Processing and Characterization of EPON 862 Reinforced with Functionalized MWCNTs

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ABSTRACT

The effects of various functionalized multi-walled carbon nanotubes (MWCNT) on morphological, thermal, and mechanical properties of an epoxy based nanocomposite system were investigated. Utilizing in-situ polymerization, a 1% by weight loading of MWCNT was used to prepare the epoxy-based nanocomposites. Compared to the neat epoxy system, nanocomposites prepared with MWCNT-COOH showed 8% increase in strength and 37% increase in modulus whereas nanocomposites with MWCNT- NH_2 exhibited 17% increase in flexural strength and modulus. A decrease in strength was observed for the MWCNT-F nanocomposites. The premature degradation is presumably catalyzed by hydrofluoric acid, HF, which evolved from the MWCNT-F during the curing process. However, only the MWCNT-F nanocomposites showed 22% increase in thermal properties (T_g).

Keywords: Epoxy resin, functionalization, multi-wall carbon nanotubes

1 INRODUCTION

Since their discovery in 1991 by S. Iijima [1], researchers have envisioned carbon nanotubes (CNTs) as the prime candidates to dominate the revolution in nanotechnology. CNTs are commonly used as fillers in base polymers to fabricate composite materials with superior mechanical, electrical, and thermal properties. Unfortunately, the fabrication of PNC with superior strength as high as the individual CNTs themselves has not been made possible so far. The achievement of such a superior PNC reinforced with CNTs is hindered by the fact that CNTs have non-reactive surfaces, lack interfacial bonding with matrix, and poorly disperses within composite matrices. Chemical functionalization of CNTs is reported by various groups to overcome these challenges promoting increase in overall properties of epoxy nanocomposites system[2-5]. Several researchers have reported noncovalent and covalent bonding of CNTs and its effects on the CNTs properties or PNC properties when utilized as the reinforcing phase in PNC [6, 7]. Simulation studies by Namilae et al. [8] have shown that the interfacial and mechanical properties of composite increase by increasing the number of functional group attachments through covalent functionalization. Chemical functionalization alters the CNTs morphology and provides an abundance of reactive sites; provide the opportunity for the CNTs to form covalent bonds with the polymer matrix. The objective of this research is to improve fundamental understanding of how surface functionalized MWCNTs affect morphology, mechanical, and thermal properties of epoxy based nanocomposites. This research focuses on three different types of functionalized multi-wall carbon nanotubes (MWCNTs) incorporated into an Epoxy resin (Epon 862) system. Characterization and analysis on the effect of the functionalized MWCNTs on mechanical, thermal, morphological properties of the nanocomposites were investigated using the most common state of the art instruments.

2 EXPERIMENTAL

Epon 862 (Part A), is a low viscosity liquid epoxy resin manufactured from epichlorohydrin and Bisphenol F, and Epicure W (part B), which is an aromatic diamine used as curing agent epoxy resins purchased from Miller Stephenson Chemical Company. The different methods and MWCNTs used in this research are; MWCNTs functionalized by oxidation (MWCNT-COOH); MWCNTs functionalized by direct-fluorination (MWCNT-F); MWCNTs functionalized by amino-functionalization (MWCNT-NH_2). Unmodified MWCNTs (MWCNT-UNMOD) and MWCNT-F were purchased from Mer Corp. The MWCNT-COOH was prepared in our lab using 3:1 ratio of sulfuric/ nitric acid and the MWCNT-UNMOd. Short thin Multi-wall amine modified Carbon Nanotubes tubes were purchased from Nanocyl (Belgium). All carbon nanotubes used in this research were synthesized by Chemical Vapor Deposition (CVD).

A desired amount of Epoxy/Epicure W (100:26.4) was heated and maintained at 60 °C. A 1 wt % loading of MWCNT was placed in acetone (10:2) and sonicated for 30 minutes in an ultrasonic bath. After the sonication process, the solution of MWCNTs and acetone was added to the Epon 862 and mixed using a digital mechanical stirrer at a constant speed of 500 rpm. During the last 15 minutes of mixing the temperature was raised to 70 ºC to remove acetone. The curing agent, maintained at 60 °C was added and mixing was continued. The mixture was then degassed under high vacuum to remove bubbles that were generated during mixing. The mixture was then poured into desired

molds that were heated at 121 ºC for 1 hour, prior to use and cured at 121ºC for 4 hours.

