-functionalized MWCNTs/epoxy composites were prepared by ultra-microtome cutting at room temperature.

Figure 3 Optical micrographs of (A) p-MWCNTs/epoxy composites (0.5/100), (B) a-MWCNTs/epoxy composites (0.5/100) and (C) f-MWCNTs/epoxy composites (0.5/100). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 4 TEM images of the network of (A) p-MWCNTs, (B) a-MWCNTs, and (C) f-MWCNTs, in MWCNTs/epoxy composites (0.5/100).
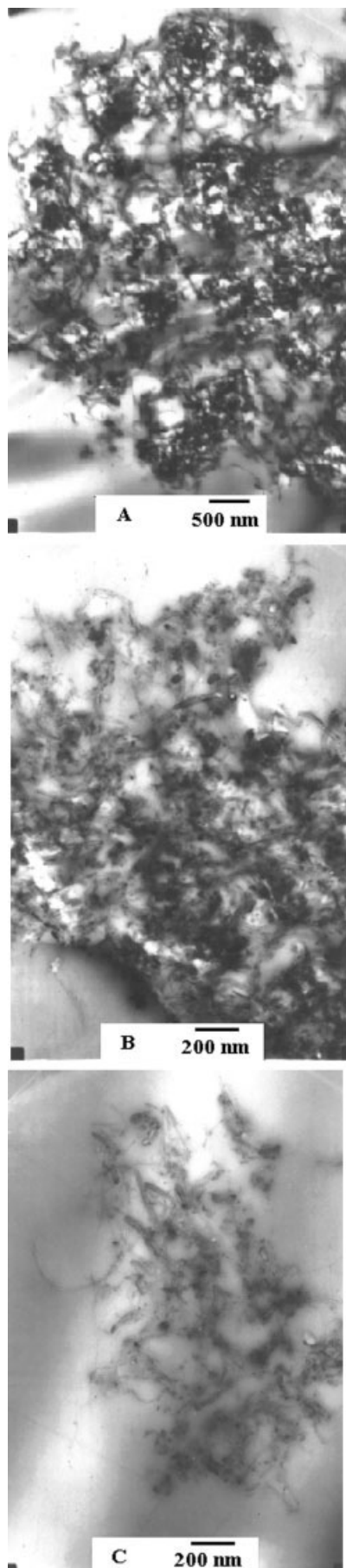
Scanning electron microscopy (SEM) of the impact cross sections were performed on a HITACM *S*-570 SEM.

Fourier transform infrared (FTIR) spectrometry measurement for the nature of the chemical groups on the surface of the MWCNTs was carried out on a Bruker Vector (Billerca, MA) 22 FTIR spectrometer by the method of KBr pellet.

Charpy impact tests of different specimens were performed at 25°C on an impact tester. The thickness of samples after polishing is between 3 and 4 mm.

Glass transition temperature (T_g) was measured by dynamic mechanical analysis (DMA), and is the peak point of tan δ–Temperature curve in DMA test. DMA was performed in nitrogen, flowing at a rate of 40 mL/min, using a Universal V3.8B TA Instruments' dynamic mechanical analyzer. All runs were performed using a frequency of 1 Hz and a heating rate of 3°C/min from 20°C to 160°C.
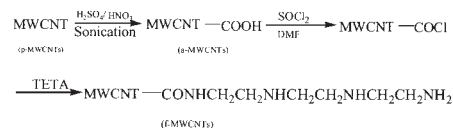
Thermal gravity analysis (TGA) was carried out on a Universal V3.8B TA Instruments' thermal gravity analyzer using a heating rate of 10°C/min from 20°C to 600°C in nitrogen. The temperature at which 2-wt % or 5-wt % sample was decomposed, was designated as T_2 or T_5, respectively.

Light transmittance was measured on an UV–vis-near infrared spectrophotometer (CARY 100 Bio, VARIAN CO., San Francisco, CA). The scanning wavelength is from 200 nm to 1100 nm, and the scanning rate is 5 nm/s. Samples for light transmittance measurement were prepared by curing the epoxy resin between two glass slices. The thickness of the samples was modulated at 1 mm.

