

Characterization and Compression Properties of Injection Molded Carbon Nanotube Composites

G. Curtzwiler,¹ J. Singh,² J. Miltz,³ J. Doi,⁴ K. Vorst²

¹Department of Polymer Chemistry, California Polytechnic State University, San Luis Obispo, California 93407

²Department of Industrial Technology and Packaging, California Polytechnic State University, San Luis Obispo, California 93407

³The Goldstein Packaging Lab, Department of Biotechnology and Food Engineering, Technion-Israel Institute of Technology, Haifa 32000, Israel

⁴Department of Statistics, California Polytechnic State University, San Luis Obispo, California 93407

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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. The CNTs are currently used to increase the modulus of common thermoplastics and thermosets, including urethanes and epoxies. The CNTs are difficult to disperse within any media because of limited chemical reactivity and potential agglomeration in their "as grown" state. This study evaluated the effect of incorporating bundled and unbundled CNTs at different concentrations into Polyurethane/CNT/woven fiber reinforced composites. Optical microscopy and atomic force microscopy (AFM) characterized the dispersion of CNTs 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. Optical microscopy and AFM qualitatively determined a decreased agglomerate size resulting in improved mechanical properties. Results of this study show significant differences in yield stress, stress at failure, and modulus of elasticity within the various treatments. No significant differences were found for yield strain, strain at failure, and toughness. However, the conservativeness of the statistical model warrants further investigation for strain at failure and toughness with possible interaction effects of CNT concentration for each composite. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 218–225, 2008

Key words: mechanical; compression; injection molding; nanotubes; composites

INTRODUCTION

Carbon nanotube (CNT) polymer composites have been shown to possess improved mechanical, thermal, and electrical properties compared to common polymeric materials. Perfect multiwall 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. A computer model of a perfect single wall carbon nanotube (SWCNT) can be seen on the top and the layering of graphene sheets in MWCNTs on the bottom of Figure 1, respectively.¹ 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. Imperfections in the walls results in a cluster of CNTs bent due to imperfections (Fig. 2).²

Production of carbon nanotubes

Different methods have been employed to produce CNTs. Arc discharge utilizes two graphite rods (anode and cathode), metal catalysts (typically Ni, Co, and Fe), iron sulfite powder, potassium chloride, and graphite powder. A mixture of the catalyst and graphite powder is filled into the anode cavity, while potassium chloride, iron sulfide powder, and graphite powder are filled into the cathode cavity. The discharge has a continuous current of 70A under a hydrogen atmosphere at 4.67×10^4 Pa.²

Another and more common method of CNT synthesis is chemical vapor deposition (CVD). A gaseous carbon source (typically acetylene, pure ethanol, or a mixture of methane and hydrogen) is injected into a flow reactor inside a tubular oven. Transitional metals are used as growth catalysts and are

Correspondence to: K. Vorst (kvorst@calpoly.edu).

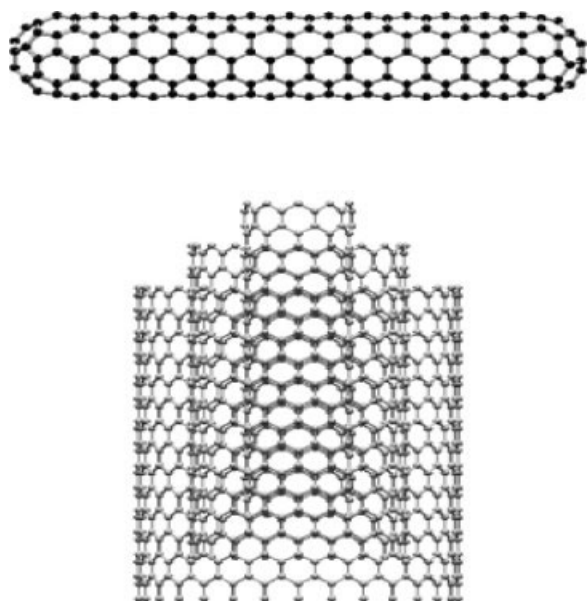


Figure 1 Simulation of single wall (top) and multi wall (bottom) carbon nanotubes.

located inside the oven. The size of the catalyst determines the diameter of the tube while the density of the particles controls the distance between the tubes.³ Catalytic nanotubes are less expensive than the arc discharge ones, have lower amounts of residual catalyst, and can be produced in large quantities. However, these catalytic nanotubes have poorer mechanical properties due to a greater number of imperfections in the tube wall. Plasma enhanced CVD (PECVD) is a variant of CVD that can produce aligned arrays of tubes with controlled diameter and length.⁴

