

INFLUENCE OF CARBON NANOTUBES ON THE CURING AND DAMAGE BEHAVIOR OF EPOXY/CARBON NANOTUBES COMPOSITES

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Abstract

Nano enriched epoxy polymers are prepared by solvent evaporation based on a commercially available epoxy system and functionalized multiwalled carbon nanotubes (COOH-MWCNTs). Three weight ratio are considered (0.05, 0.5 and 1.0 wt%) and compared to both the neat epoxy and the ethanol treated epoxy to investigate both the nanoreinforcement and the processing effects. We focus here on the modification of curing kinetics of the epoxy polymer. It has been observed that introducing the CNTs delays the polymerization process as revealed by the modification of activation energy obtained by differential scanning calorimetry. This paper also presents experimental investigation about the modification of mechanical properties induced by CNT addition into epoxy composite system. Samples with different concentrations of nanoreinforcements have been investigated by dynamic mechanical analysis.

1 Introduction

Epoxy resins are one of the most widely used thermoset polymers for high-performance applications (such as, coatings, adhesives, matrices for fiber reinforced composites) because of their good mechanical properties, excellent adhesion and good chemical and heat resistance. However, new applications demand these properties to be improved. Doping bulk epoxy resin even with a very small CNT content can largely increase the mechanical, electrical or thermal properties of the material [1, 2, 3]. For this reason, carbon nanotube based epoxy nanocomposites is one of the fastest growing areas of materials research in developing new materials with improved properties. Most of the past studies focused on investigating the mechanical, thermal or electrical properties of these modified epoxy polymers [4-10]. A specific interest has been raised about surface functionalization that is a key aspect to improve both CNT/polymer interaction and the nanoparticle dispersion. Yet, a initial stage of nanocomposite fabrication is the curing process that can be affected by this nano doping.

On top of classical processing factors such as curing cycle (temperature, time, pressure), resin/hardener ratio, the CNT ratio becomes a new parameter that can possibly affect the curing response.

However, there is still a lack of systematic study on the curing process of epoxy nanocomposites in presence of carbon nanotubes. Puglia et al [11, 12] studied the effect of

amine (-NH₂) functionalized SWNTs (5wt% and 10 wt%) on the curing reaction of diglycidyl ether of bisphenol A (DGEBA)/diethylene triamine (DETA) under dynamic and isothermal and reported that the curing was accelerated in the presence of SWCNTs. Xie et al. reported that the 1wt% MWCNTs showed a slight catalytic effect on the cure behavior of epoxy, whereas 5wt% MWCNTs induced a significantly accelerated curing [13]. Xie et al. also observed that there were negligible catalytic effect on the cure behaviour of epoxy in presence of carbon nanofiber (1wt% and 5wt%) [14]. Meanwhile, Choi et al. [15] reported that the presence of MWCNTs delays the cure of epoxy resin. Most of the research until now focused on curing behavior of CNT/epoxy system with high concentration of CNTs (>1wt%) [11-13], while few reports have presented the curing behavior with low concentration of CNTs. Yet, understanding the curing behavior modification at very low concentration (<1wt%) is of high practical interest.

The objective of the present work is to study the effect of carbon nanotubes (<1wt%) on the curing kinetics of epoxy nanocomposites. The CNT/epoxy composites were characterized through curing properties like temperature of maximum rate of polymerization (T_p), onset temperature (T_i), activation energy of polymerization reaction (E_a) and morphology through HRTEM and chemical structure through FTIR. In this study, mechanical behavior of CNT/epoxy composites is also investigated.