RESULTS AND DISCUSSION

Amino-functionalization of MWCNTs

Amino-functionalized MWCNTs were prepared by attaching TETA onto the MWCNTs. The reactions were processed in the following way:

$$\text{MWCNT} \xrightarrow[\text{Sonication}]{\text{H}_2\text{SO}_4/\text{HNO}_3} \text{MWCNT}-\text{COOH} \xrightarrow[\text{DMF}]{\text{SOCl}_2} \text{MWCNT}-\text{COCl}$$
$$\text{(p-MWCNTs)} \qquad\qquad \text{(a-MWCNTs)}$$

$$\xrightarrow{\text{TETA}} \text{MWCNT}-\text{CONHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$$
$$\text{(f-MWCNTs)}$$

After chemical functionalization, the MWCNTs are shortened and their surfaces become blurry. Entangled MWCNTs still remain in their network [Fig. 1(B)]. The existence of different chemical groups on the surfaces of MWCNTs was investigated by FTIR spectra
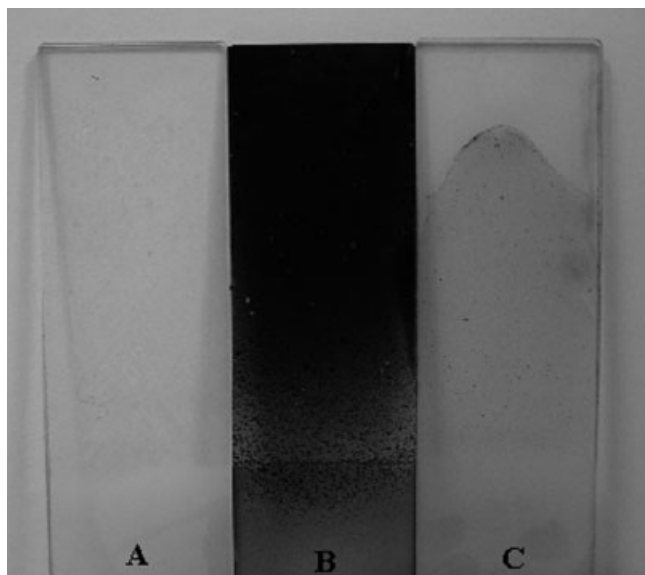
Figure 5 Light transmission samples of (A) neat epoxy resin, (B) p-MWCNTs/epoxy composites (0.5/100), and (C) f-MWCNTs/epoxy composites (0.5/100).

shown in Figure 2. FTIR spectrum of p-MWCNTs exhibits an O—H stretching band at ~3440 cm^{-1}, which is induced by the hydroxyl groups attached at the open ends and defects of the MWCNTs. After treated by acid mixture, the spectrum of a-MWCNTs exhibits a new peaks at ~1710 cm^{-1} due to C = O stretching, which means that –COOH groups are grafted on MWCNTs by acid treatment. Besides of the peaks of O-H stretching band at ~3440 cm^{-1}, the spectrum of f-MWCNTs exhibits double peaks at ~3046 and ~2945 cm^{-1} due to the N—H stretching in —CONH—, NH$_2$, and —NH— groups, and ~1641 cm^{-1} due to the C=O stretching. Other features that should be given attention are ~1580 cm^{-1}, ~1500 cm^{-1}, and ~610 cm^{-1} due to the N—H distortion, and ~1112 cm^{-1} due to C—N stretching. The features of these spectra indicate that the TETA had been attached onto MWCNTs successfully.

