

# Effect of Dispersion Conditions on the Thermo-Mechanical Properties of Functionalized Carbon Nanotube-Reinforced Vinyl Ester

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## ABSTRACT

To date, controlling the microstructure of carbon nanotube (CNT)-polymer composites remains a challenge due to high tendency of CNTs to aggregate. Proper CNT dispersion in the matrix has to be guaranteed to employ CNTs as effective reinforcement. In the current work, the dispersion of 0.25 and 0.5 wt.% functionalized multi-walled carbon nanotubes (MWCNT) into a vinyl ester (VE) resin has been studied. In order to investigate the effect of dispersion conditions, various ultrasonication parameters including mixing time and sonication energy have been examined during synthesizing process. Differential scanning calorimetry (DSC) and 3-point flexural tests have been performed on the resulting materials. The quality of CNTs dispersion/distribution in the matrix has been monitored using nanoindentation technique and correlated to the observed thermo-mechanical behavior. Based on the resulting dispersion conditions, the optimum sonication parameters and nanoparticle loading have been determined.

**Keywords:** carbon nanotube, vinyl ester, dispersion, ultrasonication, thermo-mechanical behavior

## 1 INTRODUCTION

Since the discovery of Carbon nanotubes (CNTs) by Iijima [1], numerous studies have been conducted to obtain CNT-filled composites with optimal physical, electrical, thermal, and mechanical properties [2-5]. To realize the promising potentials of CNTs, e.g. their outstanding mechanical behavior as a reinforcement in a polymer matrix, it is important to achieve a spatially even distribution of CNTs and an enhancement of the poor interfacial bonding between the CNTs and polymeric resin [6, 7]. In particular, the dispersion state of CNTs helps determine the optimal reinforcing effect of CNTs. Carbon nanotubes tend to aggregate in a matrix due to their strong van der Waals interactions. Therefore, a good dispersion of CNTs is still one of the must-resolve challenges in research associated with CNT-reinforced composites [8, 9].

Large-scale marine composite structures often use vinyl ester (VE) as a primary resin system because of its relative low cost and low viscosity, making it suitable for most of synthesizing processes [10]. To the best knowledge of

authors few researches have focused on CNT dispersion/distribution in VE matrix through different fabrication processes. Fan et al. [11, 12] examined the influence of different processing techniques on the dispersion of CNTs in VE resin. They reported that acid oxidized nanotubes were dispersed homogeneously in the matrix because nanotube length was reduced during the acid reflux. Gryshchuk et al. [13] investigated VE nanocomposites through the use of mechanical stirring and ultrasonic mixing. Poor nanotube dispersion was noted in the VE system due to nanoscale entanglement. Minor increases in the elastic properties and fracture toughness at varying nanotube concentrations. Seyhan et al. [14-17] successfully employed a 3-roll milling technique to disperse CNTs into VE/polyester hybrid resin.

Common testing methods such as tensile and flexural tests are able to evaluate the mechanical properties of bulk material at macro-level. Nanoindentation is a powerful and advanced way of measuring the micro/nano-scale mechanical behavior of nanocomposites [18]. Since the deformations in nanoindentation tests are of nanometer magnitude, the measured properties can be correlated with CNTs embedded in the matrix. This relationship would allow determining the characteristics of the CNTs distribution and its dependence on CNT content [19, 20].

In this work, thermo-mechanical properties of polymer composites containing two CNT concentrations with different CNT dispersion states are investigated. Then, the results obtained and the mechanism involved are discussed.

## 2 EXPERIMENTAL

### 2.1 Materials

Multi-walled carbon nanotubes (MWCNTs) with >8% carboxylic acid functional groups were provided by Sigma-Aldrich. The as-received MWCNTs have a mean diameter of ~9.5 nm and length of ~1.5  $\mu\text{m}$ . The thermosetting matrix used was a Derakane 8084 epoxy vinyl ester resin from Ashland Composites (Dublin, Ohio, USA) containing 40 wt.% styrene. In accordance with the supplier datasheet, Methyl Ethyl Ketone Peroxide (MEKP), Cobalt Naphtenate-6% (CoNap-6%) and dimethylaniline (DMA) were used as the curing agents.

