Effects of Carbon Nanotube Fillers on the Curing Processes of Epoxy Resin-Based Composites

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ABSTRACT: The effects of different grades of carbon nanotubes on the curing of a typical epoxy resin (EPIKOTE™ resin 862 and EPIKURE™ curing agent W) were examined via differential scanning calorimetry. It was found that nanotubes could initiate cure at lower temperatures, while the overall curing process was slowed as evidenced by lower total heat of reaction and lower glass transition temperatures of the cured nanocomposites compared to neat epoxy. This finding is practically important as it is essential to have a consistent degree of cure when the properties of thermosets with nanoinclusions are compared to neat resins. It was also found that the inclusion of carbon nanotubes might induce the thermal degradation of epoxy composites at lower temperatures. Morphological analysis done with scanning electron microscopy revealed good dispersion of nanotubes within the epoxy matrix. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 5248–5254, 2006

Key words: carbon nanotubes; nanocomposite; epoxy resin; curing process; thermal analysis

INTRODUCTION

Epoxy resins have been extensively exploited because of their comprehensive material performance (superior mechanical properties, excellent dimensional stability, outstanding adhesion and coating properties, and good corrosion resistance).[1] Epoxies already find broad application in a variety of industries, such as laminates, flooring, and caulking. They are also an important bulk structural material that can be applied in demanding aerospace projects.[2] Significant effort has focused on further improving epoxy materials using nanofillers (e.g., clay,[3–5] colloidal silica,[6,7] and carbon nanotubes[8–12]).

Since their discovery in 1991, carbon nanotubes (CNT) have become one of the most promising fillers for reinforcement and multi-functionality because of their exceptional mechanical (elastic modulus in the range of 500–600 GPa and tensile strength close to 200 GPa),[13] electrical, and thermal properties. Many studies have shown significant property enhancement in CNT-filled epoxies.[8–12] For example, a 20% increase in storage modulus at room temperature was achieved in a bisphenol F type epoxy with only 0.3 wt % of single-walled carbon nanotubes (SWNT).[12] In addition to improving properties, the incorporation of CNT influences the curing process. Studying the curing of the CNT-filled epoxies is very important for the design, analysis, and optimization of the materials fabrication. Despite significant need, this topic has not yet been addressed sufficiently and there remain controversies in this area.[14–18] Wu and Chung[14] studied the effects of carbon fillers (carbon black, carbon fibers, and carbon nanofibers) on the curing of epoxy and suggested that the presence of the carbon fillers increased the total heat of the curing reaction and accelerated the curing reaction with a lowered temperature at the exothermic peak. Puglia et al.[15] investigated the effects of SWNT on the curing of a bisphenol A type epoxy resin and claimed that SWNT acted as a catalyst to initiate the curing at a lower temperature, but it did not affect the total heat of the curing reaction based upon dynamic differential scanning calorimetry (DSC) testing. However, the isothermal DSC analysis from the same group stated that SWNT and amine functionalized SWNT tend to increase the curing degree of the epoxy composites.[17,18] Bae et al.[16] studied the effects of CNT and carbon black on the curing of a liquid-crystalline epoxy, and they found that both fillers
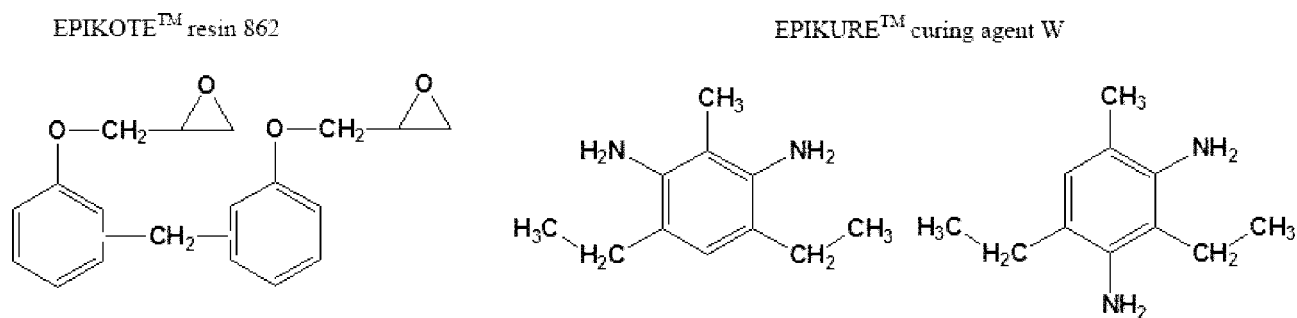
Scheme 1 Chemical structures of the EPIKOTE™ resin 862 and EPIKURE™ curing agent W.

