

Amino Functionalization of Multiwalled Carbon Nanotubes by Gamma Ray Irradiation and Its Epoxy Composites

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In this paper, γ -ray radiation technique was utilized to simply functionalize multi-walled carbon nanotube (MWCNT) with amino groups. The successful amino functionalization of MWCNTs (MWCNTs-Am) was proven and the physicochemical properties of MWCNTs before and after radiation grafting modifications were characterized using FT-IR, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). The results indicated that the γ -ray radiation had the visible effects on the surface properties of MWCNTs. The effects of various functionalized MWCNTs on morphological, thermal, and mechanical properties of an epoxy-based nanocomposite system were investigated. Utilizing in situ polymerization, 1 wt% loading of MWCNT was used to prepare epoxy-based nanocomposites. Compared to the neat epoxy system, nanocomposites prepared with MWCNT-Am showed 13.0% increase in tensile strength, 20.0% increase in tensile modulus, and 24.1% increase in thermal decomposition temperature. POLYM. COMPOS., 33:267–274, 2012. © 2011 Society of Plastics Engineers

INTRODUCTION

Carbon nanotubes (CNTs) as the strongest material are the basic material for a number of fascinating applications in materials science [1–3]. Much attention has been paid to CNT-based nanocomposites for the preparation of high-performance materials exhibiting improved or unusual mechanical and physical properties. However, the homogeneous dispersion of raw CNTs within a polymeric matrix is relatively difficult to achieve, especially in a polar matrixes such as epoxy resin. Indeed, CNTs tend to

aggregate as very long bundles due to the high surface energy and the stabilization by numerous of p–p electron interactions among the tubes [4–8]. In order to solve these problems and broaden the applications of carbon nanotubes, covalent and non-covalent functionalization approaches have been proposed in the literatures [9–11]. The non-covalent methods, including solution mixing, melt mixing and in situ polymerization are simple and convenient [12–17]; however, the dispersion of CNTs and the interfacial interaction between CNTs and polymer matrix are poor, especially in the case of melt mixing. In contrast, the covalent approaches, including “grafting to” and “grafting from,” leading to chemical linkage between the polymer and the surface of CNTs, improve the dispersion of CNTs in polymer matrices. Nowadays, covalent amino functionalization of CNTs with polar compounds is emerging as a very promising method for both the solubility of CNTs and their straightforward incorporation in polymeric matrices by chemical method [18–24]. However, the conventional chemical method is generally a complicated process involving a long reaction time, toxic coupling reagents, and strictly controlled reaction conditions. Compared with the chemical modifications methods, the γ -ray radiation method is different from the chemical modifications methods, it can be carried out at atmospheric temperature, and the γ -ray radiation method is of great importance with its nonpolluting property, which is not negligible for an industrial production, and shorter reaction time [25]. Yu et al. [26] have treated MWCNTs with glycidyl methacrylate maleic acid in aqueous solution using a single-step radiation method chemical, and the glycidyl methacrylate maleic acid were successfully grafted onto the MWCNTs; Farzi et al. [27] have studied the effect of radical grafting of tetramethylpentadecane and polypropylene on carbon nanotubes’ dispersibility in various solvents and polypropylene matrix, and it was found that this surface treatment lead to a fair solubility in various solvents. However, scanning electronic microscopy images of PP-functionalized MWCNTs/PP composites did not show a significant improvement in

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Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 21174034.

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 50973023.

DOI 10.1002/pc.22144

Published online in Wiley Online Library (wileyonlinelibrary.com).

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MWCNTs dispersion within the PP matrix. However, few investigations have been done on attempts to functionalize MWCNT with amino groups by a mutual irradiation treatment for MWCNTs with triethylenetetramine and the properties of its epoxy nanocomposites. We aim to test the feasibility of the proposed method. It is hoped that the question will be resolved with our work.

This paper focus on the amino functionalization of MWCNTs using the grafting-to approach by γ -ray mutual radiation. The functionalization reactions have been realized by free radical grafting reactions of TTA with the strained carbon atoms onto the sidewalls of MWCNTs. The characterizations of the modified MWCNTs have been evaluated by TGA, XPS, and FT-IR, and TEM. Furthermore, we will also discuss the effect of amino functionalization of MWCNTs on the properties of its epoxy composites.