## 2.2 Preparation of MWCNT/VE composites

Nanocomposites with different MWCNT contents namely 0, 0.25 and 0.5 wt.% were fabricated as follows. An appropriate amount of CNTs powder was dispersed in the VE resin first by mechanical stirring and then by using an ultrasonic horn. The ultrasonic mixing was carried out in a Sonics Vibra Cell liquid processor (Ti-horn, frequency of 20 KHz). In order to avoid rise in the temperature during sonication, the mixing beaker was kept inside a 6 °C water bath. A variety of mixing times and amplitudes were examined to determine the optimal sonication parameters. The sonication times, amplitudes and their correspondent total energy inputs are shown in Table 1. After sonication, MWCNTs/VE mixtures were degassed under vacuum for approximately 15 minutes, and then mixed with curing agents before casting into the mold. Subsequently, the samples were cured for 24 h at room temperature and post cured for 2 h at 99 °C.

CNT (wt.%)	Sonication parameter			T <sub>g</sub> (°C)
	Time (min)	Amplitude (%)	Energy (KJ)	
VE	-	-	-	117
0.25	3	70	10	119
0.25	9	50	20	119
0.25	14	50	30	121
0.25	19	50	40	123
0.25	18	70	60	130
0.25	24	70	80	125
0.5	2	70	10	119
0.5	7	50	15	122
0.5	7	70	20	116

Table 1: Sonications parameters and measured T<sub>g</sub> values.

## 2.3 Testing

A TA Instrument Q-10 differential scanning calorimetry (DSC) apparatus was used to measure the glass transition temperature (T<sub>g</sub>) of the cured materials. A small quantity of the samples (10-15 mg) was used for the measurements, using an aluminum empty pan as a reference. Each sample was first heated from 0 °C up to 200 °C with a constant heating rate of 10 °Cmin<sup>-1</sup>. After cooling down to room temperature, a similar heating cycle was applied on the sample and the data were recorded.

Room temperature flexural properties of the neat VE polymer and MWCNTs/VE composites were measured according to ASTM D790-10 [21]. A Zwick/Roell universal tension-compression testing machine with 3-point bending setup was employed. Testing was performed with a support span-to-depth ratio of 16:1 and crosshead speed of 0.5 mm/min. Five specimens were tested for each sample.

Nanoindentation tests were performed following ASTM E2546-07 [18] by using a NANOVEA hardness tester (Nanovea, CA, USA), equipped with a Berkovich indenter tip. Samples for indentation tests were cut and mounted on a holder. In order to obtain a good surface finish, samples were successively polished using 6, 3, 1 and 0.25 μm diamond paste. All nanoindentation tests were performed with a maximum normal load of 800 μN and a constant loading/unloading rate of 25 μNs<sup>-1</sup>. Prior to experiments, the tip area function was calibrated by using Oliver and Pharr method [20]. In order to reduce the creep effect, the maximum load was kept constant for 10 s. More than 50 indentations were made on each type of sample on randomly locations to obtain reliable results. Moreover, an array of 30 indents with the total length of 150 μm was made on selective.

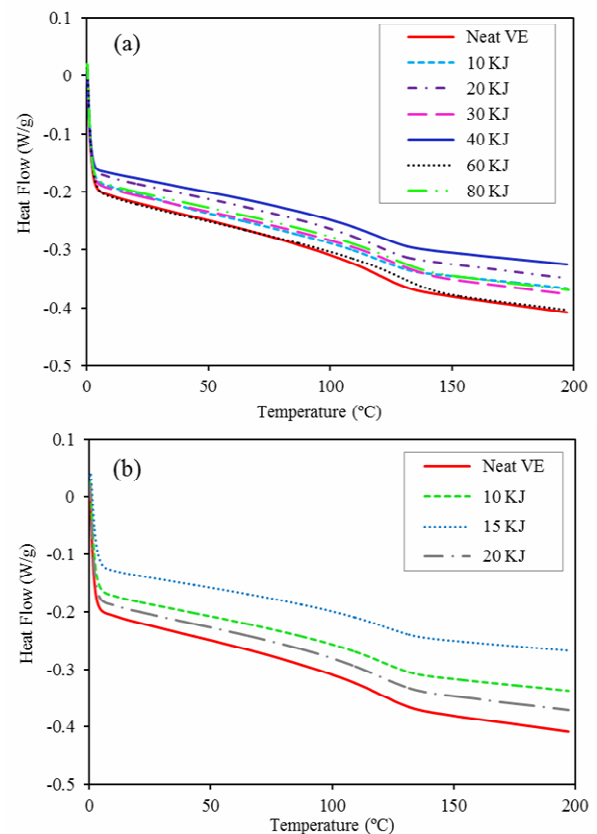


Figure 1: DSC results on the VE and its composites.

