

CHARACTERIZATION OF NH₂-MWCNT/ EPOXY NANOCOMPOSITES USING TWO DIFFERENT CURING CYCLES

M.B.A. Salam¹, M. V. Hosur², S. Zainuddin² and S. Jeelani²

¹ Mechanical Engineering Department, Tuskegee University, Tuskegee, USA

² Materials Science and Engineering Department, Tuskegee University, Tuskegee, USA

ABSTRACT

Investigations were carried out to determine an effective CNT dispersing and epoxy curing process to optimize the mechanical and thermal performance of SC-15 epoxy composites. At first, 0.1-0.3 wt. % of amino-functionalized multi-walled carbon nanotubes (MWCNT-NH₂) were dispersed in part-A of SC-15 resin using a combination of sonication and calendaring method. The mixture was then added to part-B of epoxy resin and cured using two different cycles (cycle A: at 27 °C for 24 hours and post-cure at 94°C for 4 hours, cycle B: at 66 °C for 5 hours). In addition, control samples (without MWCNTs) were also fabricated for baseline consideration under similar conditions. Rheology test results showed multiple order of increase in viscosity with increase in MWCNTs wt. % loading. Flexural and thermo-mechanical results demonstrated maximum improvement in 0.2 wt. % samples that were prepared using cycle B. Microscopic images revealed homogenous dispersion of MWCNTs in epoxy resin and coarser fracture surfaces in 0.2 wt. % samples.

Keywords: Mechanical and Thermal Properties, Dispersion Method, MWCNT.

1. INTRODUCTION

Carbon nanotubes (CNTs) were first discovered by Ijima in year 1990 [1] and exist in the form of single-walled (SWNTs), double-walled (DWNTs) and multi-walled nanotubes (MWNTs). Since the discovery of CNTs, many researchers are trying to exploit the potential of CNTs to improve mechanical performance of different polymers [2-10]. Recent experimental investigations indicated that CNTs have exceptional strength and stiffness [11-14], high flexibility [15], diameter dependent specific surface area [16] and high aspect ratio [17]. According to Reynaud et al. [18], an interface of 1 nm thick represents roughly 0.3% of the total volume of the polymers in micro particle filled composites, whereas it can reach 30% of the total volume in nanocomposites. The high specific surface area of CNTs not only provides desirable interface for stress transfer but can also introduce strong attractive forces between CNTs causing excessive agglomeration and produce unwanted stress concentrations which may act as precursors for failure. MWNTs have a specific surface area of about 200 m²/g or less which is lower than SWNTs due to their much larger diameter and multiple graphene walls and thus exhibit better dispersability.

One of the most important parameter in fabricating CNTs reinforced composites is the dispersion of CNTs itself because of their strong tendency to re-agglomerate. Various methods to disperse nanotubes in polymer resins, such as stirring, sonication and high shear mixing have been reported in literature [19-21]. Among these methods, sonication is commonly used to disperse CNTs in epoxy resin. The ultrasound energy pulse separates the

CNTs agglomeration and disperses them homogeneously in the matrix. On the other hand, acetone or methanol solvents used in isolation or in combination with sonication effectively distribute the CNTs in epoxy matrices [20, 22]. On the other hand, Liao et al. [20] reported reduction in glass transition temperature with the incorporation of SWNTs, being explained by a reduction in interfacial adhesion due to use of solvent. Interfacial adhesion between the CNTs and polymer is also a critical issue. In order to have sufficient stress transfer from the matrix to the CNTs and to efficiently use the potential of CNTs as structural reinforcements, a strong interfacial adhesion between the CNTs and polymer is desirable. The interfacial adhesion between CNTs and matrix was reported to improve by functionalizing the CNTs. Tailored amino, carboxyl or glycidyl groups enable covalent bonding between CNTs and epoxy resulting in improved interfacial bonding. Positive effects of functionalized CNTs on the mechanical properties are reported by various researchers [21, 23-25].