2 Experimental Procedure: Material and Method

2.1 Material System

Commercial functionalized MWCNTs-COOH. These were produced by Catalyzed Chemical Vapor Deposition and supplied by CheapTubes. According to the supplier's specifications, purity is over 95 wt%, residual ash being less than 1.5 wt%. The raw powder contains 2.56 wt% of COOH groups that correspond to one -COOH group for every 146 carbon atoms. In fact, as only the surface atoms of carbon nanotubes can connect to -COOH groups, we estimate there is roughly one -COOH group for every 10 surface carbon atoms. The announced dimensions (outer diameter from 8 to 15 nm, inner diameter from 3 to 5 nm, length from 10 to 50 μ m) have been confirmed by TEM observations (Figure 1(a)). The Raman spectra of these MWCNTs (Figure 1(b)) was obtained within the range of 200 to 3500 cm^{-1} using a LabRAM HR 800 Raman spectrometer (Horiba Co.). The D-band, the G-band and the G'-band clearly appear respectively at 1350, 1580 and 2710 cm^{-1} . The relative intensity (D/G) between the D and the G bands is known to be a good indicator of the quantity of structural defects within the bulk sample, the intensity of the D-band increasing largely with the presence of defects, amorphous carbon or functional groups in the sidewall [16]. These MWNTs contain multiple structural defects due to their functionalization.

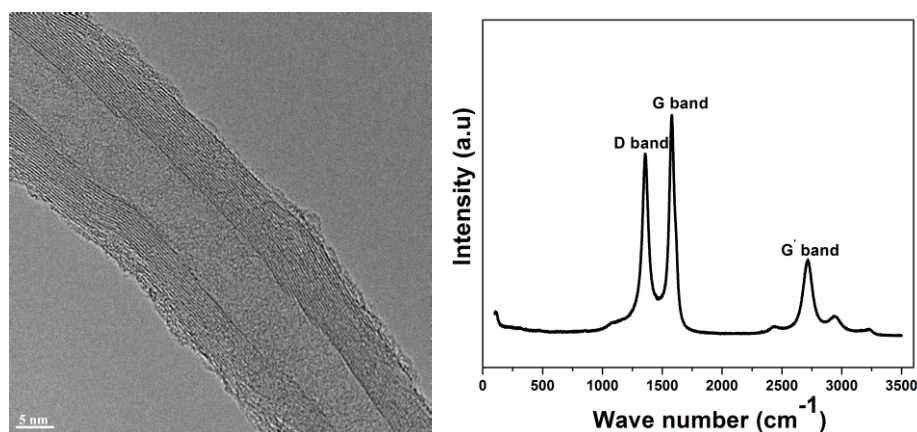


Figure 1. (a) TEM image of MWCNT and (b) Raman spectrum of MWCNT

EPOLAM 2063, provided by AXSON Technologies, is a two components epoxy system consisting of diglycidyl ether of bisphenol A (DGEBA) epoxy resin and cycloaliphatic (CA) epoxy resin. It is used with the compatible hardener (Anhydride 1,2,3,6-Tetra\hydromethyl-3,6-methanophthalique). According to the supplier's specification the tensile strength and the Young's modulus are 57 MPa and 3.1 GPa at 23°C. The glass transition temperature is expected to be between 180°C and 200°C depending on the curing cycle.

2.2 Preparation

Three different material configurations designated as M1, M2 and M3 were investigated. Material M1 is made of neat epoxy resin.

First, the epoxy resin was heated to 80°C to lower its viscosity. Next, the hardener was added into the mixture with magnetic stirring and then kept in a vacuum oven for 30 minutes at 80°C for degazing.

Material M2 is the nano-enriched epoxy. First, the MWCNTs were dispersed into ethanol by sonication (Sonicator: CPX500 Cole-Parmer Instruments, frequency: 20kHz) for 2 hours in an ice bath. Then, the CNT-ethanol solution was added to the epoxy (preheated to 80°C to lower the viscosity); this mixture was stirred continuously using magnetic stirrer for 2 hours at 80°C until all the ethanol was evaporated. Afterwards, the mixture was sonicated as well as stirred using magnetic stirrer for 30 minutes at 80°C. The required amount of hardener was added (ratio of 5:5.35 by weight as prescribed by the supplier) and it was thoroughly stirred to make a homogeneous mixture for 15 minutes. Material M2 was prepared with different MWCNT contents: 0.05 wt% (M2_{0.05}), 0.5 wt% (M2_{0.5}) and 1.0 wt% (M2_{1.0}).

