Multiwalled Carbon Nantoubes-Reinforced Poly(hydroxyaminoether) Prepared by One Pot Graft-from Method

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ABSTRACT: Multiwalled carbon nanotubes (MWNTs)-reinforced poly(hydroxyaminoether) (PHAE) was fabricated via one pot graft-from method. The modification of MWNTs and *in situ* polymerization of PHAE were combined in one reaction pot without interruption for the purification of modified carbon nanotubes. Fourier transform infrared, scanning electron microscopy, transmission electron microscopy, and Raman spectra clearly indicated that PHAE was successfully attached to the surface of MWNTs via esterification reaction between epoxy and carboxylic acid from MWNTs. Tensile tests showed that the tensile strength and modulus of PHAE/MWNTs composites were improved compared with that of pristine PHAE. Moreover, the reinforcing effect of one pot graft-from method was found to be better than that of graft-to method. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 1758–1766, 2011

Key words: multiwalled carbon nanotubes (MWNTs); poly(hydroxyaminoether) (PHAE); TGA; SEM; mechanical properties

INTRODUCTION

Carbon nanotubes (CNTs), a unique class of one-dimensional carbon nanostructure, have attracted tremendous attention because of their combination of excellent mechanical properties, high thermal stability, and unusual electrical conductivity.[1–4] One of their important potential applications is that they can be used as inorganic fillers to fabricate CNTs-reinforced polymer composites. However, because of their intrinsic van der Waals forces and poor compatibility with polymer matrices, nanotubes tend to form micrometer-sized bundles within polymer matrices.[5] The aggregation of filler has a detrimental effect on composite properties, such as load-transfer-mechanism failure resulting in inferior composite mechanical properties, processing problems, poor appearance, etc.[6–9] Therefore, a great deal of research has been carried out in recent years, focused on the formation of good dispersion of CNTs in polymer composites without aggregation.[10–13] Attaching functional groups on the surface of CNTs has been proved to be an effective approach.[14–16] Except for the improvement in the

dispersion of CNTs within the polymer matrix, this method possesses another advantage. The attached functional group can undergo further reaction with polymer matrix to form covalent bonding between polymer and CNTs.[17] The interfacial interaction between nanotubes and polymer and homogeneous dispersion of CNTs throughout the matrices are just two critical factors that affect the achievement of full potential reinforcement of CNTs based on the theoretical calculation.

Many CNTs-reinforced polymer composites have been prepared based on the chemical modification of CNTs.[18–20] The traditional method for preparing this kind of composites involves chemical modification of CNTs first, and then blending with polymers by "grafting from" or "grafting to" methods. However, this traditional method has some drawbacks involving complex processes, long time consumption, and environmental pollution for the usage of high toxic raw materials, such as thionyl. Thus, designing a relatively simple, convenient, and environmental friendly method is quite desirable.

Recently, it has been found by our research group that epoxy group could be used to react with the carboxylic acid on the surface of CNTs in the presence of triphenyl phosphine (TPP) as catalyst under mild reaction condition. The reaction mechanism of epoxy and carboxylic acid has been investigated in some published articles.[21,22] This provides a convenient and economical method for modifying CNTs
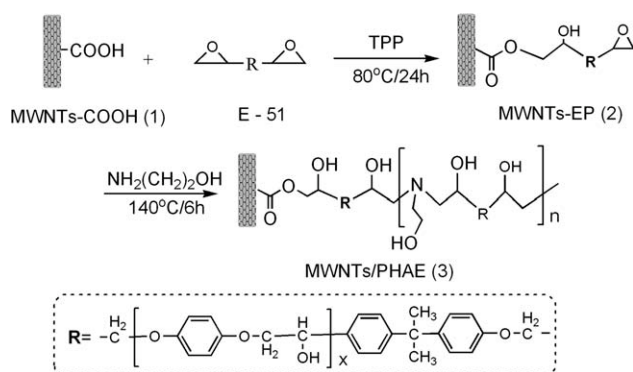
Scheme 1 Main routes for the preparation of MWNTs/ PHAE composites using "one pot graft-from" method.

because of the high reactivity of the reaction and easy availability of epoxy resins. Compared with the traditional modification method based on carbonyl chloride groups-functionalized CNTs, the method based on epoxy-modified CNTs can be carried out under relatively mild and more tolerable condition. Therefore, the method for preparing epoxy functionalized CNTs can effectively overcome the shortcomings of the traditional method.

In this study, the epoxy group-functionalized CNTs is applied in the fabrication of CNTs-reinforced poly(hydroxyaminoether) (PHAE) composites. PHAE is a kind of epoxy-based plastic resin. It has been widely used as packaging material because of its good mechanical and barrier properties.[23] This kind of polymer is typically generated through reactions of various dinucleophiles (dinucleophilic amine, bisphenol) and epoxy monomers. Therefore, a novel one pot graft-from method can be designed to fabricate the CNTs-reinforced PHAE composite, because the functionalization of CNTs and preparation of PHAE can be combined together without the interruption for the purification of epoxy-functionalized CNTs. Our proposed method is shown in Scheme 1. In the first step, epoxy resins, played a role as reactant and solvent, were used to react with carboxylic acid from CNTs. In the second step, the amine-based monomer was added into the mixture for subsequent polymerization to fabricate CNTs-reinforced composites.

