MULTIWALL CARBON NANOTUBES AFFECT THE CRACK PROPAGATION BEHAVIOR OF SINGLE PHASE BONE CEMENT

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Introduction

Understanding fracture mechanics and fatigue failure is beneficial for engineering new, high performance multiwall carbon nanotube – polymer composites. Improving fatigue performance of polymers is especially important to those that serve in structural applications. For example, improving the fatigue performance of bone cement used in Orthopaedics would extend the clinical life of the bone cement, minimize risk to the patient's health, and reduce healthcare expenditures. In general, the mechanism of fatigue failure is divided into two distinct phases: fatigue crack initiation and fatigue crack propagation. Initiation comprises the period of dynamic loading up to the initial formation of a fatigue crack. Once the fatigue crack nucleates, the material is subjected to a period nonlinear accumulation of damage (crack propagation). To counteract the increases in local stress associated with damage accumulation, the polymer molecules align in the direction of the applied stress forming an energy dissipation zone (crazing) around the crack tip. [Suresh; Beardmore] Such regions of crazing and micro-cracking often precede and limit fatigue crack growth; thus, craze failure and micro-crack nucleation are two of the rate limiting steps in the propagation of a fatigue crack. As damage accumulates and the fatigue crack grows over time, the apparent local stresses at the crack tip elevate dramatically. This is best described by the stress intensity factor (ΔK), which is a combinatorial effect of the magnitude of the applied stress and the extent of cracking. As ΔK increases, the length scale of damage processes at the tip increases; thus, ΔK is directly related to the rate of crack growth (da/dN). Unlike traditional fibers, multiwall carbon nanotubes can directly address such fatigue related issues because of their nanoscale dimensions. Given that multiwall carbon nanotubes are known to increase the fatigue performance of single phase bone cement [Marrs], the purpose of this study was to determine the affect of multiwall carbon nanotubes on the crack propagation properties of methyl methacrylate – styrene copolymer.

Materials and Methods

Material Composition

Multiwall carbon nanotubes (MWCNTs) were produced at the Center for Applied Energy Research (University of Kentucky) using a chemical vapor deposition process. [Andrews] The MWCNTs were harvested in mats and required dis-aggregation preparatory to and during dispersion into the polymer matrix. A small amount of MWCNTs (2% by weight) was dispersed into single phase bone cement (methyl methacrylate – styrene copolymer with barium sulfate) using a high temperature (220°C), shear mixing process. Single phase bone cement mixed without MWCNTs under identical conditions served as a control. The mixed materials were collected from the mixer and allowed to cool in ambient conditions (25°C; air).

Sample Preparation

Hardened composite material was crushed into pellets and hot-pressed (200°C) into films of uniform thickness. The films were then machined into rectangular specimens for constant amplitude-of-force, 4-point bend crack propagation testing. A slow turning diamond blade was used to ensure the faces of each specimen were smooth and parallel and that the thickness (W) was approximately equal to four times the width (B). The width and thickness of each specimen were measured in several locations. A single notch (<1 mm deep) was machined into one of the specimens' long edges. The faces of each specimen were thoroughly cleaned and two crack propagation gages (RDS22; HBM, Darmstadt, Germany) were mounted onto each face. Each gage was comprised of 50 conductive ties laid in parallel with spacing of 100 microns. Conductive leads were soldered onto the ends of each gage.

Fatigue Crack Propagation Testing

A conservative, increasing ΔK protocol for dynamically loading the specimens was developed and implemented. [ISO 12108] The actuator was cycled (5 Hz) in load control with a maximum load of 100 N and an R value of 0.1. If a pre-crack did not form after 100,000 cycles (signified by a change in the resistance of the gage) then the maximum load was increased by 10 N. Pre-cracking ensured that the test was isolated in the crack propagation stage of fatigue. The resistance across each gage was measured in real-time and recorded on a data logger (dataTaker DT80; Grant Instruments Ltd, Shepreth, UK). The data logger was started concurrent with the start of the fatigue test. Changes in resistance were used to mark the growth of the fatigue crack. After catastrophic failure, the rate of crack growth (da/dN) was calculated using the secant method (Equation 1):

$$\frac{da}{dN} = \frac{(a_n - a_{n-1})}{(N_n - N_{n-1})} \qquad (1)$$

The stress intensity factor (ΔK) was calculated from Equation 2:

$$K = \left(\frac{20}{2W}\right)\frac{P}{BW^{1/2}} f\left(a_{ave}/W\right) \qquad (2)$$

where P is maximum load, W is the thickness, B is the width, and a_{ave} is the average crack length over the increment $a_n - a_{n-1}$. The function f(a/W) was defined for a single edge notch four point bend specimen:

$$f(\theta) = 3(2\tan\theta)^{1/2}\left[\frac{0.923 + 0.199(1-\sin\theta)^4}{\cos\theta}\right] \qquad (3)$$

where θ = πa/2W. The resulting growth rates (da/dN) were plotted against the corresponding ΔK values. The Paris Law regression (Equation 4) was applied to each sample and the slope (m) and intercept (C) were recorded.