Benefits of carbon nanotubes

The mechanical properties of isolated nanotubes is 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 TPa⁵ and a tensile strength of 600 GPa.⁶ This makes CNTs a hundred times stronger than steel while being three to five times lighter.⁷

Chen et al.⁸ determined the stress–strain characteristics of a polyurethane (PU) elastomer/CNT composite. Young's modulus of the PU elastomer without CNTs 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). Similar results were

found by Yaping et al.⁹ for a CNT/nylon 6 system and Aglan et al.⁵ for a CNT/epoxy system. 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 that vary with each system.

Hurdles to adoption of CNTs

CNTs have a large surface area (100–1000 m²/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. CNTs have no chemical reactivity,⁴ and thus do not have a considerable interaction with the medium to be able to stay dispersed. 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.^{5,8,9} 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 nonuniform number density (number of CNTs/volume) within the



Figure 2 Scanning electron microscope (SEM) image of bent carbon nanotubes.

TABLE I
Critical Length for Various Nanotube Diameters⁷

Nanotube diameter (nm)	Observed average interfacial shear strength (MPa)	Critical length L_c from (eq. 1) (μm)
30	90	10–25
70	20	105–260
90	40	67.5–170
130	18	217–540

medium causing unpredictable stress transfers to the nanotubes.

Commercially available nanotubes are typically 0.5–5 μm 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 as⁷:

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

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 after catastrophic failure. Critical lengths were calculated based on interfacial bond strengths using AFM for MWCNT in a polymer matrix (Table I).

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 CNTs (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 later.

Overcoming obstacles with CNTs

Three major obstacles to overcome before mechanical improvements can be achieved when using CNTs are as follows: adequate wettability of the nanotubes surface; ability to transfer the applied stress to the tubes; and separation of the tubes. All are important factors that determine the performance of the system.

Several methods have been developed in an attempt of breaking apart the agglomerates that are formed during synthesis. Ball milling beats dry CNTs with glass beads at moderate mixing speeds. High and low power sonication has also been used with some success.¹⁰

Once the CNTs have been deagglomerated, 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 and tetra-hydro furan (THF) in polystyrene, although the addition of the solvents decreased the mechanical performance of the composite.⁷

Chemical modification

Chemically modifying the side walls is a common method for increasing nanotubes stability within media and preventing CNTs from reagglomeration. Examples of treatments include oxidation in acid solution, dry oxidation in oxygen, anodic oxidation, amino functionalization, and plasma treatments.⁸ Florian et al.¹¹ 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 3 h.⁴ 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.

Adding functional groups with ionic charges can not only help with dispersion but also create a repulsive force that may keep the nanotubes separated. It is also possible to crosslink the CNTs within the media through various functional groups.⁸ This would create a stronger interaction with the matrix for better stress transfer capabilities and would surpass the decrease in mechanical strength due to the disruption of conjugation.

Sonication

Sonication is a useful method to disperse CNTs without the use of additional solvents. Wang et al.¹² used sonication to disperse a poly(propylene glycol) (PPG) grafted nanotubes in dried PPG. The PPG was added by oxidizing the walls of the nanotubes in a concentrated nitric acid/concentrated sulfuric acid mixture solution then treated with thionyl chloride to produce acid chloride functional groups chemically bonded to the CNTs. PPG was then added to the CNTs in an anhydrous THF solution.¹²

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.¹³ 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.¹³

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, nondefective 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.¹³

The first objective of this study was to evaluate the effects of bundled and unbundled CNTs at different concentrations in a CNT/PU/woven carbon fiber /fiberglass mat composite. The second objective was to evaluate differences in treatments to a simple method of CNT 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 production

CNTs 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 PU 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).

Deagglomeration and dispersion of CNTs

CNTs were deagglomerated and dispersed 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). Three mixtures of different concentra-

tions (0.20, 0.30, and 0.40 wt %) were made for both bundled and unbundled CNTs. The CNT modified Rimline polyol was added to a mixing cup with the Suprasec isocyanate (1 : 1 ratio), mixed for 2 min 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 2 h at 383 K. The plaque was broken nonquantitatively to observe the break point by using AFM. Liquid samples were also characterized via optical microscopy.

