Characterization and Compression Properties of Injection Molded Carbon Nanotube Composites

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ABSTRACT

Since the development of carbon nanotubes (CNTs) in 1991, they have received much attention with improved mechanical, thermal, and electrical properties of their composites compared to common polymer composites. This study evaluated the effect of incorporating bundled and unbundled carbon nanotubes into Polyurethane/CNT/woven fiber reinforced composites. Atomic Force Microscopy (AFM) was used to characterize the dispersion of carbon nanotubes within the polymer matrix in injection molded CNT/polyurethane composites. Polyurethane/CNT/woven fiber reinforced composite plaques were prepared and then characterized by mechanical compression testing. AFM qualitatively determined a decreased agglomerate size resulting in improved mechanical properties. Results of this study show a significant difference amongst the yield stress values, but no significant differences were found for stress at failure, modulus of elasticity, yield strain, strain at failure and toughness between the bundled and unbundled samples.

INTRODUCTION

Carbon nanotube polymer composites have been shown to possess improved mechanical, thermal, and electrical properties compared to common polymeric materials. Perfect multi-wall carbon nanotubes (MWCNTs) are composed of multiple rolled graphene sheets that reside inside other graphene sheets with half fullerene ends that are 100% pure with no amorphous carbon or catalyst residues. The number of graphene sheets in MWCNTs is controlled by the method of synthesis and the conditions during the process. Perfectly straight nanotubes are rarely achieved. Most tubes do not have completely perfect hexagonal patterns as shown by the computer model; they have pentagonal or heptagonal impurities which cause the tubes to bend.

Benefits of Carbon Nanotubes

The mechanical properties of isolated nanotubes can be estimated by measuring the amplitude of their intrinsic thermal vibration in transmission electron microscopy (TEM) and found to have a Young's modulus average value of 1.8 TPa [1] and a tensile

strength of 600 GPa [2]. This makes CNTs a hundred times stronger than steel while being three to five times lighter [3].

Chen et al. [4] determined the stress-strain characteristics of a polyurethane (PU) elastomer/CNT composite. Young's modulus of the PU elastomer without carbon nanotubes was 4.96 MPa while the PU with the highest loading of 17.7 wt% nanotubes had a modulus of 135 MPa. The tensile strength, however, had a maximum increase at 9.3 wt%; the decrease in strength for a high concentration such as 17.7 wt% correlates to the increased frequency of localized agglomerates that was characterized by Scanning Electron Microscopy (SEM). It was also shown that it is possible to decrease plastic deformation without sacrificing the elongation at break for composites with MWCNTs at certain concentrations which vary by system [5].

Hurdles to adoption of CNTs

Carbon nanotubes have a large surface area (100-1000 m^2/g) and subsequently a large interface for stress transfers in a polymer matrix. This large surface area also creates a large interface for the nanotubes to aggregate due to large Van der Waal forces. Agglomeration of the CNTs introduces a major problem when trying to disperse them in any medium. Nanotubes without chemical modification added to most media tend to aggregate at the bottom of the container due to a lack of chemical reactivity. Agglomeration decreases the surface area of the nanotubes in contact with the medium and reduces the amount of stress that can be transferred to the tubes. Insufficient bonding at the nanotubes/matrix interface causes CNT composites to fail by either fracture at the interface or, in the case of MWCNTs, the layers of graphene sheets may be pulled out.

In common CNT production systems, as the concentration of CNTs increases, the modulus also increases [1,4-5]. Blau et al. [3] suggest that the tendency to form agglomerates limits the ability of the CNTs to add strength. This study also suggests maximizing structural properties by completely isolating CNTs from other tubes with a high level of dispersion. Poor dispersion creates a non uniform number density (number of carbon nanotubes/volume) within the medium causing unpredictable stress transfers to the nanotubes.

