Nanostructured Polymeric Composites for High Performance Applications
Case Study: Fracture Resistance of Baseball Bats

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ABSTRACT

Nanostructured polymeric systems can mitigate some of the severe limitations of conventional polymeric composites. In the present research, polyurethane resins with Multiwalled carbon nanotubes (MWCNT) and woven cloth graphite and glass reinforcements have been used to manufacture baseball bats. The microstructure variables included: the type of MWCNTs used (bundled and unbundled) and the percent loading of the MWCNTs. Fracture toughness tests were conducted on the developed hybrid composite rings to evaluate their fracture performance. Fracture surface analysis revealed the various mechanisms by which the MWNT-reinforced polymer nanocomposites acquired their toughness in comparison with the neat resins. Other industries such as adhesives, coatings, textiles, repairs, ultra-light durables and structural components could considerably benefit from the high-performance characteristics of such nanoreinforcements.

Keywords: *fracture toughness, hybrid composites, Multiwalled Carbon Nanotubes (MWCNT).*

1 INTRODUCTION

Carbon nanotubes (CNT) are widely being researched for their use as fillers in composite materials due to their remarkable property improvements over bulk materials. It has been widely reported that carbon nanotubes can significantly improve thermal and electrical conductivity and also mechanical properties in a wide variety of polymer matrices [1-5]. It is believed that these improvements are dependant upon the dispersion of the nanotubes [6, 7]. CNTs have strong intermolecular van der Waal forces, which create strong attractions between the nanotubes. Ordered and aligned groups of CNTs are said to be bundled, whereas exfoliated orsingle nanotubes are unbundled. Previous studies have shown that bundled CNTs are viable for use in gas sensors [8], and are suitable for use in electrically conductive applications [9]. It has also been reported that exfoliated nanotubes produce a greater improvement in mechanical properties over bundled nanotubes [6, 7]; however these studies are mostly based upon random dispersions of nanotubes. Theoretical modeling studies are currently underway to predict whether improvements over the properties of exfoliated nanotubes can be achieved when nanotube bundles are well dispersed in the polymer matrix [10]; and which configurations of bundles may yield the greatest property improvements [11].

Dispersion and interfacial bonding of CNTs in the polymer matrix are critical factors to performance. Interfacial bonds between the polymer and the CNTs promote stress transfer across the matrix, and thus increase the resistance of the material to fracture. In addition, interfacial bonding and CNT orientation lessen the occurrence of slippage of the CNTs from the host polymer when a stress is applied. Slippage is an indicator that the CNTs are not well integrated into the host polymer. Dispersion as well as slippage may be improved by promoting chemical interactions between the host polymer and functionalized CNTs. It is believed that the extent to which nanotubes are dispersed may be influenced by creating sites on the CNTs that will bond with reactive sites on the molecules of the host polymer. Several techniques for functionalizing CNTs are presently under investigation [2-4].

Prior to the advent of nanostructured polymer matrices, carbon, glass, and other macrofibers were used as matrix reinforcements in polymer matrices, including polyurethanes and epoxies. Fibers have traditionally been used as fillers because they are lightweight and strong. It has been shown that the addition of fiber reinforcement improves mechanical properties such as tensile, compressive, and flexural strengths [12-15]; and can influence viscoelastic properties as well [16].

In the present study, the role of MWCNT to enhance the fracture resistance of polyurethane composite baseball bats is studied. MWCNTs were utilized in the polyurethane resins for manufacturing of these bats with woven cloth graphite and glass reinforcements. Comparison of the fracture resistance of these hybrid nanocomposites with a neat polyurethane composite was made.