Injection molding CNT composites

The CNT modified polyol and unmodified isocyanate were added to separate hoppers followed by mechanical injection into a mold (dimensions 15.0 cm × 10.2 cm × 0.3 cm) containing a piece of woven carbon fiber/fiberglass mat reinforcing material. Each resulting plaque was cured at 380 K for 2 h. The plaques were cut via water jet to create strips of the plaque 1.3-cm wide and 10.2-cm long (Fig. 3).

Compression testing of composite samples

Two methods were used to quantify compression strength of injection molded CNT composite plaques with woven carbon fiber/fiberglass mat. The first method utilized a strip cut in accordance with ASTM D6272-02: Standard Test Method for Flexural Properties of Un-reinforced and Reinforced Plastics and Electrical Insulating Materials by Four-Point Bending.¹⁴ The strip was supported by two dowels near the outer edges of the test sample and a load was applied with two dowels equidistant from the center between the outside supports. The samples exceeded the parameters of the test and therefore this method was abandoned and a different method was employed.

The second 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.

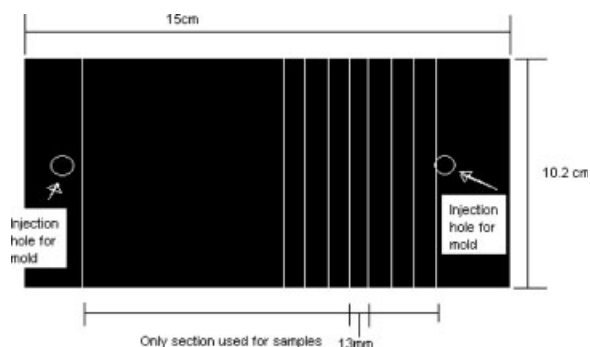


Figure 3 Dimensions of plaques and strips of a polyurethane/CNT/fiber composite.

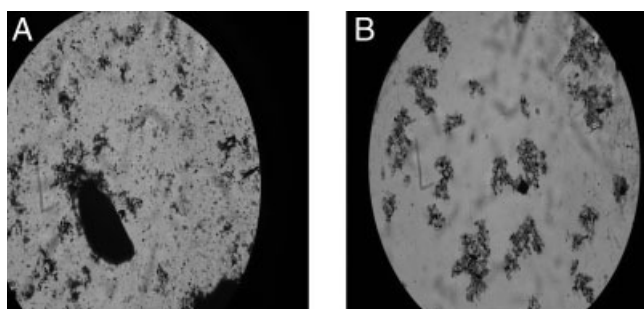


Figure 4 CNT/Polyol mixture at 400 \times before (A) and after (B) sonication and treatment.

A modification of ASTM D638-03¹⁵ 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% \pm 5% RH and STP by a universal tensile tester machine (Instron Corp model 1011, Norwood, MA). The crosshead speed was set to 4.0 cm/min¹⁴ and the gauge length of the sample was 3.40 cm.

Optical microscopy

Each specimen was prepared by adding a drop of the nonhardened CNT modified Rimline to the slide after conditioning at STP for 48 h and covering with a slide cover. The optical microscope used was a VWR VistaVision ProZoom Stereo Zoom Microscope (Batavia, IL). A Sony 6.1 megapixel (model DSC-W50, New York City, NY) digital camera was used to capture the images through the ocular lens.

Statistical analysis

All experimental treatments were replicated five times using a 2 \times 3 factorial design, and the data was analyzed using an interaction effects model. 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 (0.20, 0.30, 0.40 wt %). Data was analyzed using a general linear model and analysis of variance (ANOVA) for least significant differences with respect to treatments.¹⁶ 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" \times 5" mold and heating at 380 K for 2 h. 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 optical and atomic force microscopy

Optical microscopy was used to qualitatively determine both relative agglomerate size and dispersion within the polyol system in its liquid form (Fig. 4). The deagglomeration techniques used in the current study helped reduce the size of the agglomerates and disperse the nanotubes within the polyol (Fig. 5). A perfect dispersion would be characterized by an image in the field that is uniformly smooth gray.

The cross section of a fractured PU/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 (Fig. 6).

