

Dispersion and reinforcing mechanism of carbon nanotubes in epoxy nanocomposites

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MS received 22 October 2008

Abstract. Carbon nanotube based epoxy composites have been fabricated at room temperature and refrigeration process using sonication principle. Flexural moduli, electrical conductivity, glass transition temperature of epoxy resin as well as nanocomposite samples have been determined. Distribution behaviour of carbon nanotubes in the epoxy matrix was examined through scanning electron microscopy. Composite samples showed better properties than resin samples due to strengthening effect of the filled nanotubes. Refrigerated nanocomposites obtained increasing mechanical property because of better dispersion due to low temperature settlement of polymers. Improvement of electrical conductivity was due to the fact that aggregated phases form a conductive three-dimensional network throughout the whole sample. The increasing glass transition temperature was indicative of restricting movement of polymer chains that ascribe strong interaction presented between carbon nanotubes and epoxy chains that was again supplemented by Raman study and SEM.

Keywords. Carbon nanotubes; epoxy; flexural modulus; electrical conductivity; glass transition temperature.

1. Introduction

Polymer matrix composites with carbon nanotube (CNT) reinforcement have become popular in structural applications because of unique atomic structure, very high aspect ratio and extraordinary properties like strength and flexibility of CNT (Wagner *et al* 1998; Dagani 1999). The high bond strength of the constituent carbon-carbon bonds of multi-walled carbon nanotubes (MWNTs) are the reason behind its outstanding mechanical properties. On the other hand, epoxy resins are well established thermosetting matrices of advanced composites, displaying a series of interesting characteristics, which can be adjusted within broad boundaries (Peysner and Bascom 1977; Rosenberg 1986; Schadler *et al* 1998; Sandler *et al* 1999; Cooper *et al* 2000). They are used as high grade synthetic resins, for example, in the electronics, aeronautics, and astronautics industries. One of the major difficulties encountered during processing of carbon nanotube-reinforced epoxy composites is the inability to achieve a uniform dispersion of the nanotubes in the liquid epoxy. Nanotubes tend to cluster or agglomerate due to physical entanglements of the tubes, van der Waals forces between the carbon surfaces, and the fact that the surface energy of the nanotube clusters is thought to

be less than that of the corresponding collection of individual nanotubes.

Nanotubes in epoxy composites have been elaborated using different processes earlier and controversial results were reported concerning the improvement of their mechanical and thermal properties. Several groups (Lau and Hui 2002; Penumadu *et al* 2003; Gojny *et al* 2004) observed only marginal improvement or even a decrease in nanocomposite tensile moduli after small additions of nanotubes into an epoxy resin matrix. Lau and Shi (2002) and Lau *et al* (2003) showed the reduction in flexural strength of a CNT-epoxy composite relative to pure epoxy, probably a result of a weak interface. Electrical conductivity ($>10^{-8}$ S/cm) is needed in order to avoid the electrostatic charging of insulating matrix. Sandler *et al* (1999) showed that CNTs/epoxy composites have electrical conductivity of about 10^{-4} S/cm with the filler volume fractions as low as 0.1 wt.%. In some reports moderate or significant increase was obtained in mechanical properties as well as glass transition temperature (Allaoui *et al* 2002; Chen *et al* 2007; Song *et al* 2008).

In this work, the nanocomposites have been prepared using sonication method with very low content (0.2 wt%) of MWNTs in the epoxy matrix. Additionally, other nanocomposites were prepared for the first time at low temperature in refrigeration process. Flexural modulus, electrical conductivity and glass transition temperature of resin as well as nanocomposite samples were examined and variations in different properties between the respec-

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tive cases were observed. The purpose of this study is to optimize the conventional method of manufacturing composites and examine their effect on mechanical, electrical and thermal properties which were again supplemented by scanning electron microscopy and Raman spectroscopy.