3-point flexural tests were performed according to ASTM D790-02. The span length was maintained at 80 mm and average sample thickness was about 4.8 mm. The tests were conducted on a 2.5 KN Zwick Roell Z 2.5 machine under displacement control mode at a crosshead speed of 2.0 mm/min.

The glass transition temperature (T_g) of the fully cured samples was obtained using a TA Instruments DMA 2980 in the single cantilever mode with an amplitude of 10µm, oscillatory frequency of 1 Hz and heating rate of 3 ºC/min in air. The test was carried out according to ASTM D4065-01. Microstructures of neat and composites were examined under a Field Emission Scanning Electron Microscope (FE-SEM Hitachi S-900, JEOL JSM 5800).

Material	Strength (MPa)	Modulus (GPa)
Epon 862 neat	139.7± 7.1	3.5± 0.08
Nanocomposite/MWCNT - UNMOD	152.1 ± 20.2	4.1 ± 0.2
Nanocomposite/ MWCNT - COOH	151.1 ± 14.9	4.8 ± 0.6
Nanocomposite/ MWCNT - F	136.1 ± 12.2	3.6 ± 0.0
Nanocomposite/MWCNT-NH$_2$	162.8 ± 4.6	4.2 ± 0.1

Table 1: Flexural properties from three point test

3   RESULTS AND DISCUSSION

Interaction between the MWCNTs and the polymer matrix improved and is evident in the flexural properties as can be seen from Figure 1 and Table 1. The dispersion of the MWCNTs in epoxy resin influences its strengthening effect. However, flexural testing performed on the sample using the Zwick showed an 8–17% increase in strength and 17-37% increase in modulus in all systems except the MWCNT-F system reason for which is explained later. Brittle failure was observed in all systems which is a good indication of increase in crosslinking, better dispersion, and improved interfacial interaction between the MWCNTs and the matrix. PNC becoming more brittle with the incorporation of CNTs is a common problem seen in most research.   MWCNT-NH$_2$ composites exhibited highest increase in strength, due to the fact that the MWCNT-NH$_2$ creates a covalent bond with the polymer matrix, thus becoming an integral part of its structure forming a very strong hybrid material that increased the elongation of the composite by 8%. Subsequently, the amount of energy needed to break the sample also increased. Despite an improvement in MWCNT-NH$_2$ properties, dispersion of the MWCNT in the matrix was not the best and is evident in the morphology of the fracture surfaces discussed later.

MWCNT-NH$_2$ tends to reagglomerate rather quickly. However, MWCNT-NH$_2$ improves the dispersability by increasing the surface polarity inducing the incorporation of MWCNTs into the matrix resulting in a larger improvement in the ultimate strength [9]. Normally most fillers will increase both the modulus and the ultimate strength, but that was not the case for MWCNT-F. The MWCNT-F showed no significant increase in strength, compared to the neat. This observed behavior may be due to degradation of the sample during curing. The premature degradation is presumably catalyzed by hydrofluoric acid, HF, which evolves from the MWCNT-F during the curing process. Shofner [7]and Valentini [10] also found that residual fluorine functional groups start to detach as HF up to temperatures as high as 185º C.   HF etches the polymer matrix damaging its structure causing a loss in strength.
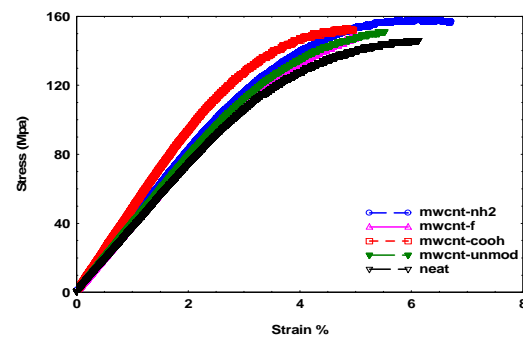