EXPERIMENTAL

Materials

Purified multiwalled CNTs (MWNTs)-COOH (purity >95%, diameter within 10–20 nm, ─COOH wt % = 0.5–3 wt %) was obtained from Chengdu Organic Chemistry Co., China. The epoxy resin (E-51) was a liquid diglycidyl ether of bisphenol A with an equivalent weight per epoxide group of 195 ± 5, obtained from Shanghai Resin Co., China. TPP was obtained

from China Medicament Group Shanghai Chemical Reagent Co. Ethanolamine, propylene glycol monomethyl ether, dimethyl sulfoxide, and N,N-dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Co., China. DMF was distilled under reduced pressure and dried over 4 Å molecular sieves before use. Other materials were used as received.

Measurements

Fourier transform infrared (FTIR) spectra were recorded on a Perkin–Elmer Paragon 1000PC spectrometer. Raman spectra were recorded on a LabRam-1B Raman spectroscope operating at a laser wavelength of 632 nm. Thermogravimetric analysis (TGA) was performed in nitrogen with a Perkin–Elmer TGA 2050 instrument at a heating rate of 20°C/min. Morphology of fracture surfaces of nanocomposite films, functionalized MWNTs, and MWNTs-COOH as received were observed using a Hitachi S4700 Field-emission scanning electron microscope. Film samples were fractured in liquid nitrogen. Powder samples were first dispersed in DMF, a drop of dispersion was then deposited on a piece of clean silicon chip, and the solvent was allowed to evaporate. All samples were gold-sputtered before scanning electron microscopy (SEM) imaging. Transmission electron microscopy (TEM) observations of the functionalized MWNTs were performed with JEOL2100F, at an accelerating voltage of 200 kV. A drop of MWNTs dispersion was deposited onto a carbon-coated copper grid (3.05 mm, 200 meshes), and the solvent was let to evaporate. Tensile tests were performed using an Instron 4465 test machine at ambient temperature, with a gauge length of 40 mm and a cross-head speed of 5 mm/min. The specimens were cut from the solution cast films with a typical size of 40 mm (length) × 4 mm (width).

Preparation of MWNTs-EP

Into a triple-necked, round-bottom flask equipped with high-torque mechanical stirrer, a condenser, and nitrogen inlet and outlet, 0.5 g MWNTs-COOH was dispersed in 30 mL DMF and sonicated for 0.5 h to give a homogeneous suspension. Then, 10 g E-51 and 0.025 g TPP (0.25 wt % by the weight of epoxy) as a catalyst were added in. The mixture was sonicated for one more hour and kept at 80°C for 24 h with mechanical stirring. At the end of the reaction, the mixture was poured into about 50 mL DMF and filtered through a 0.22 μm poly(tetrafluoroethylene) membrane. The resulting solid was dispersed in 50 mL fresh DMF, magnetically stirred for 12 h, and filtered again. The extraction routine was repeated at

least three times to remove the unattached E-51. Finally, the solid was washed with a large amount of acetone and water to remove residual DMF. The final product was dried in vacuum oven and denoted as MWNTs-EP.
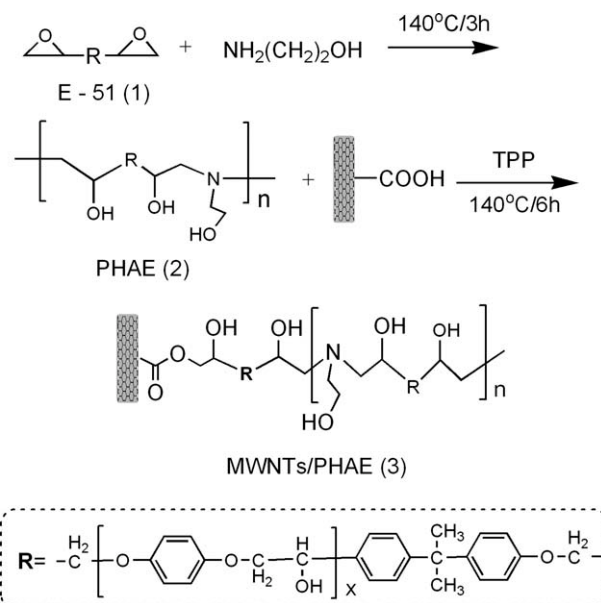
Preparation of MWNTs-PHAE

Into a 100-mL three-necked, round-bottom flask equipped with a high-torque mechanical stirrer, a condenser, and nitrogen inlet and outlet, 10 g epoxy resin E-51, 0.025 g TPP as catalyst, and 0.5 g MWNTs-COOH were charged. The resulting mixture was first stirred and sonicated at 60°C for 2 h, then further heated to 80 ~ 85°C and maintained at the temperature for 24 h with continuous stirring under dry N_2 purging. After that, 1.617 g ethanolamine and 8 mL propylene glycol monomethyl ether as solvent were added into the mixture and heated at 140°C for 3 h. The viscosity of the mixture increased rapidly; to allow further efficient stirring, more 10 mL propylene glycol monomethyl ether was added and continued to react for another 3 h. The post-treatment and extraction routine were the same as that of MWNTs-EP. The resulting product was denoted as MWNTs-PHAE.