Commercially available nanotubes are typically 0.5-5 micrometers long. When using current composites, the nanotube length has a major influence on strengthening and stiffening of the matrix. For effective load transfer, the CNT length has to exceed a critical length, $L_{c,}$ which is defined as [3]:

$$L_c = \sigma_f d/2t_c \qquad (1)$$

Where σ_f is the tensile strength of the nanotube, d is the diameter, and t_c is the fiber-matrix bond strength. If this critical length is not reached, pull out is expected to be seen instead of CNT breakage during catastrophic failure. Critical lengths were calculated based on interfacial bond strengths using AFM for MWCNT in a polymer matrix. The critical length can be reduced by chemically functionalizing the nanotubes before their addition to the polymer matrix. Functionalization compromises the structural integrity of the carbon nanotubes (by compromising conjugation on the tube wall) but allows for a better stress transfer to the CNT from the matrix. More on this subject will be discussed below.

Overcoming Obstacles with CNTs

Three major obstacles to overcome before mechanical improvements can be achieved when using CNTs are: adequate wetability of the nanotubes surface; ability to transfer the applied stress to the tubes; and separation of the tubes.

Several methods have been developed in an attempt of breaking apart the agglomerates that are formed during synthesis. Ball milling beats dry carbon nanotubes with glass beads at moderate mixing speeds. High and low power sonication has also been used with some success [6] by introducing ultrasonic waves to increase the energy of the system; it should be noted that sonication also aids in dispersion of the CNTs.

Once the carbon nanotubes have been de-agglomerated, they need to be dispersed and modified to ensure that agglomerates do not reform. Solvents like acetone, dimethyl formamide (DMF), and methanol have been used to help disperse CNTs into epoxy based composites.

Chemical Modification

Chemically modifying the side walls is a common method for increasing nanotubes stability within media and preventing CNTs from re-agglomeration. Examples of treatments include oxidation in acid solution, dry oxidation in oxygen, anodic oxidation, amino functionalization, and plasma treatments [4]. Florian et al. [7] found that functionalization of less than 1% of the nanotube wall would greatly improve interactions without significant decreases in strength improving interfacial interactions. Acid treated MWCNTs underwent esterification with stearic acid to produce nanotubes that were soluble in liquid paraffin. The process is rather short and inexpensive as only few chemicals were used and had a cycle time of about three hours [8]. If nanotubes are only acid treated, the walls are coated with some carboxyl and hydroxyl groups which allow for better dispersion in more polar solvents. It is also possible to crosslink the CNTs within the media through various functional groups [4] which can create a stronger interaction with the matrix for better stress transfer capabilities.

Compressive Failure in Fiber Composites

When a composite sample is under a compressive load, the fibers displace transversely in one of two periodic modes: an extension mode and a shear mode [9] For a total fiber volume of less than 30% in elastic polymer matrices, the extensional mode is predicted to be predominant since neighboring fibers begin to develop sinusoidal deformations completely out of phase. For total fiber volumes greater than 30%, the shear mode is predicted to be predominant since the fibers suddenly deform transversely in phase. The polymer matrix in shear mode undergoes alternating shear forces along the fiber axis while the matrix between the fibers in the extensional mode is placed in alternating transverse tension and compression [9].

Fiber matrix interactions and interface properties are well known to have important roles in compressive failure. Increasing the load leads to increasing shear dislocations and slip that laterally pushes the adjacent, non defective fibers, causing bending and shear disturbances. The disturbances observed become more intense as the matrix deforms plastically under tension or shear and can create new shear brakes if the

disturbances reach a critical level. Eventually, the compressive load is high enough for neighboring fibers to fail at both high bending locations [9].

The first objective of this study was to evaluate the effects of bundled and unbundled carbon nanotubes at different concentrations in a CNT/polyurethane/woven carbon fiber /fiberglass mat composite. The second objective was to evaluate differences in treatments to a simple method of carbon nanotube addition. These objectives were attained by analyzing structural integrity and mechanical properties of each concentration and bundling treatment using optical microscopy, Atomic Force Microscopy (AFM), and electromechanical testing. This study provides insight into performance gains realized with injection molded CNT composites for parties considering CNTs for various polymer applications.

