

## MECHANICAL AND THERMAL CHARACTERIZATION OF COOH-FUNCTIONALIZED MWCNT INFUSED EPON 862 NANOCOMPOSITES

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### ABSTRACT

Objective of current work is to optimize the mechanical and viscoelastic properties of Epon 862 polymer by infusing up to 0.2 wt. % of carboxylic acid functionalized multi-walled carbon nanotubes (MWCNTs). A combination of dispersion methods along with solvent media was used to optimize dispersion of MWCNTs in resin system. 3-point bend flexure, dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA) tests were performed. Flexural results of 0.1 wt. % system were found to be optimum with an increase of 14% in strength and 30 % in modulus comparison to control system (without MWCNTs). Storage modulus and loss modulus also increased moderately upon infusing the MWCNTs. In addition, glass transition and decomposition temperatures were also improved in 0.1 wt. % systems. Improved crosslink density and rougher fracture surface of 0.1 wt. % system can be attributed to these enhancements in properties.

**Keywords:** Carbon Nanotubes, Glass Transition Temperature, Crosslink Density.

### 1. INTRODUCTION

Since the introduction of carbon nanotubes by Iijima in 1991 [1], they have attracted the attention of all researchers in the field of CNT/polymer nanocomposites because of their outstanding thermal, mechanical and electrical properties [2-4]. Carbon nanotubes have proved to be potential candidates to act as reinforcements in nanotechnologies [5]. The main reasons for achieving such outstanding properties are the high specific surface area and flexibility, low mass density of nanotubes [3, 4]. CNTs have been extensively used in aerospace, automobile engineering, microelectronics, field emitters etc. [2, 6]. Considering that diameter of CNTs is on the same scale as the polymer chain, they are expected to reinforce the matrix at molecular level. This interaction should significantly increase mechanical and thermal properties of nanocomposite. MWCNTs have the advantage of being lower cost and easy to disperse that single walled carbon nanotubes (SWCNTs) which make them ideal for large scale production of nanocomposites [7].

The key point in achieving better properties for the polymers is to incorporate potential mechanical, thermal and electrical properties of the nanotubes into the nanocomposite. In order to do so, one needs to resolve two main issues that have been problematic [4, 8]. These issues are obtaining good dispersion of the individual CNTs in the polymer matrix and achieving good interfacial interaction between the polymer and CNTs. Surface of CNTs are chemically inert and hence they do not form strong covalent bond with polymer molecules. However, this issue can be overcome by surface

modification through chemical functionalization. Nanotubes tend to agglomerate in polymers due to Vander Waal force of attraction. When they agglomerate, they tend to act as stress raisers resulting in the premature failure of nanocomposites. High surface area of CNTs not only helps in load transfer but also contributes in forming agglomerates. Hence, to obtain a good nanocomposite comprising of CNTs, it is essential that there is proper dispersion, good alignment and proper wetting of the nanotubes in the polymer matrix [9].

Hence in this study, a combination of sonication and magnetic stir mixing was carried out to disperse MWCNTs in a high temperature curing epoxy system Epon 862. Effectiveness of dispersion methodology was evaluated through flexural, thermal and thermo-mechanical testing for different loading of nanotubes.

### 2. EXPERIMENTAL

#### 2.1 Materials

EPON 862 and COOH functionalized multi-walled carbon nanotubes (MWCNT-COOH) were the main constituents used in preparing the nanocomposite. EPON 862 a low viscosity liquid epoxy resin manufactured using epichlorohydrin and Bisphenol F (Part A: diglycidylether of bisphenol F, aliphatic diglycidyl and part B: hardener (Epicure W)) was purchased from Miller Stephenson Chemical Company (Danbury CT). Multi-Wall Carbon Nanotubes were purchased from Nanocyl (Belgium). These carbon nanotubes were synthesized by Chemical Vapor Deposition

(CVD). These nanotubes (nanocyl-3151) have a diameter of 9.5 nm, length of 1.5  $\mu\text{m}$  and carbon purity of > 95%.

## 2.2 Manufacturing Process

Incorporation of CNTs into the polymer matrix with uniform distribution is a challenging job because of its high surface area and large quantity of particles. To overcome these problems, we used a combination method of magnetic stirring followed by ultra-sonication process was used to disperse nanotubes into the resin. First, MWCNT-COOH were added to acetone to help in debundling the nanotubes. This mixture was then sonicated (Sonics Vibra Cell ultrasonic processor) for 15 minutes at 24 % amplitude on a pulse mode (20 sec. on/20 sec. off). Then Epoxy resin part A heated at 70° C to lower the viscosity was added to the sonicated nanotubes and further sonicated for 15 minutes maintaining the same parameter as mentioned earlier. After the sonication, the container with resin mixture was placed on a hot plate maintained at a temperature of 70° C and stirred using a magnetic stirrer at a speed of 750 rpm. After 2 hour of magnetic stirring, part B of the epoxy resin system which is the hardener was added as per the stoichiometric ratio (part A: part B=100:26.4) to the mixture of CNTs, acetone and Part A and stirred with a high speed mechanical stirrer for approximately 10 minutes. During this mixing, bubbles were formed entrapping air which, if not removed result in significant amount of voids. In order to remove the air, degasification was carried by placing the mixture in a vacuum oven for 50 minutes at room temperature. After degassing, the mixture was poured into a preheated mold maintained at 121° C and left for curing for 4 hours.