Despite the promising development of CNT/epoxy composites in recent years, the mechanical performance of CNT/epoxy composite falls short of theoretical value. Several researchers have tried to overcome the underlying difficulties in achieving good dispersion of CNTs through chemical functionalization, use of solvents and trying out different mixing methods. However to the best of our knowledge, the effect of processing CNT/epoxy composites by combining the best mixing methods (calendaring and sonication) and functionalization of CNTs together has not been

investigated. Thus, in the present work, we investigated mechanical, thermo-mechanical and rheological performance of amino functionalized multi-walled carbon nanotubes (MWCNTs-NH₂)/SC-15 epoxy nanocomposites that were processed by combining the dispersion methods and amino-functionalized MWCNTs. All results were compared with the baseline (reference) control epoxy composites results containing no MWCNTs.

2. EXPERIMENTAL

2.1 Materials

SC-15 epoxy resin and amino functionalized multi-walled carbon nanotube (MWCNT-NH₂) were used to prepare nanocomposites. SC-15 resin, a two part cyclo-aliphatic amine type epoxy resin (Part A: diglycidylether of bisphenol A, aliphatic diglycidyl and part B: hardener) was supplied by Applied Poleramics Inc. Amino functionalized multi-walled carbon nanotubes (MWCNT-NH₂) was procured from Nanocyl, Belgium. These nanotubes (nanocyl-3152) have average diameter of 10 nm, length of 1 micron and carbon purity >95%.

2.2 Manufacturing Process

2.2.1 Mechanical Dispersion of MWCNTs into Part-A Epoxy Resin

As previously discussed, the incorporation of CNTs into a polymer with a uniform dispersion is very difficult because of its high surface area and exceptionally large quantity of particles. In this study, a technique which is a combination of calendaring (Three roll mill) process followed by ultra-sonication process was used to disperse nanotubes uniformly into the resin.

First, MWCNT-NH₂ was mixed with Part A of the epoxy resin system as per required weight ratio. The mixture was then sonicated (Sonics Vibra Cell ultrasonic processor) for 1 hour at 35% amplitude on pulse mode (20 second on/ 20 second off). During the sonication process, there is significant increase of pressures and temperatures which is highly localized resulting in the increase in temperature of polymer-CNT mixture. Or order to reduce this temperature increase, the container is kept in a cooling bath filled with refrigerant maintained at 5° C. After the sonication process is completed, mixture was added to a three roll machine for three passes which generate high shear forces to disperse nanotubes by controlling the gap and the speed of the rollers. The gap setting among the rolls was 20 μm (1st pass), 10 μm (2nd pass) and 5 μm (3rd pass) and the speed was 150 rpm in each pass.

2.2.2 Mixing of Part A & Part B

After sonication and calendaring process, Part B of epoxy resin system which is the hardener was added as per stoichiometric ratio (Part A: Part B=10:3) to the homogenous mixture and stirred with a high speed mechanical stirrer for 10 minutes at approximately 800 rpm. The mechanical mixing introduces air bubbles into

the resin. To remove this trapped air and volatile materials from the mixture, a degasification process was introduced by placing the mixtures in a vacuum oven for 35 minutes at room temperature.

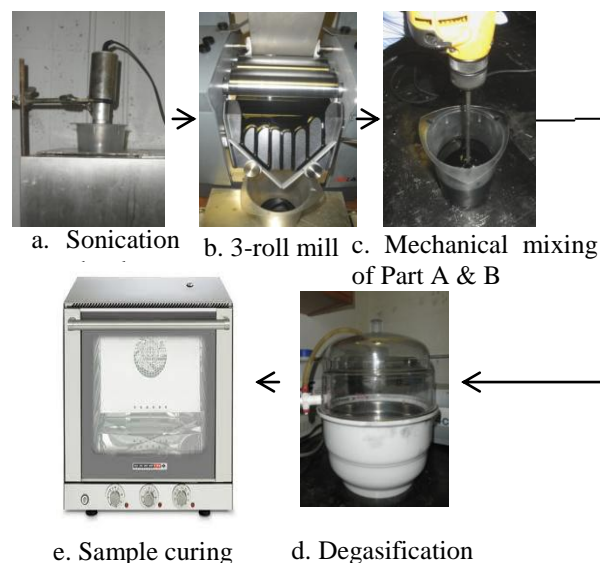


Fig 1. Fabrication process of epoxy nanocomposite.