MATERIALS AND METHODS

Carbon Nanotube (CNT) Production:

Carbon nanotubes were grown by chemical vapor deposition, with a proprietary blend of transitional metal catalysts, and were purified by Ahwahnee Technology (San Jose, CA) using strong acids. The polyurethane was a two part system (Suprasec 9702 MDI isocyanate and Rimline polyol) and was used as received (Huntsman, West Deptford, NJ). The woven carbon fiber/fiberglass reinforcing material is of proprietary composition and was used as received (CE Composites, Ottawa, Canada).

De-agglomeration and Dispersion of CNTs:

Carbon nanotubes were de-agglomerated and dispersed at a loading of 0.30 wt% by a combination of high shear mixing in a planetary mixer, model DAC 150 FVZ-K (Flack Tech, Hauschild, Germany) and sonication (Branson model 5510, Danbury, CT) in liquid Rimline polyol (Huntsman). The CNT modified Rimline polyol was added to a mixing cup with the Suprasec isocyanate (1:1 ratio), mixed for two minutes at standard temperature and pressure (STP) then poured directly into the mold. A plaque was cast with a 0.30 wt% loading and was cured for two hours at 383K. The plaque was broken non-quantitatively to observe the break point by using Atomic Force Microscopy (AFM).

Injection Molding CNT Composites:

The CNT modified polyol and unmodified isocyanate were added to separate hoppers followed by mechanical injection into a mold (dimensions 15.0cm x 10.2cm x 0.3cm) containing a piece of woven carbon fiber/fiberglass mat reinforcing material. Each resulting plaque was cured at 380ºK for two hours. The plaques were cut via water jet to create strips of the plaque 1.3cm wide and 10.2cm long.

Compression Testing of Composite Samples:

The characterization method employed an electromechanical testing machine in compression mode for evaluation of modulus of elasticity, yield stress, stress at failure, yield strain, strain at failure and toughness. A modification of ASTM D638-03 [10] was used in determining mechanical properties to account for the size of the injection molded plaques. These modifications included gauge length and compression mode to evaluate strength of the polymer composite and not the woven reinforcing carbon fiber/fiberglass mat. Toughness was determined by comparing the area under the stress-strain curve for each treatment. Five samples of each of the three mixtures were conditioned and tested at 50% ± 5 RH and standard temperature and pressure by a universal tensile tester machine (Instron Corp model 1011, Norwood, MA). The crosshead speed was set to 4.0 cm/min [10] and the gauge length of the sample was 3.40 cm.

