Carbon Nanotube-reinforced Epoxy Nanocomposites for Mechanical Property Improvement

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ABSTRACT

Mechanical properties of multi-wall carbon nanotube (MWNT) reinforced epoxy nanocomposites are evaluated and presented. MWNTs were functionalized with carboxyl functional groups (COOH-) on the surface via chemical modification. They were then dispersed in solvent followed by a microfluidic process. The mixture was then infused into the epoxy matrix at different loadings and mixed with a curing agent. Mechanical property evaluations were then performed for the epoxy nanocomposites and compared to the neat epoxy. At COOH-MWNT loading of 1.5 wt.%, compression strength, flexural strength, and modulus were improved 44%, 44%, and 16% respectively. Unidirectional carbon fiber reinforced prepreg (CFRP) were also prepared using COOH-MWNT reinforcement. The flexural strength of the CFRPs using COOH-MWNTs (1.5 wt.%) was improved by over 30% compared with the neat one. Flexural modulus was improved 18%.

Keywords: multi-wall carbon nanotube (MWNT), mechanical properties, COOH-functionalization, dispersion, CFRP

1 INTRODUCTION

CNTs possess unique mechanical properties. Their stiffness, strength and resilience exceed similar properties of any known material. For example, the Young's modulus of CNTs is larger than 1.0 TPa, and the tensile strength varies between 200 and 500 GPa [1-4]. As a result, CNTs offer a tremendous opportunity for the development of fundamental new material systems, in particular, structural nanocomposites. Unfortunately, their integration with polymer matrices present new technical challenges [5-6].

It is known that CNTs tend to aggregate with each other to form ropes or bundles due to intrinsic van der Waals forces associated with their high surface energy [7-8]. De-agglomeration and dispersion of CNTs in various media has been recognized as one of the major challenges in utilizing CNTs in commercial applications [9]. Traditional methods such as sonication, high shear mixing, stirring, and surfactants are often used in lab scale quantities to disperse the CNTs but those methods have proven not effective on an industrial scale [10-12]. Although functionalization of the surface of CNTs succeeded to improve dispersions, the end results for the mechanical properties of CNT-reinforced nanocomposites depend also on mixing procedures and CFRP making methods [13].

Obtaining interesting and unique properties of nanocomposites are not sufficient to transfer these properties to CFRPs and this goal can be realized only by successfully learning how to integrate functionalized CNTs into more complex structures [14]. Using CNTs as a reinforcing component in polymer composites requires the ability to tailor the nature of the CNT walls in order to control the interfacial interactions between the CNTs and the polymer chains [15]. Several studies have reported on the mechanical properties of CNT-reinforced polymer nanocomposites where the CNTs were used without surface modification [16-17]. These studies showed an increase in the elastic modulus of the composite at relatively low nanotube concentration (< 1% by weight). These findings show the potential of CNTs as reinforcing components, especially if the surface interface between them and the polymer matrix is optimized. Examples of such covalent linkages achieved through chemical functionalization have been utilized in CNT-reinforced polymer composites and biological systems. These interactions govern the load-transfer efficiency from the polymer to the CNTs and hence the reinforcement efficiency [18].

In the present paper, we report a unique process for preparing functionalized CNT dispersions for incorporation into CNT-epoxy nanocomposites to improve mechanical properties. The process uses a microfluidic processor that generates high shear forces in the dispersion to effectively break up CNT ropes and bundles in the solvent. MWNTs were chosen because of their cost and availability as compared to single-wall and double-wall CNTs (SWNT, DWNTs). Mechanical properties of functionalized MWNT-reinforced epoxy (Epon 828 resin) were evaluated. CNT-reinforced prepreg and CFRP using unidirectional carbon fiber was also prepared and evaluated.

2 EXPERIMENTATION

2.1 Materials

MWNTs were obtained from Mitsui Co., Japan and other vendors. The MWNTs were highly purified (>95% purity). Epon 828 epoxy resin and hardener (dicyandiamide) used to cure the epoxy were obtained from Mitsubishi Corporation, Japan. Unidirectional carbon fibers were obtained from Toray Inc. (T700).

2.2 Functionalization of MWNTs

The purified MWNTs were first put through an oxidation process by placing them in a 3:1 HNO_3/H_2SO_4 solution. The MWNTs in the solution were sonicated in an ultrasonic bath flow. The oxidation process resulted in functionalization of the MWNTs with carboxylic functional groups (-COOH) on the CNT surface. The MWNTs were cleaned using de-ionized water and filtered using a 2-μm mesh Teflon thin film filter under a vacuum. The MWNTs collected from the Teflon thin film were dried under vacuum in preparation for epoxy nanocomposite fabrication.

