Nanotube Reinforcement of Adhesively Bonded Joints

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ABSTRACT

Over the past five years there has been much excitement about the development of nanotubes and nanofibers and the potential that these materials may offer in enhancing electrical and mechanical properties of systems. The purpose of this paper is to present research into improving the mechanical performance of polymers by using nanofibers as a reinforcement to make high performance composite materials. This paper will present theoretical predictions of the composite modulus and then present the actual performance of the composite. Fabrication details will be given along with photos of the microstructure. The matrix material is polymethylmethacrylate (PMMA) and the nanofibers are vapor-grown carbon nanofibers produced by Pyrograph Products, Inc.

Keywords: carbon nanotubes, polymer matrix composites, modulus nanotube composites

BACKGROUND

The purpose of this investigation is to determine the feasibility of transferring the incredible potential of nanotubes to macroscale composites. The use of nanotubes as a structural reinforcement is a novel technique in the composites industry. As such, delving into a new realm of a composite investigation, the established structure-property relationships have to be modified for the nanoscale. In addition, assumptions must be made based on information that is currently available for nanotubes, and this information is undoubtedly incomplete.

For example, it is important to recognize that the models used in this study to predict the composite properties are built on an assumption of continuum mechanics behavior. However, at this time it is uncertain whether this assumption is entirely valid when considering nanoscale constituents.

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Evidence has been put forth by Lourie and Wagner [1] that fundamental concepts of continuum mechanics used in traditional fiber-reinforced composites are valid at least to some degree on the nanometer scale for nanotube-reinforced composites. Lourie and Wagner have drawn this conclusion from the study of damage clusters in multi-walled nanotube-epoxy composites.

While the dimensions of the nanotube present some uncertainties in modeling its behavior, the dimensions afford the nanotube a unique advantage in reinforcing materials. The nanotube configuration consistently has an extremely high aspect ratio (on the order of 1000). This dramatically increases load transfer capability. Johnson and Birt [2] have used the Cox model to clearly demonstrate this effect of aspect ratio on load carrying capacity for whisker-reinforced composites. The effect is shown in Figure 1. In addition, the curved sections of a looped and intertwined nanotube can be equated to a chain of "short" segments and still be considered fully effective in load carrying capacity due to the high aspect ratio of these short segments.

Although the length of the nanotube is beneficial as far as load transfer effectiveness is concerned,
there is a disadvantage to increased length. The longer the nanotube, the more viscous the resulting nanotube-polymer system will be. Viscosity can present problems in processing and in dispersion of nanotubes within the matrix material. Thus, the length of the nanotube presents a trade-off in effectiveness and viscosity which must be reconciled.

**MODELING**

Prediction of composite properties began with the utilization of the micromechanics models of Cox. Cox used an embedded short-fiber model to estimate the stress along the length of a discontinuous fiber loaded in tension. Johnson and Birt have discussed this further [2]. The following expression, derived by Cox to estimate the Young’s modulus in the direction of the fibers, was used to approximate the composite modulus for a nanotube-polymer composite:

$$E = E_n V_n \left[ 1 - \frac{\tanh \left( \frac{\beta L}{2} \right)}{\left( \frac{\beta L}{2} \right)} \right] + E_m (1 - V_n) \quad (1)$$