2 EXPERIMENTAL

Composite samples in the form of cylindrical rings were sliced from the baseball bats. The samples were supplied by Ahwahnee Technology, Inc. The samples were made of layers of glass and carbon fibers infused with a two-part polyurethane resin containing different loadings of multiwalled carbon nanotubes (MWCNTs). The rings' width was about 13mm, and the rings had an inner and outer diameter of about 56 and 66mm, respectively. A 2mm notch was cut in two places inside each sample, as shown in Figure 1. The samples were then tested in compression mode at a crosshead speed of 2.5 mm/min on a Sintec 5D material testing system (MTS). The body force method developed by Y. Murakami et al. [17] was used for data analysis. Figure 1 shows the specimen geometry and loading configuration used for the body force method. The maximum stress obtained from the notched samples was used to calculate the fracture resistance of the different types of samples. .

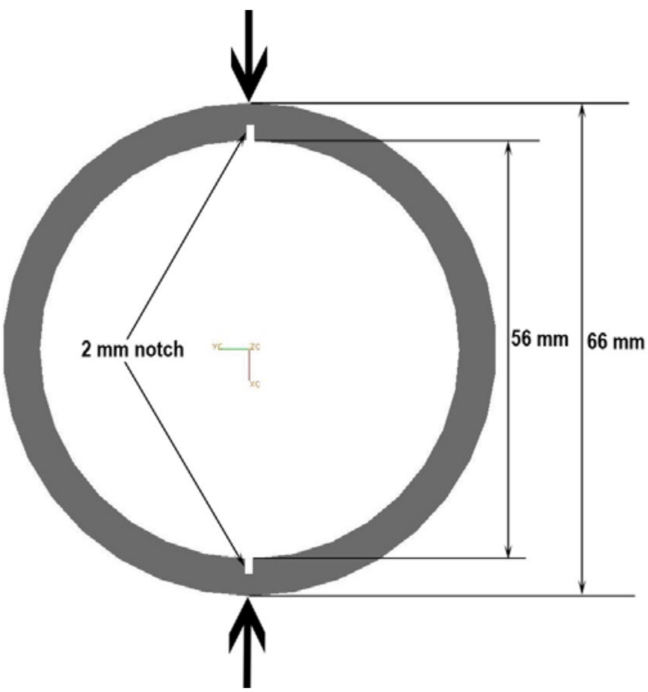

Figure 1. Specimen geometry and loading configuration of the polyurethane composite Ring.

3 RESULTS AND DISCUSSION

The stress – strain relationships of the notched bundled and unbundled 0.2% MWCNT samples as well as the neat sample are shown in Figure 2. The stress increases monotonically with the radial strain as shown in Figure 2. This is due to the presence of the notch at the point of loading which opens instead of fibers breakage, which could have caused sudden drop in the stress. The neat material showed a maximum residual strength of 151MPa and failed at a radial strain of 36%. The bundled 0.2% MWCNT sample showed a stress of 144MPa and strain of 35% while the unbundled sample showed a stress of 160MPa and a strain of 32%. It is seen that the unbundled sample shows a higher stress than the bundled MWCNT sample and also higher stress than the neat material. This may be due to a better dispersion of the unbundled MWCNTs in the matrix. The stress strain behavior of the bundled MWCNT sample is close to the neat sample, which suggests that some of the bundled nanotubes might have agglomerated, hindering dispersion in the matrix.

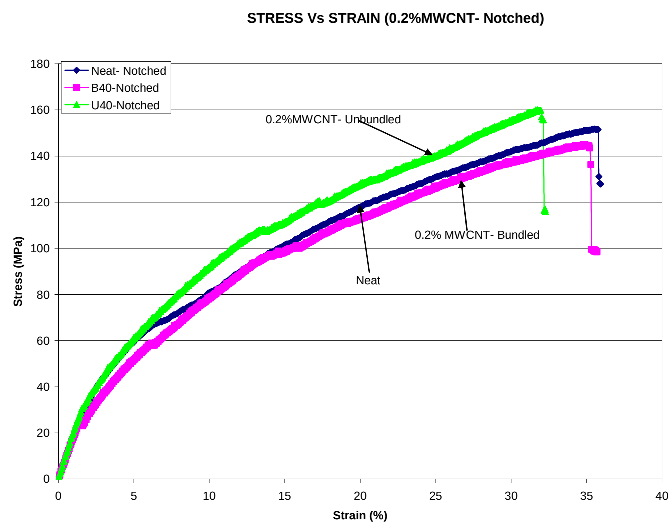

Figure 2. Stress- strain relationship of notched bundled and unbundled 0.2%MWCNTs notched.