Preparation of MWNTs/PHAE composite films using "one pot graft-from" method

The one pot graft-from method is shown in Scheme 1. Into a 100-mL three-necked, round-bottom flask equipped with a high-torque mechanical stirrer, a condenser, and nitrogen inlet and outlet, 20 g epoxy resin E-51, 0.05 g TPP as catalyst and different amounts of MWNTs-COOH (MWNTs-COOH content (α) = m(MWNTs-COOH)/m(E-51); α = 0.5%, 1%, 1.5%, 2%) were charged. The resulting mixture was first stirred and bath-sonicated at 60°C for 2 h, then further heated to 80 ~ 85°C and maintained at the temperature for 24 h with continuous stirring under dry N_2 purging. After that, 3.233 g ethanolamine and 15.5 mL propylene glycol monomethyl ether as solvent were added into the mixture and heated at 140°C for 3 h. More 19 mL propylene glycol monomethyl ether was added and continued to react for another 3 h. At the end of the reaction, the solution of MWNTs/PHAE composites with a solid content of 40% was diluted with dimethyl sulfoxide to reduce the concentration to 15%. Then, the solution was casted onto a glass plate covered with tinfoil and dried at 100°C for about 10 h to get the MWNTs/PHAE composite films.

For comparison, the pure PHAE film was also prepared and the process was similar as above. 20 g E-51, 3.233 g ethanolamine, and 15.5 mL propylene glycol monomethyl ether were first added into a

Scheme 2 Main routes for the preparation of MWNTs/PHAE composites using "graft-to" method.

three-necked flask to react at 140°C for 3 h, then more 19 mL propylene glycol monomethyl ether was added and reacted for another 3 h, and the remaining steps were the same with the composite films.

Preparation of MWNTs/PHAE composite films using "graft-to" method

The schematic of graft-to method is shown in Scheme 2. First, a certain amount of MWNTs-COOH was dispersed in 19 mL propylene glycol monomethyl ether with the aid of ultrasonic agitation. At the same time, in a 100-mL three-necked, round-bottom flask equipped with a high-torque mechanical stirrer, a condenser, and nitrogen inlet and outlet, 20 g E-51, 3.233 g ethanolamine, and 15 mL propylene glycol monomethyl ether were charged, and the mixture was heated at 140°C for 3 h. Then, the MWNTs-COOH dispersion was poured into the mixture followed by adding 0.05 g TPP and maintained at 140°C for another 6 h to allow the complete reaction between the MWNTs-COOH and PHAE. The film preparation process was the same as one pot graft-from method.

RESULTS AND DISCUSSION

Characterization of functionalized CNTs

The preparation and extraction of functionalized MWNTs are described in the Experimental section in detail. The resulted products were subjected to different characterizations, and the results are discussed as follows.
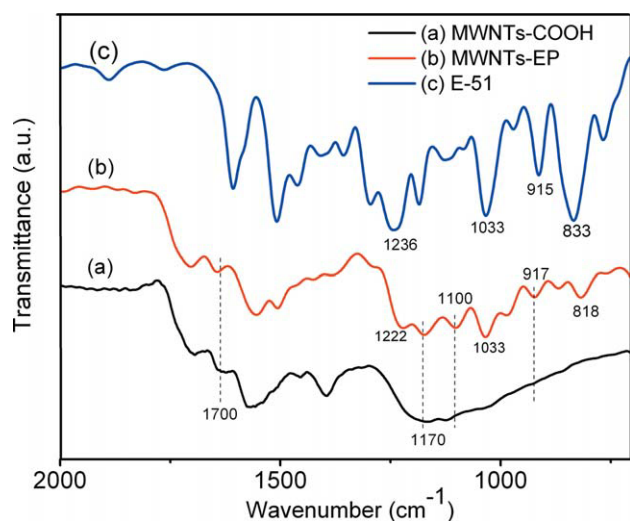
Figure 1 FTIR spectra of (a) MWNTs-COOH, (b) MWNTs-EP, and (c) epoxy resin (E-51). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

FTIR

FTIR spectrum was used to confirm the successful reaction between epoxy groups and carboxylic acid on the MWNTs. Figure 1(a) shows the characteristic FTIR spectrum of MWNTs-COOH, which has little characteristic functional groups peaks with very low intensity. The peaks at around 1700 and 1170 cm^{-1} apparently correspond to the stretching modes of the carboxylic acid. Several new infrared peaks were observed on the FTIR spectrum of MWNTs-EP [Fig. 1(b)], especially in the range of 1250–750 cm^{-1}. The peak at 1100 cm^{-1} is related to the C-O bond formed in the reaction between the carboxylic acid and the epoxy group. The peak at $\sim$ 915 cm^{-1} belongs to the stretching vibration of the epoxy group. Besides, the peaks at 818, 1033, and 1222 cm^{-1} are attributed to the characteristic bands of epoxy resin (E-51),

compared with the curve of epoxy resin [Fig. 1(c)]. Therefore, we can derive from FTIR spectrum that epoxy groups have been successfully grafted to the sidewall of CNTs through the reaction between carboxylic acid and epoxy resins.