2.2.3 Curing Cycles

Two curing cycles were used, in cycle A, the mixture containing epoxy Part-A+ B and respective weight percent MWCNT-NH₂ loading cured at room temperature for 24 hours and post-cure at 94°C for 4 hours. In cycle B, similar mixture was cured at 66° C for 5 hours in convection oven. These curing cycles were selected using a DSC thermo-gram that indicated curing started at 27° C and finishing at 66° C respectively.

3. RESULTS AND DISCUSSION

3.1 Rheological Properties

Rheology measurements were performed to observe the effect of increasing weight percent loading of MWCNTs on viscosity, and the changes in viscosity as a measure of shear rate at constant temperature. The measurements were performed with AR 2000 Rheometer in ETC control mode using parallel plate geometry at 1000 μm gap settings. Flow sweep was used to vary the shear rate from 0.1 rad/sec to 100 rad/sec by keeping the temperature constant. Viscosity calculations were performed immediately after the degasification of mixture (Part A & B + MWCNTs). Figure 2 shows viscosity as a function of shear rate for neat and 0.1-0.3 wt. % MWCNTs-NH₂ loaded epoxy resin. Shear viscosity of a polymer is principally divided into Newtonian and shear thinning regions respectively. With increasing shear rate, a shear thinning behavior was observed and a declining trend in shear viscosity was noticed. However, at high shear rate, a Newtonian region was observed in all the samples independent of shear rate. The viscosity of 0.1 wt. % MWCNTs reinforced epoxy sample remains at comparable range with neat resin. However, an increasing trend in viscosity was observed with increasing weight percent of MWCNTs content. Viscosity of 0.3 wt. % resin samples was found to

increase more than 100% in comparison to neat resin samples. This implies that strong particle-particle interaction of CNTs is one major factor that leads to an increase in shear viscosity with increasing CNTs content resulting in poor dispersion.

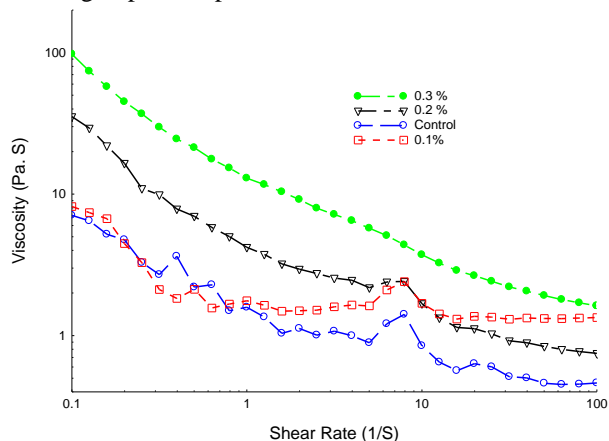


Fig 2. Viscosity vs shear rate response of neat and 0.1-0.3 wt. % MWCNT-NH₂ epoxy resin.

Figure 3 shows the micrograph of 0.2 wt. % MWCNTs samples prepared using a combination of sonication and calendaring methods and cured using cycle B. It is evident from the micrograph that use of a combination dispersing methods not only helped in CNTs separation but they were also uniformly dispersed in the epoxy resin. Separation of CNTs eliminates the unwanted stress raisers that can built inside the epoxy samples due to the excessive particle-particle interaction of CNTs in polymers. Additionally, enhanced dispersion of CNTs provides more sites in the polymer for particle-polymer interaction and can provide significant improvements in mechanical and thermal properties.

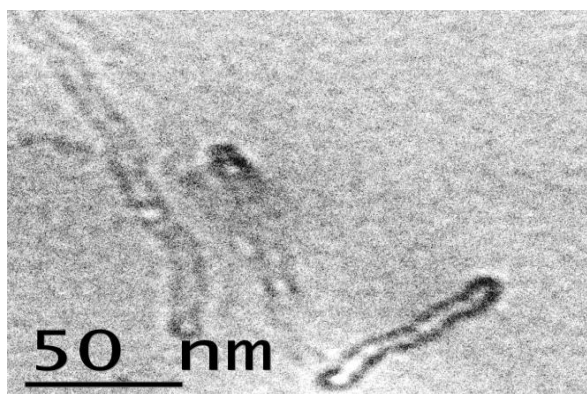


Fig 3. Transmission electron micrograph (TEM) of 0.2 wt. % epoxy composite prepared using cycle B.