The fracture toughness of the specimens was calculated using the maximum stress, obtained from the tested notched specimens and is given by:

$$f_I = \frac{K_I}{\sigma_m \sqrt{\pi c}} \tag{1}$$

Where the maximum stress (σ_m) is given by:

$$\sigma_m = \sigma_o \left[\frac{6(1+\beta)}{(1-\beta)^2} \right] \left[\frac{(0.995)}{\left[\left(1+\frac{\beta}{0.338}\right) - \left(\frac{\beta}{0.523}\right)^2 + \left(\frac{\beta}{0.840}\right)^3 \right]} \right] \tag{2}$$

where σ_0 and β are given by:

$$\sigma_o = \frac{P}{\pi R_2} \quad , \quad \beta = \frac{R_1}{R_2} \qquad (3)$$

The value for f_I was found from graphs that were developed using empirical data by Murakmai [17]. Table 1 shows the fracture toughness of the specimens tested. The average fracture toughness for the neat composite samples is 14 MPa √m. The average fracture toughness for the 0.2% MWCNT bundled and unbundled samples is 15and 17 MPa √m respectively. It is seen that the fracture toughness of the nanocomposites is higher than the neat material. This shows that the MWCNTs improved the fracture resistance of the polymeric composite components. Further, the unbundled MWCNTs specimen had higher fracture toughness than that of the bundled. This correlates to the stress strain data, which also showed that the unbundled MWCNTs had a higher residual strength than the bundled. Again, it is believed that the improvement in the fracture resistance for the unbundled MWCNTs can be attributed to a more uniform dispersion of the MWCNTs in the polyurethane resins.

Table 1. Data showing calculation the fracture toughness of all the materials tested

	Neat	B40	U40
P_{max} (N)	814	778	816
σ (MPa)	0.6	0.56	0.59
C (mm)	1.9	2.3	0.0024
σ_{max} (MPa)	158	147	157.56
f_1	1.16	1.21	1.24
K_1 (MPa √m)	**13.5**	**15**	**17**

4 FAILURE MECHANISM

A tested notched specimen is shown in Figure 3. The two inner notches are aligned with the loading axis. Initially, crack mouths of the notches opened without noticeable delamination at the crack tips as depicted in Figure 3. Beyond the crack tip of the neat samples, cracks developed along the fiber direction, showing de-bonding from the laminates. This suggests that the matrix dominates the failure. A similar failure pattern is seen beyond the crack tips in the bundled MWCNTs samples. The unbundled MWCNTs samples cracked across the fibers just beyond the crack tip. These events were captured in Figures 4 and 5 for the neat and the unbundled MWCNT rings, respectively. This suggests the presence of a tougher matrix, which may be attributed to a better dispersion of the unbundled MWCNTs in the polyurethane matrix. This also corresponds to the stress- stain relationship shown previously in Figure 2. After the samples cracked at the notch tip, they started to crack at 90° to the notch (Figure 3). The neat and bundled MWCNTs samples again cracked along the fiber direction. The unbundled MWCNTs samples cracked across the fibers similar to that observed beyond the crack tip. This means that the unbundled MWCNTs have increased the toughness of the matrix. This is also in good agreement with the fracture toughness of the materials shown in Table 1. The ultimate failure of all samples occurred at the sides of the samples, 90° from the notch tips. The failures occurred via a combination of matrix cracking, localized delamination, and fiber breakage at the outer diameter of the rings. These outer layers are the graphite woven cloth laminates.