SEM

Figure 2 shows the field-emission SME results for MWNTs-COOH before and after modified reactions. As shown in Figure 2(a), the pristine MWNTs-COOH have relatively smooth surface without extra phase or stain attached on its sidewall, which is consistent with the results reported elsewhere.[24] After modified with epoxy resins, MWNTs' surface became rough with some attached organic coatings [Fig. 2(b)]. With further modification with PHAE via *in situ* polymerization, MWNTs were clearly enwrapped by a nanometer-thick layer of polymer [Fig. 2(c)]. The attached PHAE significantly increased the surface roughness and diameter of the tubes. In the meantime, the attached polymer chains also imparted strong surface charging effects to MWNTs, which caused the vagueness of the images.

TEM

The morphology of MWNTs-PHAE is also observed by TEM in terms of the diameter and surface of the CNTs. It can be taken as an additional and more direct evidence for the covalent attachment of PHAE onto MWNTs. Figure 3(a) shows that the surface of MWNTs-COOH is smooth; no extra phase or stain is detected to adhere on the sidewall. For MWNTs-PHAE [Fig. 3(b)], the tubes' surfaces are obviously coated with polymer shell, about 4–6 nm in thickness. Based on both SEM and TEM image analysis, it is concluded that PHAE is indeed attached to the surface of MWNTs.
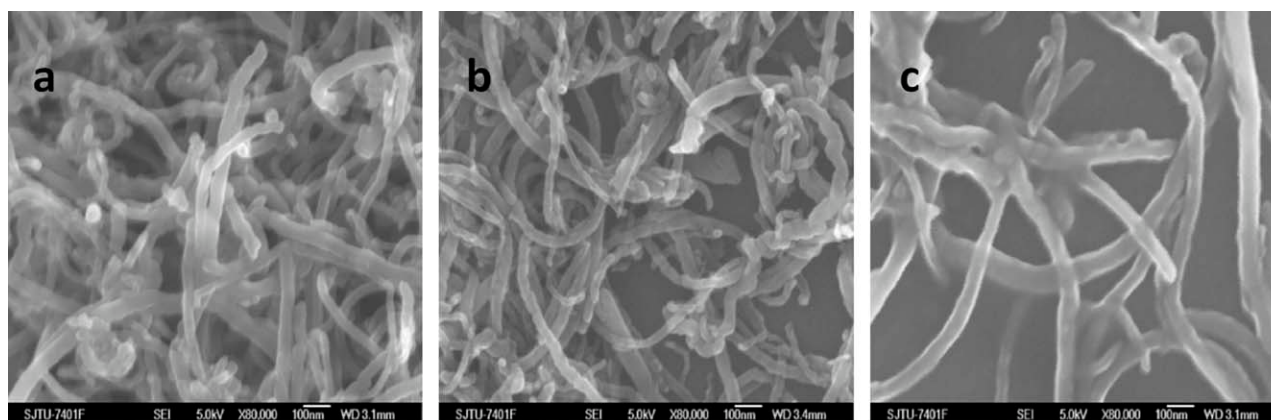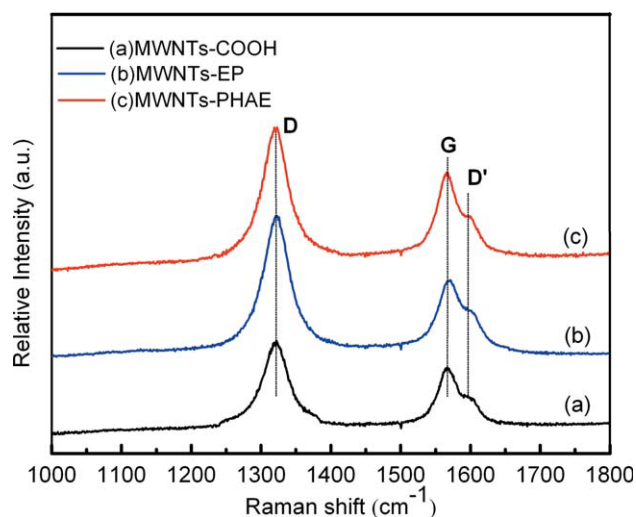