3.2 Flexural Response

Flexural tests were performed according to ASTM D790-03 under a three-point bend mode. The tests were conducted in a Zwick-Roell testing machine at a crosshead speed of 1.2 mm/min. All tests were performed at room temperature. Typical stress-strain behavior from the flexural tests is shown in Fig. 4. The stress-strain curves showed considerable non-linearity before reaching the maximum stress, but no obvious

yield point was found in the curves. Five specimens were tested for each condition.

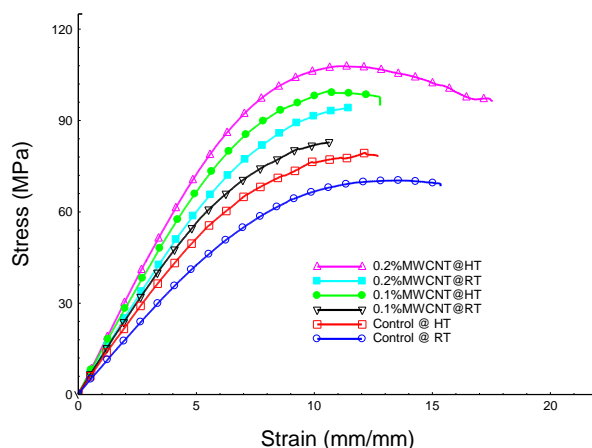


Fig 4. Flexural stress vs. strain response of control and MWCNT epoxy composites prepared with cycle A and B.

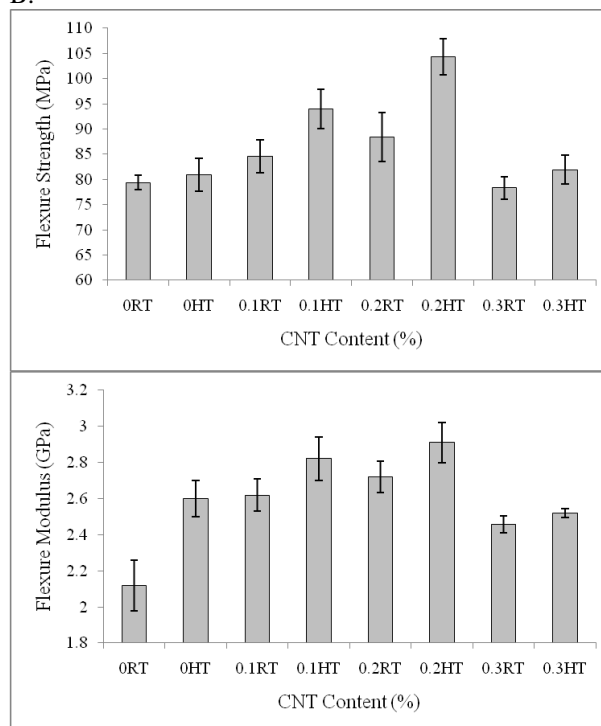


Fig 5. Flexural response of control and MWCNT- epoxy composites prepared using cycle A and B.

Strength and modulus of the nanophased epoxy in both cycles increased continuously with higher MWCNTs content up to 0.2 wt. % loading as shown in Fig. 5. Flexural strength and modulus of cycle A 0.2 wt. % MWCNTs- NH₂ samples improved by 11.3% and 28.3%. Samples with similar 0.2 wt. % MWCNTs loading prepared with cycle B showed best properties with 28.87% and 12% improvement in flexural strength and modulus, respectively in comparison to control samples similarly prepared. The improvements in flexural properties were found lowering with increase in cure time under isothermal condition. Similar results have been reported in the literature [26-27]. Comparing the two curing cycles, the flexural properties found to be affected by the curing process (see figure 5).