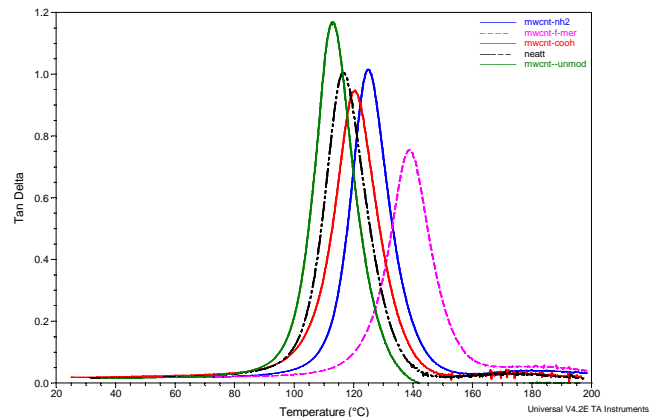Figure 1: Flexural response of nanocomposites

Figure 2: Variation of tan δ with temperature for nanocomposites

Enhancement in T_g is a highly desirable property for high temperature applications. Using DMA, the T_g value listed in Table 2 was determined as the temperature corresponding to the peak of tan δ curves (Figure 2). Enhancement in T_g can be attributed to several factors: increase in crosslink density, restriction in molecular motions at molecular level, and decrease in free volume. The MWCNT-F epoxy nanocomposites showed the highest

increase of 22%, shifting from 117ºC to 141 ºC, in the glass transition temperature (T_g). MWCNT-F introduces a steric repulsive force between the carbon nanotubes and the fluorinated polymer matrix strong enough to overcome the Van Der Waals attractive force between the individual carbon nanotubes and the polymer matrix. This effect will basically appear around and above the T_g, due to the limited potential movement of the polymeric matrix. However, the decreased magnitude in the tan delta suggests a decrease in damping capability. The MWCNT-F nanocomposites will only be suitable for applications where thermal stability is the only desirable property. There was an 8% increase in the case of epoxy-nanocomposites made with the MWCNT-NH_2. This increase in T_g, indicates that both the MWCNT-F and MWCNT-NH_2 inhibits the mobility of the polymer chain to different degrees, respectively, causing an increase in T_g. The MWCNT-NH_2 nanocomposites systems shows less of an increase compare to the MWCNT-F composite because creating a covalent bond with polymer matrix forms a linear chain as opposed to a highly cross-linked network, which would cause a higher increase in T_g. Although enhancement of interfacial interaction by functionalization should lead to a stronger shift of T_g no significant increase in T_g was observed for composites made with MWCNT-COOH. This observation suggests that MWCNT-COOH do not hinder the mobility of the polymer matrix by no means as a result of no chemical interaction with the matrix.

Material	(T_g) ˙C
Epon 862 neat	117
Nanocomposite/MWCNT -UNMOD	121 ± 10
Nanocomposite/ MWCNT -COOH	121 ± 6
Nanocomposite/ MWCNT -F	141 ± 1
Nanocomposite/MWCNT-NH_2	125 ± 1

Table 2: Glass transition temperature, T_g of nanocomposites
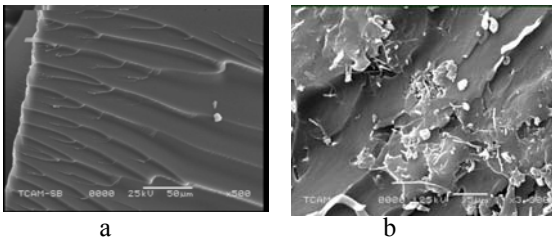

a   b

Fig. 3 Fracture surfaces of the flexure samples: a) neat composite, b) MWCNT-UNMOD composite

SEM was employed to determine the morphology and dispersion of the functionalized MWCNTS in the matrix. The fracture surface of the samples from the three point bend test was investigated. Figures 3-6 illustrate the scanning electron micrographs of the samples observed under the microscope after the flexure tests. Most common failure observed in polymer nanocomposites reinforced with short fiber as well as continuous fibers are fiber

fracture, fiber pullout, debonding/crack bridging, or matrix cracking. From Figure 3a, it is obvious that the neat composite has a clean and smooth surface. Incorporation of pristine MWCNT into the matrix increases the roughness.
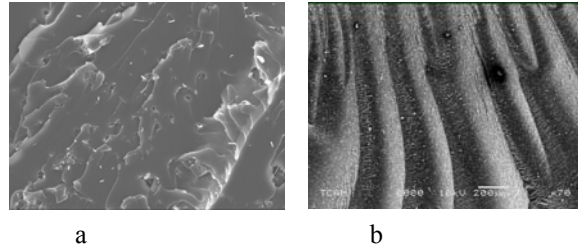

a   b

Figure 4: Fracture surface of the MWCNT-COOH composites flexure sample at different magnifications