## 3. RESULTS AND DISCUSSION

### 3.1 Flexure Response

Flexure tests were conducted according to the ASTM D790-03 under three point bend mode in a Zwick-Roell testing machine at a crosshead speed of 2 mm/min. All samples were tested in room temperature. Stress-strain behavior from the flexure test is shown in Fig.1. The stress-strain curves showed considerable non-linearity till maximum stress. No yield point was observed for any samples.

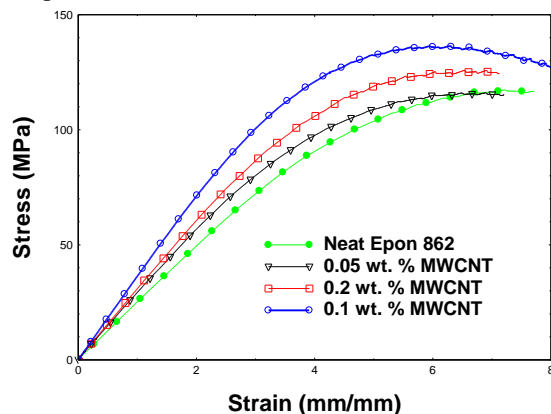


Fig 1. Typical Stress-Strain response of the nanocomposite.

Strength and modulus of the nanocomposite were

increased continuously up to 0.1 wt. % loading. For 0.1 wt. % loading of MWCNTs there was 14 % increase in flexure strength and 30 % increase in flexure modulus over the neat sample as shown in figures 2 & 3.

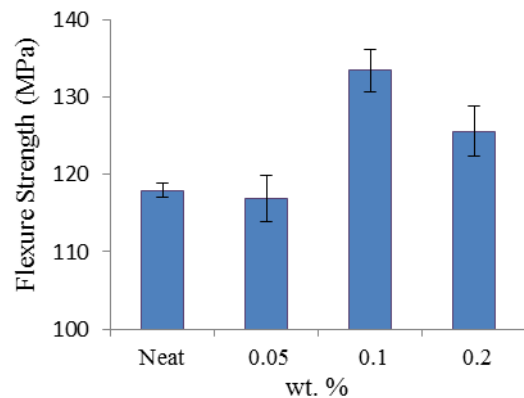


Fig 2. Flexure strength of the nanocomposite with different MWCNT loading.

As mentioned earlier, better dispersion of the CNTs in the polymer matrix is the key factor for improved properties of nanocomposites. But this contribution of better dispersion is sometimes minimized by the entrapped air bubbles which are really difficult to remove and see as the samples become opaque by the addition of the CNTs.

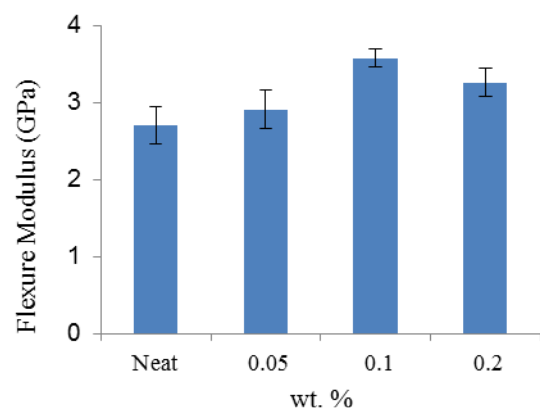


Fig 3. Flexure Modulus of the nanocomposite with respect to carbon loading.