EXPERIMENTAL

Materials and Modification Procedure

MWCNTs were provided by Shenzhen Nano Port Company. Their average diameter varies from 40 to 60 nm and their length from 1 to 4 μm , purity >95%. Triethylenetetramine (TTA) was purchased from Guangdong Guanghua Sci. Tech. Co. Ltd. Then the purified MWCNTs were mixed with TTA according to the ratio of 1:100 by weight. The mixture was dispersed by ultrasonic at 25°C for 3 h. The resin matrix is Wuxi Resin plant diglycidyl ether of bisphenol A epoxy resin (DGEBA) with 3,3-diethyl 4,4-diaminodiphenylmethane (H-256) as hardener. The two components were mixed in the ratio of 100 parts resin to 40 parts hardener by weight.

Radiation-Induced Grafting of MWCNTs Treatment

To remove the impurities, the amorphous carbon of the MWCNTs was eliminated by thermally treatment at 350°C under air for 6 h, the thermally purified MWCNTs were immersed in a flask in a 1:3 mixture of concentrated HNO_3 and H_2SO_4 at room temperature and sonicated for 30 min. The purge process was carried out at 110°C for 30 min. The produced MWCNTs were washed with excess deionized water until the pH was approximately 7 and finally washed with acetone. The product was dried at 60°C for 24 h in a vacuum oven. Consequently, the purified MWCNTs (denoted as p-MWCNTs) were mechanically dispersed in TTA solution in a glass vessel. After bubbling N_2 for 10 min to remove O_2 , the vessel was sealed and subjected to ultrasonication for 60 min.

A mutual irradiation treatment for MWCNTs with TTA was carried out with the energy of 1.17–1.33 MeV and intensity $1.5 \times 10^4 \text{ Ci}$ in a room temperature atmosphere using a ^{60}Co gamma ray source. The irradiation dose rate was 6.0 KGy h^{-1} and the total irradiation dose was 200 KGy. After irradiation treatment, the resultant product (denoted as MWCNTs-Am) was thoroughly

washed by distilled water and filtered. The washed MWCNTs-Am were dried overnight at 120°C in a vacuum oven. The dried MWCNTs-Am were ready for characterizations.

MWCNTs Characterizations Analysis

FTIR spectra were recorded on a Perkin–Elmer spectrometer 2000 using powder-pressed KBr pellets. Specimens for the measurements were prepared by mixing 2 mg of the sample powder with 100 mg of KBr and pressing the mixture into pellets. FTIR spectra were obtained at a resolution of 2.0 cm^{-1} at room temperature in the range of 4,000 to 400 cm^{-1} wavenumber and averaged over 16 scans.

XPS were utilized to demonstrate the surface chemical compositions of unmodified and irradiated MWCNTs. Different functional groups were evaluated by curve fitting of C1s spectra using Gaussian–Lorentzian distribution.

TEM was carried out with a Philips CM-120 microscope (Philips Consumer Electronics BV, Eindhoven, The Netherlands) operated at 80 kV. For test of solvent dispersion ability, the mixture of MWCNTs and acetone was ultrasonicated for 30 min, filtered in the above purification process, the MWCNTs were transferred onto a 400-mesh size copper with carbon film for examination by TEM.

Preparation of Epoxy Nanocomposites

MWCNTs-Am was added to the epoxy DGEBA according to a ratio of 1:100 and mixed using a digital mechanical stirrer at a constant speed of 500 rpm at 80°C and sonicated for 30 min in an ultrasonic bath at 60°C, and then the curing agent H256 was added. The viscous mixture was agitated for 30 min. The resulting viscous mixture was poured into dog-bone molds. The sample molds were placed into vacuum at 60°C for 2 h to remove the bubbles formed. Finally, the nanocomposite samples were cured at 120°C for 3 h and then 150°C for 3 h in an oven after which it was left to cool to ambient temperature and released from the molds.

Thermogravimetric Analysis of Epoxy Nanocomposites. TGA was performed on SDT Q600 (TA Instruments) from room temperature to 700°C at a heating rate of $10^\circ\text{C}/\text{min}$ in air atmosphere.

Tensile Characterization of Epoxy Nanocomposites. The tensile properties of neat epoxy matrix and MWCNTs/epoxy nanocomposites were investigated. The specimens were tested on a tensile test machine according to ASTM D 638 standard. The machine was run under displacement control mode at across head speed of $2.0 \text{ mm}/\text{min}$, and all the tests were performed at room temperature.