These nanocomposites contain agglomeration of MWCNTs that seem to be sitting on top of the matrix as opposed to being embedded in the matrix (Figure 3b). These results are signs of poor dispersion resulting from lack of interfacial interaction and adhesion to the matrix. Incorporating functionalized MWCNTs increased the roughness to an even higher degree making the composites more resistant to
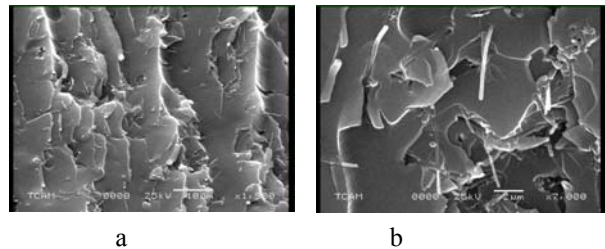

a   b

Figure 5: Fracture surface of the MWCNT-F composites flexure sample at different magnifications.
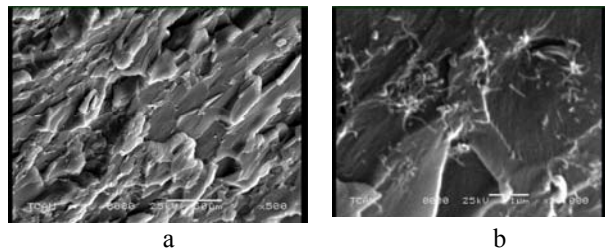

a   b

Figure 6: Fracture surface of the MWCNT-NH_2 composites flexure sample at different magnifications

deformation. It also improves dispersion within the matrix. The fracture surface of composite shows that it is resisting or delaying the fracture process by forming vivid ridges which dissipate energy. It is believed that randomly oriented MWCNT is responsible for such resistance. The increased number of features on the surface (vivid ridges) gives rise to a larger area for fracture energy absorption, simultaneously, increasing the stress intensity factor. In the MWCNT-COOH composites a continuous and uniformed river pattern was formed at the fracture surface and the MWCNT-COOH were very well dispersed (Fig. 4). In the MWCNT-F composites, matrix cracking is observed

creating debonding in some areas (Figure 5). As mentioned earlier, the matrix cracking could be the consequences resulting from the damages created by the HF. The MWCNT-NH$_2$ contains the most rigid fracture surface with some agglomeration-rich areas and fiber fracture (Figure 6). The concentration was still less than that of the MWCNT-UNMOD. Even though dispersion was not the best in MWCNT-NH$_2$, breaking of the MWCNTs indicate that interfacial interaction between the MWCNT-NH$_2$ and polymer matrix is the strongest. Increase in roughness, improvement in dispersion, and fiber fracture are all indications of enhancement in interfacial interaction.

4 CONCLUSIONS

In this study, MWCNTs were functionalized through oxidation, fluorination and amine modification. The modified as well as unmodified MWCNTs were then dispersed in EPON 862 polymer at 1% loading by weight. Performance of the nanocomposites samples was compared with that of neat epoxy. The effect of functionalization on the nanocomposite samples to determine the mechanical and thermal behavior of the samples was characterized utilizing a 3-point bend flexure test, DMA, and SEM analysis. Finally, the fracture surfaces of flexure samples were observed under scanning electron microscope to determine the failure modes and morphology of the functionalized MWCNTs in the resin. Following conclusions were made: Chemical functionalization, in most cases, is a useful method to improve dispersion, mechanical, and thermal properties. Improvement in interfacial interaction and dispersion also manifested itself by improving the mechanical and thermal properties of the composites. The improvements in the mechanical properties of the polymer matrix by addition of functionalized MWCNTs are the results of two major factors, dispersion and surface modification. SEM investigation of the fracture surface showed evidence of improvement in the dispersion of MWCNTs in the matrix and the chemical interaction between them. Unfortunately, chemical functionalization by direct-fluorination produces HF which degrades the ultimate strength but enhanced the T$_g$ of polymer nanocomposites.

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