The two phase images in Figure 6 indicate the degree of nanotubes dispersion within the PU matrix. The authors suggest that the white spots in the phase image indicate relatively harder sections (CNTs) while the darker regions show softer mate-

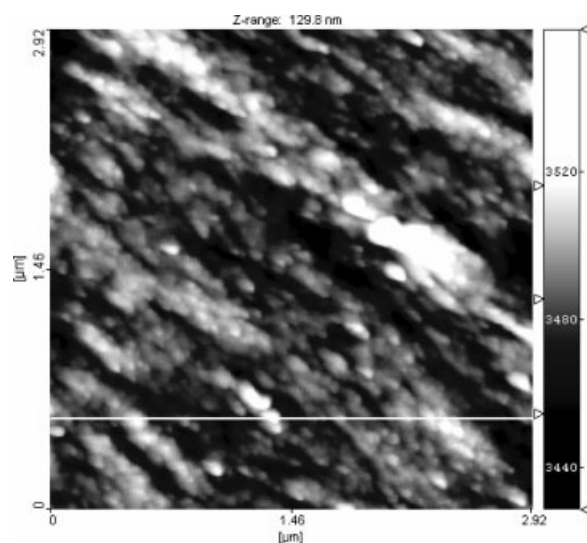


Figure 5 Height image of the cross section surface of a broken polyurethane/CNT composite (3 μm \times 3 μm).

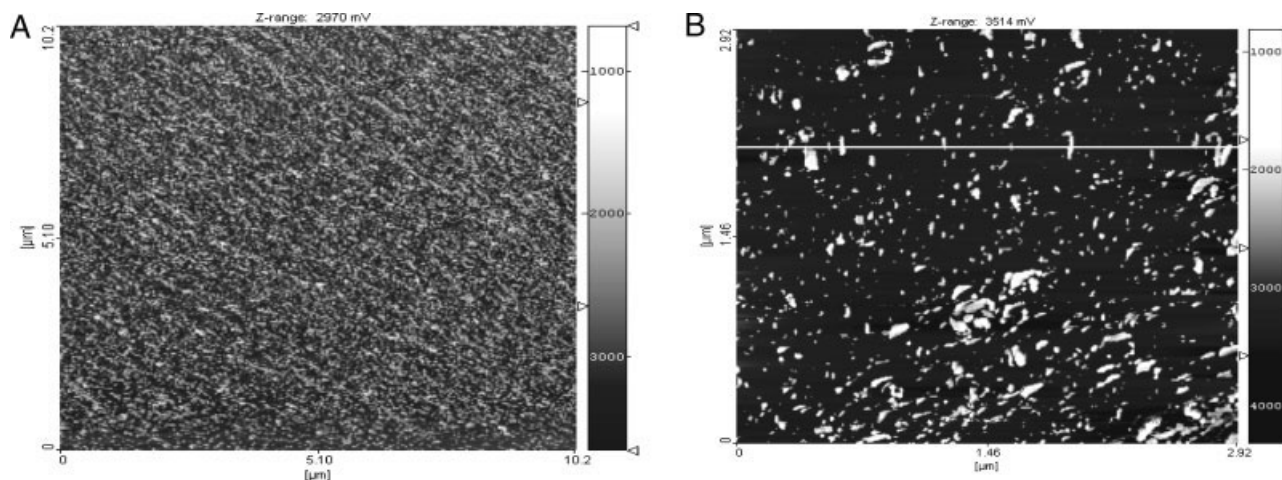


Figure 6 Phase image of the cross section surface of a broken polyurethane/CNT composite 10 μm × 10 μm (A) and 3 μm × 3 μm (B).

rial (PU 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 nm (figure not shown). Using the critical length table (Table I), 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 CNT composites is well known and reported in other studies^{7,8,12} thus the comparison between samples without nanotubes was not considered. For materials that show a nonlinear 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.

In both types of CNTs (bundled and unbundled), the observed yield stress values at 0.40 wt % were lower than those at 0.30 wt %. The lower yield stress at the higher concentration can be attributed to a lack of sufficient interaction between the nanotubes and the polymer matrix causing the nanotubes to agglomerate and to be poorly dispersed.

The 0.30 wt % CNT loading created the largest increase in mechanical properties of this system with bundled CNTs offering a better load transfer in ultimate strength applications. Among the stress at failure values, a higher degree of variability was found in the bundled 0.20 wt % group (Table II). Con-

TABLE II
Average Yield Stress and Stress at Failure of Polyurethane/CNT/Woven Fiber Composites at Various CNT Concentrations

Bundled	Mean conc. (wt %)	Yield stress ^a (MPa)	Std. dev. yield stress (MPa)	Stress at failure ^b (MPa)	Std. dev. stress at failure (MPa)
N	0.20	49.5	5.12	25.2	3.14
N	0.30	49.1	4.09	37.7	5.24
N	0.40	44.1	2.66	14.9	+1.72
Y	0.20	63.1	*11.2	28.2	*17.2
Y	0.30	62.8	*11.4	40.4	*6.55
Y	0.40	40.5	4.62	17.4	2.66

*, high amount of variability within values; +, low amount of variability within values.