2.3 Dispersing CNTs by Microfluidic Process

We have developed a readily reproducible microfluidic process for achieving highly homogeneous dispersions of CNTs. CNT dispersions were prepared utilizing a microfluidizer processor to generate high shear forces in the dispersion to effectively break up CNT ropes and bundles. CNTs were mixed with acetone and dispersed using the microfluidic processor at an elevated pressure. After dispersion, well dispersed mixtures of CNTs in the acetone solvent manifest themselves as a gel. Figure 1 shows a picture of CNTs in acetone solution dispersed by the microfluidic process compared to a dispersion by an ultrasonic horn (a traditional method used to disperse CNTs) one hour after the dispersion process (0.5 g CNTs in 200 ml acetone in each glass beaker). The higher quality of the microfluidic dispersions is observed.

Figure 1 CNT/acetone solution dispersed by a microfluidic process (left) and ultrasonication (right)

2.4 Sample Preparation

Epon 828 resin was then added in the CNT/acetone gel at the ratios needed for sample preparation. The mixing process used a stirrer at 70°C for half an hour at a speed of 1,000 rev/min followed by an ultrasonication process to evaporate the acetone and disperse the CNTs in the epoxy matrix. The hardener (dicyandiamide) was then added into the mixture at a ratio of 4.5 wt.% and mixed by stirring at 70°C for 1 hour. The mixture was degassed in a vacuum oven at 70°C for 2 hours. The mixture was then poured into a release agent-coated Teflon mold and cured at 160°C for 2 hours. The specimens were polished using fine sandpaper to create flat and smooth on the surfaces for ASTM evaluation.

In this study, neat, non-functionalized, and COOH-functionalized MWNTs reinforced epoxy nanocomposites were synthesized for comparison. MWNT-reinforced prepreg and CFRP were also prepared for mechanical property evaluation. A hot-melt method was used for prepreg fabrication. The MWNT-reinforced resin was first coated onto a releasing paper. The unidirectional carbon fiber (Toray T700) was then impregnated into the CNT-reinforced Epon 828 thin film. The volume of the carbon fibers was controlled at 60 % in the prepreg. Multi-layered prepregs were then integrated and cured in an autoclave facility at 160°C for 2 hours. The CFRP laminate was then cut to standard specimens for mechanical properties evaluation.

2.5 Characterization

An MTS Servo Hydraulic test system (capacity 22 kips) is used for 3-point bending testing for flexural strength and modulus evaluation (based on ASTM D790). It is also used for compression strength testing (ASTM E9). Impact strength was tested based on ASTM D256. Vibration damping was tested based on ASTM E756.

A Hitachi S4800 FEI XL50 High Resolution SEM/STEM system was used for SEM imaging of the fracture surfaces of both reinforced epoxy nanocomposites and CFRP specimens.

3 RESULTS AND DISCUSSION

Table 1 shows mechanical properties of the CNT-reinforced epoxy nanocomposites compared with the neat epoxy. Compression strength, flexural strength and modulus were measured for all the samples.

From the results in Table 1, one can conclude that proper functionalization and loading of MWNTs has great effect on the mechanical properties of the epoxy nanocomposites. Compared with the neat epoxy, improvement of flexural strength was 7% and 36% respectively for the non-functionalized and COOH-functionalized MWNT-reinforced epoxy nanocomposites at 1.0 wt.% loading. Best results were obtained for COOH-MWNT loading of 1.5 wt.%. Compression, flexural strength, and modulus were improved 44%, 44%, and 16% respectively. It is important to note that initially the mechanical properties were improved with increasing loading of CNTs and then started to degrade. The reason may be because the viscosity of the resin at higher loading of the CNTs was high which left voids in the specimens after the curing process.

Epon 828-based materials	**Compression strength (MPa)**	**Flexural strength (MPa)**	**Flexural modulus (GPa)**
Neat	125	116	3.18
COOH-MWNT (0.5 wt.%)	131	144	3.38
COOH-MWNT (0.75 wt.%)	138	151	3.57
COOH-MWNT (1.0 wt.%)	158	159	3.61
COOH-MWNT (1.25 wt.%)	170	162	3.70
COOH-MWNT (1.5 wt.%)	180	168	3.72
COOH-MWNT (2.0 wt.%)	147	150	3.68
Non-functionalzed MWNT (1.0 wt.%)	130	124	3.48

Table 1 Mechanical properties of the nanocomposites

Samples were chosen for SEM testing of the flexural surfaces. SEM testing revealed no agglomeration of the CNTs in the matrix. As shown in Fig. 2, COOH-MWNTs were very well dispersed in the matrix.