retarded the cure reaction and the retardation effect is more remarkable for carbon black due to its larger particle size, and thus the more significant steric hindrance effect. These discrepancies inspired the present investigation. In this study, three different types of carbon nanotubes were evaluated with regard to their influence on the curing behavior of a bisphenol F-based epoxy resin by means of DSC. DSC was also used to assess the morphology in the cured samples along with imagery from scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

The EPIKOTE™ resin 862 (862) and EPIKURE™ curing agent W (W) were supplied by Hexion Specialty Chemicals. (Houston, TX). The 862 is a bisphenol F type epoxy resin (diglycidyl ether of bisphenol F) and W is a nonmethylene dianiline, aromatic amine curing agent (diethyltoluenediamine). Their chemical structures are shown in Scheme 1. These are commercial products suitable for fabricating composite parts via resin transfer molding (RTM), vacuum-assisted RTM (VARTM), and filament winding processes because of their viscosity (2200 cP) and long working life (> 20 h) at ambient temperature. The manufacturer suggested cure cycle is 2.5 h at 177°C and the curing formula is 100/26.4 (862/W in weight ratio).

Three kinds of carbon nanotubes were used in this work. Short SWNT (S_SWNT, 96.3% carbon content) was purchased from Sigma Aldrich (Milwaukee, WI). The residue includes 2.92 wt % of cobalt, 0.41 wt % of chlorine, 0.29 wt % of sulfur, and 0.08 wt % of aluminum. The diameter is in a range of 0.8–1.6 nm and the average length is about 500 nm according to the vendor. HiPco® SWNT (HiPco-SWNT) was purchased from Carbon Nanotechnologies (CNI, Houston, TX). There is approximately 20 wt % ash content, 8 wt % of which is Fe catalyst residue. The XD-grade CNT (XD-CNT), designed for electrostatic discharge applications, was also obtained from CNI. It has 96 wt % of carbon content and is a mixture of single-walled, double-walled, and triple-walled carbon nanotubes. The transmission electron microscope (TEM) pictures of these carbon nanotubes are shown in Figure 1. It is clear that HiPco-SWNT contains many residue catalyst particles (3–5 nm in diameter), while the XD-CNT and the S_SWNT are cleaner without obvious signs of metal particles.
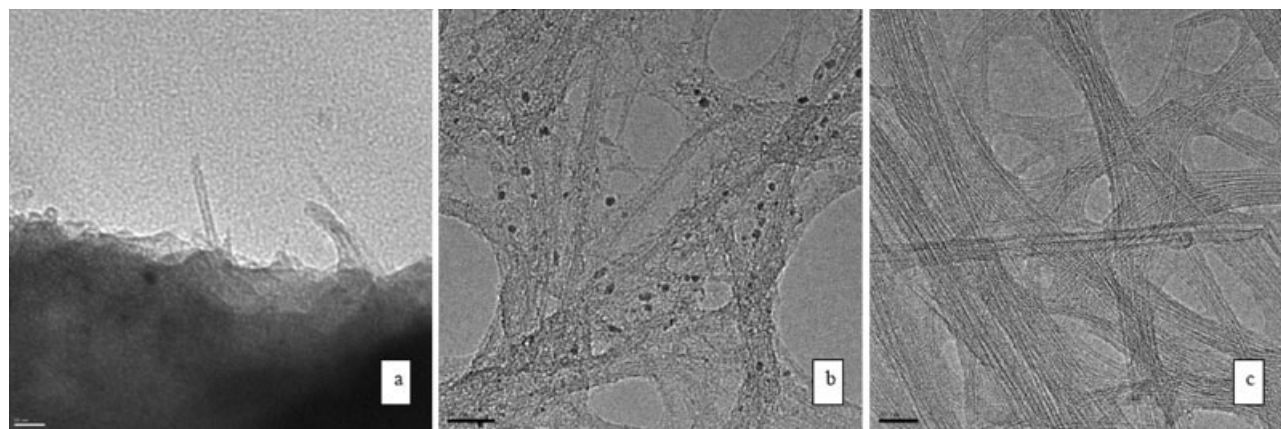