Figure 6 (a-d) shows the scanning electron micrographs (SEM) of neat, 0.2 and 0.3 wt. % fractured (tested) samples prepared using cycles A and B. Rougher fracture surface in 0.2 wt. % samples irrespective of the curing cycle were noticed in comparison to neat samples. A densely rough surface was observed in 0.2 wt. % sample (see Fig. 6c) prepared using cycle B indicating that the failure was accompanied with plastic deformation evident from Fig. 4. However, the smooth and ridged fracture surface on 0.2 wt. % sample prepared using cycle A (see Fig. 6b) demonstrated comparatively brittle type of failure evident from Fig. 4. When the MWCNT loading increased to 0.3 wt. %, the failure mode of nanocomposite changed. A crack was initiated at a localized region that appears to be an agglomeration of several MWCNTs. The stress concentration caused by the agglomerated particle initiated a crack, which made the sample to fail rather quickly. Therefore, a decrease in flexural strength and modulus was observed in 0.3 wt. % MWCNTs sample prepared using both cycles.

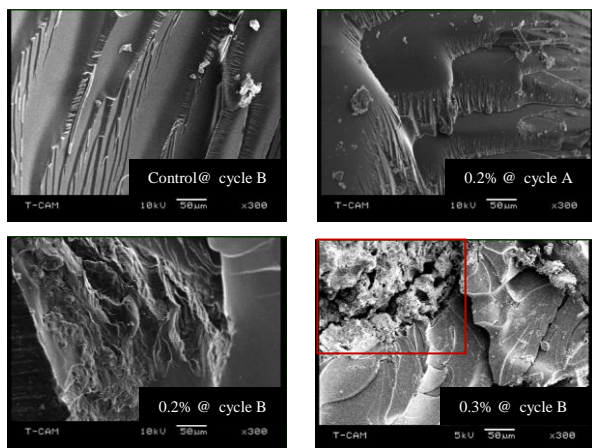


Fig 6 (a-d). Scanning electron micrographs (SEM) of neat, 0.2 and 0.3 wt. % fractured samples prepared with cycles A and B.

Homogeneous dispersion of MWCNTs evident from Fig. 3 may have restricted the mobility of polymer chains under loading resulting in rougher fracture surfaces and thus improving the strength and modulus of 0.2 wt. % samples. Further, modification of MWCNTs with NH_2 (amino) functional groups develops covalent bonding between the MWCNTs and epoxy that might have enhanced interfacial stress transfer leading to the improvement in flexural properties. Similar results have been reported by Gojny and Bai et al. [24-25]. High aspect ratio, high modulus, strength of MWCNTs, and good interfacial adhesion between the MWCNTs and matrix contributed to the improvements in flexural properties. However, the decrease of strength with high 0.3 wt. % MWCNTs loading can be attributed to the MWCNTs agglomeration in higher loading systems as shown in Fig. 6d.

3.3 Thermo-Mechanical Properties

Figure 7 shows the dynamic mechanical analysis

(DMA) results of neat and MWCNTs epoxy composites prepared using cycle A and B. The modulus drop is credited to an energy dissipation phenomenon involving cooperative motions of the polymer chain. In this study, storage modulus at 30 °C and glass transition temperature (T_g) from the peak position of $\tan \delta$ curve is used to study the viscoelastic behavior of samples. Addition of 0.2 wt. % NH_2 -functionalized MWCNTs samples prepared using cycle B yielded an optimal increase of 37.64%, 73.65% and 13.1 % in storage modulus, loss modulus and glass transition temperature respectively.

