Enhanced Fatigue Life of Carbon Nanotube-Reinforced Epoxy Composites

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The effects of carbon nanotube (CNT) inclusion on cyclic fatigue behavior and the residual mechanical properties of epoxy composites after different degrees of fatigue have been studied. Tension–tension cyclic fatigue tests were conducted at various load levels (25–50 MPa) to establish the relationship between stress and the number of cycles to failure (S–N curves). The residual strength and modulus were measured after loading at 30 MPa for 5000, 15,000, and 25,000 cycles. The incorporation of a small amount of CNTs increased the fatigue life of epoxy in the high-cycle, low-stress-amplitude regime by 1550%. Micrographs indicate the key mechanisms for enhancement in fatigue life such as CNT crack-bridging and pullout. POLYM. ENG. SCI., 00:000–000, 2012. © 2012 Society of Plastics Engineers

INTRODUCTION

Because of the outstanding mechanical and physical properties and large specific surface area of carbon nanotubes (CNTs), CNT-based composites are expected to show significantly improved mechanical performance, when compared with the neat matrix material [1]. Most of the prior work reported on this topic focuses on the effect of CNT addition on the stiffness and strength of composites [2], but improvements in fatigue resistance can also be expected.

Fatigue is the progressive and localized structural damage that occurs when a material is subject to cyclic loading and is one of the primary causes for catastrophic failure in structural materials. Enhancement of fatigue life is desired for improving the utility of polymer composites. Epoxies have significantly lower fracture toughness and fatigue resistance in comparison with other polymers, which limits their reliability and operating life [3]. In the wind-energy industry, the main structural/dynamic requirements for wind turbine blades are: (i) sufficient turbine blade bending stiffness; (ii) at least a 20-year fatigue life (>10⁸ cycles); and (iii) high-strength-to-mass ratio. CNTs have shown a huge potential in enhancing such properties in epoxy-based composites [4–8]. Relatively few studies have been devoted to the fatigue life of two-phase CNT/polymer composites [5–9], whereas the fatigue life cycle of hierarchical three-phase (glass- or carbon-fiber/CNT/polymer) composites has been more often analyzed [4, 10]. An understanding of the long-term performance of CNT-reinforced composites under repeated mechanical loads will enable the potential of CNTs to be better realized for long-term structural applications, such as wind turbine blades.

Ren et al. [9] investigated the tension–tension cyclic fatigue behavior of unidirectional, aligned 100-mm long single-walled CNT (SWCNT) rope-reinforced epoxy composites. The results suggested that the fatigue strength of SWCNT composites is at least twice that of carbon fiber composites. Scanning electron microscope (SEM) images of local failures around SWCNT ropes showed ductile-like failure with plastic deformation of the epoxy and pullout of the CNTs. The bridging of cracks by CNTs was also observed, and the fatigue life curves (cyclic stress vs. lifetime, S–N) were reported. In another work by the same group, the fatigue failure mechanisms of SWCNT bundles embedded in epoxy were studied [11]. The observed damage and failure modes included splitting

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of SWCNT bundles, kink formation and subsequent failure in SWCNTs, and fracture of SWCNT bundles.

Zhang et al. [5] reported an order of magnitude reduction in the fatigue crack propagation rate for an epoxy system with the addition of ~0.5 wt% CNTs. They showed that the crack suppression is caused by pullout of nanotubes that bridge the crack interface. In another work by the same group, the effect of CNT dimensions on fatigue crack growth suppression in epoxy composites was studied [7]. They observed that fatigue crack growth rates can be significantly reduced by (i) reducing the diameter of the CNTs; (ii) increasing the CNT length; and (iii) improving the nanotube dispersion. An over 20-fold reduction in the fatigue crack propagation rate was demonstrated.