Material M3 is made by repeating exactly the same steps as for material M2, except that the MWCNTs are not introduced. The purpose of material M3 is to investigate clearly the respective effects of processing and MWCNT in any modification observed between materials M1 and M2.

All samples were prepared by moulding in a 80°C preheated steel mold. The mold was kept at 80°C for 6 hours followed by 6 hours at 180°C to ensure high quality curing of the samples.

2.3 Characterization Techniques

The curing behavior and the glass transition temperatures of the different material formulations were measured by differential scanning calorimetry (DSC) using a Netzsch DSC 204 F1 calorimeter. Samples were heated from 25°C to 250°C under pure nitrogen at a rate of 5, 10, 15°C/min.

The activation energy during polymerization of epoxy was calculated from DSC data using the Kissinger's equation given below (equation 1) [17]:

$$d(\ln(\beta/T))/d(1/T) = -E_a/R \quad (1)$$

where β is the heating rate °C. min⁻¹, T is the most rapidly polymerization temperature (K), E_a is the activation energy (kJ/mol), R is the gas constant (J/mol.K).

To investigate the mechanical behavior, tensile tests were performed for all the materials using molded samples per the ASTM/D638-03 type I standard (Figure 2). All tests were performed using an Instron 8252 universal testing machine with an extension rate of 2

mm/min. Load and longitudinal strains were monitored during the test using strain gages and a Vishay 7000 Strain Smart acquisition system.

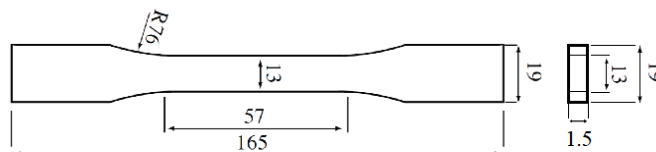
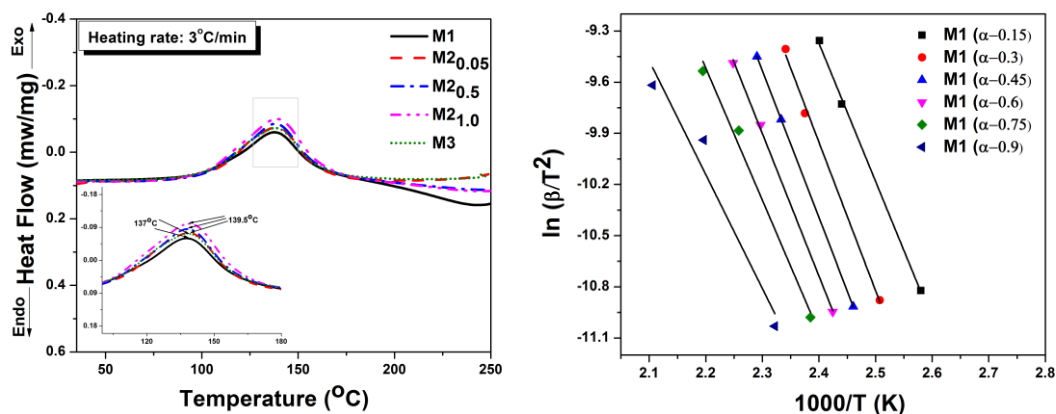


Figure 2. Geometrical specification according to ASTM/D638-03 type-I standard for the bulk epoxy resin.

