

Mechanical Characterization of XD-Grade Carbon Nanotube/Epon 862 Processed by Dual Phase Dispersion Technique

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ABSTRACT

In this research, a dual-phase dispersion method is studied combining a high intensity ultrasonic liquid processor with a three roll milling technique. Xd-grade carbon nanotubes (xd-CNTs) were infused into Epon 862 epoxy and then mixed with epicure curing agent W using a high-speed mechanical agitator. Flexural and dynamic mechanical analysis (DMA) were performed on neat, 0.015 wt.%, and 0.15 wt.% xd-CNT-filled epoxy to identify the loading effect on the mechanical properties of the composite materials. Flexural tests were performed using Zwick Roell testing unit. Flexural results indicated homogeneity with improvements in mechanical properties of up to 15% in strength as well as modulus enhancement of up to 25%, respectively. Interfacial adhesion and dispersion are improved with viscosity reduction and secondary three roll mixing method. Scanning electron microscopy (SEM) performed using Joel 2001 at 5 and 10kV depict the fracture morphology of the tested specimens indicating proper dispersion of the xd-CNTs by fracture propagation and cleavage plane displacement. DMA studies performed using TA Instrument Q800 operating in three-point bending mode at an oscillation frequency of 1Hz revealed an increase in storage modulus in the nanophased specimens as CNT loading increased.

Keywords: XD-CNT's, high shear mixing, ultrasonic, DMA, SEM

1. INTRODUCTION

Recent and ongoing research on polymer nanocomposites has shown dramatic enhancements in thermal, mechanical, and chemical properties over other materials without compromising density, toughness, or storage life [1]. Important drivers in the growth of polymer composites have been the reduced weight and parts consolidation opportunities, design flexibility, corrosion resistance, material anisotropy, and mechanical properties [1]. There have been several approaches taken in effort to discover the potential mechanical enhancements of polymer matrices adding a small amount of nanomaterials. Typical nanomaterials have enhanced various characteristics in a given polymer material [2-3]. However, these enhancements have had limitations at higher loadings with poor dispersion and increased agglomeration causing premature failure. Zhou et al. [4] studied multi-walled carbon nanotubes (MWCNT) dispersed in Epon 862 by a high intensity ultrasonic liquid processor to determine the optimal loading weight percentage. They documented that the system with 0.3 wt.% MWCNT loading produced the best results in both flexural strength and modulus because of the uniform dispersion of the MWCNT into the resin. However, the higher CNT loading causes agglomeration that result in a less homogenous structure. This resulting agglomeration acts as an area of weakness that causes premature failure during applications. In addition, due to the increased viscosity as CNT content increases, more trapped air is inherent in the samples creating voids helping initiate fracture propagation.

Utilizing sonication Chisholm et al. [5] observed a 39% enhancement in flexural strength by infusing 1.5 wt.% SiC

nanoparticles in carbon/epoxy composite. These fundamental improvements in mechanical properties have also translated to the thermal properties of the matrix material. The addition of nanofillers at lower levels has been studied and proven to be increased the glass transition temperature (T_g) of a given matrix. Wang et al. [6] observed slight improvements to the T_g at low loading levels. Pristine vapor grown carbon nanofibers (pVGCNFs) and functionalized vapor grown carbon nanofibers (fVGCNFs) were processed using a high intensity ultrasonic processing and analyzed using differential scanning calorimetry (DSC) and the T_g was studied for five different loadings. For the epoxy/fVGCNF at 0.1 and 0.3 wt.% , the T_g increased at 1 and 4 °C, respectively. However, as the weight percentage was increased to 10 wt.%, the T_g value began to decrease. The glass transition temperature decreased from 141 °C to 109 °C. Similarly, for the pVGCNFs, the T_g value begins to degrade after the 0.1 wt.% loading point. Wang et al. claim that the slight increase in the glass transition temperature is caused by the reinforcement effect of VGCNF on the polymer chains. However, they are uncertain as to what causes the degradation at higher loading levels. They concluded that the degradation takes place because of interference in the cross-linking between the monomer and the amine curing agent resulting in uneven distribution of the cross-linked sites. Poor dispersion can also be attributed to the reduction in the glass transition temperature, the agglomerated sites would separate the cross-linking sites between the monomer and the amine curing agent therefore causing a decreased T_g .