Morphology of MWCNTs in epoxy matrix

Figure 3 shows the optical micrographs of p-MWC-NTs/epoxy composites, a-MWCNTs/epoxy composites, and f-MWCNTs/epoxy composites with 0.5 wt % MWCNTs content. With 640 times magnifying magnitude, it is seen that the p-MWCNTs [Fig. 3(A)] and a-MWCNTs [Fig. 3(B)] are poorly dispersed. In the p-MWCNTs/epoxy composites [Fig. 3(A)], there are many huge, but relatively loose conglomerations of tubes, while in a-MWCNTs/epoxy composites [Fig. 3(B)], only huge and extremely tight conglomerations are seen. In the f-MWCNTs/epoxy composites, the f-MWCNTs are dispersed uniformly and the size of

the conglomerations becomes tiny [Fig. 3(C)]. Observing the ultra thin films of p-MWCNTs/epoxy composites (0.5/100), a-MWCNTs/epoxy composites and f-MWCNTs/epoxy composites (0.5/100) with TEM [Fig. 4], it can be seen that the conglomerations of p-MWCNTs and a-MWCNTs are tight, and there are many holes which are the areas not wetted by epoxy resin in the network, indicating that the p-MWCNTs and a-MWCNTs are poorly wetted [Fig. 4(A) and 4(B)], while the conglomeration of f-MWCNTs is very loose and no matrix holes exist in the network of f-MWCNTs [Fig. 4(C)], which indicates that though there exist aggregates more or less, the f-MWCNTs is still wetted well by the epoxy resin, and thus f-MWC-NTs can act as strengthening element. In fact, the conglomerations of f-MWCNTs are "soft" (epoxy resin exists between tubes), while the conglomerations of p-MWCNTs and a-MWCNTs are "rigid" (no epoxy resin exists between tubes), further more the conglomerations of a-MWCNTs are the most "rigid". For the reasons mentioned above, the f-MWCNTs exhibit best dispersion in epoxy resin among the three kinds of MWCNTs used in this paper, thus the interfacial interaction between MWCNTs and epoxy resin can be strengthened by this method.

Light transmission property of the f-MWCNTs/epoxy composites can also prove the good dispersion of the f-MWCNTs in epoxy resin matrix too. Photos of cured epoxy resin, and its composite with 0.5 wt % of p-MWCNTs or f-MWCNTs, all cured between glass slices, are shown in Figure 5. It is seen that the neat epoxy resin has perfect light transmission property [Fig. 5(A)]. The f-MWCNTs/epoxy composite still keeps relatively high light transmission [Fig. 5(C)], while the p-MWCNTs/epoxy composites become nearly opaque [Fig. 5(B)]. The relationships between the light transmittance and the scanning wavelength
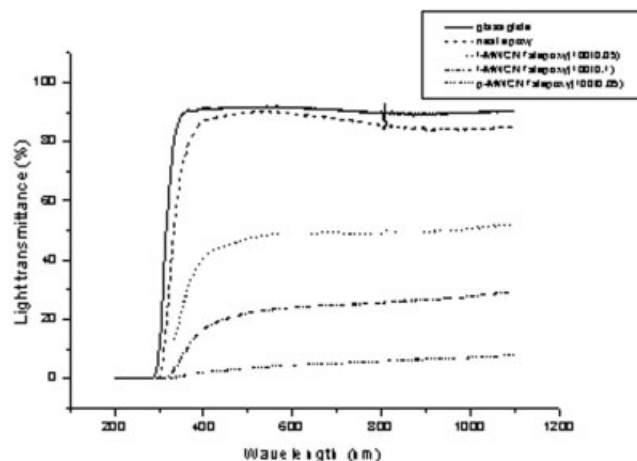

Figure 6 Light transmittance spectra for neat epoxy resin, p-MWCNTs/epoxy composites and f-MWCNTs/epoxy composites.
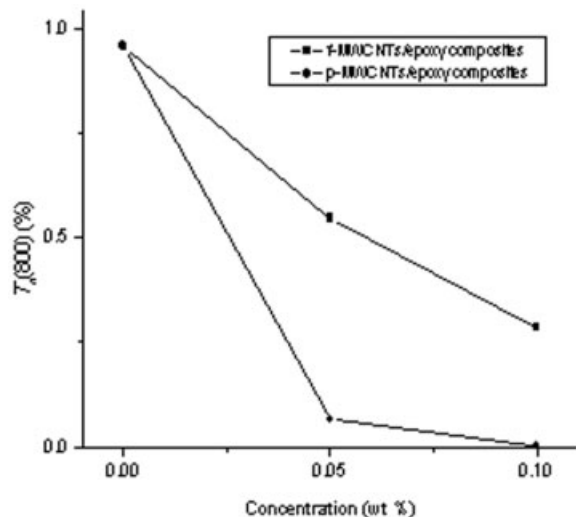
Figure 7 Plots of $T_n(800)$ versus MWCNTs contents.

