

Effect of multi-walled carbon nanotube reinforcement on the fracture behavior of a tetrafunctional epoxy

S. GANGULI, M. BHUYAN, L. ALLIE, H. AGLAN*
Tuskegee University, 218 Luther Foster Hall, Tuskegee, AL 36088, USA
E-mail: aglanh@tuskegee.edu

Epoxy resins are the most common class of thermosetting resins used in various applications. These include adhesives, composite matrices, coatings, potting compounds, and encapsulates. The high content of rigid groups and high cross-linking density, normally make an epoxy resin after curing a brittle high-modulus material. To retain its modulus and to improve toughness, engineering thermoplastics either at a high molecular weight or in functionalized oligomer forms have been incorporated into epoxy thermosetting systems. A poly(ether imide) has been incorporated for the preparation of toughened high-performance epoxy thermosets [1]. Though there was improvement in the toughness, the dynamic mechanical analysis of the cured blend showed that the glass transition temperature was greatly reduced indicative of the plasticization of poly(ether imide) content in the blends. Amine terminated oligo(aryl ether ketones) was synthesized and incorporated into epoxy thermosetting systems to improve toughness. Similar to the previous study, toughness increase was achieved with a significant decrease in the glass transition temperature [2]. Though much research has been done to improve the mechanical properties of bifunctional epoxy resins, improvements have been achieved in some properties while some other properties have deteriorated. Addition of rubber or thermoplastics to increase toughness results in an increase in toughness but a decrease in modulus and strength.

Nanocomposite technology using reinforcements such as layered silicates, carbon nanofibers and multi-walled carbon nanotubes MWCNT offers an interesting yet challenging alternative for the modification of polymer matrix properties. Nanocomposites can provide improvements in toughness without degrading the stiffness and or strength. This concept was first introduced by researchers from Toyota [3] who discovered the possibility to build a nanocomposite from polyamide 6 and an organophilic clay. Their new material showed dramatic improvements in physical and mechanical properties. Various researchers have used this concept for nanocomposites based on epoxy systems [4–8]. However, the most commonly used epoxy resins, such as diglycidyl ether of bisphenol A and their modified forms after curing with conventional curatives possess inadequate dimensional stability, high water uptake, and unacceptable dielectric properties for advanced material applications [9].

The majority of these studies have so far been performed on low temperature thermosets. Nanocomposites of high temperature thermosets have not been extensively researched. Polyimide-Clay nanocomposites utilizing a PMR-15 thermoset matrix were prepared [10] and improvement in the mechanical and thermal properties was observed. Cyanate ester organo clay nanocomposites were also investigated [11, 12]. At only 2.5 wt% clay loading the cyanate ester systems showed 30% increase in toughness and flexural modulus. This was accompanied by 30% increase in the flexural strength. Kornman *et al.* investigated the nanocomposites of tetrafunctional epoxy [13]. Though the toughness of the system increased, the thermal and viscoelastic properties degraded.

In the present work, the effect of MWNT reinforcement on the ultimate strength and fracture toughness of a tetrafunctional epoxy resin was investigated. The origins of strength and toughness of multiwalled carbon nanotube reinforced tetrafunctional epoxy system were examined using scanning electron microscopy.

A tetrafunctional TGDDM Araldite MY720 epoxy, supplied by Ciba Specialty Chemicals, was used. The curing agent was diaminodiphenyl sulfone (DDS), of Ciba Specialty. The chemical structures of the resin and amine are illustrated in Figs 1 and 2, respectively. Multi-Walled Carbon Nanotubes (MWNTs) were obtained from Mer Corp. The MWNT were formed in the cathode deposit during the Kratschmer-Huffman arc process. The deposit consists of a tube-rich core surrounded by a fused carbon shell. The core material contains tubes that are 2–15 nm in diameter, 1–10 μm long, with 5–20 graphitic layers. The core contains 10–40% tubes. The remainder is multi-layer polygonal carbon nanoparticles and amorphous and graphitic carbon nanoparticles.

The tetra-functional epoxy resin, MY-720 was mixed with 1% by weight MWNT. Dispersion of the MWNT in the epoxy resin was achieved by using a novel mixing technique. The mixer works by spinning a high speed-mixing arm at speeds up to 3,500 rpm in one direction while the basket, containing both the resin and the nanotubes, rotates in the opposite direction. It is an asymmetric FlackTek Speed Mixer, DAC 150 FV(Z). The mixing time was 1 min at 3500 rpm. Diaminodiphenyl sulfone (DDS) was added to the resin at 44 wt% and the mixture was mixed in the FlackTek mixer for another

*Author to whom all correspondence should be addressed.

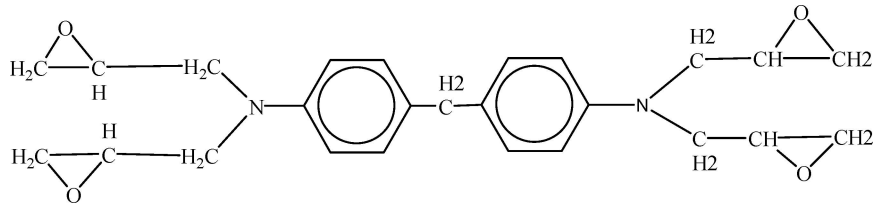


Figure 1 Structure of TGDDM—tetraglycidyl-4,4'-diaminophenylmethane.