Statistical Analysis

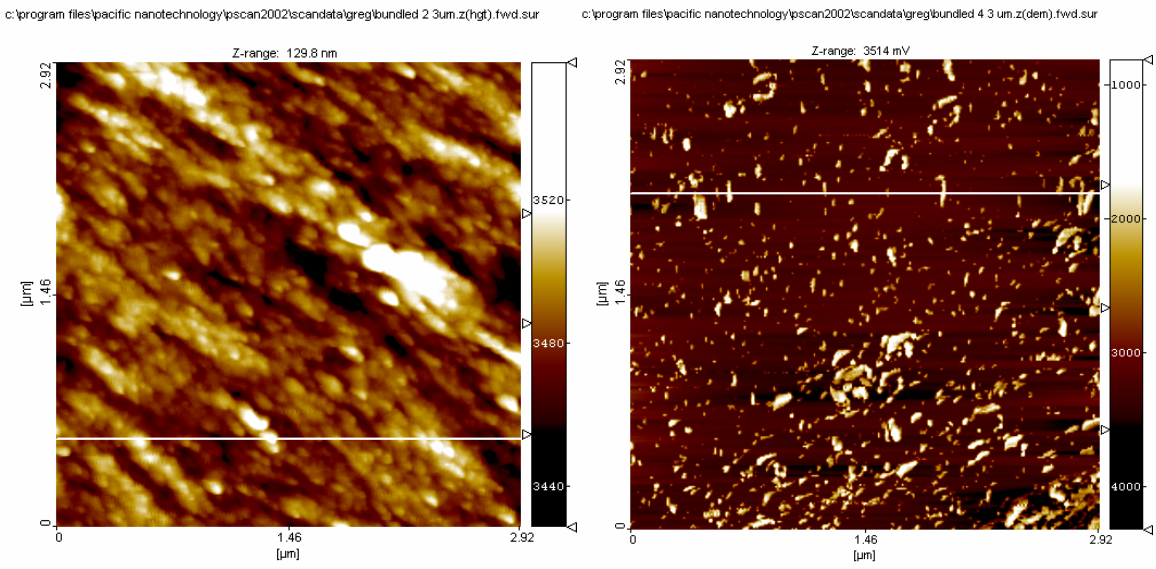
All experimental treatments were replicated five times using a factorial design. The yield stress, stress at failure, modulus of elasticity, strain at yield, and strain at failure were defined as response variables for each bundled (B) and unbundled (U) treatments. Data was analyzed using a general linear model and analysis of variance (ANOVA) for least significant differences with respect to treatments [11]. The data analyses below are based on the ordinary least squares method. To account for the variability among standard deviations for each response variable, the data was analyzed using a weighted least squares approach. The results, however, were consistent with the ordinary least squares analysis.

Atomic Force Microscopy

A CNT/PU plaque was prepared by mixing the CNT/polyol (0.30 wt%) mixture with Suprasec 9702 MDI isocyanate (Huntsman, West Deptford, NJ), pouring into a 3" x 5" mold and heating at 380 K for two hours. The cured material was fractured into two pieces at STP and the fractured surface was scanned using a Pacific Nanotechnology atomic force microscope (PACIFIC Nanotechnology, Santa Clara, CA) model: Nano-R-AFM

Characterization using Atomic Force Microscopy:

The de-agglomeration techniques used in the current study helped reduce the size of the agglomerates and disperse the nanotubes within the polyol (Figure 5). The cross section of a fractured polyurethane/CNT plaque was characterized by AFM. The height image shows a very rugged and random surface which suggests a successful stress transfer from the polymer matrix to the CNTs (Figure 5A).



A B

Figure 5. The height image (A) and the phase image (B) is shown above for a fractured CNT nanocomposite.

The phase image (Figures 5B) indicate the degree of nanotubes dispersion within the polyurethane matrix. The authors suggest that the white spots in the phase image indicate relatively harder sections (CNTs) while the darker regions show softer material (polyurethane matrix). The CNTs in this region are fairly uniform throughout the matrix which increases the ability of the nanotubes to relieve the stress from its surroundings. Line analysis of the phase image indicates that the width of the nanotubes were between 30 and 80 nanometers (Figure not shown). Using the critical length equation (Equation 1), it was possible to determine that only some of the nanotubes present in the matrix could successfully receive the stress applied to the material.

RESULTS AND DISCUSSION

The total volume fraction of the fibers in the present system was well above 30% (woven fiber mat plus nanotubes) and followed the predicted shear failure mode. It could be seen macroscopically via digital photography (figure not shown) that enough compressive load was applied to cause the samples to fail at both high bending locations. This behavior could also be observed by visual inspection.

Compression Testing

The increase in mechanical properties of carbon nanotube composites is well known and reported in other studies [5, 7-9] thus the comparison between samples without nanotubes was not considered. For materials that show a non linear elastic region, the slope of the stress-strain curve at low strain is used to determine the elastic modulus. Toughness was calculated from the area under the stress-strain curves.