Figure 1 TEM micrographs of carbon nanotubes S_SWNT (a), HiPco-SWNT (b), and XD-CNT (c). The scale bars are 20 nm.
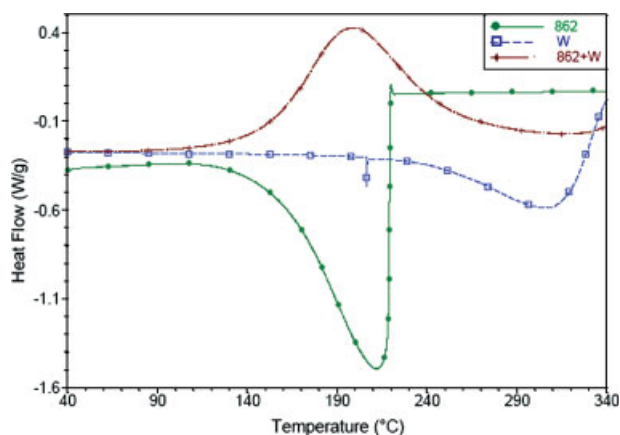
Figure 2 Dynamic DSC thermograms of 862, W, and the mixture (862/W = 100/26.5). [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

Composite preparation

About 1 g of 862, 0.264 g of W, and carbon nanotubes were mixed with a mortar and pestle for 30 min to achieve visual homogeneity. The amount of carbon nanotubes used in this study was fixed at 1 wt %. Next, about 10 mg of the homogenized mixture was precisely weighed in a DSC sample pan where the curing process was characterized. Preparation of the control sample (neat epoxy) also followed the same procedure.

Thermal analysis

Thermal characterization was performed on a Q1000 DSC from TA Instruments (New Castle, DE). The curing processes of the epoxies were monitored under dynamic and isothermal conditions. The procedure for a dynamic mode involved ramping ~10 mg of uncured sample from room temperature to 340°C with a heating rate of 10°C/min. For the isothermal procedure, ~10 mg uncured samples were ramped from room temperature to 177°C, then kept isothermal for 150 min. The cured samples from isothermal procedures were also tested with another DSC ramp to determine the glass transition temperatures. All DSC tests used aluminum sample pans and 50 mL/ min of N_2 purge. For all the DSC thermograms reported, upward peaks are exothermic.

SEM/TEM characterization

SEM images, of the freshly impact-fractured surfaces of the epoxy nanocomposites, were obtained with a Zeiss 1530 VP FE-SEM system. The surfaces were sputter coated with platinum prior to imaging. TEM observation of the carbon nanotubes was carried out with a JEOL JEM-1230 instrument. TEM samples are

prepared using acetone solution casting on 200-mesh copper grids coated with lacey carbon films.

RESULTS AND DISCUSSION

Dynamic DSC measurements of the curing process

Curing of the epoxies was first examined using a temperature ramp. Figure 2 shows the thermograms of the 862, the W, and the mixture of the two. Both 862 and W alone showed endothermic evaporation peaks. The mixture exhibited one broad exothermic peak ranging from 80 to 310°C corresponding to the curing. It also showed a beginning of another exothermic process at higher temperature, which might be an overlap of the unfinished curing and the initial thermal degradation of the cured resin and/or the unreacted monomers.[19] The curing of the epoxy with the inclusion of 1 wt % of CNT is shown in Figure 3. The thermograms are similar to that of the neat epoxy with a broad exothermic peak followed by a degradation process. It was obvious that for the epoxy nanocomposites, the exothermic peak was smaller than that of the pure epoxy control, implying that the inclusion of nanotubes decreased the curing degree of the epoxies, possibly due to the physical hindrance of the nanotubes to the mobility of the monomers. The onset temperature of curing (T_{on}) and the exothermic peak temperature (T_p) are summarized in Table I. Some data, such as the temperature of completion of the curing or the total enthalpy of curing, could not be precisely determined here because of the onset of the thermal degradation. From Table I, it is clear that all carbon nanotubes facilitated the curing initially by lowering the onset temperature of curing (T_{on}). The HiPco-SWNT demonstrated the most noticeable effect on T_{on} (lowering it by 14°C compared to neat epoxy), while the other
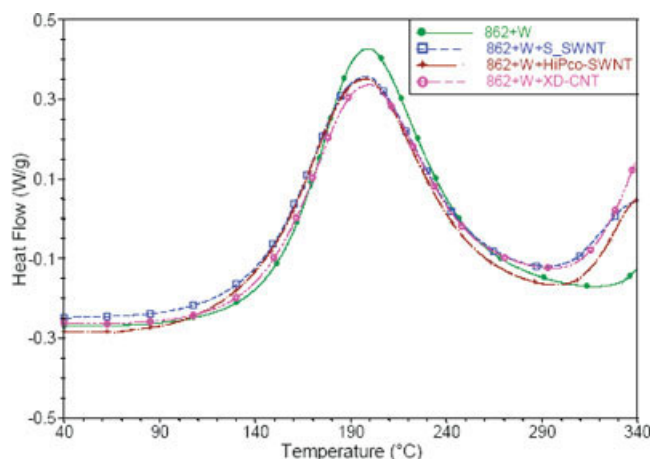