Fracture Morphology of Epoxy Nanocomposites. A field emission scanning electron microscopy (SEM, Hitachi S-4700) was used to observe the morphologies of the MWCNTs/epoxy nanocomposites surfaces and the dispersion of MWCNTs from the fracture surfaces of samples.

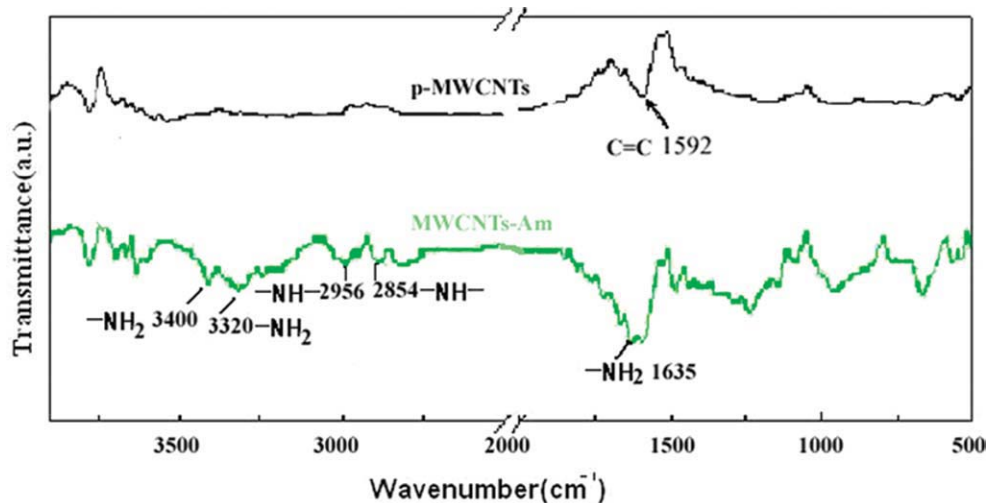
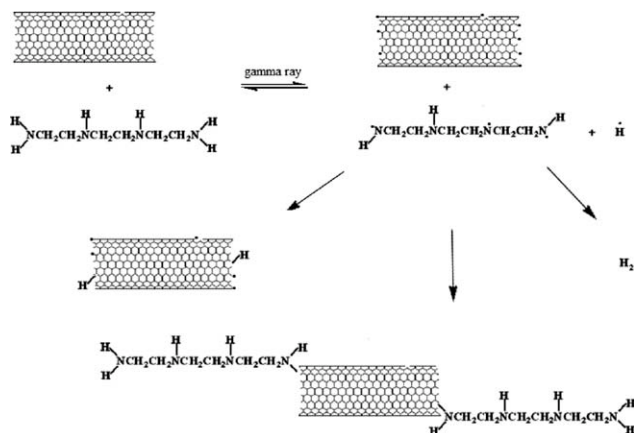


FIG. 1. FTIR spectra for p-MWCNTs and MWCNTs-Am. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS AND DISCUSSION

Characterization of MWCNTs-Am

FTIR Analysis. Direct evidence for MWCNTs' surface functionalization can be confirmed with the aid of FTIR spectra analysis. The FTIR general spectra of MWCNTs before and after irradiation treatment were presented in Fig. 1. There was no significant functional group detected on the untreated nanotubes. After irradiation treatment, the emergence of nearly identical series of vibrational bands suggested the successful grafting of TTA onto MWCNTs. The peaks at wave numbers of 2,926 and 2,854 cm^{-1} corresponded to the N—H stretching vibrations, and the peaks at 3,100–3,400 cm^{-1} and 1,660 cm^{-1} were related to amine vibrations, although the hydroxyl group also had the similar vibration at 3,100–3,400 cm^{-1} . The results may be attributed to the free grafting radicals between TTA and MWCNTs by γ -ray radiation energy. The main reactive pathways of free radical grafting of TTA onto MWCNTs by common irradiation as follows.



However, the main drawback of free radical grafting was low selectivity of radicals, and the radicals can undergo additional reactions including hydrogen radicals leading to the formation of amino radicals or attack onto the sp^2 carbon of the MWCNTs and with other radical species via the common radical coupling reactions. The formed radicals through hydrogen abstraction of TTA were able to react with MWCNTs by radical addition onto sp^2 carbon of the MWCNTs. Compared with chemical method, this method was also a simple way to directly incorporate organic molecule onto the MWCNTs' surface.