$$da/dN = C(\Delta K)^m \qquad (4)$$

Results and Discussion

The rate of crack growth was plotted as a function of increasing ΔK. (Figure 1) The Paris Law regression produced the material constants, m and C, for each sample. (Table 1) The intercept (C) of the regression line for 2wt% MWCNT material was nearly one order of magnitude greater than that of the 0wt% MWCNT material. The slope of the regression line (m) for the reinforced single phase bone cement (2wt% MWCNT) was 187% greater than that for the unreinforced single phase bone cement. This suggested that at lower values of ΔK, the MWCNTs effectively reinforced the single phase bone cement. Conversely, at high values of ΔK, the rate of crack growth for the reinforced single phase bone cement converged with that for the unreinforced material.

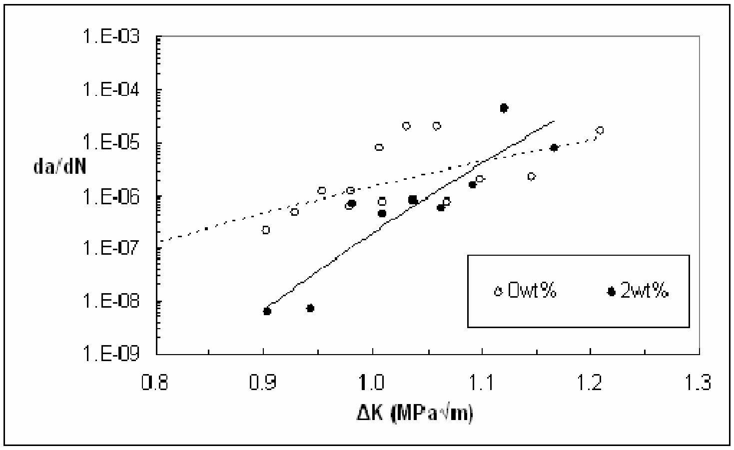

Figure 1. The rate of crack growth (da/dN) plotted against increasing stress intensity factors (ΔK).

Table 1. Material Constants from the Paris Law Regression

	C	m
0wt% MWCNT	1.0 E-6	11.02
2wt% MWCNT	2.0 E-7	31.62

Further investigation with scanning electron microscopy revealed the presence of small agglomerations within the reinforced single phase bone cement (Figure 2). As these are anticipated to be sites of stress concentration it is probable that the agglomerates may have accelerated the rate of crack growth. As stress intensity levels rise, the probability of such agglomerates interacting with the crack tip increases (the volume of highly stressed material at the crack tip rises as K^4). As crack tip and crack wake opening distances increase with stress intensity levels (both as K^2) it is also possible that crack 'reinforcing' effects of MWCNTs (e.g. crack bridging, as seen in earlier work [Marrs]) may become less effective, further contributing to the high *m* exponent of the CNT loaded material. These observations suggested that MWCNTs more effectively reinforce single phase bone cement during the short crack/early propagation stages of failure (i.e. low values of ΔK), which are well known to dominate total fatigue life (cycles to failure) in most structural applications.

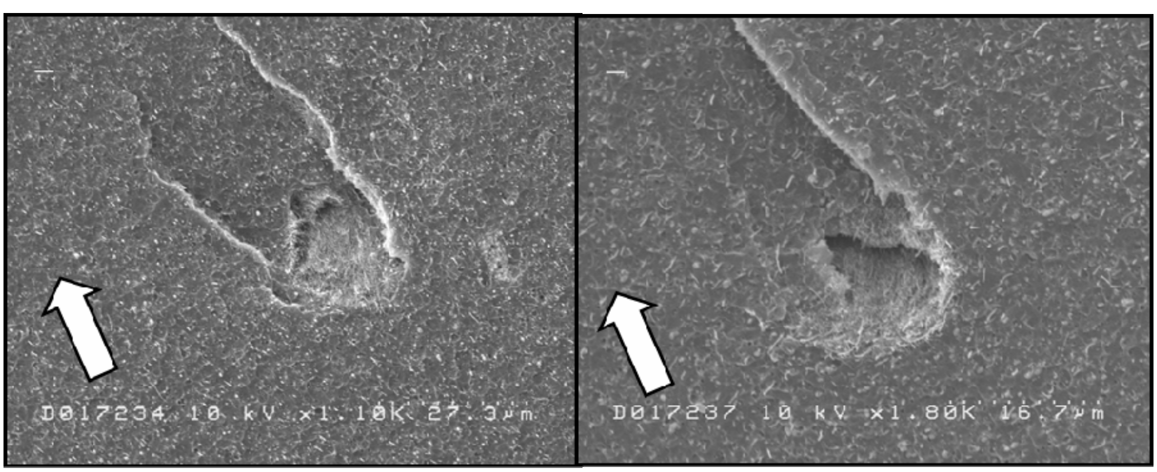

Figure 2. SEM micrographs revealed the presence of MWCNT agglomerations. The white arrows indicate the direction of crack growth. The agglomerates likely accelerated the rate of crack growth.

References

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