3 Results and Discussion

3.1 Influence of the CNT content on the curing process

The dynamic DSC scans for materials M1, M2 and M3 are shown in Figure 3(a). The crosslinking reaction of the epoxy curing is analyzed by an exotherm peak in the DSC heat flow curve. In the DSC plot, the exothermic peak appeared in the M1 sample at 137°C. The detail of the graph surrounded by the rectangle is presented as an inset, which shows exothermic peak temperatures clearly. The peak temperature has remained the same for the M3 sample. Therefore, it can be observed that there is not any significant modification of curing process of epoxy by treating through ethanol. For all samples, the onset point of the exotherm corresponds to the first crosslinking of epoxy polymer chains. It has been observed that the onset cure temperature was shifted to a lower temperature in presence of CNTs, whereas, peak temperature was shifted to a higher temperature in the same condition. The occurrence of early onset temperature in the presence of CNTs is due to the outstanding thermal conductivity of CNT. The heat of curing reaction (area under the curve) of the M₂ sample is higher than the M₁ and the M₃ sample. The difference in the value of heat reaction is due to the presence of CNTs [18, 19].



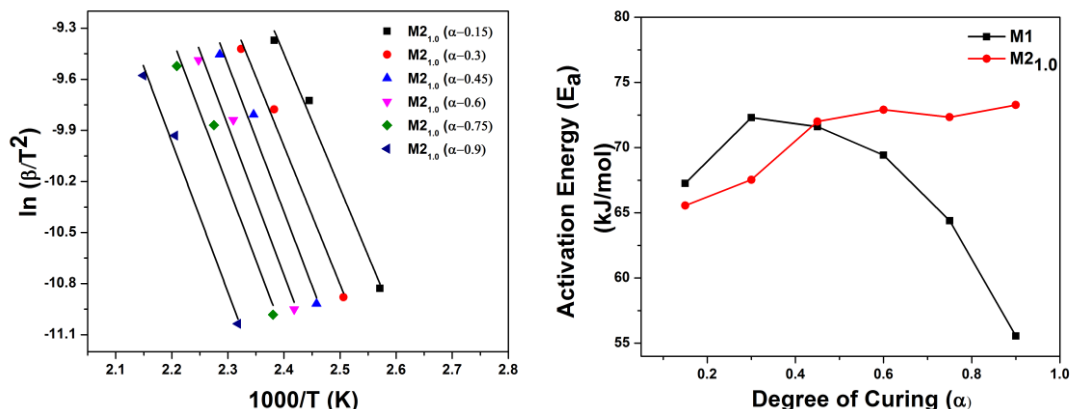


Figure 3. (a) DSC plots for CNT-epoxy with different condition, (b) isoconversional plots at various conversions for M1 sample at different heating rates (c) isoconversional plots at various conversions for $M_{2,1,0}$ sample at different heating rates and (d) activation energy of M1 and $M_{2,1,0}$ with the variation of degree of curing

The activation energy (E_a) for the M1 and $M_{2,1,0}$ samples were evaluated by dynamic DSC. In the Kissinger's method, a DSC experiments at different heating rates are analyzed assuming the curing reaction, as expressed by equation 1.

To estimate the activation energy at different degree of curing through the Kissinger's equation, the slope of the plot between $1000/T$ and $\ln(\beta/T^2)$ was measured for each configuration (Figure 3(b) and Figure 3(c)). Figure 3(d) illustrates the relationship between activation energies and degree of curing. The activation energy of polymerization of M1 increases up to 0.3 degree of curing, and then it decreases, while the activation energy for $M_{2,1,0}$ sample increases during the whole curing cycle. In the presence of the CNTs, epoxy monomer traps between the CNTs during curing process and increases the activation energy.

3.2 Characterization of dispersion and chemical structure

After the curing cycle, the cured samples were characterized through TEM and FTIR. The TEM observations (Figure 4) show that the CNTs have been efficiently dispersed within the resin. No clusters of CNTs are visible even for the maximum load of 1 wt%.

