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Morphology and properties of carbon nanotubes modified epoxy

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Abstract. Multi-walled carbon nanobutes (MWNTs) reinforced epoxy resin nanocomposites were fabricated by functionalizing the MWNTs with amino group. The functionlization of MWNTs was characterized by FTIR, elementary analysis, and TEM, and the MWNTs dispersion was characterized by optical microscopy and SEM. MWNTs functionalization with ethylene diamine improved the nanotube dispersion in the epoxy matrix composites. The dynamic mechanical thermal properties and thermal properties of MWNTs/epoxy nanocomposites are briefly discussed in terms of the MWNT loading and dispersion.

Introduction

Carbon nanotubes (CNTs) have attracted considerable attention because of their unique atomic structure, high aspect ratio and excellent electronic, mechanical and thermal properties[1-2]. They have a wide range of potential applications including nanoelectronic, sensors, fillers in composite materials and others. While uniform dispersion is the big challenge for CNTs modified materials. Two methods are based on physical interactions or chemical bonding, so called noncovalent or covalent approaches respectively. Efforts to obtain homogeneous and fine dispersion of CNTs in polymer matrix have been previously undertaken[3-5]. Although some of studies show good CNT dispersion state in polymeric matrices, in-depth research on how to combine uniform distribution of CNTs in the polymer matrix and improve interfacial interaction between CNTs and the polymer with the demand for high performance of CNTs/polymer composites has been still deficient. In the face of the demand of industrial applications, more efforts need to devote on CNTs and its polymer matrix composites.

Experiments

The multi-walled carbon nanotubes (MWNTs) were purchased from Chengdu Organic Chemicals Co., Ltd., Chinese Academy of Sciences with diameters at 10-20 nm and lengths at 5-15 μm . Epoxy resin (E51) was purchased from Shanghai Resin Factory Co., Ltd. 1-Methy Jimidazole was donated by BASF SE. Other chemical reagents used in this research were purchased from Sinopharm chemical reagent Co., Ltd.

The MWNTs were functionalized using a procedure involved 1 hour reflux in 3:1 (in volume) H_2SO_4 and HNO_3 mixture followed by washing with deionized water repetitiously. So the functional MWNTs with carboxyl was received, marked as MWNTs-COOH. The MWNTs-COOH were sonicated for 5 hours at 50 $^\circ\text{C}$ in 35 ml DMF with 4 g 4-toluene sulfonyl chloride. Added 5 ml ethylene diamine into the former solution for 24 hours at 120 $^\circ\text{C}$, followed by washing with deionized water repetitiously. Then the MWNTs with amino group were received, marked as MWNTs-NH₂. The MWNTs-NH₂ were sonicated in alcohol for 2 hours, added epoxy resin with stirring. Degassed alcohol and added 1-Methy Jimidazole, the mixture was cast into a glass mold for curing at the following parameters: 80 $^\circ\text{C}$ /2h + 120 $^\circ\text{C}$ /3h. A neat resin sample was prepared for comparison with the composite as same procedure.

An AVATAR FTIR-360 and an Vario EL III elementary analysis instrument were performed for monitoring elemental change of the MWNTs. A JEM-2100 transmission electron microscope (TEM) was used for observing morphology of the MWNTs. Dispersion achieved in the nanocomposites was observed with a ME600 optical microscopy and a LEO 1530 scanning electron microscopy (SEM). A differential scanning calorimetry (DSC 204) was performed at a heating rate of 10 °C/min from 25 to 220 °C. DMTA was performed in bending mode using a Rheometric Scientific DMTA-V, and the samples were heated from 25 to 220 °C at a rate of 3 °C/min at a frequency of 1 Hz.

Results and discussion

FTIR and elementary analysis of the MWNTs

Figure 1 shows there are characteristic absorption of carboxyl group at 1710 cm^{-1} in curve b and amino group at 1640 cm^{-1} in curve c. Results of elementary analysis in Table 1 show that there is 2.949 % nitrogen element of the MWNTs-NH₂. Results in Figure 1 and Table 1 indicate that ethylene diamine chains were grafted onto the MWNTs successfully. TEM images in Figure 2 suggest that the MWNTs-NH₂ have less impurities than raw MWNTs through acidification and amination process, while surfaces of the MWNTs-NH₂ are almost no change.