where \( \beta = \left[ \frac{H}{E_n \pi r_0^2} \right]^{\frac{1}{2}} \),

\( H = 2\pi G_m / \ln[1/(V_n^{1/2})] \),

\( E = \) composite Young’s modulus,

\( E_n = \) Young’s modulus of the nanotube,

\( E_m = \) Young’s modulus of the matrix,

\( G_m = \) shear modulus of the matrix,

\( V_n = \) volume fraction of nanotubes,

\( L = \) average nanotube length, and

\( r_0 = \) average nanotube radius.
PMMA/CARBON NANOFIBER COMPOSITE

Constituent Materials

A nanocomposite was fabricated from polymethylmethacrylate (PMMA) and two types of carbon nanofibers. The nanofibers were produced by Pyrograf Products, Inc., a subsidiary of Applied Sciences, Inc. The product is marketed as Pyrograf III® carbon nanofiber. The specific nanofibers used are designated by the manufacturer as PS21 and PS24. These fibers have been cleaned after manufacturing. The two nanofibers have different diameters; however, their other characteristics are approximately the same. The manufacturer's data indicates that the PS21 nanofibers have an average diameter of 200 nm while the PS24 nanofibers have an average diameter of 100 nm. Both types of nanofibers have a length of approximately 100 μm. The tensile modulus for both types is estimated by the manufacturer to be 600 GPa. The density is approximated as 2.0 g/cm³. [3]
Extrusion Process
The two previously mentioned carbon nanofibers were added to PMMA compounding pellets in amounts of 5 wt% and 10 wt%. The two constituents were mixed by hand. The mixture was then extruded using a conventional extrusion machine. The product was water-cooled and then chopped into pellets. After drying, these pellets were again extruded. In this case, the product was gravity extruded and cooled in air. A Bradford University Research Ltd. Melt Spinner was used (see Figures 2-4). The ram speed was 1.5 mm/min. The samples containing PS21 were processed at 250°C. The samples containing PS24 were processed at 260°C and are therefore smaller in diameter due to a reduced die swell effect.

EVALUATION

SEM Characterization
A scanning electron microscope (SEM) was used to study fracture surfaces of the PMMA/nanofiber extrudate. The specimens were mounted on aluminum stubs using silver paste and coated with gold. The purpose of the SEM characterization was to observe the dispersion and distribution of nanofibers within the extrudate. SEM micrographs were also used to analyze the alignment of the nanofibers within the sample. Specimens were studied after the first extrusion process. Additional specimens were studied after the second extrusion processes. All micrographs

![Figure 6. SEM Micrographs at 2000X. (a) 5% PS24. (b) 5% PS21. Scale bars 5 μm.](image)

![Figure 7. SEM Micrograph at 2000X. 15% PS24. Scale bar 5 μm.](image)
shown are from samples after the second extrusion process.

The dispersion and distribution of nanofibers showed similar trends for the first and second extrusion processes. All specimens are mounted such that the plane viewed under the microscope is a cross-sectional cut perpendicular to the direction of extrusion. In the micrographs, the cross sections of the nanofibers are visible as white dots. This fact can be substantiated by looking at these white spots at high magnification. Such investigation shows that their dimensions are on the proper order for the nanofibers. Figure 5 shows an example of a nanofiber lying on the surface of a 10% PS21 sample at 17,000X. The scale bar is 500 nm.

SEM micrographs such as the ones in Figures 6 and 7 show that the nanofibers are well distributed throughout the sample and well dispersed from each other. Figure 6 shows (a) 5% PS24 and (b) 5% PS21 at a magnification of 2000X. Both scale bars are 5 μm.

Conclusions regarding the alignment of the nanofibers can also be drawn from the micrographs. The samples show significant alignment (more nanofibers in the extrusion direction than randomly oriented). Since nearly all nanofibers are visible as circular or nearly circular cross sections, this indicates that most of the nanofibers are aligned in the extrusion direction. The micrograph in Figure 7 shows 5% PS24 at a magnification of 2000X. The alignment is even more obvious in samples in which the fracture surface is not perpendicular but at a slight angle to the extrusion direction, such as in Figure 8. This micrograph shows 10% PS21 at 2000X. The scale bar is 5 μm.

The micrographs also reveal what appears to be evidence of nanofiber pullout. Micrographs such as the one in Figure 9 show holes where apparently nanofibers once were located but were pulled out under the stress of the testing load. This micrograph is of a 5% PS21 sample at 4000X. The scale bar is 5 μm. This pullout indicates that the fiber/matrix interface was too weak to support the maximum shear load transfer.

**Tensile Testing**

Five types of specimens were produced: the PMMA control and PMMA containing 5wt% PS21 nanofibers, 10wt% PS21, 5wt% PS24, and 10wt% PS24. These specimens were mounted using copper tubing as the tabs and an epoxy adhesive. The specimens were then loaded in tension using a conventional Instron machine. Using an extensometer, load vs. displacement data was collected. From this data and specimen dimensions, stress vs. strain curves were generated, and thus, the tensile modulus of each specimen. The results are summarized in Table 1.