are shown in Figure 6. It is seen that the light transmittance, at wavelength below 300 nm, is nearly zero, which is the result of the molecular lever light absorption of the glass slice, while at wavelengths over 300 nm, nearly no light is absorbed by glass slices. Though introduction of f-MWCNTs lowers about 50% of the light transmittance of the cured epoxy resin, the f-MWCNTs/epoxy (0.5/100) composite has relatively higher light transmittance compared with p-MWCNTs/epoxy composite at the same concentration of MWCNTs. The introduction of p-MWCNTs greatly decreases the light transmittance of the epoxy resin to near zero. To exclude the influence of the glass slices, normalized light transmittance of p-MWCNTs/epoxy composites and f-MWCNTs/epoxy composite are obtained. Figure 7 shows the normalized transmittance at 800 nm wavelength ($T_n(800)$).

$$T_n(800) = T_s(800)/T_g(800)$$

where $T_s(800)$ is the light transmittance of sample and $T_g(800)$ is the light transmittance of glass slice.

The high light transmittance of the f-MWCNTs/epoxy composites prove that a proportion of the f-MWCNTs in term of individual tube or small sized conglomeration, which can not block off the visual and near infrared light to transmit through the com-

posites, are dispersed in the matrix. In other words, the f-MWCNTs have better dispersion in matrix than the p-MWCNTs.

Charpy impact strength

Charpy impact tests of the MWCNTs/epoxy composites were performed, and the results are shown in Table I. It is seen that the introduction of different MWCNTs into epoxy resin can enhance the toughness of the cured epoxy resin in different degrees. The f-MWCNTs enhance the impact strength of the cured epoxy resin nearly one time. Figure 8 shows the SEM images of impact cross sections. Large aggregations of p-MWCNTs and a-MWCNTs are seen in the epoxy matrix [Figs. 8(B,C)], while no obvious conglomerations of f-MWCNTs are seen in the matrix [Fig. 8(D)], indicating the most uniform dispersion of the f-MWCNTs in the matrix. Further more, it is seen that the cured neat epoxy resin shows obvious brittle rupture [Fig. 8(A)], while, with the introduction of different MWCNTs (0.5 wt %), the epoxy matrix shows plastic rupture more or less [Figs. 8(B–D)]. The plastic distortion of the matrix in f-MWCNTs/epoxy composites is the most and finest, which can explain why the toughness of the matrix is enhanced most efficiently by the f-MWCNTs. Possibly, because the f-MWCNTs adhere to epoxy matrix through chemical bonds —NH$_2$ and —NH— groups on the MWCNTs combined with epoxy groups in the epoxy resin, they can be dispersed in the matrix more sufficiently and have great interfacial interaction with the epoxy matrix. When the f-MWCNTs/epoxy composite is impacted, the f-MWCNTs can initiate great number of plastic distortions in the epoxy matrix.

Thermal properties

Thermal properties of cured epoxy resins and epoxy resin composites with different MWCNTs are shown in Table I. It is seen that introducing p-MWCNTs or a-MWCNTs or f-MWCNTs by the content of 0.5 wt % to the epoxy resin increases the T_g of the cured epoxy resin, but the f-MWCNTs have the greatest ability to increase the T_g, about 14.5°C. Because the MWCNT dispersed in the cured epoxy resin can retard the movement of macromolecules under outside force, so

TABLE I
Thermal Properties and Charpy Impact Strength of Cured Epoxy Resin and Different MWCNTs/Epoxy Composite