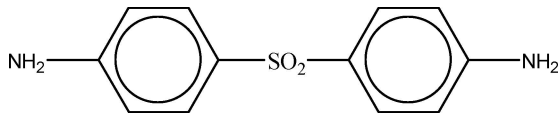


Figure 2 Structure of the diaminodiphenyl sulfone (DDS) curing agent.

30 s. Similar mixing was performed for the neat resin and curing agent to prepare a neat resin panel. Both the nanocomposite and the neat resin were molded into panels of about 3 mm thickness. They were then cured for 2 hr at 80 °C, 1 hr at 100 °C, 4 hr at 150 °C, and 7 hr at 200 °C in a programmable Blue M oven. Five unnotched and five notched specimens were machined from each material; the neat epoxy and the MWNT composite. The dimensions of each specimen were 30 mm long by 8.5 mm depth. For the fracture toughness experiments, specimens were notched using a saw with a 1 mm blade thickness and the notch length to specimen depth ratio was 45%. Three point bending tests were used to compare the flexural behavior and fracture toughness of the nanocomposite with the neat resin. A Minimat 2000 testing machine manufactured by Rheometric Scientific Inc. was used at a cross-head speed of 5 mm per min.

The flexural strength versus the deflection curves for the neat tetra-functional epoxy resin and the nanocomposite are shown in Fig. 3. It can be seen that the addition of 1% by weight of MWCNT has significantly increased the strength and deflection to failure of the neat resin. The strength has increased from about 70 MPa to 170 MPa and the deflection from 0.4 mm to about 1 mm. The flexural behavior of the nanocomposite depicted in Fig. 3 displays some nonlinearity in comparison with the neat resin. Thus, it is evident that the MWCNT

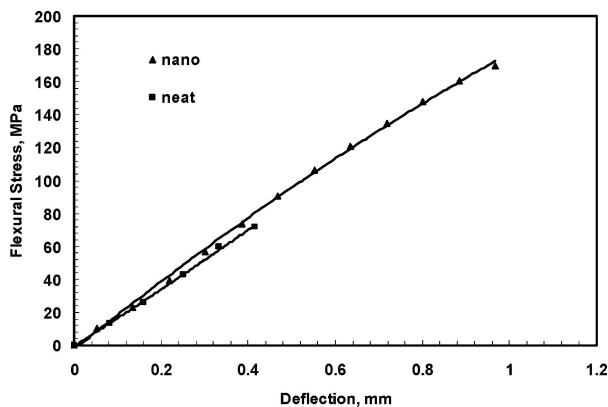


Figure 3 Overloading three-point bend mode stress-strain behavior of the tetra-functional neat epoxy resin and the 1% (wt) MWCNT tetra-functional epoxy composite (Unnotched Specimens).

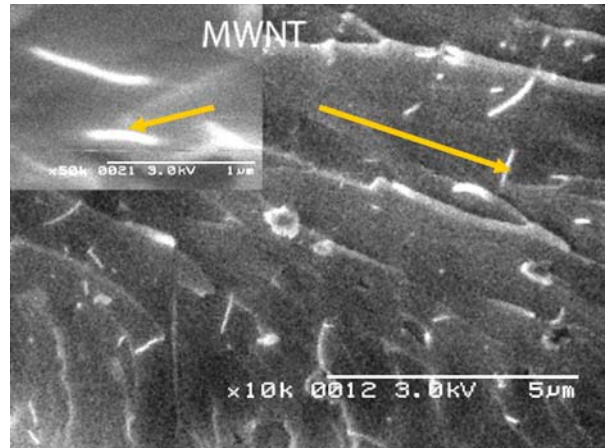


Figure 4 SEM micrographs of the MWNT overloading fracture.

reinforcement has enhanced the flexural performance of the brittle high temperature epoxy. The fracture surface morphology of a typical unnotched specimen from the MWCNT nanocomposites is shown in Fig. 4. The Scanning Electron Microscopy (SEM) reveals well dispersed nanotubes in the matrix. No evidence of agglomeration of the nanotubes can be found in this micrograph. This lends support to our proposed innovative mixing method using an asymmetric speed mixer.