Table 1. Stress Characteristics of Bundled and Unbundled CNT Nanocomposites

Bundled	Mean Conc. (wt%)	Yield Stress[a] (MPa)	Std. Dev. Yield Stress (Mpa)	Stress at Failure (Mpa)	Std. Dev. Stress at Failure (Mpa)
N	0.30	49.1	4.09	37.7	5.24
Y	0.30	62.8	*11.4	40.4	*6.55

a) Significantly different (P<0.01)

Table 2. Modulus of Elasticity and Strain Characteristics of Bundled and Unbundled CNT Nanocomposites

Bundled	Mean Conc. (wt %)	Modulus of Elasticity (MPa)	Std. Dev. Modulus (MPa)	Average Yield Strain	Std. Dev. Yield Strain	Average Strain at Failure	Std. Dev. Strain at Failure
N	0.30	30.5	3.28	0.27	0.05	0.82	0.13
Y	0.30	31.0	5.14	0.21	0.02	0.69	0.12

The yield stress values were found to be significantly different with a P value less than 0.01 with the bundled CNTs offering a better load transfer from the matrix. The yield stress values displayed a high variability in the unbundled treatment (Table 1). The variability seen within the samples can be attributed to non-uniform wetting of the fibers during the curing process and localized agglomerates of CNTs.

The stress at failure response variable had a P value greater than 0.10 and so it was omitted from the model. The strain at yield and toughness (data not shown) as the response variables both had P values greater than 0.05 thus they are not considered to be significantly different at the 95% interval. The modulus of elasticity values were also not found to be significant between the bundled and unbundled samples.

CONCLUSION

The objectives of this study were achieved showing a significant difference in yield stress values for bundled and unbundled samples. The methods used in this study for dispersing nantubes in a polyurethane matrix decreased the CNT agglomerate size as demonstrated by AFM. No significant differences were found for stress at failure, modulus of elasticity, yield strain, strain at failure and toughness at the 5% significance level. This study determined that bundled CNTs offer better stress transfers from the polymer matrix at the yield point, but not statistically different for any other properties evaluated by electromechanical testing. In general, bundled CNTs are cheaper to manufacture than unbundled, thus, bundled CNTs are recommended over unbundled.

Though this study reduced the agglomerate size, more research is needed to improve dispersion and completely isolate the nanotubes. Calendaring and higher power sonicators may allow for better dispersion with smaller agglomerates which can increase the mechanical properties of the nanocomposites.

REFERENCES:

1. Aglan, H., Dennig, P., Ganguli, S., Irvin G. *J. Reinforced Plastics and Composites* 2006, **25**,175.
2. Chen, Peng., He, Jiasong., Hu, Guo-Hua., Zhang, Baoqing., Zhang, Jun., Zhang, Zhinan. *Carbon* 2006, **44**, 692.
3. Esawi, Amal M.K., Farag, Mahmoud M. *Materials and Design* 2007, **28**, 2394.
4. Chen, Wei., Tao, Xiaoming., Liu Yuyang. *Composites Science and Technology* 2006, **66**, 3029.
5. Yaping, Zheng., Aibo, Zhang., Qinghua, Chen., Jiaoxia, Zhang., Rongchang, Ning. Materials science and Engineering, 2006, **435**, 145.
6. Chen, Wei., Tao, Xiaoming. *Applied Surface Science* 2006, **252**, 3547.
7. Florian H, Jacek N, Zbigniew R, Karkl S. *Chem Phys Lett* 2003, **370**, 820.
8. Bonard, Jean-Marc. *Thin Solid Films* 2006, **501**, 8.
9. Wang, Xinling., Xiong, Jiawen., Yang, Xiaohui., Zheng, Zhen., Zhou, Dongsheng. *Polymer* 2006, **47**, 1763.
10. ASTM, *D638-03*. Standard Test Method for Tensile Properties of Plastics. Association for Standard Testing of Materials (ASTM) International 2003, West Conshohocken, PA.
11. SAS Institute, Inc. 2004. *SAS/STAT 9.1 User's Guide*, North Carolina: SAS Institute Inc.