^a Significant differences for both main effects and the interaction effect (*P* < 0.01).

^b Significant differences for the concentration main effect (*P* < 0.01).

TABLE III
Average Modulus of Elasticity, Yield Strain, and Strain at Failure of Polyurethane/CNT/Woven Fiber Composites at Various CNT Concentrations

Bundled	Mean conc. (wt %)	Modulus of elasticity ^a (MPa)	Std. dev. modulus (MPa)	Average yield strain	Std. dev. yield strain	Average strain at failure ^b	Std. dev. strain at failure
N	0.20	25.3	7.20	0.25	0.05	0.71	0.09
N	0.30	30.5	3.28	0.27	0.05	0.82	0.13
Y	0.20	26.8	1.69	0.33	0.16	0.88	0.12
Y	0.30	31.0	5.14	0.21	0.02	0.69	0.12

^a Significant differences for the concentration main effect ($P < 0.05$).

^b Significant differences for the interaction effect ($P < 0.05$).

versely, a relatively low variability was observed in the unbundled 0.40 wt % group. Yield stress values also displayed a high variability in the bundled 0.20 wt % and unbundled 0.30 wt % treatments (Table II). The high and low variability seen within treatments can be attributed to nonuniform wetting of the fibers during the curing process and localized agglomerates of CNTs. However, the range of 0.30–0.40 wt % should still be explored.

Using yield stress as the response variable, both main effects and the interaction effect were found to be significant ($P < 0.01$). Given the significant interaction effect, a *post-hoc* analysis was performed (using Tukey-Kramer multiple comparisons). Seven pairwise comparisons were found to be significant, and the data suggests the following relationships hold:

B20 > U30; B20 > U40; B30 > U20; B30 > U30; B30 > U40; B20 > B40; B30 > B40

where the bundled and unbundled treatments are represented by B and U, and respective numbers correspond to the fraction of percent loading (20 = 0.20 wt %). Bundled CNT samples performed better than the unbundled in all treatments scenarios.

Using stress at failure as the response variable, the interaction effect was found to be nonsignificant ($P > 0.10$) and so it was omitted from the model. Only the main effect of concentration was found to be significant ($P < 0.0001$). A *post-hoc* analysis was performed (using Tukey-Kramer multiple comparisons) and all three pair comparisons were found to be significant. The mean at 0.20% loading was found to be significantly higher than that at 0.40%. Also, the mean at 0.30% was found to be significantly higher than that at both 0.20 and 0.40%.

For the strain at failure response variable, the interaction between bundling and concentration yielded a P -value of 0.014. However, due to the multiple hypothesis tests that are considered across all response variables, a multiple comparisons adjustment should be applied. Based on a Bonferroni adjustment, a significance level of 1% was applied. Given this, the

concentration and interaction effect cannot be declared to be significant. However, due to the conservative nature of Bonferroni adjustments, this P -value suggests a potentially significant interaction effect and warrants further investigation (Table III).

For the modulus of elasticity response variable, the main effect of concentration yielded a P -value of 0.041. As previously stated, the Bonferroni adjusted significance level of 1%, this main effect cannot be declared as significant and warrants further investigation.

Using strain at yield as the response variable, none of the main effects or interaction effects was found to be significant. Toughness was not found to be significantly different for any of the CNT treatments ($P > 0.05$).

CONCLUSION

The objectives of this study were achieved showing an increase in mechanical properties for yield stress and stress at failure for each bundled and unbundled treatment with modulus of elasticity demonstrating performance gains for bundled treatments.

The methods used in this study for dispersing nanotubes in a PU matrix decreased the CNT agglomerate size as demonstrated by optical microscopy and AFM, resulting in significant differences for yield stress ($P < 0.01$), stress at failure ($P < 0.01$), modulus of elasticity ($P < 0.05$), and strain at failure ($P < 0.05$) within the various treatments.

No significant differences were found for yield strain, strain at failure, and toughness at the 1 and 5% significance levels. However, the statistical model used in this study identified areas of further research due to interaction effects resulting from potential agglomeration of CNTs during the injection molding process.

This study identified an increase in mechanical properties but not all of the structural gains from the CNTs were realized utilizing the testing and statistical methods previously identified.

More research is needed to improve dispersion and reduce agglomerate size. Calendaring and higher power sonicators may allow for better dispersion with smaller agglomerates. This study suggests the possible advantage of bundled CNTs over unbundled for various polymer applications.

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