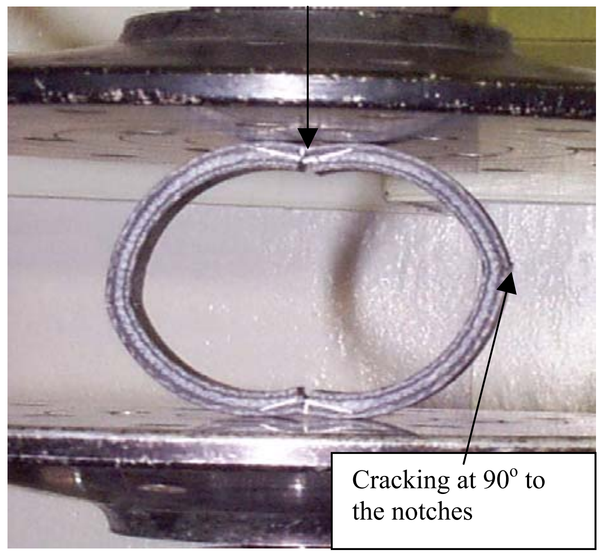

Figure 3. Photograph of notched specimen after tested.

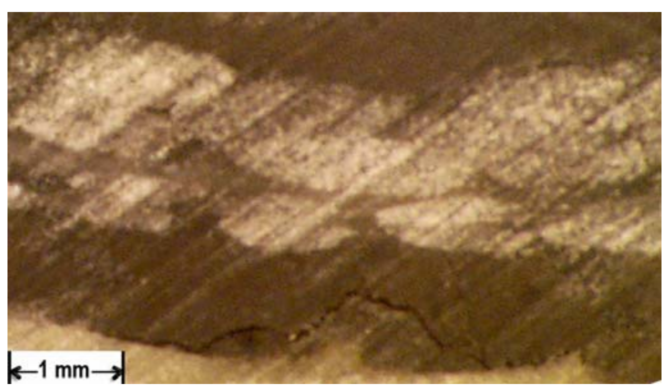

Figure 4. Micrograph showing delamination in the neat polyurethane composite baseball bat.

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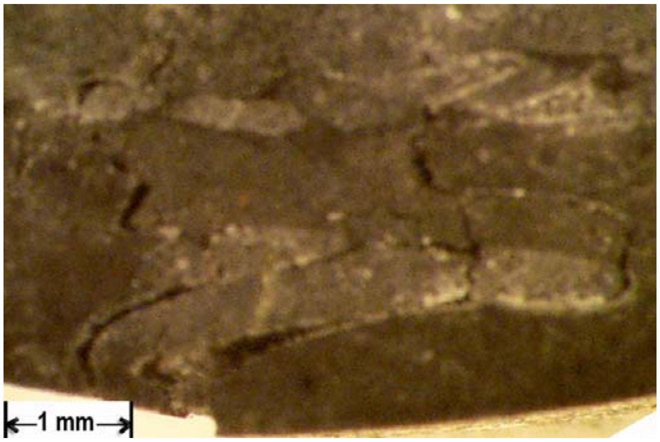

Figure 5. Micrograph showing microcracks perpendicular to the laminates of the unbundled MWCNT polyurethane composite baseball bat.

5 CONCLUSIONS

The role of MWCNT to enhance the delamination fracture resistance of polyurethane composite baseball bats was studied. The MWCNTs were either bundled or unbundled and kept at 0.2%w to manufacture the bats. Comparison of these hybrids nanocomposite components with a neat polyurethane composite was made. It can be concluded that:

- The MWCNT did not increase the brittleness of the polyurethane matrix.
- The fracture toughness of the unbundled MWCNT specimen is slightly higher than that of the bundled, however both the MWCNT systems showed a higher fracture toughness than the neat system. This attests to the better interfacial interaction between the MWCNTs and the polyurethane resin.
- The unbundled MWCNTs appear to have better dispersion in the polyurethane resin in comparison with the bundled ones.
- Delamination was not as pronounced as at the notch tips, in comparison to the outer layer of the rings at 90 degrees perpendicular to the notches.
- The failure occurred via a combination of matrix cracking, localized delamination, and fiber breakage at the outer diameter of the baseball bat rings.
- Future studies would be beneficial, looking at more loadings and sample geometry configurations.

Acknowledgements

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