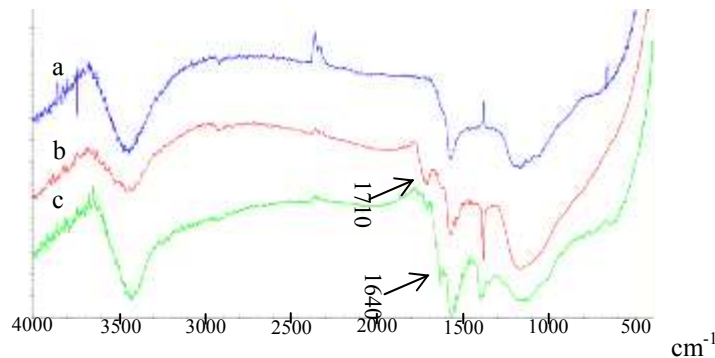


Fig. 1. FTIR spectra of (a) raw MWNTs, (b) MWNTs-COOH, (c) MWNTs-NH₂

Table 1. Elementary analysis of raw MWNTs and MWNTs-NH₂

Sample	Weight / mg	C/N Ratio	Content / %	Peak area
raw MWNTs	5.5920	0.000	N: 0.000	N: 0
			C: 94.93	C: 132479
			H: 0.507	H: 1339
MWNTs-NH ₂	5.3330	28.20	N: 2.949	N: 5441
			C: 83.19	C: 111054
			H: 1.339	H: 4230

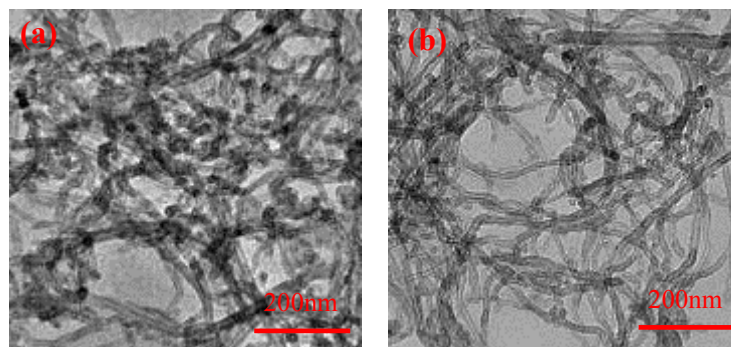


Fig.2. TEM images of (a) raw MWNTs and (b) MWNTs-NH₂

Dispersion of MWNTs in the nanocomposites

Dispersion of nanofillers within polymer matrix is a stubborn task in scientific. The MWNTs were shown single dispersion in the nanocomposites containing less than 1 wt% raw MWNTs in Figure 3a and 3b. However, the nanocomposites containing no more than 2 wt% MWNTs-NH₂ show much better dispersion in Figure 3e, 3f, and 3g. While the composite containing 3 wt% MWNTs-NH₂ has a similar dispersion with the composite containing 2 wt% raw MWNTs. Figure 4 indicates that the composites containing MWNTs-NH₂ were shown less aggregation than the composites containing raw MWNTs. That means enhanced reaction between the epoxy matrix and the MWNTs-NH₂ improved nanofillers dispersion within the composites.

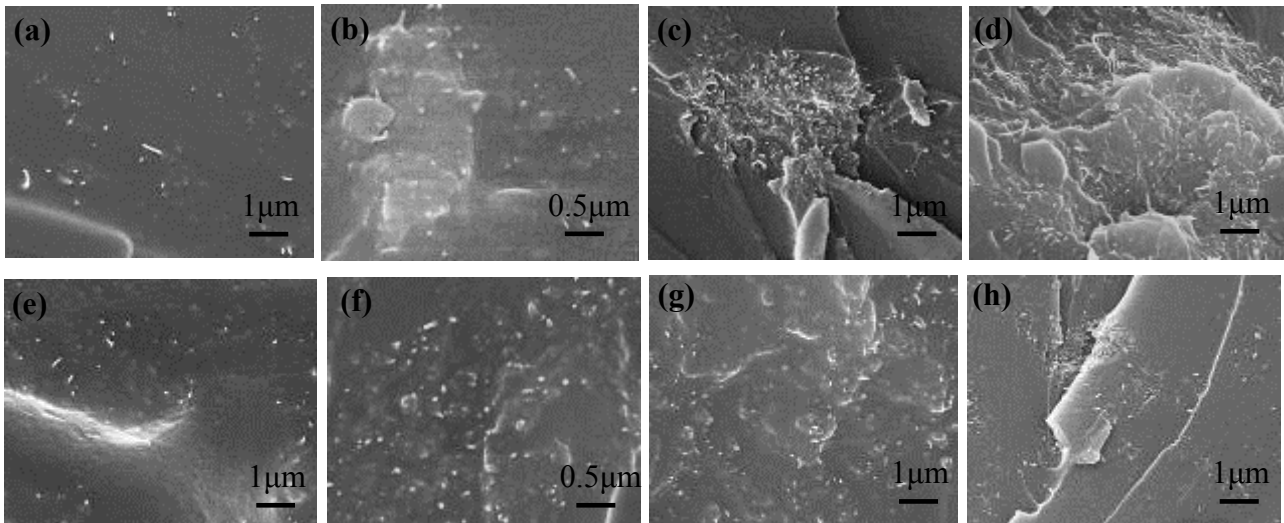


Fig.3. SEM images of MWNTs/epoxy composites, a. 0.5 wt% raw MWNTs, b. 1 wt% raw MWNTs, c. 2 wt% raw MWNTs, d. 3 wt% raw MWNTs, e. 0.5 wt% MWNTs-NH₂, f. 1 wt% MWNTs-NH₂, g. 2 wt% MWNTs-NH₂, h. 3 wt% MWNTs-NH₂