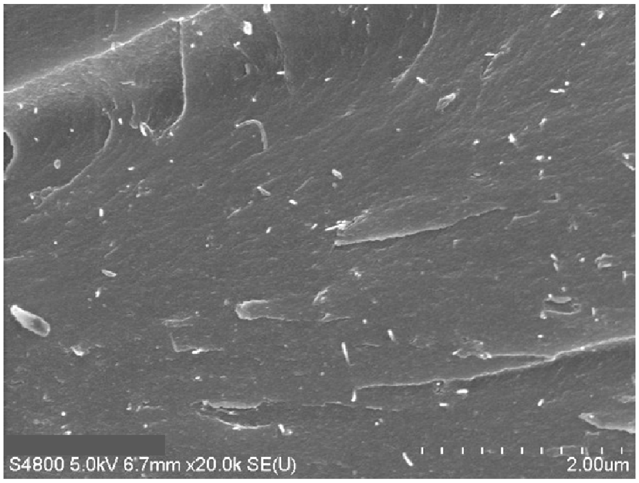

Figure 2 SEM image of flexural surface of the MWNT-COOH (1.5 wt.%) epoxy nanocomposite

We believe that significantly improved mechanical peroperties of the epoxy nanocomposites were due to proper functionalization and good dispersion of the CNTs. As for the COOH-MWNT reinforced epoxy nanocomposite, the surface of the MWNTs affects the wettability between the surface of CNTs and the matrix. It is very possible that the COOH-CNTs are hydrophilic to the epoxy matrix after the functionalization which improves their dispersion in the epoxy matrix [18]. The COOH-functional groups attached onto the CNTs offer an opportunity for chemical interactions with the epoxy matrix and enhance mechanical properties.

Based on the results above, we prepared prepreg using a hot melt process. The COOH-MWNT (1.5 wt.%) resin was first coated onto a releasing paper. The unidirectional carbon fiber (Toray T700) was then impregnated into the thin film. The volume of the carbon fibers was controlled at 60 % in the prepreg (average carbon fiber weight is 125 g/m^2). Multi-layered prepregs were then integrated and cured in an autoclave facility at 160°C for 2 hours. The CFRP plate was then cut to standard size specimens for 3-point bending testing. For comparison, neat epoxy CFRP specimens were also prepared for flexural testing. Figure 3 shows the graph of load vs. displacement of both CFRPs. The ultimate load increased to 958.8 N of COOH-MWNT (1.5 wt.%) CFRP compared with 730.8 N of the neat epoxy CFRP. That means a 30% improvement using MWNT-reinforcement in flexural strength. Flexural modulus improved 18 %.

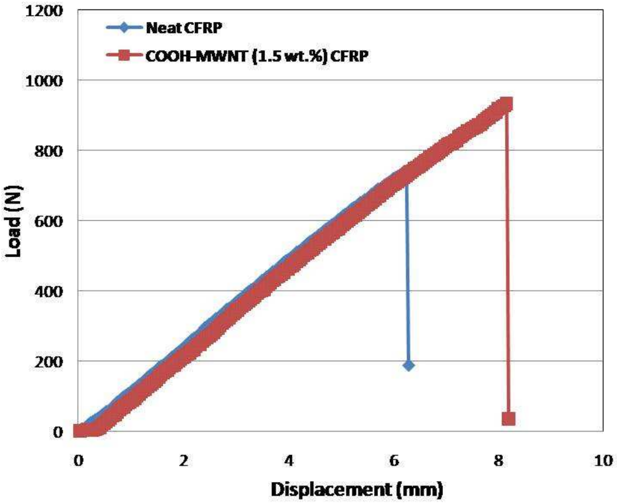

Figure 3 Load vs displacement of 3-point bending testing for both neat and COOH-MWNT (1.5 wt.%) CFRPs

Further testing will be performed for other mechanical properties such as open hole compression strength of the COOH-MWNT (1.5 wt.%) reinforced CFRPs.

Viscosity is very problematic for high loading of the CNTs in the epoxy matrix. We intend to use modifiers to lower the viscosity of the resins while increasing the loading of the CNT. Additional experimentation related to

NH_2-functionalized MWNTs will be performed to further improve desired mechanical properties.

4 CONCLUSIONS

In this study, mechanical properties of functionalized MWNT reinforced epoxy nanocomposites were evaluated. COOH-MWNTs show excellent reinforcement of the epoxy nanocomposites. Optimal results were shown at the COOH-MWNT loading of 1.5 wt.%. Compression strength, flexural strength, and modulus were improved 44%, 44%, and 16% respectively. The microfluidic process is a reliable technology for dispersing CNTs in solvent.

The flexural strength of COOH-MWNT (1.5 wt.%) reinforced CFRP was improved over 30% as compared with CFRPs of neat epoxy. The mechanical properties improvement of COOH-MWNT-reinforced resin has been successfully transferred to the improvement of CFRP.

We believe that our functionalization and dispersion methods for obtaining CNT-reinforced epoxy and other thermosetting nanocomposites is a very promising technology with many applications in fields such as aviation, aerospace, marine and sporting goods.

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