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Mechanical and thermal enhancements are correlated with the uniform dispersion of the nanoparticles within the given polymer nanocomposite. Without proper dispersion, degradation in mechanical and thermal properties is seen at increased loading levels. This research strives to produce a well dispersed composite matrix using xd-grade carbon nanotubes distributed in Epon 862 epoxy resin in an effort to enhance the thermal and mechanical properties.

Xd-grade carbon nanotubes consist of single and double walled nanotubes along with carbon black [7]. The xd-grade has the tendency to become highly agglomerated due to the variation in sizes and structure of the nanotubes. For this reason we will test the capacity of the dual phase dispersion technique.

Epon resin 862/Epikure curing agent W system consists of a bisphenol-F epoxy resin and an aromatic amine for fabricating composite parts. This resin system is at low viscosity and allows for long working life at room temperature [8]. The work life was utilized for extended processing at room temperature.

2. EXPERIMENTAL

2.1 Materials

Xd-grade carbon nanotubes were received from Carbon Nanotechnology Inc. (now Unidym) Houston, TX.

Epon Resin 862 and epikure W curing agent was purchased from Hexion (now Momentive) Specialty Chemical, Inc. Danbury, CT.

2.2 Fabrication of epoxy/xd-grade carbon nanotube plaques

Pre-calculated amounts of carbon nanotubes and epon 862 resin were carefully weighed and placed in a beaker. The mixture was then mechanically mixed with a mechanical stirrer for 10 minutes before placing into a sonicator for 1 hour on a pulse mode: 40 sec. on and 20 sec. off (Ti-horn, 20 kHz Sonics Vibra Cell, Sonics & Materials, Inc). This mixture was submerged continuously in a cooling bath to prevent preemptive polymerization. Once the cycle was completed, the mixture was then placed in a three roll milling processor for 6 successive cycles incrementally reduced from 20-5 μm gap spacing at 140 rpm. Epikure W curing agent was added to the modified resin and mixed using a high-speed mechanical stirrer for 10 minutes. The ratio of epon 862 resin to epikure W curing agent was 100:26. The mixing process produced highly reactive, volatile vapor bubbles, which create voids and can be detrimental to the properties of the plaques. To reduce the chance of voids formation, the mixture was preheated to 70 °C to reduce its viscosity and placed in a high vacuum system for 30 min. Once bubbles were completely removed, the mixture was then transferred into an aluminum mold and cured at 121° C in a Fisher-Scientific convection oven for 2 hour and post cured at 177

°C for 2 hour. Plaques were made at loadings of 0, 0.015 and 0.15 wt.%.

2.3 Characterization

Flexural tests were performed according to ASTM D790-86 under a three-point configuration using a Zwick Roell 2.5 kN load cell servo-hydraulic testing machine equipped with Test Ware data acquisition system. The machine was run under displacement control mode at a crosshead speed of 2.0 mm/min. The standard sample size recommends a span length to thickness ratio of 16:1. The sample length was 100 mm and average thickness 5 mm, respectively.

Scanning electron microscopy (SEM) was performed using a Field Emission Scanning Electron Microscope (FE-SEM Hitachi S-900) JOEL JSM 5800). Microstructure of the fracture surfaces of both neat and nanophased composite was analyzed. A 10-15 kilovolt accelerating voltage was applied to achieve desired magnification. Micrographs were taken after completion of flexural tests. All neat and nanophased composites were gold coated by sputtering prior to loading under SEM.

Dynamic mechanical analysis (DMA) tests were performed using TA Instrument Q800 operating in three-point bending mode at an oscillation frequency of 1Hz. Data were collected from room temperature to 200 °C at a scanning rate of 10 °C/min. The sample specimens were cut and sanded to 60 mm x 13 mm x 3 mm.