XPS Analysis. To further confirm the covalent bonding between TTA and MWCNTs, qualitative and quantitative chemical element analysis was performed based on XPS results (as shown Table 1). According to Table 1, p-MWCNTs did not contain any nitrogen element (in amide groups). By contrast, MWCNTs-Am contained 1.76% nitrogen, which implied that amino peaks appear on the surface of MWCNTs after irradiation treatment. Most possible, the N_2 in the irradiation vessel was introduced onto the groups existing on the MWCNTs surface. Another possible reason was that the high irradiation energy may initiate nitrogen (amide groups) onto MWCNTs.

Figure 2 presented the general XPS spectra of MWNTs before and after irradiation treatment. It was interesting to note that there was a peak of C1s spectrum at a binding energy of 284.3 eV and a peak of O1s at a binding energy

TABLE 1. Elemental composition of p-MWCNTs and MWCNTs-Am from XPS.

	C (wt %)	O (wt %)	N (wt %)
MWCNTs	98.39	1.61	—
MWCNTs-Am	95.37	2.87	1.76

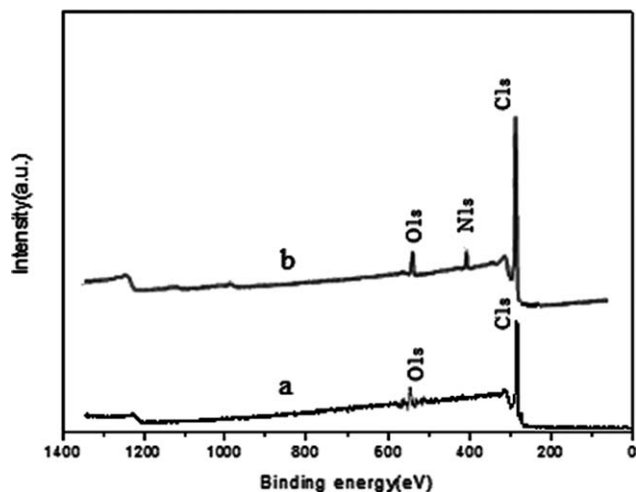


FIG. 2. XPS general spectra of p-MWCNTs (a) and MWCNTs-Am (b).

of 534.0 eV for p-MWCNTs. After the irradiation treatment followed by functionalization with TTA, there was an extra peak of N1s at 401.0 eV except for the peaks of C1s and O1s for the MWCNTs-Am. Various functional groups on the nanotubes surface were identified by means of high resolution deconvolution of the XPS C1s peaks, as shown in Fig. 3. As shown in Fig. 3a, the C1s peak of p-MWCNTs located at 284.3 eV can be deconvoluted into four fitting curves with binding energy located at 284.3, 286.1, 288.1, and 290.5 eV, which were assigned to C—C, C—O, C=O and O—C=O, respectively. In Fig. 3b, there appeared a prominent peak at a binding energy of 285.80 eV, which represented amide functional groups (C—N). The summarized results obtained by curve fitting of C1s peak area to surface functional groups of p-MWCNTs and MWCNTs-Am were listed in Table 2. It was noted that the irradiation enrich the surface of

MWCNTs with not only nitrogen but also oxygen arising probably from the presence of C—N functional group with the similar binding energy in the attached TTA molecules on the nanotubes. Since the C to N ratio in C—N group was 1:1, the area percentage of amide from the curve fitting analysis was 4.6%, comparable to the content of TTA molecule was 4.6% on the nanotubes, as shown in Fig. 3b. This observation further confirmed the above finding that TTA molecule was successfully attached on the nanotubes.

Solubility Observation of MWCNTs. As an additional evidence for the functionalization of TTA onto MWCNTs, the dispersion stability of the p-MWCNTs and the MWCNTs-Am in acetone was investigated. The samples were placed in the same amount of acetone followed by sonication for 30 min (a1, b1) and then leaving them free standing for 60 min (a2, b2) and 30 days (a3, b3). As illustrated in Fig. 4, for p-MWCNTs (Fig. 4a2 and a3), we found unstable dispersions in acetone solvent meaning that it is not possible to well disperse p-MWCNTs in the solvent even after sonication. There are two factors affecting p-MWCNTs dispersion: nanotube morphology and attractive forces between the tubes. Not only the tube surfaces are attracted to each other by molecular forces, but the extremely high aspect ratios coupled with the flexibility also dramatically increase the possibilities for entanglements. In contrast, for MWCNT-Am, because of the dispersions in acetone the CNTs could not be centrifuged down easily (Fig. 4b2 and b3). The obvious improvement in the suspension stability of the MWCNTs-Am confirms that the TTA molecule is covalently linked onto the surface of MWCNTs that ensure fine dispersion. The relatively high solubilities of MWCNT-Am in acetone solvent provide the possibility to easily disperse