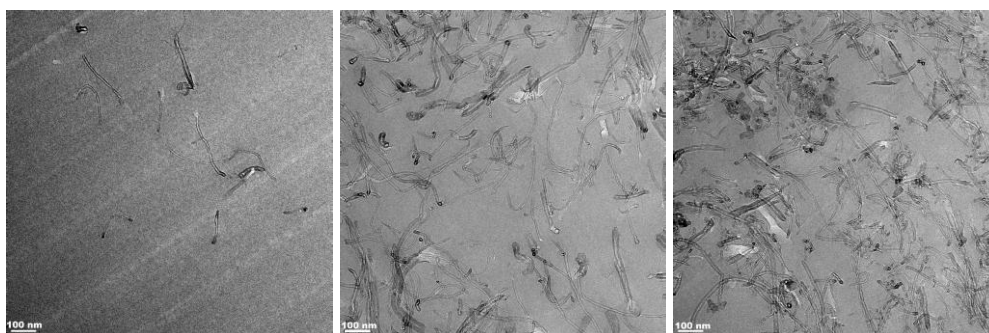


Figure 4. TEM images of CNT/epoxy composites. (a) $M_{2,0,05}$, (b) $M_{2,0,5}$ and (c) $M_{2,1,0}$

Figure 5 shows the FTIR spectra of the samples M1, M2 and M3. It is clear that the absorption bands spectrum matched well with each other, indicating no strong modification of the chemical structure by neither ethanol nor the CNTs. The peak in the ranges of $800-900\text{ cm}^{-1}$ are appears due to the presence of epoxide group [20]. The characteristic absorption bands of carboxylic C=O stretching vibrations at 1730 cm^{-1} and C-H stretch at 2918 cm^{-1} were observed. It is also clear that the appearance of band near 3400 cm^{-1} suggested that there was certain number of hydroxyl groups on the surface of the sample that might create

intermolecular hydrogen bonds with other nucleophilic groups. The absorption intensity of this band (3100-3600 cm⁻¹) is minimum for pure epoxy (M1).

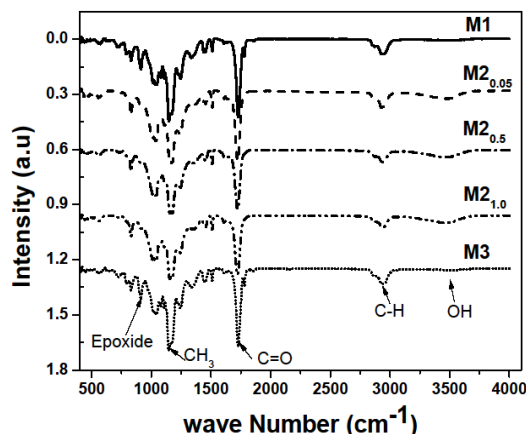


Figure 5. FTIR spectra for CNT enriched epoxy

This increase in intensity might be attributed to the following reasons: First, the reaction between -COOH groups of CNTs with epoxy. Second, the unreacted carboxylic absorption at the same wavelength as the hydroxyl group and, finally, the creation of hydrogen bonding between carboxylic group and -OH groups within the mixture. Also, the absorbance of the unreacted epoxy group near 900 cm⁻¹ decreased drastically upon addition of CNTs.

3.3 Characterization of mechanical behavior

The storage moduli (E') of M1, M2 and M3 samples are presented in Figure 6(a). No changes of storage modulus of epoxy was observed after treating it through ethanol. A significant improvement is observed in storage modulus for M2 samples as compared to M1 and M3 sample. The storage moduli of M2_{0.05}, M2_{0.5} and M2_{1.0} sample at room temperature are 3440, 3680 and 4250 MPa, respectively, whereas the E' values at room temperature for M1 and M3 both samples are 3440 MPa. It is clear that at the room temperature the E' of the nanocomposite is enhanced by more than 7% (M2_{0.5}) and 24% (M2_{1.0}), whereas no changes of storage modulus of epoxy was observed upon addition of 0.05 wt% CNTs into the epoxy. This improvement testifies of a good interaction between the CNTs and the bulk matrix [21].