### 3.2 Thermo Mechanical Properties

Figures 4 and figure 5 show the storage modulus and loss modulus values as a function of temperature respectively, for nanocomposites infused with COOH-functionalized MWCNTs. These values are measured using Dynamic Mechanical Analysis (DMA) testing. Addition of functionalized nanotubes has some remarkable effect on the polymer properties in both glassy region and the rubbery region depending on the amount of nanotube added to the resin blend. This is basically attributed by the stiffening effect of MWCNTs and the interfacial interaction due to interfacial interactions between the MWCNTs and the polymer matrix. As a consequence, CNTs reduce the molecular motion of the surrounding polymer matrix to some extent helping in increasing the modulus values. Though the functionalization of MWCNTs reduces the length (aspect

ratio) of the nanotubes which lead to reduced modulus value but the good dispersion of the CNTs compensate the loss resulting in much better modulus value [10]. The modulus value shows a increasing trend in the glassy region up to 0.1 wt. % loading which is an indication of good dispersion of the CNTs, better cross-linking and improved interfacial interaction between the CNT and the polymer matrix. However, another drawback of good dispersion is a significant increase in the viscosity of the mix which starts affecting the dispersion. Hence, when higher percentage of CNTs are introduced into the mix, increase quantity of tubes combined with significant increase in viscosity hinders dispersion resulting in agglomeration as well as entrapment of air during mixing which becomes difficult to remove. Entrapped air makes the material weaker and also less stiff. This effect when combined with agglomeration at higher loading results in decreasing trend for stiffness, glass transition temperature and dynamic mechanical properties.

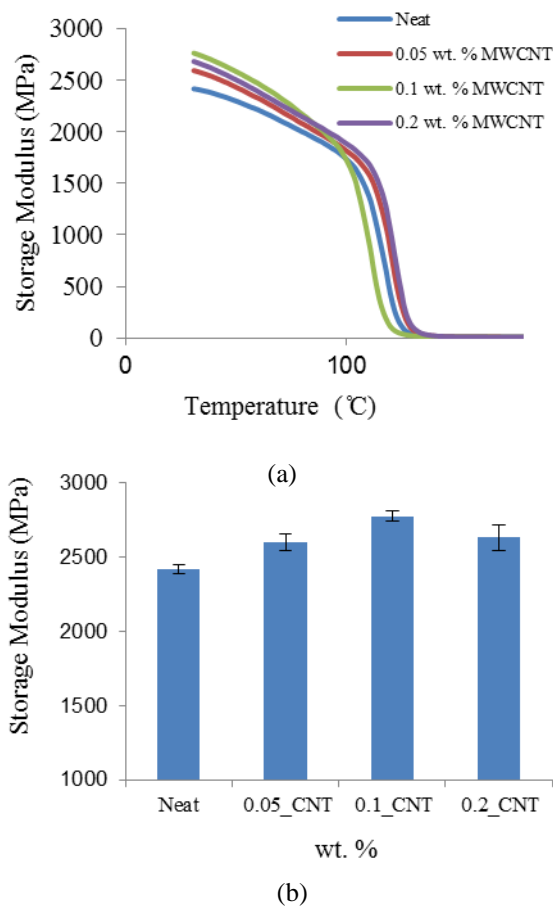


Fig 4. Storage Modulus (a) as a function of temperature (b) for different MWCNT loading.

Loss Modulus is nothing but the measure of the viscous behavior. It is one of the important design parameter in many engineering applications. Loss modulus indicates the energy converted in to heat or the viscous component or unrecoverable oscillation energy per cycle. By taking the advantage from the interfacial friction between the CNT and the resin, the loss modulus can be increased. In the viscous region, the bonds between the CNTs and the resin get weaker for slippage

to occur as will be the case with any polymer. In this study, an increment of 10 % in loss modulus was observed for 0.1 wt. % MWCNT loading over the control system. It can be concluded that well dispersed nanotubes can assist in dissipating energy under viscoelastic deformation of the surrounding resin matrix due to the slippage between the nanotubes and the resin matrix [11]. But with increasing loading, the loss modulus decreases due to the lack of slippage between the CNTs and the matrix.