2. Experimental

2.1 Materials

Multiwall carbon nanotubes (MWNTs) used for the preparation of nanocomposites were obtained from MER corporation, USA. They were produced by arc plasma method (purity 95%, length, 10–50 μm and diameter, 20–70 nm). SEM morphology of the products (figure 1) was carried out with a 'JEOL JSM-6480 LV Scanning Microscope'. Epoxy polymer matrix was prepared by mixing epoxy resin (Ciba-Geigy, araldite LY-556 based on Bisphenol A) and hardener HY-951 (aliphatic primary amine) in wt. ratio 100/12. Epoxy resin (5.3–5.4 equiv/kg) was of low processing viscosity and good overall mechanical properties.

2.2 Nanocomposite preparation

Nanocomposites were prepared by dispersing MWNTs kinetically by ultrasonication. To achieve better state of dispersion first the nanotubes were treated with alcoholic medium (ethanol) for the deagglomeration of the tube bundles. The treated tubes were then added to the epoxy resin and sonicated for 2 h at room temperature. Then the mixture was cured under vacuum at 90°C for 10 h followed by hardener addition by manual stirring. One part of sample was allowed to set at room temperature and another part under refrigeration. The prepared samples were treated at 80°C for 6 h in the oven to remove the moisture contents of the samples. Pure resin and refrigerated resin samples were also fabricated for comparison purpose. Four types of test samples were fabricated. The pure resin sample was named as epoxy and the nanocomposite sample as epoxy/MWNT. Respective resin samples and nanocomposite samples settled in refrigerator were named as epoxy and epoxy/MWNT.

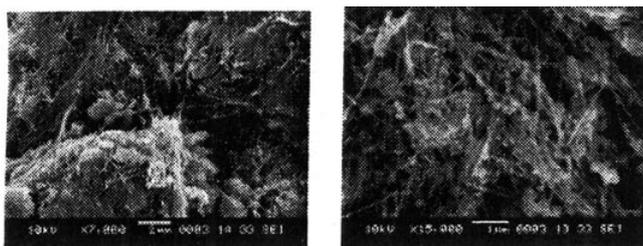


Figure 1. SEM of multiwall carbon nanotubes (MWNTs).

2.3 Flexural test

From each sample, five rectangular specimens were taken for three-point bend test as per ASTM D790 (width = 2.7 cm, thickness = 0.7 cm, span = 11.2 cm, length = 12 cm). Flexural tests were carried out at ambient temperature using Instron 1195 keeping a cross-head speed of 2 mm/min. Flexural modulus of each sample was determined from the average value of five specimens.

2.4 Electrical measurements

The d.c. electrical conductivity values of resin and MWNT reinforced epoxy composites of $4 \times 0.5 \times 0.4$ cm were obtained. Electrical resistance was measured at room temperature (25°C) by two-probe method using Keithley Electrometer-617 having maximum input resistance $\sim 10^{17} \Omega$. Two-probe method was chosen instead of four-probe method because the sample shows relatively high resistance. Silver paints were used at the electrode point for ohmic contact. Respective resistivities of samples were determined taking the cross-sectional areas (0.2 cm^2) and length (4 cm) of the sample into account. From this information, conductivities of respective samples were calculated.

2.5 Differential scanning calorimetry (DSC) study

The DSC measurements were performed on a Mettler-Toledo 822^e with intra-cooler, using the STAR (version 9.0 \times) software with Alternating DSC (ADSC) module. The temperature calibration and the determination of the time constant of the instrument were performed by standards of In and Zn, and the heat flow calibration by In. The underlying heating rate of 5°C min^{-1} was used. In order to calibrate the heat flow signal, a blank run with an empty pan on the reference side and an empty pan plus a lid at the sample side was performed before the sample measurements. All measurements were conducted in air atmosphere. About 20 mg of sample was sealed in 40 μL aluminum pan. The experiments were performed in the temperature range from 25–120°C.

2.6 Raman spectroscopy

All Raman scattering spectra were recorded by using a Renishaw plc in Via MicroRaman spectrometer equipped with 514 nm green laser having 2 cm^{-1} spectral resolution of Raman shift, X–Y step resolution of 0.1 μm and confocal resolution of 2.5 μm .