Figure 2 SEM images of (a) MWNTs-COOH, (b) MWNTs-EP, and (c) MWNTs-PHAE. The scale bars for all images are 100 nm.
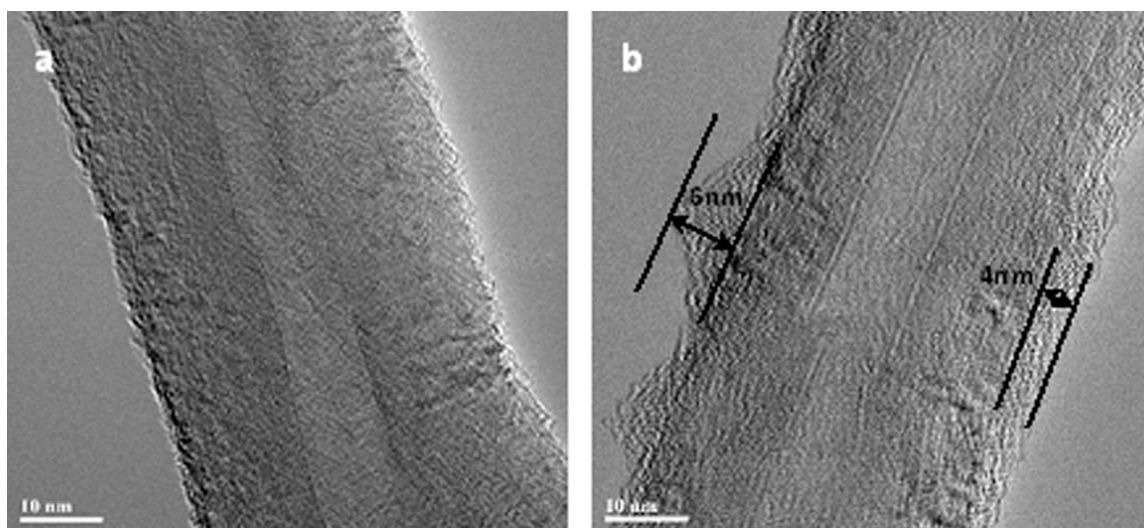
Figure 3   TEM images of (a) MWNTs-COOH and (b) MWNTs-PHAE.

Raman spectra

Figure 4 shows Raman spectra of MWNTs-COOH, MWNTs-EP, and MWNTs-PHAE. The spectra of MWNTs-EP and MWNTs-PHAE show characteristic tangential mode peaks at 1566 cm^{-1} (G band, in-plane E_2g zone-center mode) and a disorder-band peak at 1321 cm^{-1} (D band, the defects and disor-der-induced modes),[25,26] which are similar to those observed for MWNTs-COOH. The existence of G band and D band indicates that the graphite struc-ture of MWNTs was not destroyed during modifica-tion and polymerization reactions.[27,28] The small peak showing on the Raman spectra, teamed as D' band, is related to the degree of disorder in nano-tubes.[29,30] The higher the grafted quantity, the more strongly the peak appeared. Besides, the ratio of the

intensity of D band to G band, which indicates the generation of surface defects due to functionaliza-tion,[31] increased from 1.28 for MWNTs-COOH to 1.59 for MWNTs-EP and 1.32 for MWNTs-PHAE, respectively. It revealed a partial destruction of the conjugation structure of the MWNTs sidewall after the modification. All the results mentioned above indicate that epoxy groups and PHAE have been successfully attached to the surface of MWNTs-COOH.

TGA

Figure 5 displays the TGA curves of raw MWNTs-COOH, MWNTs-EP and MWNTs-PHAE in nitrogen. The curve of MWNT-COOH shows a continuous but insignificant weight loss before 700°C, which is
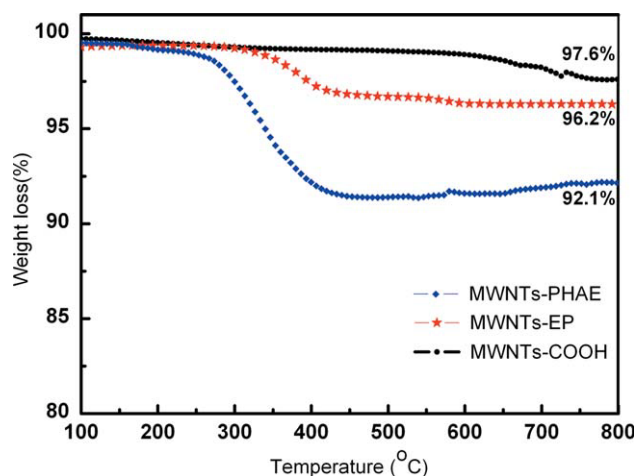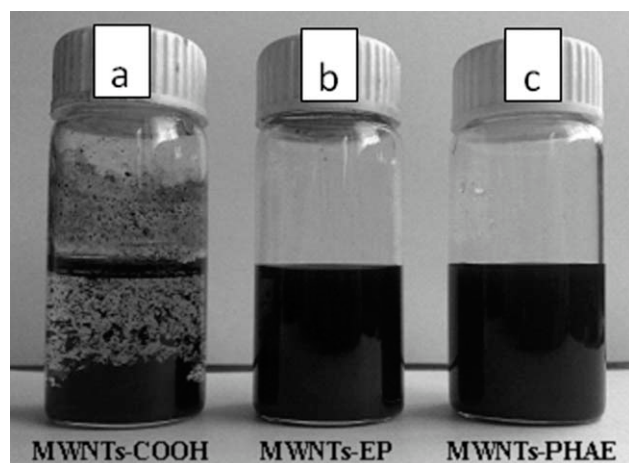

Figure 4   Raman spectra of (a) MWNTs-COOH, (b) MWNTs-EP, and (c) MWNTs-PHAE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5   TGA curves of MWNTs-COOH, MWNTs-EP, and MWNTs-PHAE under nitrogen at 20°C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6 Observation of (a) MWNTs-COOH, (b) MWNTs-EP, and (c) MWNTs-PHAE dispersions in DMF, 1 day after ultrasonication.

consistent with the results reported elsewhere.[32] The large weight loss at 700°C is caused by decomposition and volatilization of impurities (amorphous carbon and catalyst). On the contrary, there is obvious weight loss stage between 250°C and 450°C for the modified MWNTs (MWNTs-EP and MWNTs-PHAE). The weight loss comes from the organic part attached on the surface of MWNTs, which also indicates that chains of epoxy resin and PHAE have successfully attached to the surface of MWNTs. From char yields of MWNTs-COOH, MWNTs-EP, and MWNTs-PHAE, weight percentage of epoxy and PHAE in modified MWNTs was calculated to be about 1.4% and 5.4%, respectively.