Figure 3 Dynamic DSC thermograms of the curing of the neat epoxy and epoxy nanocomposites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Results of Dynamic DSC Scans
(Temperature Ramp to 340°C)

Sample	T_{on} (°C)	T_p (°C)	$T_{on, d}$ (°C)
862 + W	149	198	335
862 + W + S_SWNT	141	197	306
862 + W + HiPco-SWNT	136	197	314
862 + W + XD-CNT	141	198	317

T_{on} is the onset temperature of curing, T_p is the exothermic peak temperature, and $T_{on, d}$ is the onset temperature of degradation.

two carbon nanotubes exhibited similar but more modest effect on T_{on} (lowering it by 8°C). This similar effect had been observed in a SWNT-filled bisphenol A-type epoxy resin[15] and carbon fiber/carbon nanofiber/carbon black-filled bisphenol F-type epoxy resins.[14] The stronger effect from the HiPco-SWNT may be attributed to its relatively higher catalyst residues (20 wt % ash content vs. 3.5 and 4.0 wt % for S_SWNT and the XD-CNT, respectively). Although the carbon nanotubes induced curing to lower temperatures, there is no obvious effect on the exothermic peak temperature. A closer look at the tails of the DSC thermograms reveals that the CNT-filled epoxy composites underwent earlier and more severe thermal degradation compared to the neat epoxy. For qualitative comparison, the onsets of degradation temperatures ($T_{on,d}$) obtained from the partial degradation process are also listed in Table I. A lowering of at least 20°C in $T_{on,d}$ is observed in the CNT-filled composites. In previous literature, a fluorinated SWNT-filled epoxy also showed a similar trend.[12] The lowered $T_{on,d}$ might be explained as follows: First, the CNT-filled epoxy composites experienced less degree of curing and therefore there were more unreacted constituents that decomposed at lower temperatures. Second, the metallic catalyst residues within the CNT might also catalyze the thermal degradation process, which is consistent with ABS and POM-based nanocomposite systems.[20]

Isothermal DSC measurements of the curing process

For isothermal testing, all the samples were ramped from ambient temperature to 177°C with a heating rate of 10°C/min followed by holding at 177°C for 150 min. This procedure is similar to the practical condition in the epoxy curing process suggested by the vendor. Only the data after the system reached 177°C were reported here, as the temperature ramp before the isothermal step had been investigated in the dynamic DSC study (section 3.1). Figure 4 presents the curing of the neat epoxy and the CNT-filled epoxy composites. The thermograms demon-
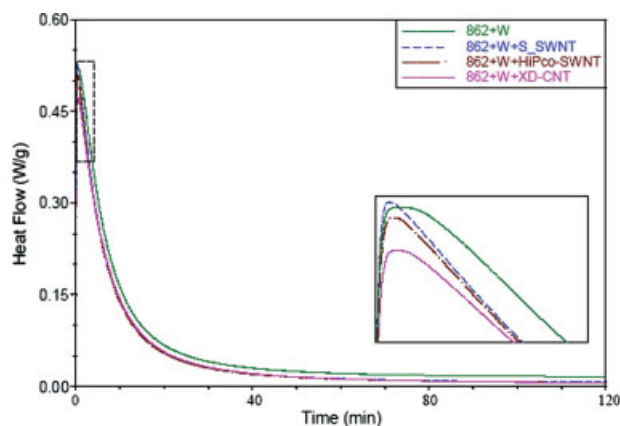