2.7 Scanning electron microscope (SEM) study

Scanning electron microscope (Jeol JSM-6480 LV) was used to conduct the dispersion behaviour and fracture

surface topography characterization. The composite samples were fractured and the fracture surfaces were coated with a thin platinum layer.

3. Results and discussion

3.1 Flexural measurements

Flexural modulus of pure resin and refrigerated resin samples are found to be 24.52 MPa and 44.15 MPa, respectively (figure 2). The composite samples show greater modulus than pure resin samples (136.86 MPa and 176.38 MPa). This may be due to the high mechanical strength of CNT. Moreover, refrigerated samples (repoxy and repoxy/MWNT) have 4–5 times more flexural modulus value than room temperature settled samples that implies variation in polymerization process under the action of low temperature. This may be due to contraction of matrix that increases frictional force between nanotubes and matrix. At low temperatures, polymeric chains get frozen and thermal vibrations and mechanical deformations (moduli) are controlled mainly by the weak inter-chain binding (van der Waals) forces (Hartwig 1994).

3.2 Electrical measurements

It is observed that electrical conductivity values of composite samples are higher compared to that of resin samples (figure 3). Epoxy and repoxy samples have conductivity values of 0.027 $\mu\text{S}/\text{cm}$ and 0.054 $\mu\text{S}/\text{cm}$, respectively. Composite samples of epoxy/MWNT and repoxy/MWNT offer conductivity values of 2.00 $\mu\text{S}/\text{cm}$ and 2.35 $\mu\text{S}/\text{cm}$, respectively. This clearly indicates a significant increase of conductivity by 43–74 times. MWNTs are generally conducting (Sandler *et al* 1999) and typically have aspect ratio of around 1000. Improvement of electrical conductivity was due to the fact that aggregated phases form a conductive three-dimensional

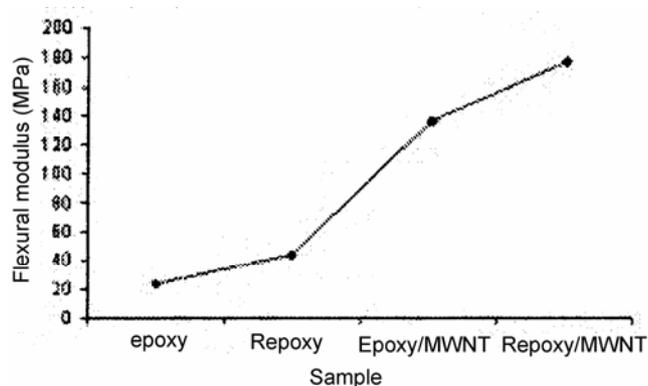


Figure 2. Flexural moduli of resin as well as composite samples.

network throughout the whole sample. Previous workers (Allaoui *et al* 2002) have found that with 0.5 wt.% CNT, composite still behaved like an insulator. However, present investigation indicates good results even with 0.2 wt% taking into account the random orientation of MWNTs. Composite sample conductors (conductivity order of 10^{-6} S/cm) agrees with the earlier report (Song and Youn 2004) of obtaining a percolation threshold with less than 0.5 wt% of CNTs.

3.3 DSC study

Figure 4 shows the changes occurring in the glass transition temperature of epoxy and nanocomposites. The measurement of glass transition temperature (T_g) is very important because it determines the critical service temperature of the polymer composites and finally their engineering application (Clegg and Collyer 1993).

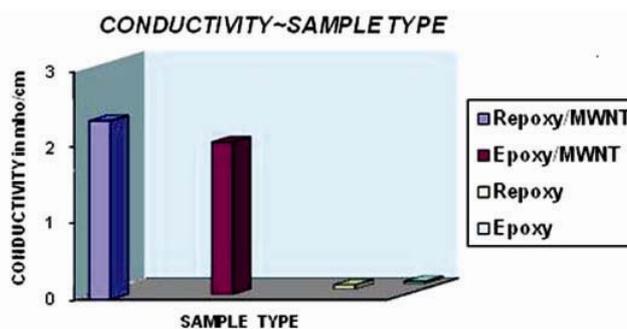


Figure 3. Electrical conductivity of epoxy and nanocomposite samples.