![Figure 8. SEM Micrograph at 2000X. 10% PS21. Scale bar 5 μm.](image-url)
Comparison of Tensile Results to Model Prediction

The reinforcement offered by the nanofibers for this particular system prepared in this manner is minimal. For the PS21/PMMA system, the Cox model predicts a composite tensile modulus of 29.79 GPa for 5% unidirectional reinforcement and 18.85 GPa for 5% random reinforcement. For the system containing PS24, the model predicts 30.52 GPa and 19.54 GPa for the 5% unidirectional and 5% random, respectively. This data and that for the 10% cases is summarized in Table 1. The inputs assumed for this case were 600 GPa for the nanofiber modulus, a matrix Poisson’s ratio of 0.32, a nanofiber length of 100 μm, and a composite strain of 0.001. Again, the diameters for the PS21 and PS24 nanofibers are 200 nm and 100 nm, respectively. For this system, since SEM micrographs show high alignment of the nanofibers, results near the high end of these predictions (29-30 GPa for 5% and 57-59 GPa for 10%) were expected.

Obviously, the results do not follow the trends that were expected. The measured results are much closer to the modulus of the unfilled polymer than to the predicted results, indicating that the load is not being sufficiently transferred. While the moduli of the reinforced polymer increased slightly from that of the unfilled polymer, the moduli for the 5 and 10% cases are very close. In fact for PS21 reinforcement, the average modulus of the samples containing 5% nanofiber were higher than those containing 10% nanofiber. This is obviously contrary to expectation.

Table 1. Average Tensile Modulus v. Predicted Tensile Modulus

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average Tensile Modulus (GPa)</th>
<th>Predicted Modulus for Unidirectional (GPa)</th>
<th>Predicted Modulus for Random (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA control</td>
<td>2.00</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>5% PS21</td>
<td>3.07</td>
<td>29.79</td>
<td>18.85</td>
</tr>
<tr>
<td>10% PS21</td>
<td>2.27</td>
<td>57.93</td>
<td>36.11</td>
</tr>
<tr>
<td>5% PS24</td>
<td>3.23</td>
<td>30.52</td>
<td>19.54</td>
</tr>
<tr>
<td>10% PS24</td>
<td>3.55</td>
<td>59.21</td>
<td>37.34</td>
</tr>
</tbody>
</table>
Figure 10. Cox Predicted Composite Modulus. (a) For 5% PS24, varying nanofibers modulus. (b) For 5% nanofibers, varying nanofibers diameter.

CONCLUSIONS AND RECOMMENDATIONS

Composite modulus has been predicted as a function of nanotube modulus, volume fraction, length, diameter, and orientation. Nanotube orientation, volume fraction, and nanotube modulus were the most significant factors determining the composite modulus. However, changes in nanotube length and diameter within the range corresponding to those of available nanotubes produced very little overall effect.

Assuming 5% volume fraction, random orientation, a nanotube modulus of 600 GPa, and typical nanotube dimensions (rather than those of nanofibers), the composite modulus predicted using the aforementioned models is relatively low (25-35 GPa) in comparison to predictions supplied by NASA [4] which expect a theoretical value on the order of 240 GPa for a SWNT-polymer composite in the timeframe of 15-20 years in the future. This is not surprising since the projected value has factored in improvements that are likely to be made during that timeframe but are not currently available. These improvements may be in the nanotube properties themselves, in interfacial strength, or in processing.

The measured tensile values in this study are low compared to currently available conventional carbon fiber reinforced composites. However, such composites are typically used in structural applications that require higher moduli. The moduli predicted in the present models offer substantial improvement over typical values for adhesives. Such an improvement may open the door to new applications for adhesives. The value assumed for the neat adhesive in the models was 2.0 GPa. Thus, at 2.3 GPa to 3.6 GPa, the nanofiber-polymer composite still offers an improved tensile modulus.
Although the models predict a significant modulus improvement for polymer systems, these models are based on many assumptions. This study has shown the importance of the assumption of sufficient load transfer from polymer to nanoparticle. The system used in this study was PMMA reinforced with carbon nanofibers (5% and 10%). The vapor-grown carbon nanofibers were made by Pyrograf Products, Inc. and designated as PS21 and PS24. While for this particular system the observed tensile modulus was closer to that of the unfilled polymer than the predicted composite modulus, the potential remains to exploit carbon nanotubes and nanofibers as a superior structural reinforcement. Perhaps with the proper surface treatment or functionalization of the nanofibers, sufficient interfacial bond strength (and thus load transfer) will be achieved and a higher composite modulus will be observed in future attempts to fabricate nanocomposite structures.

REFERENCES