3. RESULTS

3.1 Morphological characterization

3.1.1 Scanning electron microscopy (SEM)

The fracture surfaces of the neat and nanophased plaques were comparatively examined. The fracture surface of the neat epoxy plaques displayed relatively smooth surfaces and the micrographs seen in Fig. 1 (a,b), indicate a typical brittle fracture behavior. The distance between the cleavage steps range from 200-250 μm . The smooth surface brittle fracture is attributed to ease of fracture propagation [9-10]. In Fig. 1 (c,d), the 0.015 wt.% nanophased plaques show shrinkage in the distance between cleavage planes from 200-250 μm to 100-150 μm , which is attributed to the nanotubes being present in the polymer. The fracture propagation has been inhibited by the nanotubes in the polymer. Once the load force is applied to the sample the polymer molecular chains begin to move, the sample undergoes deformation, moving towards its elastic limit and yield strength [11-12]. The nanotubes inherent in the sample slow the movement of these molecular chains therefore increasing the youngs modulus and flexural strength. In addition, by adding the secondary three roll mixing method the spacing between cleavage planes have been reduced even more. The cleavage planes formed become much smaller due to the improved dispersion

of the nanotubes creating more barriers for fracture propagation.

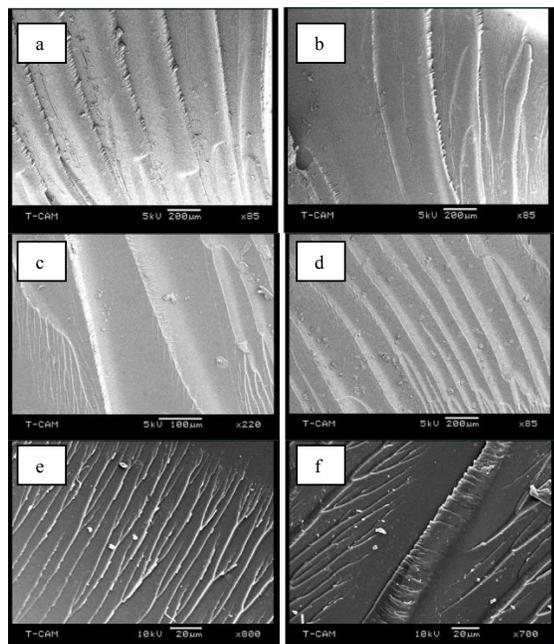


Fig. 1. Fracture surface of neat epon 862 resin (a, b) plaque, 0.015% x-d-grade CNT/epon 862 (c,d) plaques (c) sonication only, (d) sonication and three roll milling and 0.15% x-d-grade CNT/epon 862 (e,f) plaques (e) sonication only, (f) sonication and three roll milling

3.2 Mechanical characterization

3.2.1 Flexural results

Stress-strain curves shown in Fig. 2, showed incremental improvements in flexural strength and flexure modulus as x-d-grade CNT was increased. Flexural strength improved by 11.1% in the dual phase mixing method with an improvement in flexure modulus of 16.51%. The improvements observed in the dual phase mixing method of sonication and three roll versus the sonication only have been attributed to better dispersion of the nanoparticles within the matrix. The reduction of agglomeration enabled uniform load transfer and allowed the nanotubes to act as reinforcement within the matrix [13]. Similarly, the 0.15% nanophased plaques showed improvements in flexure strength of 12.39% and flexure modulus of 25%, refer to Table 1.

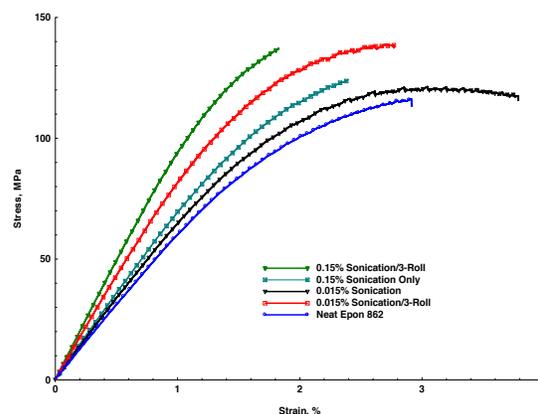


Fig. 2. Flexural results for neat and nanophased sonication only (SO) and sonication with 3 roll (S_3Roll)