There are few works reporting the fatigue life cycle of randomly oriented CNT-based composites. Yu et al. [6] investigated the fracture toughness and fatigue behavior of multiwalled CNT (MWCNT)/epoxy composites. The fracture toughness was increased by 62% by the addition of 3 wt% CNTs. The fatigue lives of 0.5 wt% MWCNT/epoxy composites were 10.5 and 9.3 times the average fatigue life of neat epoxy, when they were subjected to stress amplitudes of 8.67 and 11.56 MPa, respectively. The fatigue life (S–N) curves were presented, but the interpretation of the results was based on only one or two specimens tested. In addition, the fatigue-life data roughly followed a power-law model. From a phenomenological standpoint, fatigue damage can be evaluated in terms of the reduction in residual strength and stiffness [12]. Therefore, the measurement of residual properties brings about the possibility of tracking fatigue damage development in composite materials. To the best of our knowledge, there are no studies reporting the effect of CNTs on the residual properties of nanocomposites.

Herein, we report the effects of incorporating small amounts of CNTs on the fatigue life of a structural epoxy system widely used in the wind-energy industries. We also investigate the damage accumulation during fatigue cycling in terms of the residual modulus and strength of the composites.

**EXPERIMENTAL**

**Materials**

In this study, the epoxy matrix used is a modified diglycidyl ether of bisphenol-A (DGEBA, L135i, Hexion) with an amine hardener (RIMH 1366, Hexion). The MWCNTs (Baytubes C70P) were supplied by Bayer Material Science and exhibit an average diameter of 13 nm and a length larger than 1 μm. A dispersing agent, BYK-9077 consisting of block-copolymers with pigment affinity groups (BYK-Chemie) was used to aid the dispersion of CNTs in the epoxy system. The potential of BYK-9077 for the dispersion of CNTs and their stabiliza-

**Sample Preparation**

For the preparation of the samples, MWCNTs and the block copolymer were dispersed in epoxy using simultaneous magnetic stirring (400 rpm) and sonication for 2 h. Centrifugation and filtration were performed on the suspensions of CNTs prepared in epoxy, before casting the composites. The centrifugation at 150g lasted for 1 h, and the supernatant part of the solution was collected and filtered using a polypropylene filter with a pore size of 90 μm followed by filtration with a polyethylene filter with a pore size of 15–20 μm. The suspension of MWCNTs was then degassed by applying vacuum for 30 min to remove trapped bubbles. Furthermore, the suspension was mixed with the second component of the system for 3 min by stirring, and the mixture was allowed to cure at room temperature overnight and finally postcured at 90°C during 6 h. Reference samples of neat resin were also prepared following the same route. The starting concentration of CNTs and block copolymer were chosen to be fixed at 0.3 wt% in relation to epoxy, which would nominally render composites to have 0.225 wt% MWCNTs. However, some large CNT agglomerates are removed in the filtration and centrifugation processes, and thus, the amount of CNTs present in the composite is lower than this value. Experiments were designed to assess the amount of CNTs lost through filtration and centrifugation showed that the actual concentration of CNTs in the composite to be 0.19 ± 0.0042 wt%.

**Characterization**

The tensile properties of the composites were investigated according to the American Society for Testing and Materials (ASTM) 638-03 using an Instron 1011 universal tensile tester at a crosshead speed of 1 mm/min. Fatigue tests were conducted at room temperature on a servo-hydraulic test machine (MTS Model 20Kip). Dog-bone shaped specimens (Type IV, ASTM 638-03) were prepared, and their edges were sanded to reduce the possibility of edge-related failures. Aluminum tabs (6061-T6) with dimensions 40 × 25 × 1.6 mm³ were bonded to the ends of the specimens using a two-component epoxy adhesive to facilitate gripping. The specimens were fatigue tested under load-control mode, and the stress ratio defined as the ratio of the minimum stress to the maximum stress was set to be R = 0.1. The shape of the loading waveform was sinusoidal, and the frequency used was 3 Hz to avoid sample heating. The number of cycles to failure (N) was recorded for each specimen. At least three specimens were tested for each condition to ensure the reliability of the fatigue data. Additional fatigue tests were performed to assess the residual modulus and strength of the materials. The maximum stress level of...
the cyclic loading was set to 30 MPa, and cycling was halted after 5000, 15,000, and 25,000 cycles. The measurements of residual properties were performed with the same method as the static tests. Fracture surfaces of the fatigue tested samples were observed using a SEM (JEOL JSM-6510LV) with an operating voltage of 30 kV. Dynamic mechanical analysis (DMA) was performed using a TA instrument Q800 with a film tension mode at a frequency of 1 Hz and 0.01 N initial static force under a nitrogen atmosphere. The temperature was varied from 30°C to 150°C at a heating rate of 3°C/min.

