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Heat absorbability of single-walled, coiled and bamboo nanotube/epoxy nano-composites

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Carbon nanotubes and nanoparticles have become attractive as nano-fillers for improving the mechanical properties and thermal stability of polymer-based nanocomposites. Most research has focused on the use of straight single-walled (SWNTs) or multiwalled (MWNTs) carbon nanotubes as ultrastrong reinforcements for epoxy-based composites. However, due to the uncertainty of the bond interface between the nanotubes and matrix, the stress transferability of these composites is doubtful [1]. The latest development of coiled multiwalled carbon nanotubes (CCNTs) provides an improvement in the stress transferability due to the generation of mechanical interlocking in composite systems [2]. However, there is no comprehensive study which has addressed the thermal properties of these nanocomposites. In this letter, we report on the thermal properties of different epoxy-based nanocomposites formed by adding 0.5 wt% of SWNTs, CCNTs (Fig. 1a), and bamboo multiwalled (BCNTs) nanotubes (Fig. 1b) to pure epoxy.

The low viscosity, commercially available ARALDITE GY 251 epoxy resin was used with CIBA HY 956 amine hardener. The sample preparation for 0.5 wt% nanotubes (SWNTs, CCNTs, and BCNTs) reinforced epoxy beam was based on four steps:

(i) Nanotubes were dispersed into acetone with strong sonication for 1 hr.

(ii) The desired amount of epoxy resin was added into the nanotubes suspension and then the mixture was sonicated for another hour.

(iii) The mixture was placed on a hot plate to evaporate the solvent for 1 hr, followed by a degassing process in vacuum for 4 hrs.

(iv) The nanotube-epoxy mixture was cast in a polypropylene mold, and then cured after the hardener was added, by first precuring on a hot plate at 50 °C for 10 min with stirring and then curing at room temperature for 24 hrs.

The three nanocomposites were heated from −50 to 250 °C at a scan rate of 10 °C min^{-1}, in a Perkin-Elmer Pyris 1 DSC apparatus coupled with an intercooler. Fig. 2 shows DSC curves for the different nanocomposites and for the pure epoxy from which the glass transition temperatures can be determined. With the DSC curve of the pure epoxy as reference, the most noticeable feature in the curves for the composites is the disappearance of the exothermic peak at 44.33 °C. This indicates that the nanotubes prevent the epoxy from releasing heat energy at this temperature. The endothermic peak located at ∼50 °C in each curve represents the glass transition temperature range for the corresponding composite. The total area under the heat flow peak, based on the extrapolated baseline at the end of the transition, is used to calculate the total heat of the transition process. The initial temperature of the transition (T_{i}), the maximum endothermal peak temperature (T_{p}), the final temperature of the transition (T_{e}), the glass transition temperature (T_{g}), and the heat of the transition (the transition enthalpy, ΔH) for each type of composite are reported in Table I. It is clear that T_{i}, T_{p}, and T_{g}, decrease in order of SWNT/epoxy, BCNT/epoxy, and CCNT/epoxy. Compared to the pure epoxy, a shift of T_{g} to higher temperatures is observed in the composites with SWNTs and BCNTs, while there is an obvious decrease in T_{g} and ΔH in the CCNT/epoxy system. These observed changes reveal that the tubes' surface

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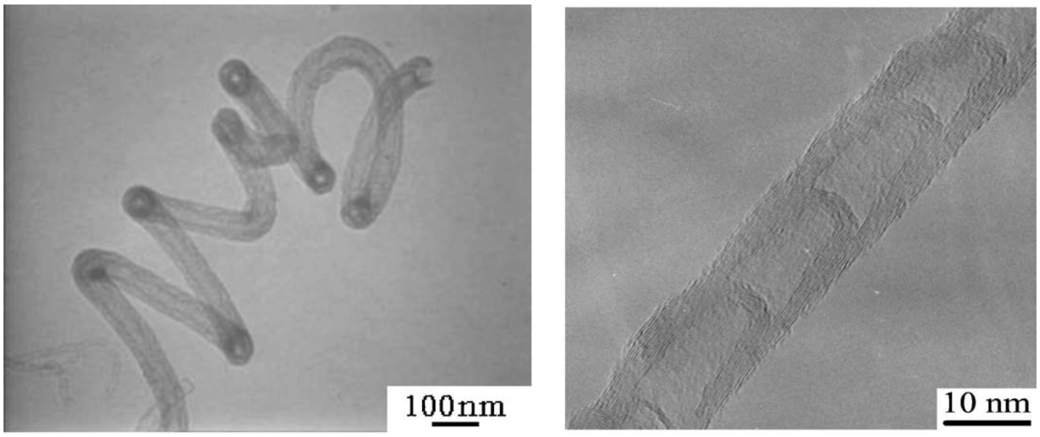

(a) (b)

Figure 1 (a) Coiled and (b) bamboo carbon multiwalled nanotubes.