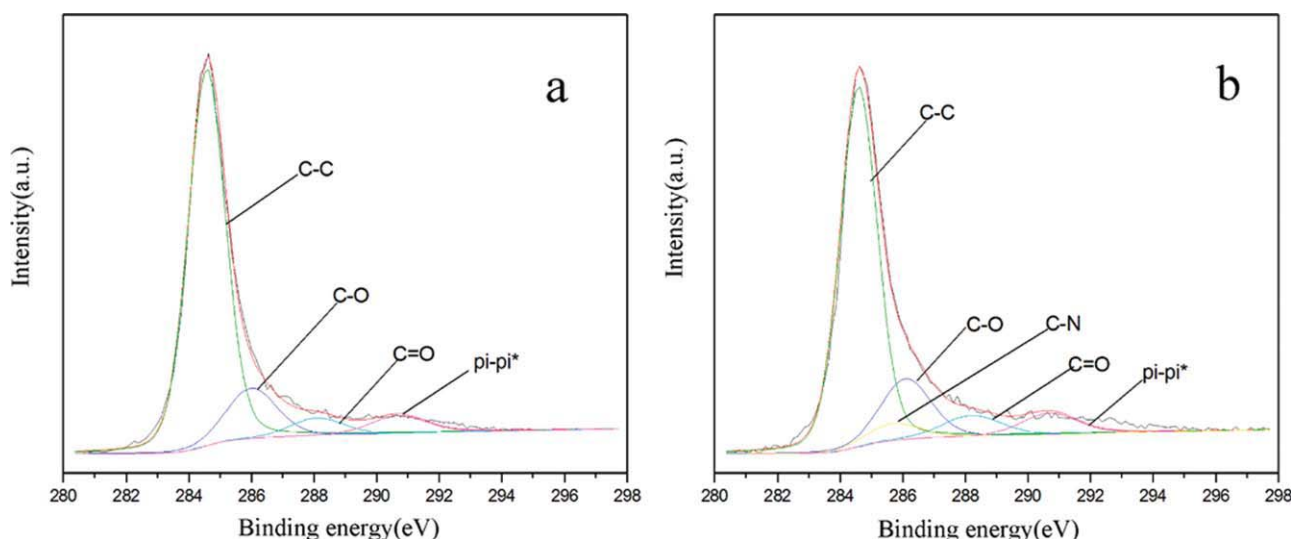


FIG. 3. XPS C1s spectra of p-MWCNTs (a) and MWCNTs-Am. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

TABLE 2. Surface functional groups of p-MWCNTs and MWCNTs-Am by C1s curves fitting.

	C—C (%)	C—N (%)	C—O (%)	C=O (%)	C—O—C (%)
p-MWCNTs	75.87	—	13.78	5.05	5.30
MWCNTs-Am	67.77	4.57	15.54	6.2	5.92

MWCNTs which allows preparing MWCNTs/epoxy composites.

To further investigate dispersity, TEM observations of the p-MWCNTs and the MWCNTs-Am in acetone were made (leaving for 60 min after sonication), which are shown in Fig. 5. It is apparently seen on the morphologies of p-MWCNTs in Fig. 5a and illustrates the heavily entangled nature of CNTs within these agglomerates leading to the presence of large bundles and ropes scattered around. An obvious difference between the number and the size of agglomerates in p-MWCNTs and MWCNTs-Am is observed from the TEM micrographs (Fig. 5b). In contrast, for the MWCNTs-Am sample, TEM micrographs at nanoscale show that the CNTs are mostly debundled into individual tubes leading to a fine nano-dispersion in the acetone solvent. Even at the microscale, the image shows a large amount of light passing through the TEM sample, which gives an evidence of spacing between the individual nanotubes. Here the loosely entangled swelled mass shows that the functionalization has untied the otherwise tightly held bundles of p-MWCNTs. This morphology might better be understood considering the behavior of MWCNTs-Am in the acetone solvent (Fig. 4b). These results highlight that radical grafting of TTA molecules onto the surface of MWCNTs is a promising way to irradiation grafting of TTA onto MWCNTs.

