Multiwall Carbon Nanotubes Enhance the Fatigue Performance of Methyl Methacrylate Copolymer

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Statement of Purpose: Total joint arthroplasty, vertebroplasty/kyphoplasty, and most dental prostheses use polymer based bone cements as structural materials. The fatigue performance of these polymers is critical for prosthesis longevity, but the ideal material has not yet been developed. Conventional fibers (≥ several µm dia.) are too large to effectively bridge fatigue micro-cracks, but the nanoscale dimensions of multiwall carbon nanotubes (MWNTs) are comparable with the scale of fatigue related matrix damage; therefore, MWNTs may directly address fatigue related phenomena such as crazing and micro-cracking. To evaluate this central hypothesis, the present study was conducted to test the null hypothesis that small amounts of MWNTs will not alter the fatigue performance of a bone cement based copolymer maintained under physiological conditions.

Methods: MWNTs (O.D. ~10^1 nm) were manufactured to high purity in our labs by using a chemical vapor deposition process. Methyl methacrylate – styrene (MMA-co-Sty), a copolymer commonly used as a base material for commercial bone cements, was mixed with MWNTs (0%-5% by weight) using previously established methods. (1) The resulting materials were aged in phosphate buffered saline (PBS) at 37ºC for ≥ 6 days and were subsequently tested (n = 11 or 12) to failure in fully reversed tension-compression fatigue (peak stress amplitudes of 20, 30, and 35 MPa; test frequency of 5Hz) in a physiological environment (PBS; 37º). These stresses are larger than the predicted ≤10 MPa stresses modeled in bone cement mantles. (2) The cycles to failure data were analyzed by using the linear form of the 3-parameter Weibull model. The three Weibull parameters (minimum fatigue life, shape parameter, and location parameter) were incorporated into the calculation of the Weibull mean (N_{WM}), a widely-used parameter of fatigue performance. (3)

Results: Scanning electron microscopy of freeze fractured surfaces clearly showed the ability of MWNTs to bridge fatigue cracks. (Fig. 1)

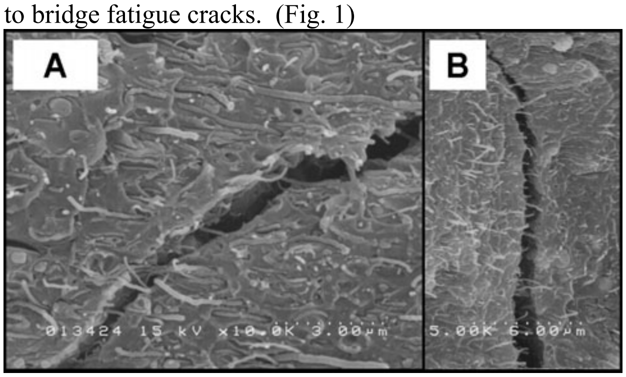

Fig. 1. These SEM images show MWNTs as finger-like projections extending into and across cracks in the matrix.

Table 1.

MWNT Concentration	Weibull Mean (N_{WM}), Cycles 20 MPa	30 MPa	35 MPa
0wt %	124,754	20,097	16,055
0.5wt %	507,953	29,943	15,209
1wt %	714,810	49,782	10,959
2wt %	830,028	69,784	13,467
5wt %	863,216	54,417	3,508

The addition of 2wt% and 5wt% MWNTs increased the fatigue life (as quantified by N_{WM}) of MMA-co-Sty in the 20 MPA peak stress group by 565% and 592%, respectively. (Table 1) Similarly, in the 30 MPA test group the addition of 2wt% MWNTs increased the fatigue life by 247% and the 5wt % loading was associated with a 171% enhancement in N_{WM}. Curiously, in the 35 MPa peak stress group, all MWNT loadings resulted in slight decreases in N_{WM}, as compared to controls. This effect peaked with a 78% reduction in N_{WM} with the 5wt% loading.

This study clearly shows that MWNTs can effectively bridge incipient cracks, retard crack propagation and, extend the fatigue life of the copolymer matrix. The reduction in fatigue performance enhancement with increasing stress amplitude suggests that these mechanisms of reinforcement are more effective at lower stresses. Reasons why MWNT enhancement of fatigue life diminish as peak stress increases is currently unclear, but the chief potential culprit may be sub-optimal MWNT dispersion and a stress dependant trade-off between performance enhancement (perfectly distributed MWNTs) and matrix defect production (imperfectly distributed MWNTs). Although this work exclusively focuses on a MMA-co-Sty matrix, these results have implications for a wide variety of other medically useful polymers, especially those that are amorphous or semi-crystalline.

Conclusions: We reject the null hypothesis and conclude that multiwall carbon nanotubes substantially enhance the physiologically relevant fatigue performance of this copolymer. This enhancement depends on the concentration of MWNTs and the peak stress amplitude. Translation of these performance improvements into clinical application would help enable "lifetime" implant devices, which are especially beneficial for younger or more active patients.

References: 1. Marrs BH. JBMR 2006; 77A(2):269-276.
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