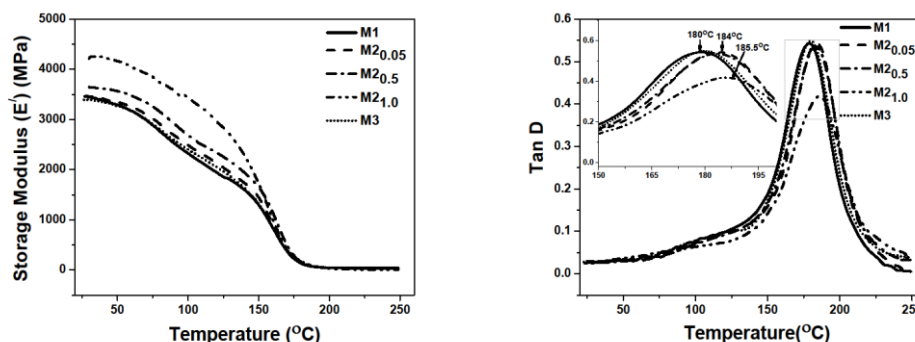


Figure 6. (a) storage modulus (E') and (b) phase angle (Tan D) of CNT/epoxy composites.

It is well known that the peak temperature of the TanD curve is the glass transition temperature (T_g), as shown in Figure 6(b). The inset indicated that the T_g of the M1, M2_{0.05},

M2_{0.5}, M2_{1.0} and M3 samples are observed at 180°C, 184°C, 184°C, 185.5°C and 180°C, respectively. It is worth to mention that the T_g is shifted slightly to the higher temperatures in presence of CNTs, because, the movement of polymer backbone is restricted by CNTs [22]. It has also been observed that the height of the peak decreases as the CNT concentration is increased signifying a decrease in the damping. This can be attributed due to the incorporation of CNTs into the epoxy which significantly increases the storage modulus of the composite.

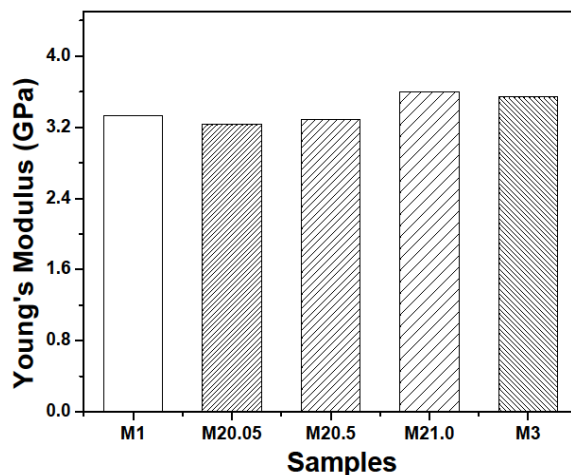


Figure 7. Young's modulus of CNT/epoxy composites.

Figure 7 shows the Young's modulus of neat epoxy and CNT enriched epoxy system. There is a not significant change of the Young's modulus after doping CNTs into the epoxy.

4. Conclusions

The curing, physical and mechanical behavior of EPOLAM 2063 resin system by introducing CNTs has been studied. Based on the experimental results and analysis, following conclusions have been drawn.

- From DSC analysis, it has been observed that the onset temperature and peak temperature during curing was shifted to lower value by increasing CNT content into the epoxy. These changes occurred due to the outstanding thermal conductivity of CNT.
- FTIR result indicates that ethanol did not modify the chemical structure of the epoxy. The formation of various reactive groups was confirmed by FTIR spectroscopic analysis.
- TEM image revealed that the CNTs are well dispersed into the epoxy resin.
- Due to the restriction of polymer chain by CNTs, the T_g has been shifted to a higher temperature. The storage modulus of epoxy is enhanced due to the presence of CNTs, but no significant change of young's modulus.

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