FATIGUE PERFORMANCE OF MULTIWALL CARBON NANOTUBE – POLYMER COMPOSITES

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Introduction

High performance materials are typically thought of as those that exhibit elevated quasi-static mechanical properties (i.e. high strength, high modulus); however, performance in real world applications is largely based on the materials ability to withstand fatigue failure. Improving the performance of a polymer such as polymethylmethacrylate (PMMA) can be achieved by adding a reinforcing phase. Carbon fiber reinforced polymers are commonly found in sporting goods, automotive, and aerospace industries because of their high strength and low weight. Multiwall carbon nanotubes (MWNTs), which have nanoscale dimensions and superior specific strength, are an alternative to carbon fibers. The nanoscale dimensions of the MWNTs confer them with the ability to directly address the sub-microscale damage (i.e. crazing) that is associated with fatigue failure of polymers. Crazes form when the molecules of the polymer realign in the direction of the applied stress. [Suresh] This not only creates fibrils of aligned polymer but it also generates regions of micro-cracking. Typically, the dimensions of the fibrils and micro-cracks are larger than MWNTs but much smaller than carbon fibers; therefore, the MWNTs are more likely to affect craze formation and growth. Since crazing often precedes fatigue crack growth, MWNTs should exhibit a greater effect on fatigue performance than carbon fiber. In this study, the fatigue performance of PMMA reinforced with MWNTs and chopped carbon fibers are measured and compared.

Materials and Methods

Sample Production

Multiwall carbon nanotubes (MWNTs) were produced in our laboratory to high purity (>95%) using a chemical vapor deposition process. [Andrews] Small amounts (0.1% by volume) of MWNTs and chopped carbon fiber (CCF) were dispersed in molten PMMA using a high temperature (220°C), shear mixing protocol. [Marrs] PMMA mixed under identical conditions without an additive served as a control. After mixing, the material was removed and allowed to cool in ambient conditions (25°; air). Once the material hardened, it was crushed into pellets (<5mm) and, subsequently, hot-pressed (200°C) under vacuum into films of uniform thickness. The films were machined into rectangular specimens (60mm x 10mm x 1.7mm) suitable for constant amplitude-of-deflection fatigue testing. The rough surfaces of each specimen were smoothed with a rotary polishing device and annealed (120°C) for approximately 20 hours. This relaxed residual stresses that developed during the machining processes. The specimens were aged in air (25°C) for an additional 20 hours.

Fatigue Testing

Each sample (n=11-12) was tested to failure in a custom built, constant amplitude-of-deflection fatigue tester. The specimens of each sample were tested simultaneously with amplitudes of 0.5” (12.7mm) and 0.4375” (11.1mm) and a test frequency of 5 Hz. The run-out value was 1,000,000 cycles. The numbers of cycles to failure were recorded and analyzed using the linear version of the 3-parameter Weibull model. [Marrs] This analysis produced three parameters: the minimum fatigue life (N_o) [Janna], the shape parameter (α), and the location parameter (β). To simplify the comparisons between each material, the three Weibull parameters were used to calculate the Weibull mean (N_{WM}), an accepted single number indicator of fatigue performance. The fractured surfaces of randomly selected failed specimens were investigated with scanning electron microscopy.

Results and Discussion

The Weibull parameters and Weibull means for each material and deflection are presented in Tables 1 and 2. The MWNT reinforced PMMA outperformed unreinforced PMMA and PMMA reinforced with CCF at both deflections. The effect of MWNT reinforcement was more pronounced at the smaller deflection. In fact, the Weibull mean was 37.6% greater than that of PMMA and 90.1% greater than that of PMMA reinforced with CCF. At the smaller deflection (i.e. 0.4375"), the reinforcing effect of the MWNTs was amplified (i.e. the Weibull mean of 0.1vol% MWNT – PMMA was 74.7% greater than unreinforced PMMA and 30.9% greater than 0.1vol% CFF – PMMA). These results are similar to those reported by Marrs et al for MWNT reinforced methyl methacrylate – styrene copolymer (i.e. as stress amplitude decreased, the effect of MWNTs increased). [Marrs]

Table 1. Weibull Parameters and Weibull Means at 0.5" Deflection

	Minimum Fatigue Life (N_o)	**Shape Parameter (α)**	**Location Parameter (β)**	**Weibull Mean (N_{WM})**
PMMA	9795	0.756	30021	**33718**
PMMA + 0.1vol% MWNT	6529	0.944	45382	**46405**
PMMA + 0.1vol% CCF	2429	2.676	27152	**24408**

Table 2. Weibull Parameters and Weibull Means at 0.4375" Deflection

	Minimum Fatigue Life (N_o)	**Shape Parameter (α)**	**Location Parameter (β)**	**Weibull Mean (N_{WM})**
PMMA	42569	0.959	342355	**348047**
PMMA + 0.1vol% MWNT	0	0.982	603355	**608005**
PMMA + 0.1vol% CCF	88337	0.825	427605	**464633**