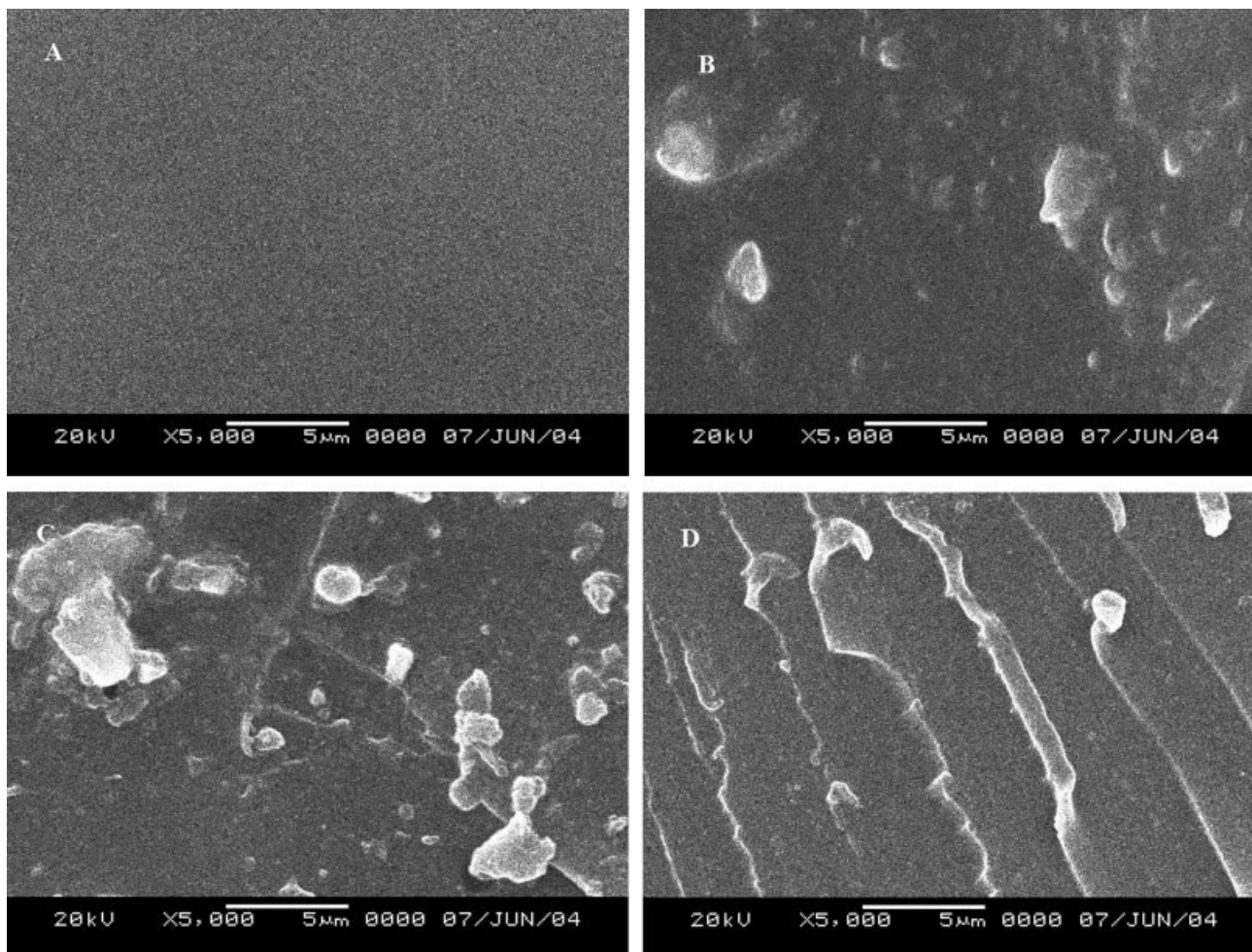| Sample	T_g (°C)	T_2 (°C)	T_5 (°C)	Impact strength (KJ/m^2)
Cured neat epoxy resin	77.8	273.19	327.65	11.7
p-MWCNTs/epoxy (0.5/100)	80.6	268.69	319.88	15.3
a-MWCNTs/epoxy (0.5/100)	89.4	258.67	350.01	15.7
f-MWCNTs/epoxy (0.5/100)	92.3	327.10	358.62	23.1