3.2.2 Dynamic mechanical analysis (DMA)

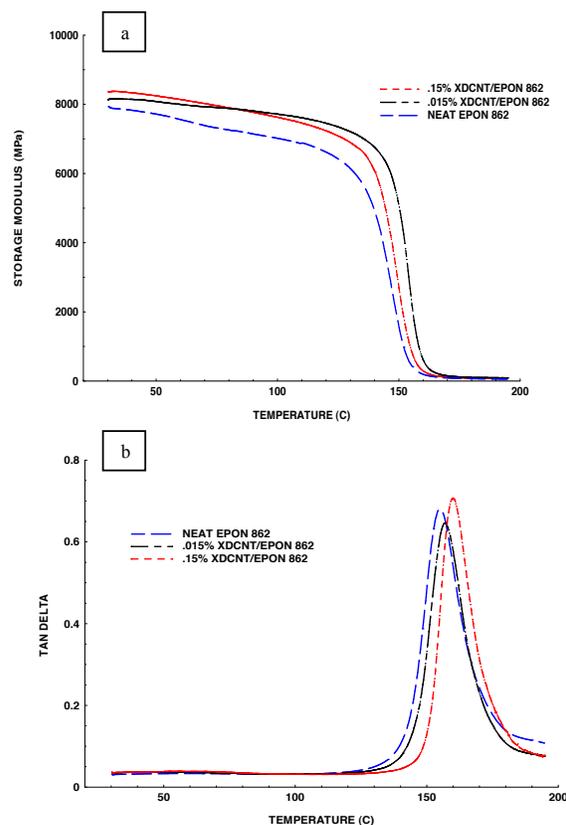


Fig. 3. Dynamic mechanical analysis of neat and x-d-grade CNT/epon 862 plaques (a) storage modulus, (b) tan delta curve

Table 1	Flexural Strength (Mpa)	% Improvement	Youngs Modulus	% Improvement	Strain of Failure	% Improvement
Neat Epon 862	114 ± 4.5	-	2.62 ± .1	-	2.31	-
0.015% SO	126 ± 1.2	9.15	2.81 ± .1	6.76	3.93	70.1
0.015% S_3 Roll	129 ± 1.1	11.1	3.14 ± .2	16.5	2.88	24.6
0.15% SO	119 ± 3.8	4.02	3.22 ± .1	18.53	2.38	3
0.15% S_3 Roll	133 ± 2.6	12.39	3.49 ± .2	25.01	1.86	-19.4

Fig. 3. shows improvements of 10% in the 0.15 wt.% nanophased plaques. The storage modulus steadily increases with the increase of CNT content. However, there is an improvement seen in the 0.015 wt.% plaques at the rubbery plateau region which may indicate better interfacial adhesion helping reduce the movement of the polymer chains at elevated temperatures [14]. Upon analyzing the tan delta curve proportional improvements were seen in the glass transition temperature in the nanophased plaques. This would deduce that at elevated temperatures, around T_g , the inherent nanotubes restrict the polymer chain movement through glass transition and thereby slightly enhance the glass transition temperature of the polymer matrix.

4. CONCLUSIONS

There is a desperate need to develop approaches to achieve the optimum dispersion and processing method. It has been observed with the use of CNTs, enhancements can be made to the mechanical and thermal properties of a given polymer matrix. However, it is apparent that there are limitations to CNT loading capacity prior to property degradation. The main contributor to the premature failure in higher loading nanocomposites is poor dispersion forming agglomeration and voids in the fabricated sample. It has been seen that the use of high shear mixing methods has the capability of uniformly dispersing higher nanoparticle content within a polymer matrix.

Xd-grade CNT's have been infused in epon 862 resin system by sonication and three roll milling method. Based on mechanical and thermal experimental results, the following conclusions can be reached. Sonication and three roll milling is an efficient method for infusing xd-grade CNTs into epoxy resin. Mechanical characterization show up to 14% increase in flexural strength for each loading case as well as increased modulus of up to 25%. Dynamic mechanical analysis (DMA) show an increase in the storage modulus in the 0.015 and 0.15 wt% nanophased specimens with up to 10% improvement and 0.015 wt% plaques showing improvements in the rubbery plateau region. These improvements are due

to uniform distribution and proper dispersion of the xd-grade nanotubes, which creates homogenous reinforcement throughout the plaque and improved interfacial interaction culminating in improved strength and modulus values.

Acknowledgments

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