Dispersibility

Figure 6 gives the digital photos of dispersions for MWNTs-COOH, MWNTs-EP, and MWNTs-PHAE in DMF after ultrasonication, kept at room temperature for 1 day. It is clear that the dispersion for MWNTs-COOH is unstable, and there was much sedimentation (several hundred micrometer-scale aggregations) at the bottom of vial, 1 day after ultrasonication. In a sharp contrast, MWNTs-EP and MWNTs-PHAE dispersed well in DMF with the aid of ultrasonication and remained stable after 1 day, as shown in Figure 6(b,c). There was no precipitate observed even after half a month. Therefore, we can conclude that the modification of MWNTs-COOH with epoxy resins and PHAE has effectively improved the dispersibility of MWNTs in a high polar solvent.

Characterization of MWNTs/PHAE nanocomposites

Mechanical properties

It is well known that the mechanical properties of polymer can be improved with incorporation of well-dispersed CNTs as reinforced agents.[33,34]

Figure 7(a) shows the stress–strain curves of MWNTs/PHAE composite films prepared by one pot graft-from method. The resulting mechanical properties, namely Young's modulus, tensile strength and break elongation, are listed in Table I. It is observed that the yield strength increases from 41.85 MPa for pure PHAE to 58.12 MPa for the composites containing 0.5 wt % MWNTs-COOH, and its data progressively increase to 69.42 MPa as the content of the MWNTs-COOH increase to 2 wt %; about 58% improvement. The Young's modulus also increases simultaneously from 1506 to 2580 MPa, as the MWNTs-COOH content rise from 0 to 2 wt %; almost 71% improvement. Although the strain ratio at break progressively decreases with increasing the MWNTs-COOH content, the break elongation of the composites with less than 1.5 wt % of MWNTs-COOH is still above 15%. Such data on ductility could still meet with the requirements for the application of PHEA.
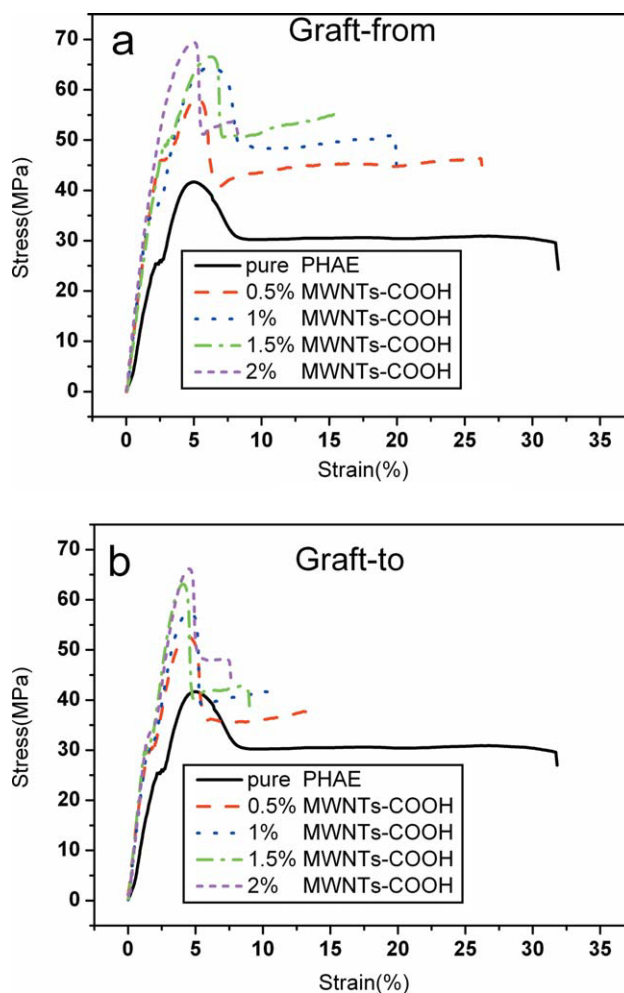
Figure 7 Representative stress–strain curves for poly (hydroxyaminoether)-based composites with different contents of MWNTs-COOH via (a) one pot graft-from method and (b) graft-to method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
Mechanical Properties of Composites with Different Contents of MWNTs-COOH