Figure 4 Isothermal DSC thermograms of the curing of the neat epoxy and epoxy nanocomposites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

strated typical isothermal behaviors in the cure of thermoset polymers. In fact, these systems are often characteristic of a maximum reaction rate at time zero, when the concentrations of reactive species are the highest. The minor shift of the maximum reaction rate to a nonzero time observed in Figure 4 might be explained by the "auto-catalytic" behavior in epoxy systems.[15] The resultant reaction peak time (t_p) was also listed in Table II. It was found that the CNT-filled epoxies are slightly faster in reaching the exothermic peak than the neat epoxy. To take a better look at the initial curing, the thermograms during the first 5 min are presented as an inset in Figure 4. The inset indicated that the neat epoxy exhibited a higher exothermic curing peak than the CNT-filled systems, which is consistent with the result from the dynamic DSC analysis. The three carbon nanotubes investigated here showed a difference in the initial curing stage as evidenced by the initial curing slopes and exothermic peak heights. However, after about 15 min curing, all the curves converged and no significant difference was observed thereafter. The curing degree can be characterized by the total heat of reaction (ΔH). The total area under the exothermic peak was used to calculate the total

TABLE II
Isothermal DSC Data

Sample	t_p (min)	ΔH_{150} (J/g)	ΔH_{250} (J/g)
862 + W	0.50	298	300
862 + W + S_SWNT	0.26	283	287
862 + W + HiPco-SWNT	0.37	280	283
862 + W + XD-CNT	0.41	280	282

t_p is the exothermic peak time, and ΔH_{150} and ΔH_{250} are the total heat of reaction for the samples isothermally cured for 150 and 250 min, respectively.
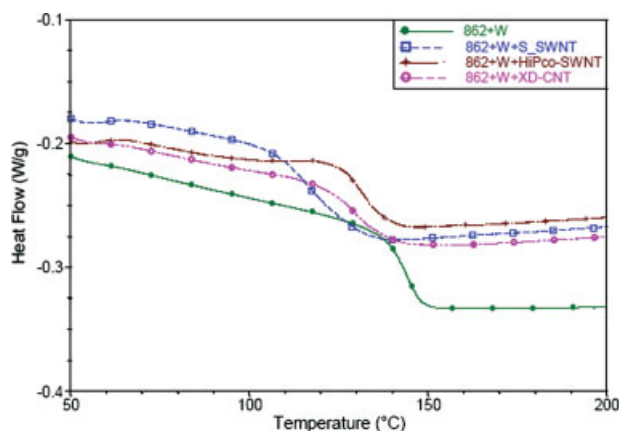
Figure 5 DSC thermograms of the epoxy samples cured at 177°C for 2.5 h. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 6 Comparison of the DSC plots of the neat epoxy and S_SWNT filled composites cured at 177°C for 2.5 and 24 h. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

heat of reaction and these values are reported in Table II. The enthalpy data confirmed that the inclusion of CNT in epoxy hindered the cure to a certain degree. Even when our isothermal study was extended to 250 min, we found that there was very little increase in the total heat of reaction for all of the samples and the curing degree of the CNT-filled composites was always lower than that of the neat epoxy. The data for the total heat of reaction within 250 min are also summarized in Table II. This observation is in contrary to Wu and Chung's findings with the carbon fillers' (carbon fiber, carbon black, and carbon nanofiber) effect on the curing of the same type of epoxy.[14] It should be noted that: (1) their heat of reaction data were obtained from dynamic DSC testing; (2) their curing agent was also different (the peak curing temperature was around 80°C); and (3) they used a much higher filler concentration (20 wt %).