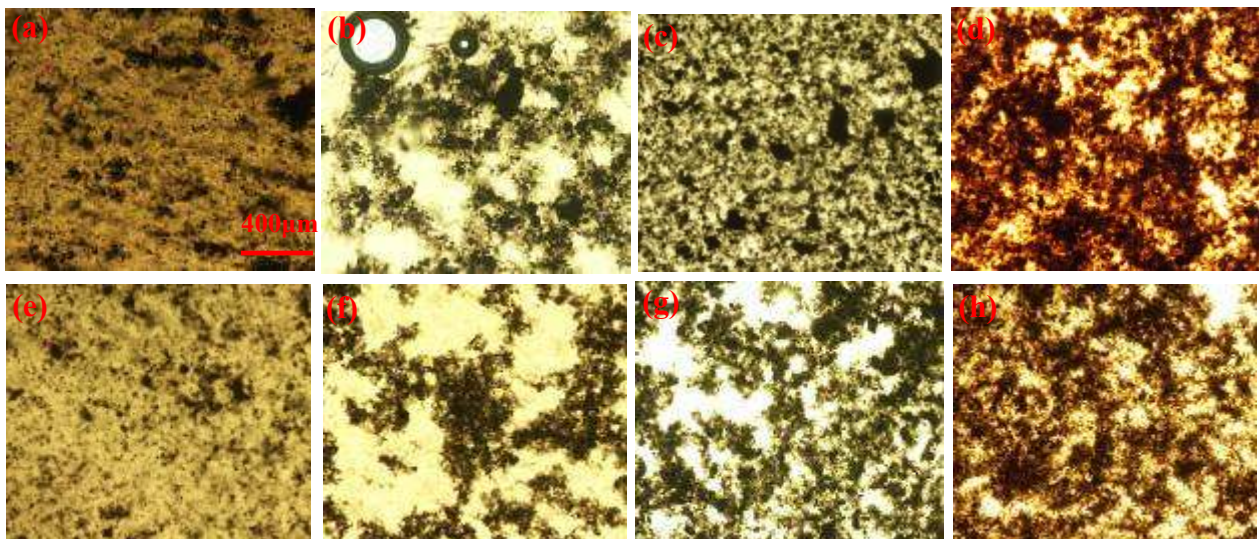


Fig.4. Optical microscopy images of MWNTs/epoxy composites, a. 0.5 wt% raw MWNTs, b. 1 wt% raw MWNTs, c. 2 wt% raw MWNTs, d. 3 wt% raw MWNTs, e. 0.5 wt% MWNTs-NH₂, f. 1 wt% MWNTs-NH₂, g. 2 wt% MWNTs-NH₂, h. 3 wt% MWNTs-NH₂, all images have same scale bar with a.

Dynamic mechanical thermal analysis (DMTA) of MWNTs/epoxy nanocomposites

Table 2 suggests that glass transition temperature (T_g) of the composites containing 0.5 wt% raw MWNTs and MWNTs-NH₂ are increased than the epoxy resin, indicating that one-dimensional MWNTs are imposed on polymer chains, which are constrained by MWNTs. However, the constrain effect only occurred in the composites with less 0.5 wt% nanofillers. T_g of the composites with more than 1 wt% MWNTs are lower than epoxy matrix, probably indicating that more air bubbles and cavities within the composites brought by MWNTs aggregations, more movable spaces are provided within the nanocomposites lead to more mobility of the polymer chains, thus usually decreasing T_g of the nanocomposites. Results in Figure 5 also indicate a similar trend of the nanocomposites. Even storage modulus of the nanocomposites containing raw MWNTs are varying degrees of decline than epoxy matrix, while storage modulus of the composites with MWNTs-NH₂ show varying degrees of increased in Figure 6.