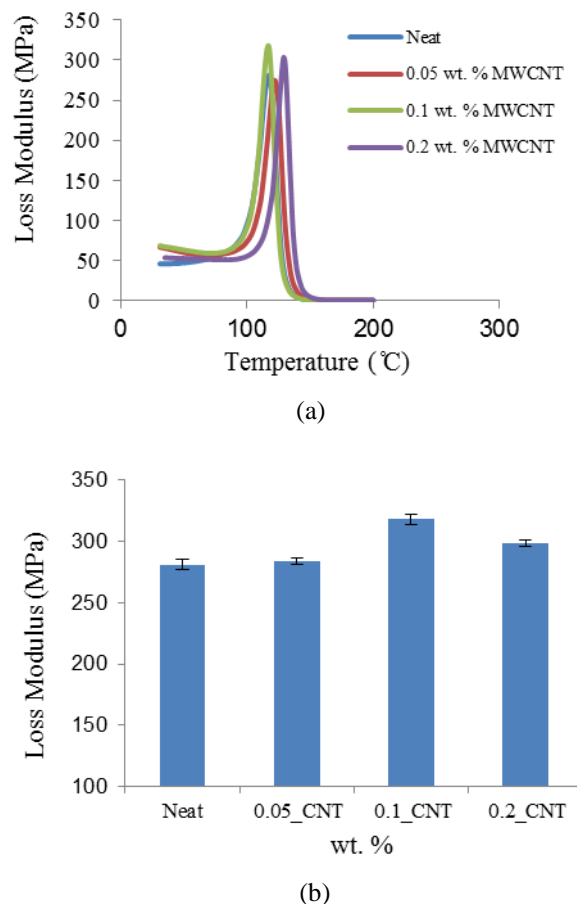


Fig 5. Loss Modulus (a) as a function of temperature (b) as a function of amount of MWCNT loading.

Figure 6 shows the glass transition temperature of the nanocomposite with different loading percentage of the nanotubes obtained from the dynamic mechanical analysis (DMA). This is nothing but the peak value of the  $\tan \delta$  curve which is the ratio of loss modulus and storage modulus. Addition of nanotubes in the resin blend improves the glass transition temperature significantly. From the figure it is clear that an improvement in the  $T_g$  up to 10° C was achieved over the control system. This improvement is attributed to the fact that the mobility of the polymer chain around the nanotubes is reduced due to the presence of the nanotubes. Thus, for well dispersed nanotubes a strong interfacial bonds are supposed to occur between the functionalized nanotube and the resin matrix and enhance the  $T_g$ . For higher loading of nanotubes, the same fact as in storage modulus and loss modulus also contribute here.

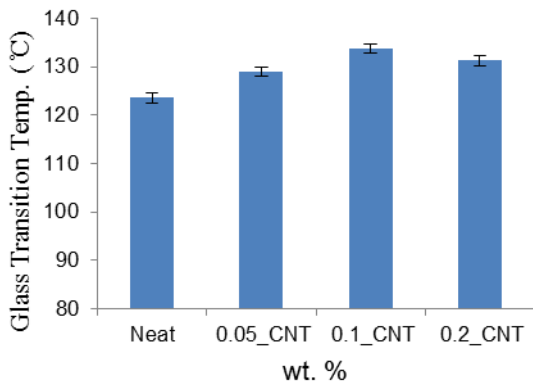


Fig 6. Glass transition temperature as a function of carbon loading.

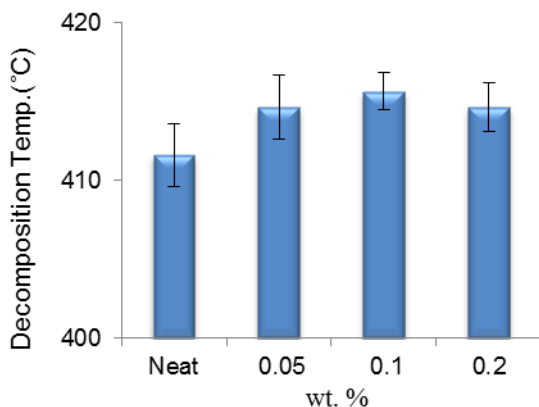


Fig 7. Decomposition temperature as a function of CNT loading.

### 3.3 Thermal Properties

Thermo gravimetric analysis (TGA) was conducted with a TA Instruments TGA 2950, which was fitted to a nitrogen purge gas. The temperature was increased from ambient temperature to 800° at a ramp of 10° C/min. TGA results shown in Fig. 7 represent the decomposition behavior of the nanocomposite infused with functionalized MWCNT. The incorporation of CNTs increases the decomposition temperature in nitrogen because functionalization not only removes the carbonaceous material and metallic impurity but also improves the interfacial interaction between the nanotube and the matrix. An improvement over 5° C was noticed for 0.1 wt. % loading compared to control system which was attributed to well dispersed nanotubes.

## 4. CONCLUSIONS

A combination method using sonication and magnetic stirring was adopted to disperse carboxylic acid functionalized MWCNTs into a high temperature curing epoxy resin system. Mechanical, thermomechanical and thermal properties were determined to study the effectiveness of the dispersion method. Following conclusions were drawn from the study.

(1) Combination process of sonication and magnetic stirring proved to be an effective way of dispersing the CNTs.

(2) 0.1 wt. % loading of MWCNT is the optimum amount to get better mechanical and thermal properties of the nanocomposites.

(3) The flexure strength and the flexure modulus both were improved by incorporating nanotubes because of the reduced mobility of the polymer chain near the CNTs.

(4) The DMA properties (storage modulus, loss modulus and glass transition temperature) were maximum for 0.1 wt. % MWCNT.

(5) The decomposition temperature for the nanocomposite was also maximum for 0.1 wt. % loading.

## 5. ACKNOWLEDGEMENT

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