The micrograph in Figure 1 revealed the ability of a carbon nanotube to span a micro-crack that most likely developed during crazing of the PMMA matrix. This type of bridging helps to prevent micro-crack growth and slows the coalescence of multiple micro-cracks. Since crazing typically precedes fatigue crack growth, the MWNTs slow the rate of crack growth by reinforcing the regions of crazing. This is not the case, however, for chopped carbon fiber. In fact, the diameter of a typical carbon fiber is too large to effectively address the development of a craze zone. (Figure 2) In the suspected regions of crazing, traces of carbon fibers are present, which suggests that during crazing the carbon fibers de-bonded from the matrix and offered little to no resistance to crack growth. (Figure 3) Such de-bonding was more prevalent at the higher deflection, which explains why the difference between MWNT and CCF reinforcement diminished when the deflection was decreased. These images support our initial claim that the fatigue performance of MWNT – PMMA is superior to CCF – PMMA. We conclude that multiwall carbon nanotubes enhance the fatigue performance of PMMA and outperform chopped carbon fiber.

Figure 1. This micrograph represents the craze zone surrounding a secondary fatigue crack. The white arrow points to an isolated carbon nanotube bridging the faces of a micro-crack.

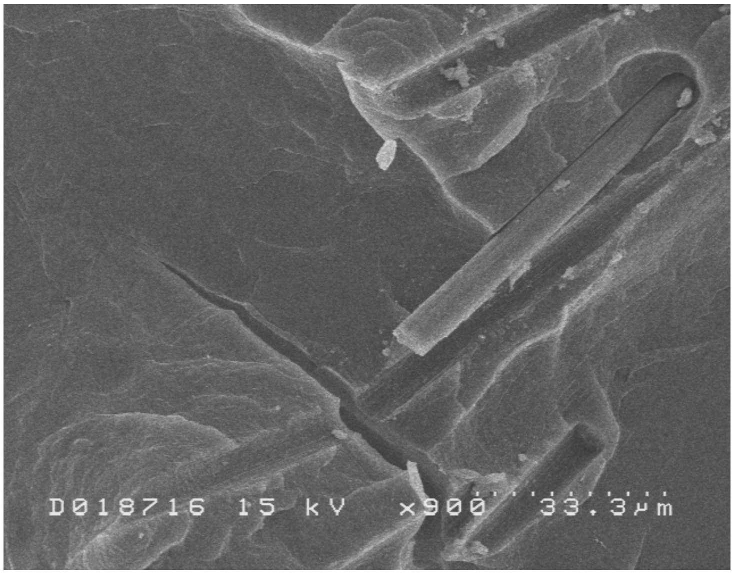

Figure 2. This micrograph of a 0.1vol% CFF – PMMA specimen reveals a carbon fiber that is de-bonding from the PMMA matrix. This also shows the trace of a carbon fiber that spans perpendicular to a secondary crack.

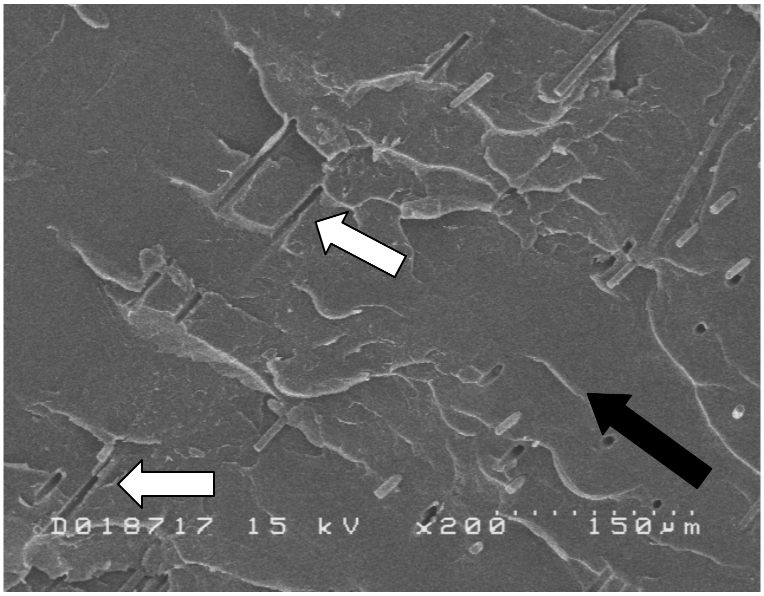

Figure 3. This SEM micrograph shows the fracture surface of a 0.1vol% CFF – PMMA specimen. The black arrow indicates the direction of crack growth. The white arrows point to traces of de-bonded carbon fibers within the "rough" region. This is a suspected region of crazing.

References

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