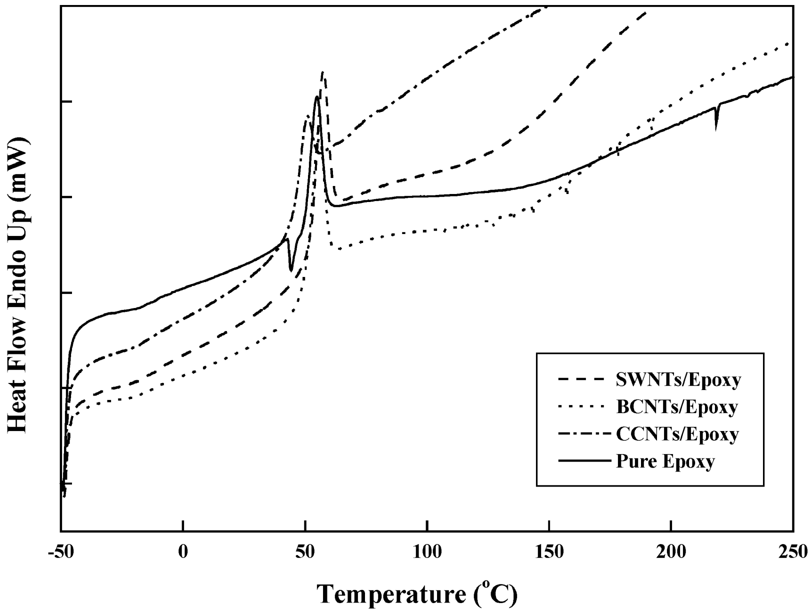

Figure 2 DSC curves at a heating rate of 10 °C min^{-1} for different types of nanotube/epoxy nanocomposites and pure epoxy.

configuration plays an important role in the glass transition behavior of the epoxy. It has been demonstrated that the incorporation of carbon fillers can affect the structure of the cured epoxy by restricting the nucleophile-electrophile interaction during the curing reaction by steric hindrance. Accordingly, nanotubes with different shapes would have different steric hindrance effects on the curing reaction between the epoxy and the hardener. The helical shape of CCNTs should have a larger steric hindrance effect than the straight nanotubes, such as SWNTs and BCNTs. As a result, the curing reaction of the epoxy would be influenced more by CCNTs than by the SWNTs and BCNTs.

TABLE I Initial temperature, peak temperature, final temperature, glass transition temperature and transition enthalpy of different types of nanotube/epoxy composites and pure epoxy

Sample	T_i (°C)	T_p (°C)	T_e (°C)	T_g (°C)	ΔH (J g^{-1})
SWNT/epoxy	52.727	57.333	61.949	57.338	7.852
BCNT/epoxy	50.218	55.666	60.338	55.278	6.752
CCNT/epoxy	46.595	50.833	55.291	50.943	0.745
Pure epoxy	49.979	54.833	58.952	54.466	7.282

Also from Table I, the ΔH values for the three composites are ordered SWNT/epoxy > BCNT/epoxy > CCNT/epoxy. This ordering is consistent with that of the T_g results. Meanwhile, the ΔH value of the SWNT/epoxy composite was higher than that of the pure epoxy, while the ΔH values of the BCNT/epoxy and CCNT/epoxy are slightly, and significantly, lower than that of the pure epoxy. It is thus inferred that during the glass transition process, SWNTs can act as a heat sink to accelerate the heat absorption of the epoxy, while CCNTs can act as heat-shielding fillers and prevent the epoxy from exchanging energy with the outside system. This is because BCNTs and CCNTs are essentially multiwalled nanotubes that, in addition to the inner tube space, have extra space between the graphite layers to absorb energy. On the other hand, CCNTs should have a more effective tube length than BCNTs, and thus more space to absorb energy. In principle therefore, the sequence of endothermic ability or ΔH value should be CCNTs > BCNTs > SWNTs, which is in contradiction to the experimental results. However, because the weight percent of nanotubes in all nanocomposites was the same, the total number of the nanotubes in CCNT/epoxy nanocomposite was much less than the number of nanotubes in the BCNT/epoxy and SWNT/epoxy nanocomposites, so the total surface contact area between the nanotubes and epoxy matrix decreases. Therefore the measured enthalpy of the CCNT/epoxy composite was less than that of the SWNT/epoxy and BCNT/epoxy composites.

It is a fact that functional groups can be introduced on the tube wall during nanotube purification by acid treatment. These polar groups can act as a curing agent because of their affinity to the epoxide group. As a result, the curing reaction should be due to two kinds of hardeners, amine hardener and polar groups. Epoxy cured by these two hardeners should possess different properties from that of the pure epoxy cured by a single amine hardener. Considering this, CCNTs which have many more pentagon-heptagon-pair defects and nodes on the tube sidewall than straight nanotubes (SWNTs and BCNTs), would have more polar groups after acid oxidation treatment. The polar interaction effect of the CCNTs is the most prominent attribute among the three composites. With the CCNTs/epoxy composites exhibiting the lowest ΔH, it can be concluded that if more polar groups in the nanotube contributed to the curing reaction, the ΔH value of the resulting composites would be even lower. It should be pointed out that for SWNTs, the polar interaction effect is no more important a factor than its heat sink effect. This is why SWNT/epoxy has the highest ΔH value among the three composites and the pure epoxy.

By adding a few percent of SWNTs we enhance the heat absorbability of the epoxy-based composite structure. This might be of use for building materials with high heat storage capacity for solar energy storage systems. In contrast, the use of CCNTs in polymer-based structures has great potential in the development of heat shielding polymer structures.

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