Characterization of MWNTs/Epoxy Nanocomposites

Thermal Properties of MWNTs/Epoxy Nanocomposites. Thermogravimetric analysis was performed on the produced neat MWCNTs (a), WMCNTs-Am (b), WMCNTs-Am/epoxy nanocomposite (c), and neat epoxy

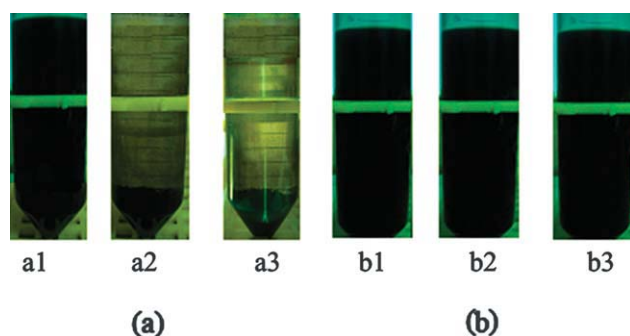


FIG. 4. Solubility of p-MWCNTs (a) and MWCNTs-Am (b) in acetone. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

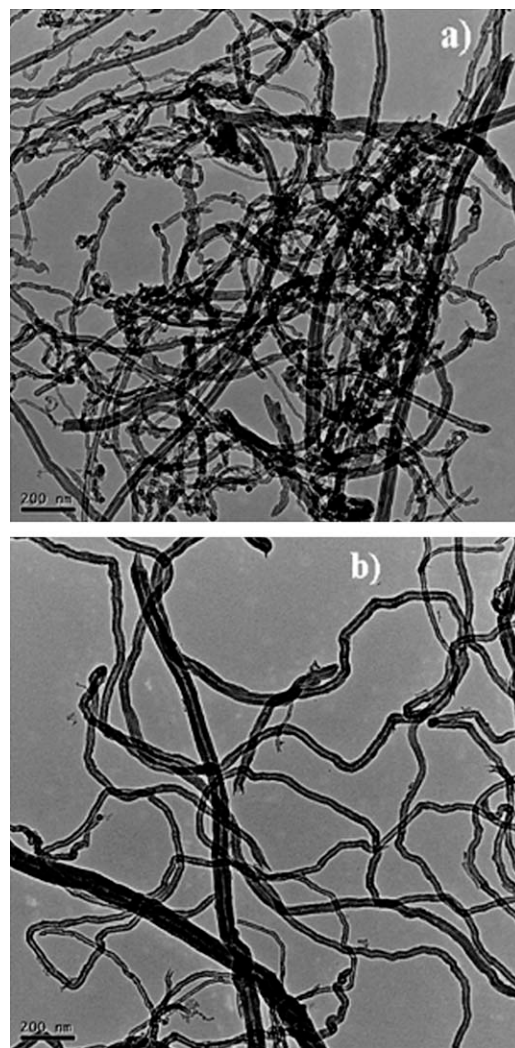


FIG. 5. The dispersion of p-MWCNTs (a) and MWCNTs-Am (b) in acetone by TEM.

matrix (d) as shown in Fig. 6. The results commented that the weight loss of the neat MWCNTs was not obvious before 550°C (less than 1.3 wt%), their thermal decompo-

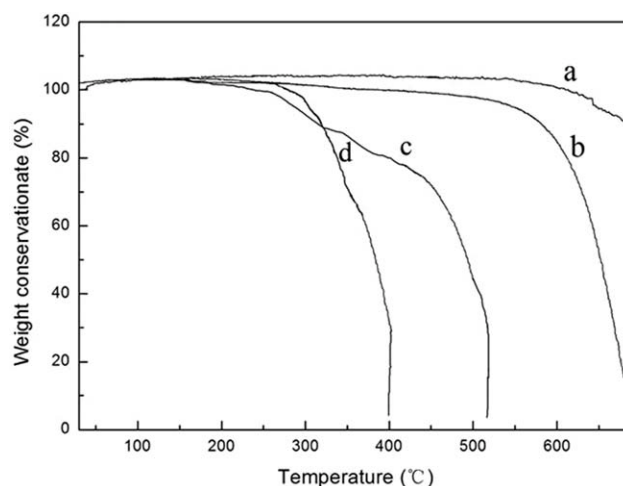
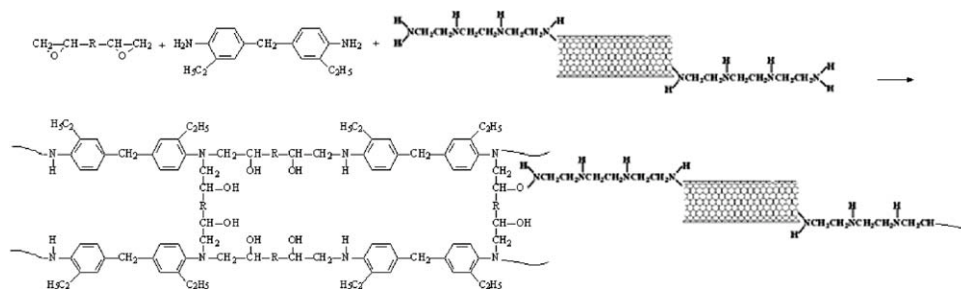