Samples	Yield stress (MPa)	Young's modulus (MPa)	Break elongation (%)
One pot graft-from method			
Pure	41.85 ± 0.49	1506 ± 31	31.88 ± 0.42
0.5% MWNTs-COOH/PHAE	58.21 ± 1.21	2235 ± 19	26.25 ± 1.58
1% MWNTs-COOH/PHAE	64.32 ± 0.18	2364 ± 34	19.95 ± 1.75
1.5% MWNTs-COOH/PHAE	66.68 ± 0.25	2489 ± 41	15.75 ± 1.2
2% MWNTs-COOH/PHAE	69.42 ± 0.63	2580 ± 10	8.23 ± 1.51
Graft-to method			
Pure	41.85 ± 0.49	1506 ± 31	31.88 ± 0.42
0.5% MWNTs-COOH/PHAE	52.65 ± 0.2	2212 ± 13	13.80 ± 0.63
1% MWNTs-COOH/PHAE	57.64 ± 0.82	2291 ± 40	10.65 ± 0.5
1.5% MWNTs-COOH/PHAE	63.23 ± 0.78	2408 ± 36	9.03 ± 0.92
2% MWNTs-COOH/PHAE	66.47 ± 0.42	2564 ± 38	7.63 ± 0.83

For comparison, the composites made by graft-to method were also subjected to mechanical measurements. The representative stress–strain curves are shown in Figure 7(b). The mechanical properties are also listed in Table I. It is found that their reinforcement effect is inferior to that made by one pot graft-from method. Take the composites with 1 wt % of MWNTs-COOH for example. For the graft-from method, Young's modulus and tensile strengths are increased to 2364 and 64.32 MPa, respectively, and the break elongation is kept at 19.95%. However, for the graft-to method, Young's modulus and tensile strengths are just increased to 2291 and 57.64 MPa, and the break elongation greatly reduced to 10.65%. Such differences are relevant to different dispersion of MWNTs in matrix and different interaction between CNTs and polymer matrices provided by two methods. For the sample prepared by one pot graft-from method, good dispersion and strong interface interaction between CNTs and polymer chains were obtained via the formation of covalent linkage. However, by graft-to method, the polymer chains were not easily attached to the surface of MWNTs because of the high viscosity of polymer and limited grafting sites available. These all resulted in poor dispersion of MWNTs in the matrix and low interface interaction between them.

Interface structure of the composites

To explain the difference in mechanical behaviors provided by two different preparation methods, the dispersion of CNTs in PHAE matrix was further investigated by SEM measurements. Figure 8(e–h) shows the SEM images of the sample prepared by one pot graft-from method. It is found that CNTs dispersed well in PHAE matrix. Most of the CNTs are broken in the interface rather than pulled out from the polymer matrix. However, samples, prepared by graft-to method, show different morphology [Fig. 8(a–d)]. Most of the CNTs are pulled out from the PHAE matrix with some aggregation. Such discrepancy demonstrated that a stronger interfacial adhesion existed between MWNTs and PHAE matrix by using one pot graft-from method. For the one pot graft-from method, most of the polymer chains were interacted with MWNTs through covalent bond. For the graft-to method, the initial attached polymer chains sterically prevents grafting of additional macromolecules to the surface of MWNTs,[35] leading to the low grafting efficiency. Moreover, some polymer chains were just physically blended with MWNTs. All the observations of fracture surfaces are in accordance with the mechanical properties discussed above.

Thermal stability

TGA measurements are also conducted on the composites prepared by graft-from method to elucidate their thermal stability with the presence of MWNTs-COOH. The results are depicted in Figure 9. Overall, dynamic thermal stabilities of composites in nitrogen are improved. It is obviously reflected on the increase in the maximum weight loss velocity temperature (T_{max}). For the composites containing 0.5, 1, 1.5, and 2 wt % MWTNs-COOH, T_{max} are 373, 383, 401, and 423°C, respectively, almost 20–70°C increase compared with 353°C (T_{max}) for the pure PHAE. Also, the initial degradation temperature (T_0) and the char yields are improved for the samples with incorporation of MWNTs-COOH. 0.5–2 wt % MWNTs-COOH addition can increase the T_0 and char yields from 280°C and 7.6% for pure PHAE to about 340°C and 13.3% for the composites, almost 60°C and 6% increase, respectively.