## 3 RESULTS AND DISCUSSION

Fig. 1 shows the result of DSC tests on the neat polymer and its composites. The T<sub>g</sub> of each material was determined according to ASTM D7426-08 [22], resulting a T<sub>g</sub> value of 117 °C for the neat VE polymer. This value is pretty close to the reported T<sub>g</sub> by the manufacturer (115 °C). The resulting T<sub>g</sub> values are given Table 1. It can be seen that in composites with 0.25 wt.% CNT, increasing the sonication energy up to 80 KJ can improve the T<sub>g</sub> of the resulting material. By applying a sonication energy of 60 KJ, the

maximum  $T_g$  value (130 °C) is obtained, which corresponds to an improvement of about 11% compared to the neat polymer. At loading rate of 0.5 wt.% CNTs, the  $T_g$  improves by introducing up to 15 KJ energy and applying more energy results in a drop in the  $T_g$ .

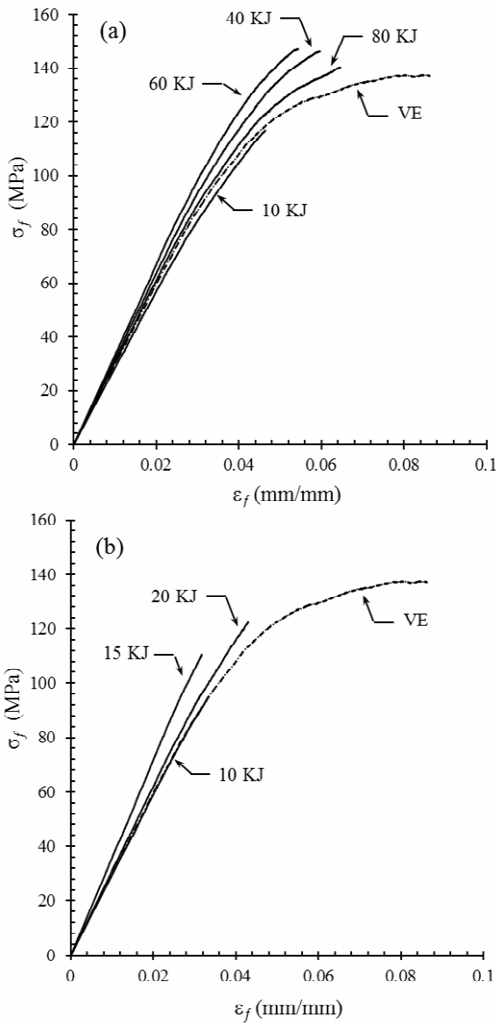


Figure 2: The effect of sonication conditions on the flexural behavior of composites with (a) 0.25 and (b) 0.5 wt.% MWCNT content.

Some researchers have also observed this dual effect of MWCNTs on the  $T_g$  of thermosetting polymers [17, 23, 24]. Gryschuck et al. [13] reported that MWCNTs, dependent on their surface condition and aspect ratio, may have some adverse effects on the chemical reactions during free radical polymerization of VE resins. They concluded that nanotubes with higher aspect ratio would be more beneficial to the ultimate performance of VE polymers. Therefore, it can be proposed that excessive amounts of sonication energy may initiate some defects in CNTs, resulting in lowering their average aspect ratio. This can seriously affect the rate of polymerization reaction and thus reduce the cross-linking density of the final product.

Typical flexural stress-strain curves of nanocomposites with different sonication conditions are depicted in Fig. 2. As is seen, the ductility of the neat polymer is reduced by incorporation of CNTs. This result is more pronounced in composites with 0.5 wt.% CNTs. The flexural strength of the neat VE is slightly enhanced (about 7%) by introducing 60 KJ sonication energy to the 0.25 wt.%/VE mixture. It can be found out from DSC and flexural test results that at each nanotube loading rate, composite with the highest  $T_g$  possesses the highest flexural modulus (Fig. 2). For instance, for 0.5 wt.% CNT – 15 KJ composite (let us call this sample A), the average flexural modulus is 3.71 GPa, showing a 24% improvement in comparison with pure VE polymer (3.00 GPa). At loading rate of 0.25 wt.%, a maximum improvement of 15% in flexural modulus can be achieved when introducing energy of 60 KJ to the mixture (let us call this sample B).