FIG. 6. TGA curves of MWCNTs and epoxy nanocomposites.

sition started at about 550°C. However, the thermal decomposition curves for MWCNTs-Am showed steps at 280°C. The steps were within the range of decomposition temperatures of the TTA molecules. It can be further demonstrated that TTA molecule was introduced onto the MWCNTs surface. Also, the amount of TTA that covalently attached to the MWCNTs is estimated by the weight loss of TTA-grafted MWCNTs sample at 550°C. For the MWCNTs-Am, an obvious thermal decomposition appeared at 280°C, and the weight losses were about 5.0 wt% at 550°C. In addition, nanocomposites with MWCNTs-Am exhibited increases in degradation temper-

ature comparing with neat epoxy matrix, and the neat epoxy matrix showed a degradation at 290°C, but epoxy/MWCTNs-Am nanocomposite exhibited a two-stage degradation at a higher temperature, it started to degrade around 360°C, which increased with 24.1% compared to the neat epoxy matrix. We speculate that MWCNT-Am was introduced into the crosslinking coupling nets of epoxy matrix. Thus, the epoxy/WMCNTs network structure had higher thermal stability than the network structure of the neat epoxy matrix. The MWNTs-Am were expected to have a chemical reaction with epoxy as follows:



Tensile Properties of MWNTs/Epoxy Nanocomposites. The tensile properties of neat epoxy matrix and its nanocomposites were tested and shown in Table 3. Results showed a maximum increase of 13.0% and 20.0% in tensile strength and Young's modulus of modified MWCNTs/epoxy nanocomposites compared to the neat epoxy matrix, respectively. However, the tensile strength and Young's modulus with unmodified MWCNT loading did not exhibit the increase in degree comparable to those of modified MWCNTs/epoxy nanocomposites. For the both of unmodified and modified MWCNTs/epoxy nanocomposites, the failure strain to failure decreased with increasing MWCNTs additive. That was due to the formation of a covalent bond between the MWCNTs-Am and epoxy matrix so as to induce efficient load transfer from the matrix to the MWCNTs, so they can increase the composites mechanical properties. However, with unmodified MWCNTs loading, there were no interfacial reactions between the p-MWCNTs and the epoxy matrix due to a lack of functional groups on the MWCNTs and a poor dispersion in the epoxy matrix, so that it cannot increase the composites mechanical properties.

TABLE 3. Mechanical properties of epoxy and its nanocomposites.

	Tensile strength (MPa)	Young's module (GPa)	Failure strain (%)
Neat epoxy	75.5	2.75	2.3
MWCNTs-Am/epoxy	85.3	3.30	2.1
p-MWCNTs/epoxy	74.9	2.90	2.0

Microstructure Analysis of the Nanocomposites. An important function of the surface treatment of carbon nanotubes was to allow more uniform dispersion within the polymer matrix for composite fabrication. Microstructure analysis of the nanocomposites was very important for the evaluation of dispersion in the polymer matrix. Therefore, the fracture morphology of the unmodified and modified MWCNTs/epoxy nanocomposites state was studied using SEM as shown in Fig. 7. For the p-MWCNTs/epoxy sample in Fig. 7a, SEM images showed only clusters of a few tens micrometers of diameter evidencing a poor interfacial adhesion in the material. In some areas, the concentration of MWCNTs was high, and the nanotubes were entangled together, whereas none of the MWCNTs can be found in other areas. In contrast, for the MWCNTs-Am/epoxy sample in Fig. 7b, the degree of agglomeration decreased in the MWCNTs-Am/epoxy composite. Nevertheless, the sizes of the aggregates were obviously reduced in comparison with those of untreated MWCNT composites, indicating that the agglomerates have been destroyed through amino functionalization. The composite was particularly efficient in achieving a fairly homogeneous dispersion of the nanotube agglomerates owing to the creation of amino functional groups, which were reactive with the functional groups in the epoxy matrix. The improved surface functionality also helped better dispersion of the carbon nanotubes in the matrix. It was then clear from these results that the grafting of TTA onto MWCNTs provided a high steric barrier against the strong intermolecular Van der Waals interactions among nanotubes within the epoxy matrix.