Table 2. T_g of the composites with different MWNTs content (°C)

Sample	0	0.5 wt%	1 wt%	2 wt%	3 wt%
raw MWNTs	181.0±1.5	183.8±0.4	179.4±0.1	173.5±0.9	170.5±0.5
MWNTs-NH ₂	181.0±1.5	182.6±0.2	178.6±0.2	177.8±0.3	173.6±0.6

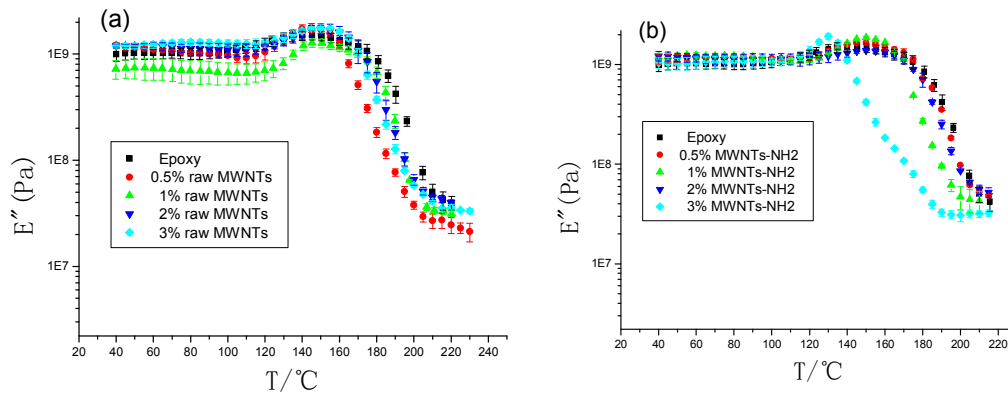


Fig.5. Loss modulus of the nanocomposites with (a) raw MWNTs and (b) MWNTs-NH₂

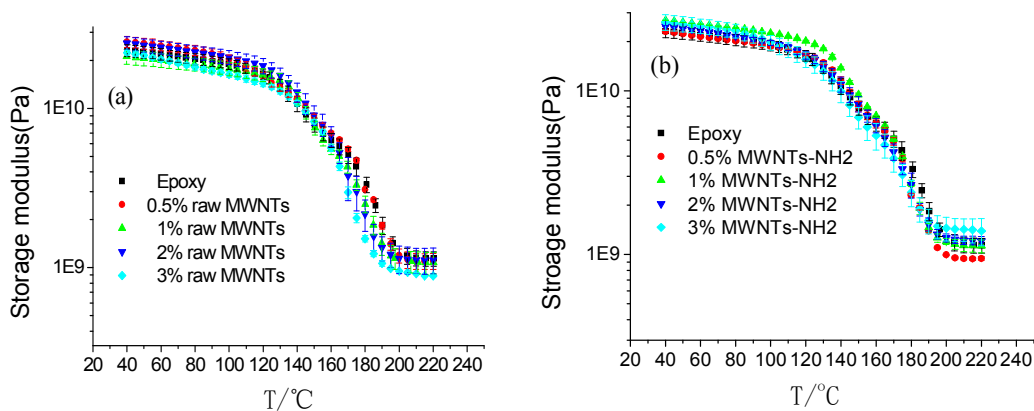


Fig.6. Storage modulus of the nanocomposites with (a) raw MWNTs and (b) MWNTs-NH₂

Differential scanning calorimetry of MWNTs/epoxy nanocomposites

Results in Table 3 exhibit that curing temperature of the nanocomposites containing MWNTs shift to higher temperature than epoxy matrix. However, the curing temperature of the composite with 3 wt% raw MWNTs decreased than the other nanocomposites, probably indicating that poorer dispersion has less impact on interfacial interaction between MWNTs and epoxy matrix, which lead to almost no change on curing reaction of the nanocomposites.

Table 3. T_p of DSC curves of epoxy matrix and its composites ($^{\circ}\text{C}$)

Sample	0	0.5 wt%	1 wt%	2 wt%	3 wt%
raw MWNTs	126.5 \pm 0.7	128.8 \pm 2.5	129.4 \pm 1.4	128.8 \pm 0.9	126.5 \pm 0.3
MWNTs-NH ₂	126.5 \pm 0.7	128.5 \pm 2.1	128.5 \pm 1.9	129.8 \pm 0.2	128.0 \pm 1.0

Conclusion

We have adapted an surfacial functionalization method to the fabrication of MWNTs/epoxy nanocomposites. In the case of MWNTs, functionalizing with ethylene diamine chains promotes the nanofiller dispersion in epoxy matrix and surfacial reactivity of MWNTs/epoxy nanocomposites. The properties of the various MWNTs/epoxy composites were explored. Notably, addition of the nanofillers caused obvious change on T_g of the nanocomposites. The T_g was increased of the nanocomposites with 0.5 wt% raw MWNTs and MWNTs-NH₂ than the epoxy matrix, subsequently decreased T_g with more nanofillers for nanotubes agglomeration. Composites containing nanotubes were postponed curing reaction of the epoxy, but the nanocomposites with 3 wt% raw MWNTs has hardly affect on the curing reaction for poorer nanofiller dispersion.

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