To compare the fracture toughness of the two materials, single edge notch three-point bend (SENB) tests were performed on five identical specimens from each material. A representative specimen from each material was examined using SEM for the analysis of the fracture surface morphology. The average maximum load sustained by each material was calculated and used in Equation 1. The stress intensity factor for the SENB specimen was calculated as follows:

$$K_I = \frac{3SP}{2tW^2} \sqrt{\pi a} f(a/W) \quad (1)$$

where, S , t , and W are the span length, specimen thickness, and width, respectively. The geometrical

TABLE I Flexural properties of the MWCNT epoxy composite in comparison with the neat resin

Properties	Neat resin, flexural	1% Nano, flexural
Flexural strength (MPa) unnotched specimens	70	170
Maximum deflection (mm) unnotched specimens	0.42	0.97
Stress intensity factor, K_I (MPa-m ^{1/2})	1.3	4.0

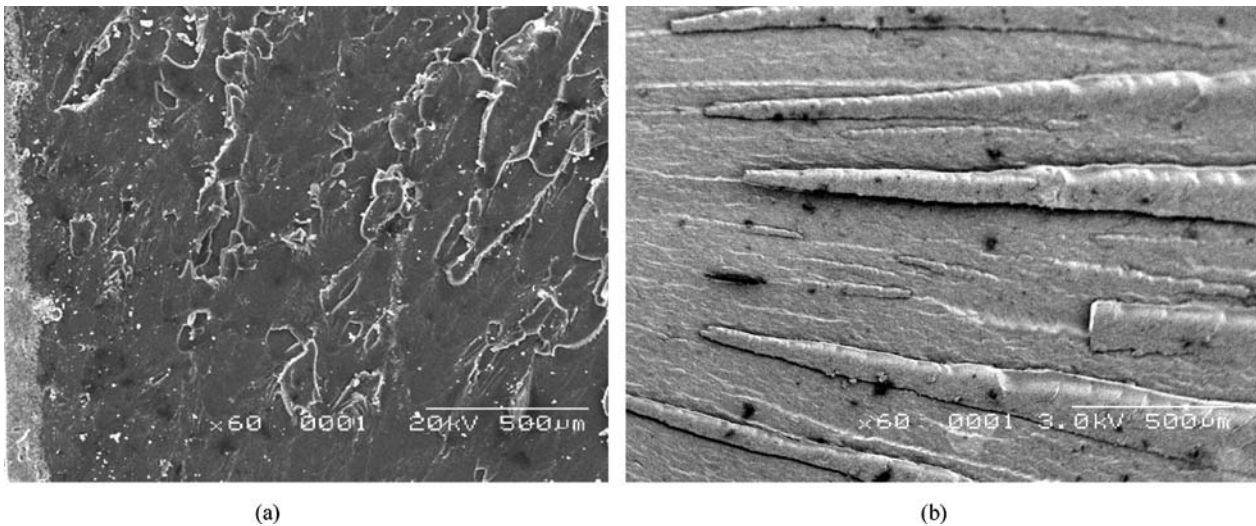


Figure 5 Fracture surface of notched neat epoxy (a) and MWNT epoxy (b) composite specimens. The notch is to the left side of the micrographs.

correction factor $f(a/W)$ is given as [14]:

$$f(a/W) = [1.107 - 2.12(a/W) + 7.7(a/W)^2 - 13.55(a/W)^3 + 14.25(a/W)^4] \quad (2)$$

The values of K_I for these two materials are given in Table I together with the average ultimate strength and deflection sustained by the unnotched specimens. It is found that the stress intensity factor for the neat epoxy is about $1.3 \text{ MPa m}^{1/2}$ and that for the nanocomposite is $4.0 \text{ MPa m}^{1/2}$. This represents a three-fold increase in the stress intensity factor. This is a significant enhancement in the toughness of the epoxy in addition to the enhancement of the ultimate strength.

The fracture surface morphology of the notched specimens is shown in Figs 5a and b. These micrographs are taken ahead of the crack tip. The notch is on the left side of the micrographs in Figs 5a and b. Brittle fracture features are displayed on the flat surface of the neat epoxy resin, as shown in Fig. 5a. These features appear to be very shallow elongated hackle marks oriented about 45 degrees from the direction of crack propagation. The fracture surface of the MWCNT composite exhibits both large and small ridges indicating a higher resistance to fracture. The fracture surface in Fig. 5b indicates that MWCNT composite is resisting the fracture process by forming these vivid ridges which dissipate energy during their formation providing high resistance to material separation. It is believed that the randomly oriented MWCNT is responsible for such high resistance to separation of the composites. The increased number of features on the surface (ridges) gives rise to more area for the absorption of the fracture energy; giving rise to a higher stress intensity factor.

A nanocomposite of a tetra-functional epoxy resin has been synthesized and characterized. Multi-walled carbon nanotubes were used as reinforcement at an optimum loading of 1% by weight. It was found that the MWNT has significantly increased the stress and strain to failure of the neat resin. An increase of about 2.5 times and about 2 times was achieved in the ultimate flexural strength and deflection to failure, respectively.

The MWNT increased the fracture toughness of the neat resin by more than three folds in the three-point bend mode. Examination of the fracture surface of the notched specimen of the MWNT epoxy composite revealed that the randomly oriented MWNT has enhanced the mechanical performance of the neat resin by making it more compliant. This was manifested in the creation of fracture ridges along the crack propagation direction. It is this mechanism by which the MWNT epoxy composite acquires its increased resistance to fracture.

Acknowledgments

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