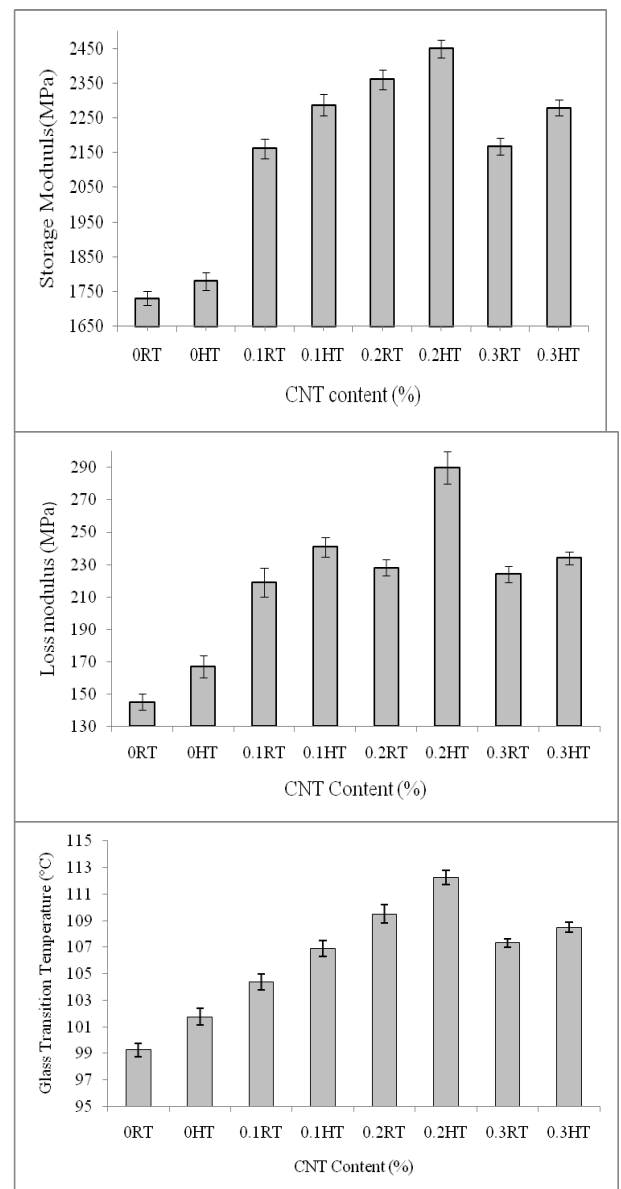


Fig 7. Thermo-mechanical response of control and MWCNT- epoxy samples prepared using cycle A and B.

Figure 8 and 9 show typical storage modulus vs. temperature, loss modulus vs. temperature curves as additional two figures for both cycle A and cycle B.

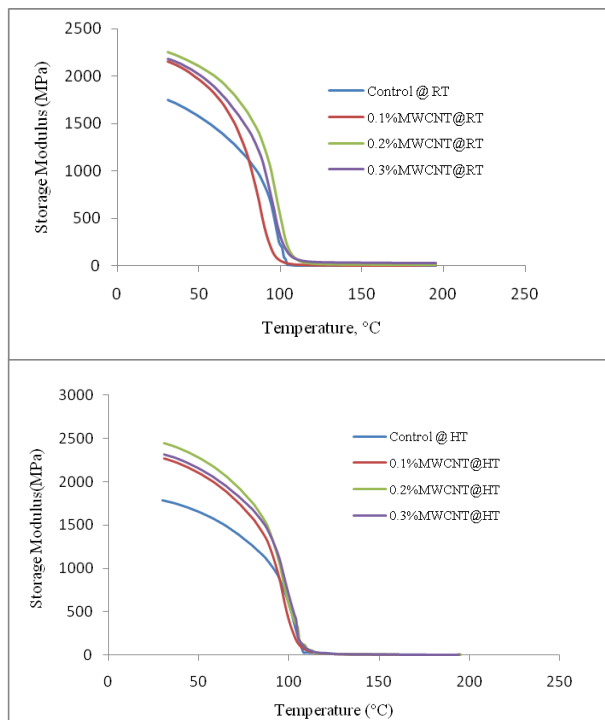


Fig 8. Typical storage modulus vs. temperature for curing cycle A and B.