DSC measurements of cured samples

A temperature ramp was performed on samples cured isothermally at 177°C for 2.5 or 24 h to further study the effects of CNT and curing time. Figure 5 shows the DSC thermograms of the samples cured for 2.5 h. All curves showed typical one-step changes corresponding to glass transitions. It is clear that all CNT-filled composites exhibited lower glass transition temperatures (T_g) regardless of the rigidity of the nanotubes, which is a strong indication of less curing of the nanocomposites compared to the neat epoxy. The viscosity increase caused by nanotubes inclusion was noticeable during mixing, which suggested that the physical hindrance of the carbon nanotubes might be a major factor impairing the mobility of the active groups in epoxy and the curing agent, thus leading to significantly lower curing
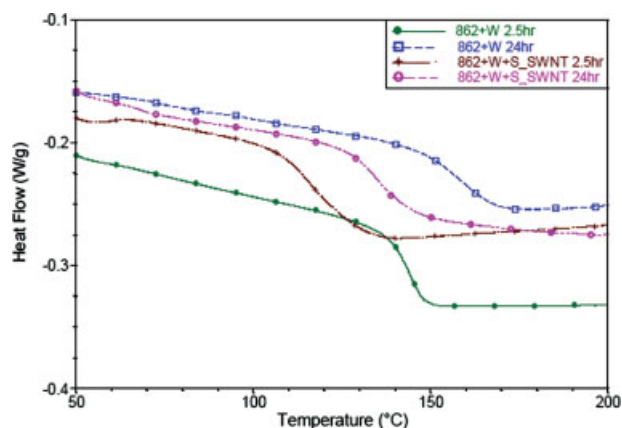
degrees. As expected, the cure would continue given longer curing time. Figure 6 shows the comparison of DSC thermograms of the neat epoxy and the S_SWNT filled composite cured for 2.5 and 24 h. The 24 h cured samples showed higher T_g than the 2.5 h cured counterparts. A more significant observation is that even after 24 h of curing, which is much longer than the vendor's recommended curing time (2.5 h), the S_SWNT filled composites still showed much lower T_g than the neat epoxy. Similar trends were also observed in the other two CNT-filled systems and the T_g values were tabulated for comparison (Table III). It is clear that, with only 1 wt % of carbon nanotubes, the T_g of epoxy composites was lowered by 10–30°C approximately. As evidenced by the lower total heat of reaction in the isothermal DSC study (the previous section 3.2 and Table II), the significantly decreased T_g would be primarily ascribed to the lower degree of cure, while it might also be partially attributed to the well-dispersed filler particles (as demonstrated in the SEM pictures in the next section 3.4) that weakly bonded with the epoxy matrix and therefore increased the distance between polymer chains, resulting in a decrease in intermolecular forces thus further lowering the T_g.[21] This effect may be found especially substantial in

TABLE III
Glass-Transition Temperatures (T_g) of the Cured Samples from DSC Analysis

Sample	T_g (°C), 2.5 h	T_g (°C), 24 h
862 + W	144	159
862 + W + S_SWNT	115	135
862 + W + HiPco-SWNT	133	148
862 + W + XD-CNT	130	143

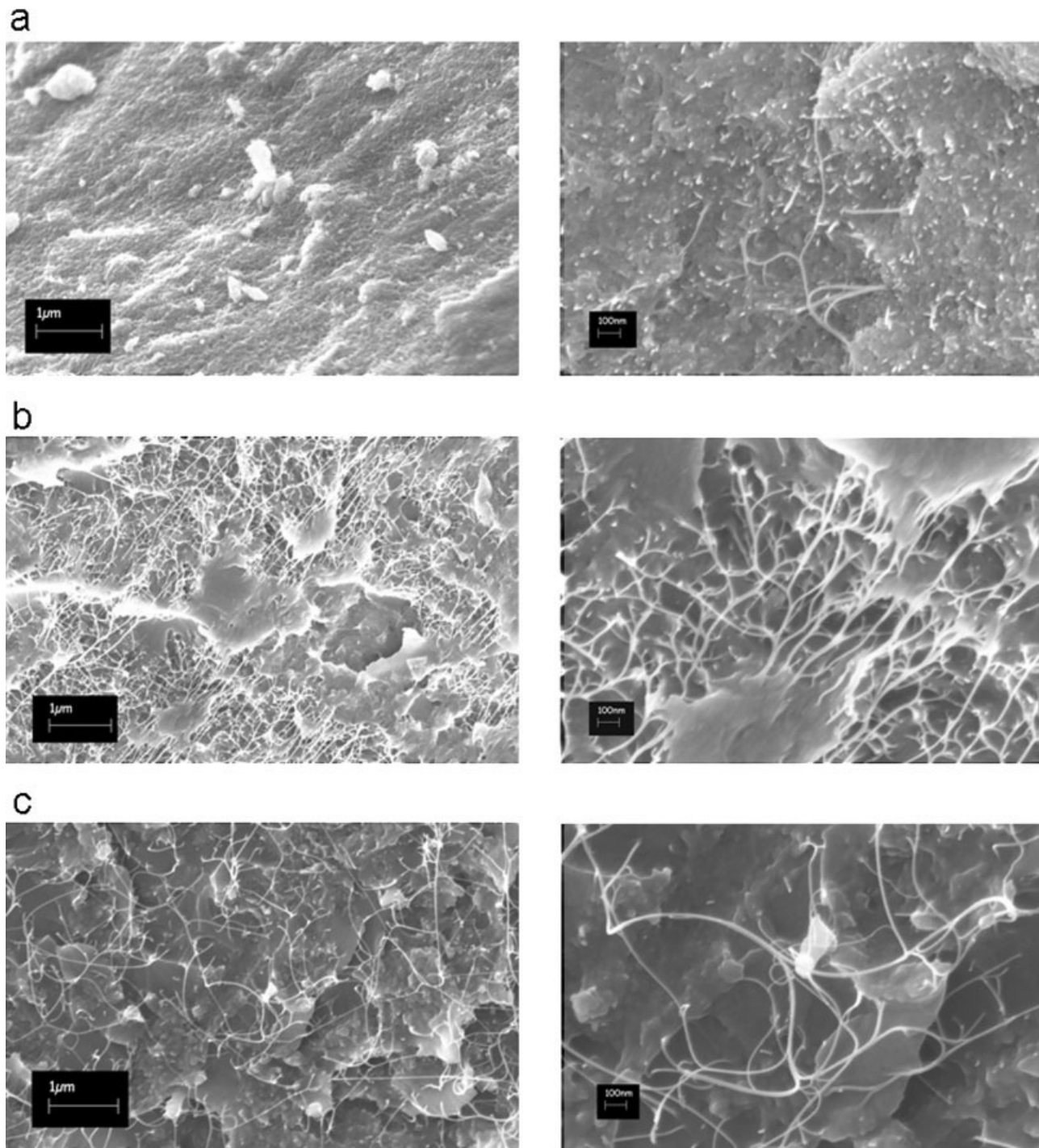T_g, 2.5 h and T_g, 24 h are the T_g values for the samples isothermally cured for 2.5 and 24 h, respectively.