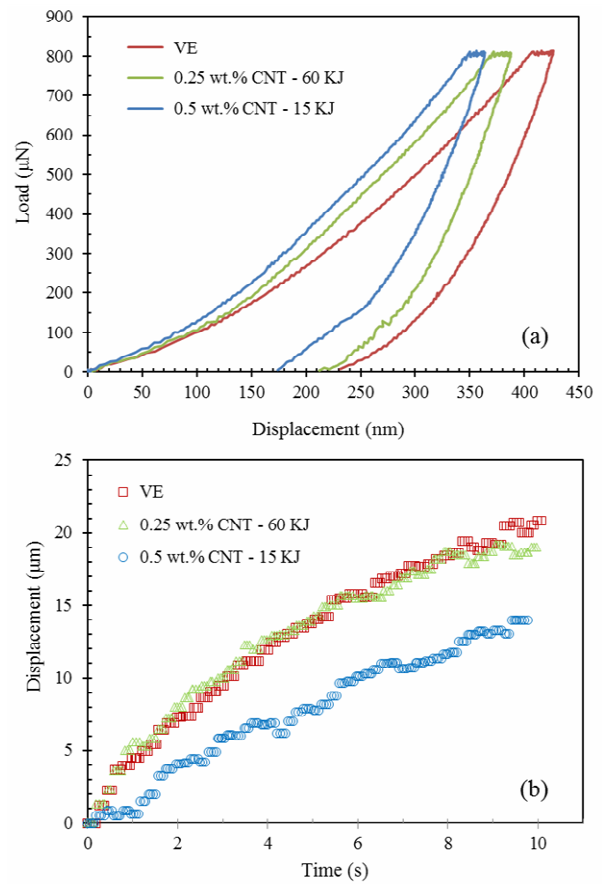


Figure 3: (a) Representative load-displacement curves from nanoindentation tests, (b) Nanoindentation creep tests at maximum load of 800  $\mu$ N.

To make a better understanding of the observed thermo-mechanical behavior, nanoindentation results of samples A and B are compared with the neat VE in Fig. 3. By increasing CNT content, nanoindentation curve is shifted to the left and the slope of unloading curve is increased. It is well known that the modulus and the slope of unloading

(i.e., stiffness) have a direct relationship [18]. Therefore, growth in stiffness will result in a higher modulus. The time-displacement data under constant indentation creep load are illustrated in Fig. 3b. Addition of MWCNTs results in a noticeable decrease in creep rate, particularly for 0.5 wt.% CNT content. Fig. 4 shows the modulus variation along an array of indentation for the neat VE and samples A and B. It is evident that the average modulus of composites are higher than that of VE, which is consistent with the results of DSC and flexural tests. It can also be seen that sample A has relatively uniform modulus values along the indentation array, demonstrating a good distribution of CNTs in the matrix. For sample B, a considerable heterogeneity in modulus variation can be found in two regions of the indentation array (20-60  $\mu\text{m}$  and 100-130  $\mu\text{m}$ ). Sonication under high amplitude of 70% for relatively long times may be responsible for aggregation of CNTs at small regions, resulting in a locally non-uniform variation of modulus along the array. Based on the aforementioned phenomena, it can be concluded that high CNT content along with a good distribution state of nanotubes in the matrix may play a significant role in decreasing the creep rate of sample A.

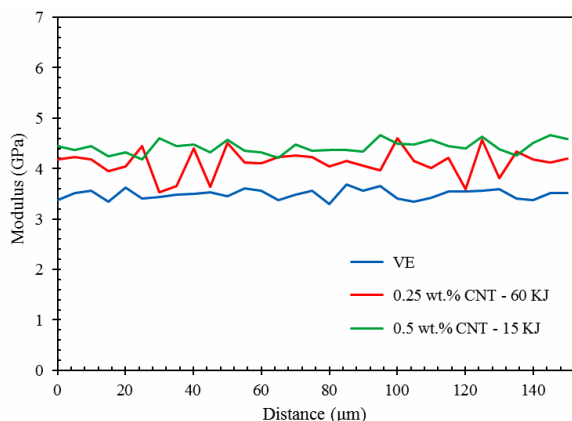


Figure 4: Modulus variation along the indentation array.

#### 4 SUMMARY

- DSC results show that the 0.25 wt.% CNT/VE composite with 60 KJ sonication energy exhibits 11% enhancement in  $T_g$  compared to VE polymer.
- A 24% improvement in the flexural modulus can be achieved by adding 0.5 wt.% CNT to the VE resin with applying 15 KJ sonication energy.
- Array indentation results demonstrate that incorporation of 0.5 wt.% MWCNTs into the VE resin with the total sonication energy of 15 KJ generates a relatively uniform distribution state of nanotubes in VE matrix.
- Uniform distribution of nanotubes in the matrix is shown to play a significant role in decreasing the creep deformation rate of VE polymer.

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