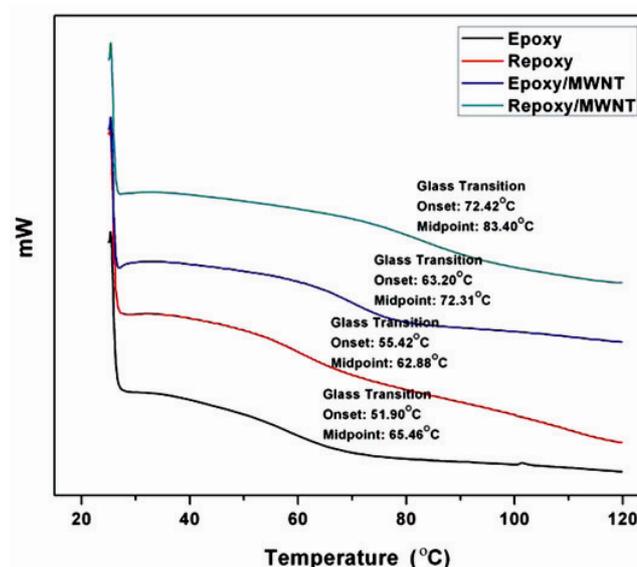


Figure 4. DSC of resin and composite samples.

In the present study an increase in glass transition temperature was observed in case of refrigerated samples. In case of epoxy and re epoxy, T_g increased slightly while T_g of epoxy/MWNT was about 10°C lower than that of re epoxy/MWNT. This difference indicates that polymer/filler interaction influences glass transition temperature. It has been reported that increase in T_g is due to increase in density and decrease in the mobility of the polymer chains (Ajayan *et al* 2003).

3.4 Raman characterization

Figure 5(a) shows the Raman scattering spectra of MWNT in the regions of $100\text{--}1800\text{ cm}^{-1}$. A strong peak at 1587 cm^{-1} can be assigned to the G -band due to tangential C–C bond stretching motions generically stem from the E_{2g} mode in graphite. The weak peak at 1367 cm^{-1} was assigned to D -band arising from disorder induced $A(g_1)$ mode and corresponds to the amorphous carbon (Saito *et al* 1998). The signal intensity ratio of the G -band to the D -band (G/D) is high, indicating that high-quality MWNTs contain few impurities. The Raman spectra recorded on the same sample in the low-frequency part (figure 5a) shows a broad and weak peak. This band is attributed to the breathing-type vibration (RB modes, A_{1g} symmetry) of nanotubes that is usually too weak to be observable for large diameter tubes (Jorio *et al* 2003).

Raman characterization was also applied to highlight the effects of MWNTs on the epoxy matrix composites. Presence of RBM peaks in both epoxy/MWNT and

re epoxy/MWNT confirms the presence of carbon nanotubes in composite samples. It can be seen that D band (1365 cm^{-1}) in epoxy/MWNT is more intense than the band observed for re epoxy which indicates MWNT at 1352 cm^{-1} (figure 5b). This indicates in epoxy/MWNT, more number of CNTs showed defect sites and change to amorphous carbon than in case of re epoxy/MWNT (Sulong *et al* 2006). Again, increase in peak intensity and a little shift in G -band are found in case of re epoxy/MWNT in comparison to epoxy/MWNT. It has been reported that increase in peak intensity related to G -band corresponds to the debundling of MWNT (Lefrant *et al* 2003) and shifting of G -band indicates stress transfer from CNT to matrix and reinforcement (Bokobza 2007).

3.5 Morphological characterization

To check the dispersion, as well as the reinforcing mechanism of carbon nanotubes in CNTs reinforced epoxy resin composites, the fracture surfaces of samples were observed by SEM.