CONCLUSIONS

Esterification between epoxy and carboxylic acid from MWNTs and the *in situ* polymerization of
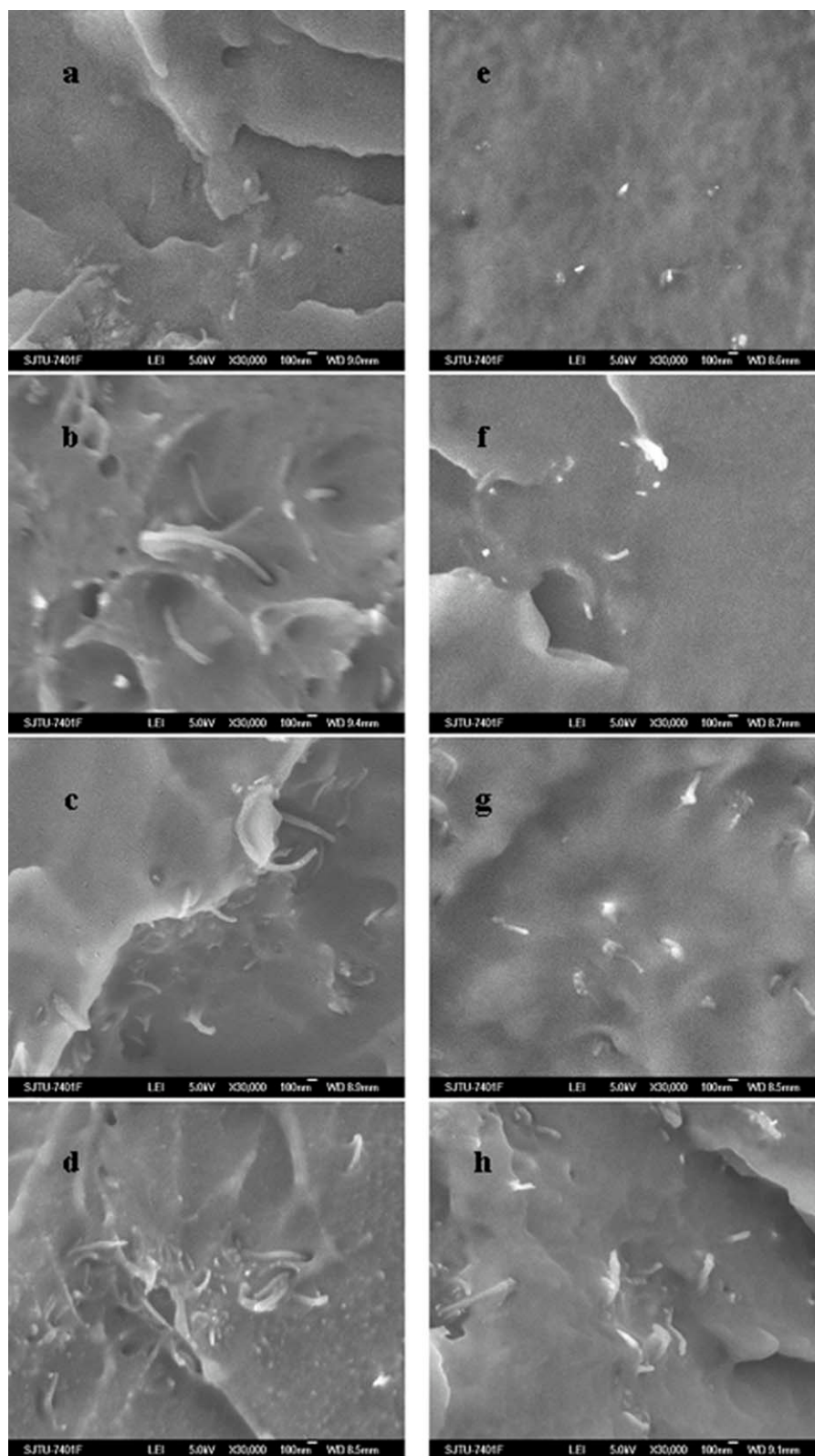
Figure 8 SEM images of fractured surfaces. MWNTs/PHAE composites containing (a) 0.5 wt %, (b) 1 wt %, (c) 1.5 wt %, and (d) 2 wt % MWNTs-COOH, prepared via graft-to method. MWNTs/PHAE composites containing (e) 0.5 wt %, (f) 1 wt %, (g) 1.5 wt %, and (h) 2 wt % MWNTs-COOH, prepared via one pot graft-from method. The scale bars for all images are 100 nm.
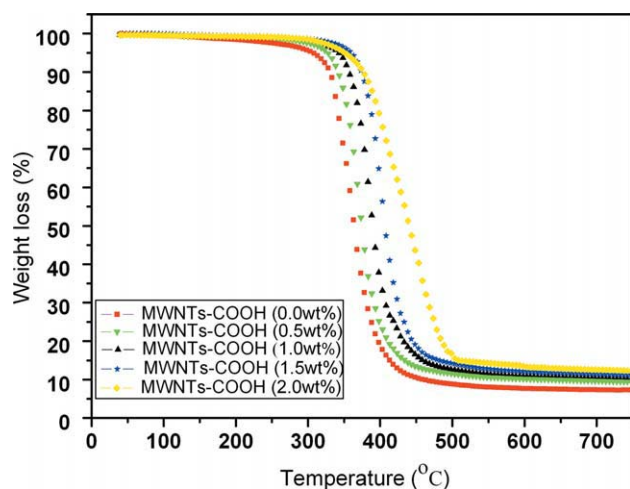
Figure 9 TGA curves for pure PHAE and MWNTs/PHAE composites prepared via graft-from method, under nitrogen at 20°C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PHAE was combined together in one reaction pot to prepare MWNTs-reinforced PHAE composites. This combination effectively simplified the traditional methods to prepare MWNTs-polymer composites. FTIR, SEM, TEM, and Raman spectra analysis confirmed the successful attachment of epoxy groups and PHAE onto the surface of MWNTs. Such modification has greatly improved the dispersion of MWNTs in polymer matrix, resulting in the efficient load transfer between the polymer matrix and CNTs. As a result, the thermal and mechanical properties of composite films, especially the maximum weight loss velocity temperature (T_{max}), tensile strength, and modulus, are all improved compared with the pure PHAE and the composites prepared by graft-to method.

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