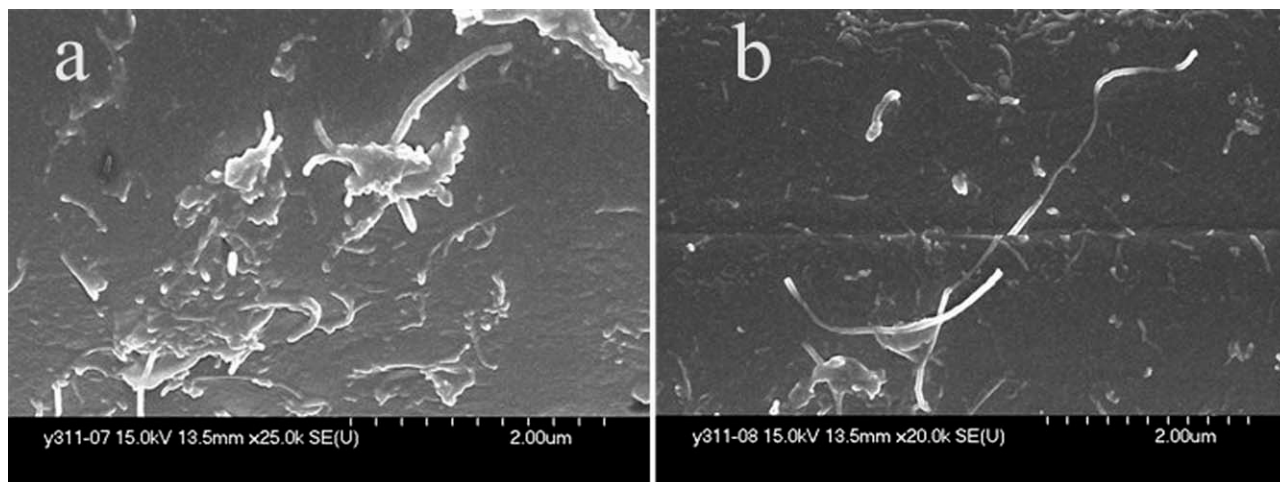


FIG. 7. The fracture morphology of epoxy nanocomposites by TEM.

CONCLUSIONS

In this study, MWCNTs were functionalized through γ -ray radiation technique. The modified as well as unmodified MWCNTs were then dispersed in the epoxy matrix at 1% loading by weight. The performance of the nanocomposites samples was compared with that of neat epoxy. The effect of functionalization was characterized through FTIR, XPS, and TGA. The tensile property was carried out, and the samples were observed under scanning electron microscopy to understand the failure modes. The following conclusions were made:

- (1) Irradiation amino functionalization is a useful method to improve the dispersion of MWCNTs in acetone and epoxy.
- (2) FTIR, XPS, and TGA conformed that TTA molecule was successfully grafted onto MWCNTs using γ -ray radiation treatment.
- (3) Comparing with the neat epoxy matrix, the thermal decomposition temperature, tensile strength, and Young modulus of modified MWCNTs/epoxy nanocomposites increased with 24.1%, 13.0%, and 20.0%, respectively.
- (4) SEM investigation of the fracture morphology of the nanocomposites showed evidence of better dispersion and chemical interaction of MWCNTs-Am in the epoxy matrix than that of p-MWCNTs in the epoxy matrix. Improvement in interfacial interaction and dispersion is dependent upon the surface medication, and it manifested itself by improvement in the mechanical properties for the epoxy system reinforced with MWCNTs-Am.

Presumably, a better dispersion in the epoxy matrix and further improvement in the content of the amide groups existing on the surface of the MWCNT could be obtained by optimizing the grafting parameters.

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