Compared to epoxy/MWNT (figure 6), relatively homogeneous distribution of nanotubes was observed in re epoxy/MWNT (figure 7). Raman study also proved more debundling of MWNT is happening in re epoxy/MWNT. This may be due to delay in settling procedure that facilitates better dispersion in case of refrigerated samples. This also supplements and compliments flexural results that uniform distribution of nanofillers inside polymer matrix enhances flexural value.

From all the measurements, it is clear that cooling process at refrigeration temperature facilitates improvement in electrical conductivity and increase in flexural modulus. Better dispersion is possible because ethanol helps to deagglomerate nanotubes and high-energy sonication action breaks the entanglement, which helps to distribute MWNTs homogeneously in the polymer matrix. Low temperature offers delay in the settling procedure that ultimately has an impact on the matrix structure and crosslinking ratio and by this way the molecular motions. Further work can be aimed at the alignment of CNTs in the matrix and improvement in interfacial bonding between CNTs and matrix that would still improve

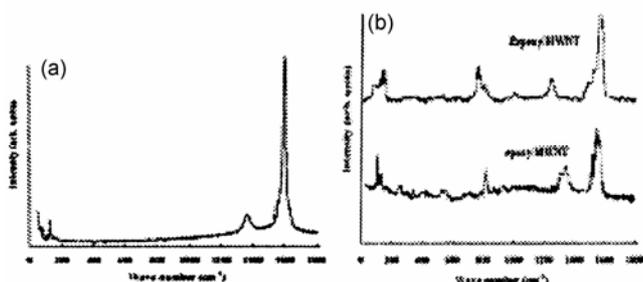


Figure 5. Raman spectra of (a) MWNT, (b) epoxy/MWNT and re epoxy/MWNT.

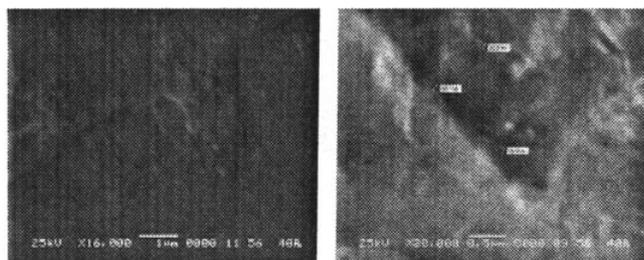


Figure 6. Distribution of nanotubes in epoxy/MWNT.

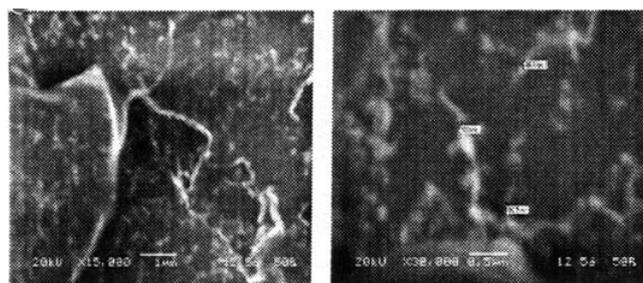


Figure 7. Distribution of nanotubes in re epoxy/MWNT.

the results in terms of electrical and mechanical parameters.

4. Conclusions

Epoxy composites filled with a little wt% CNTs yield better mechanical and electrical properties than pure resin samples due to high strength carbon nanotubes. Improved results of refrigerated sample as compared to other samples indicated that settling the composite at lower temperature brings improvement in physical properties. Morphology study supported this by showing improvement in dispersion of nanotubes in the epoxy matrix. Enhancement in electrical conductivity was due to the fact that aggregated phases form a conductive three-dimensional network throughout the whole sample. The increasing T_g ascribe to the strong interaction existing between MWNTs itself and epoxy chains, restricting the movement of polymer chains. This conclusion is clearly supported by the Raman results, which suggests a direct association of the observed shift of the G modes with a coupling of MWNT with the epoxy matrix.

Acknowledgement

The author is thankful to the Department of Science and Technology, Govt. of India, for the financial support to carry out this research.

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