Figure 8 SEM images of impact cross sections of (A) cured neat epoxy resin, (B) p-MWCNTs/epoxy composites (0.5/100), (C) a-MWCNTs/epoxy composites (0.5/100), and (D) f-MWCNTs/epoxy composites (0.5/100).

the T_g value of epoxy resin is heightened. For the a-MWCNTs and f-MWCNTs, they adhere to the matrix with strong chemical bonds, so the degree of increase of the T_g by them is higher than p-MWCNTs. The f-MWCNTs, with the best dispersion in and the strongest interfacial interaction with the epoxy matrix, can retard the movement of the macromolecules most efficiently, so the T_g of cured epoxy resin is heightened to the maximum value.

Introducing different MWCNTs to epoxy resin brings changes to the initial thermal decomposing temperature of neat resin more or less. The introduction of p-MWCNTs and a-MWCNTs into the epoxy resin decreases the initial decomposing temperature (T_2 and T_5.), while the introduction of f-MWCNTs brings increase to the cured epoxy resin, by 54°C for T_2 and 31°C for T_5. Because of their best dispersion in and the strongest interaction with epoxy resin matrix of the f-MWCNTs, the introduction of f-MWCNTs can retard the diffusion and extravasations of small molecules from matrix under high temperature most efficiently, so the initial decomposing temperature is

heightened. What is different with p-MWCNTs and a-MWCNTs is that the bad dispersion of them may result in lots of defect in epoxy matrix, which can quicken the thermal decomposition of the matrix.

Glass transition temperature (by DMA) of the f-MWC-NTs/epoxy composites with different contents of f-MWCNTs is shown in Figure 9. It is seen that the T_g of the composites keeps rising with the increase of the f-MWCNTs content initially, then begins to fall when the f-MWCNTs content exceeds 1.0 wt %. When the content of f-MWCNTs exceeds 1.0 wt %, serious congregation of f-MWCNTs possibly occurs, and the "soft" conglomerations of f-MWCNTs at low loading level transforms to "rigid" conglomerations. The conglomerations and matrix holes existing in the network of f-MWCNTs performing as matrix defects make the macromolecules to move easily, so the T_g of matrix is decreased.

CONCLUSIONS

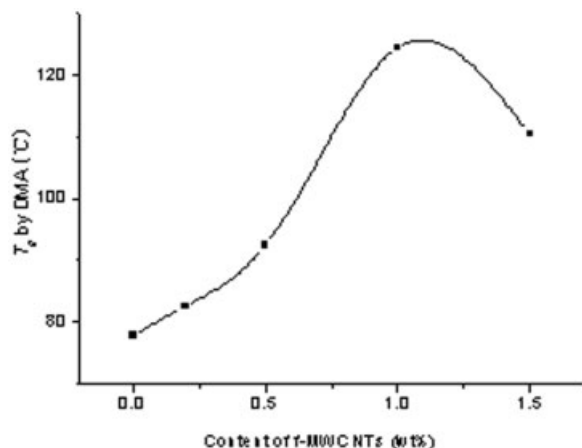Amino-functionalized MWCNTs were obtained using efficient acid–thionyl chloride route. TEM, SEM, and

Figure 9 The relationship between T_g and content of f-MWCNTs.

optical microscopy testified the improved compatibility of the f-MWCNTs with epoxy resin and, as a result, more homogenous dispersion in the matrix. The mechanical, optical, and thermal properties of the f-MWCNT/epoxy composites were also investigated. It was found that the introduction of amino-functionalized MWCNTs to the epoxy resin could increase the charpy impact strength, T_g and initial decomposing temperature of cured epoxy resin. In addition, with a certain small loading of f-MWCNTs, for example 0.05 wt %, the f-MWCNTs/epoxy composites still kept near 50% light transmittance of the neat epoxy resin, which was much higher than that of p-MWCNTs/epoxy composites at the same loading level. The relatively high light transmittance of the amino-functionalized MWCNTs/epoxy composites not only proved the good dispersion of the amino-functionalized

MWCNTs in epoxy matrix, but also expanded the potential application of the MWCNTs/epoxy composites in future.

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