Figure 7 SEM micrographs of the epoxy composites filled with S_SWNT (a), HiPco-SWNT (b), and XD-CNT (c), at lower (10,000×) and higher (50,000×) magnifications.

the case of S_SWNT filled epoxy composite where a large number of nonfunctionalized fine filler particles were evenly distributed in the epoxy matrix. This finding of decreased T_g is practically important for applications where CNT are expected to enhance the thermal properties of the nanocomposites. In addition, when the properties of nanocomposites are compared to the pristine polymers, it is also necessary to

perform such comparison on a basis of a uniform degree of cure.

Morphological analysis

The morphology of the epoxy nanocomposites cured for 2.5 h was characterized by SEM and is shown in Figure 7. Despite the simple method used in our

materials preparation (grinding for 30 min), nice dispersion and distribution of nanotubes were achieved in the epoxy matrix. No large bundles of nanotubes were observed on the fractured surface. Actually, molecular simulation by Wong et al. showed that nonbond interactions (electrostatic and van der Waals forces) between CNT and epoxy matrix resulted in a shear stress of about 138 MPa at 0 K[22] and strong interactions of 862 and W to a (10,10) SWNT were also observed by another group through molecular dynamic simulation.[23] The interactions between CNT and epoxy helped reduce the probability of agglomeration, so good wetting on CNT by epoxy matrix could be expected. Among the three different CNT, relatively better wetting was observed in the HiPco-SWNT filled epoxy composite. The epoxy was pulled out together with carbon nanotubes during fracture, and bridging of epoxy was seen on the fracture surface which suggested a strong interfacial interaction and strong stress transfer in the interface. On the contrary, for XD-CNT and S_SWNT filled epoxy composites, naked nanotubes were observed on the fracture surface, indicating a relatively poor interface.

CONCLUSIONS

The effects of three carbon nanotubes on the curing of a bisphenol F-type epoxy resin were examined via DSC. From dynamic DSC analysis, it was found that all carbon nanotubes initiated curing at lower temperatures while the overall degree of cure was decreased compared to the neat epoxy. From isothermal DSC analysis, it was found that the three carbon nanotubes only showed a difference during the first 20 min of curing, after that all the curves converged. All CNT-filled composites exhibited lower degrees of curing than the neat epoxy. It was also found that the inclusion of CNT helped induce the thermal degradation at lower temperatures. The T_g of the 1 wt % CNT-filled composites was lowered by 10–30°C compared to neat epoxy system. Morphological analysis of the cured composites revealed good dispersion of

nanotubes within epoxy matrix and relatively better wetting was observed in the HiPco-SWNT filled epoxy composite.

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