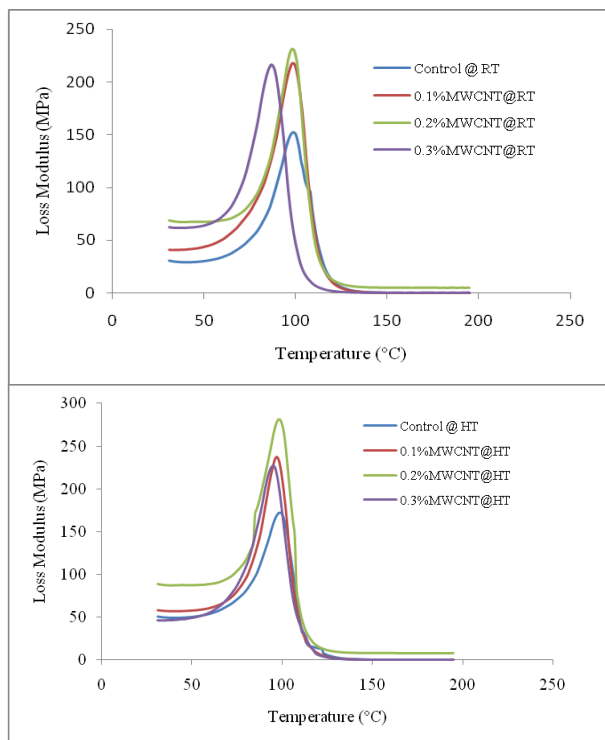


Fig 9. Typical loss modulus vs. temperature for curing cycle A and B.

Functionalization of MWCNTs with amino functional groups develops covalent bond and thus enhances interfacial bonding between epoxy and MWCNTs. Improved interfacial bonding increases the crosslink density and restricts polymer chain sliding in MWCNTs epoxy samples. This behavior can be attributed to better dispersion and an improved interaction between CNTs

and epoxy due to the formation of covalent bonds between them which leads to stronger shift of elastic properties of final composites below rubbery region as this interfacial interaction reduces mobility of epoxy matrix around nanotubes [28]. Above glass transition temperature i.e. in rubbery region, a slight increase of storage modulus was observed. It might be due to relatively higher molecular motion and higher amplitude of this motion in rubbery region. As the macromolecule is not practically in contact with particles, there is no shear force between them [28]. This increase of the storage modulus was seen up to 0.2 wt. % loading. When nanotubes loading reach to 0.3 wt. %, a decrease was observed in storage modulus. It might be due to increase of density and incapability of de-agglomeration which facilitates the molecular motion and movement of chain.

The loss modulus indicates that the energy has been converted into heat and can be used as a measure of viscous component or unrecoverable oscillation energy dissipated per cycle. Addition of nanotubes has a positive effect on loss modulus too. Well dispersed nanotubes must dissipate energy due to resistance against viscoelastic deformation of the surrounding matrix [29]. Also covalent bonds between amino-functionalized CNTs and epoxy improved the efficiency of load transfer from matrix to fillers, resulting in an increase in loss modulus due to more energy loss and dissipation in composites [29]. Decrease of loss modulus for higher nanotube contents can be attributed to increasing inclination of agglomeration which leads to less energy dissipating in the system under viscoelastic deformation [30].

Addition of nanotubes to epoxy results in a shift of the glass transition temperature. The glass transition temperature was shifted from 101.75°C for control samples to 112.25 °C for 0.2 wt. % loading CNTs, both prepared with cycle B. This gain in thermo-stability can again be interpreted as a reduction of the mobility of the epoxy matrix around the nanotubes by the interfacial interactions. An improved interaction between nanotubes and epoxy matrix should lead to a stronger shift of the glass transition temperature. Basically, amino-functionalized nanotubes are supposed to react with the epoxy resin with the formation of covalent bonds between them. This covalent bond inducing different cross-linking region into the epoxy matrix will reduce the matrix mobility, for which a strong shift of T_g in the composites was observed.

4. CONCLUSION

In this work, effect of cure temperature on the performance of epoxy nanocomposites infused with amine functionalized carbon nanotubes was investigated. Following conclusions were made from the study.

- (1) Combining sonication and calendaring methods proved to be an effective pathway for improving nanotube dispersion in epoxy systems.
- (2) Viscosity of 0.3 wt. % epoxy resin was increased in multiple orders in comparison to control counterpart.
- (3) Epoxy resin modified with amino functionalized MWCNTs showed linearly increasing trend in properties upto 0.2 wt. % in both cycle A and B systems.

(4) Improvements in MWCNT-epoxy samples prepared using cycle A (room temperature curing) were comparatively lower than samples prepared with cycle B.

(5) 0.2 wt. % samples fabricated with cycle B showed the optimum enhancement in strength, and modulus. Similar improvements were observed in thermo-mechanical properties.

5. ACKNOWLEDGEMENTS

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7. MAILING ADDRESS

M.B.A. Salam

Mechanical Engineering Department,
Tuskegee University, Tuskegee, AL 36088
E-mail: hosur@mytu.tuskegee.edu