RESULTS AND DISCUSSION

Materials Response Under Quasi-Static Loading

The comparison between the tensile properties of the different materials has shown that CNT-filled composites and neat epoxy have similar elastic modulus, tensile strength, and elongation at break. Figure 1 shows a typical stress–strain curve of pure resin and composites containing CNTs under monotonic loading. It can be seen that for the neat epoxy, there is a large nonlinear response beyond a stress of about 20 MPa. The composites on the other hand show an extended linear response up to about 30 MPa. Also, the response of the composites beyond the proportionality limit is considerably more linear than that of the neat material. Therefore, it could be expected that the neat epoxy samples will be susceptible to plastic deformation at lower load levels than the composites. These results suggest that at a given stress level, the amount of damage generated in a composite specimen would be probably lower than that created in a neat epoxy and consequently it can be speculated that composites would have a longer fatigue life. To confirm that the composites behave more elastically than the neat epoxy, DMA tests were performed. The effect of nanotubes addition on the damping behavior was obtained by the analysis of the plot of tan-delta versus temperature. The height of the peaks provided additional information about the relaxation behavior of these samples. The height of the peak for the neat resin has a value of 0.8, while the sample reinforced with nanotubes has a peak value of 0.7. This implies that the composites exhibit more elastic behavior than the neat epoxy.

Material Response Under Cyclic Loading

To study the influence of CNTs on the fatigue life of epoxy systems, neat epoxy and CNT/epoxy composites were tested under five different peak loading levels: 25, 30, 40, 45, and 50 MPa. Cyclic stress versus lifetime (S–N) curves are shown in Fig. 2a, and the data are listed in Table 1. The fatigue life data were fitted by the log-normal function \( \sigma_a = A N^B \), where \( \sigma_a \) is the stress amplitude and \( N \) is the corresponding fatigue life. High coefficients of determination were obtained \( (R^2 = 0.95) \) for both systems. The fitting parameters used for the curves presented...
in Fig. 2a are $A = 118.05$ MPa and $B = -0.13$ for the neat epoxy and $A = 94.34$ MPa and $B = -0.097$ for the CNT/epoxy composites. It is noteworthy that these values for $A$ and $B$ are in agreement with reported values for CNT/epoxy composites [6].

Under identical loading conditions, composites have longer fatigue lives than those of the neat epoxy systems. Although fatigue life is enhanced along the entire range of cyclic stresses used during testing, the addition of CNTs more significantly enhanced the fatigue life in the high-cycle, low-stress amplitude regime (Fig. 2b). Testing at 25 MPa peak stress showed the median fatigue life of CNT composites increased by 1550% over the neat epoxy. It has been demonstrated that CNTs can suppress failure in polymers via crack-bridging and a frictional pullout mechanism [5]. Crack-bridging has been shown as the dominant mechanism for energy dissipation during crack propagation [7]. As the fillers are in nanoscale, the chance that a propagating crack encounters them is statistically higher than in composites with microsized fillers. In principle, the dramatic enhancement of fatigue life observed in this study can be rationalized by the aforementioned mechanisms. However, further characterization, such as microscopy, is necessary to confirm such mechanisms.

As discussed previously, the most significant effect of CNT addition on the fatigue life of composites is seen for high-cycle, low-stress amplitudes (Fig. 2b). Similar results have been reported for carbon nanofibers and CNT/epoxy composites [6, 14]. At low stress levels, the CNT/matrix interface is preserved, and the load is effectively transferred from the matrix to the CNTs. The behavior of the composites at high-applied stress levels is suspected to be correlated to the breakdown of the CNT/epoxy interface. At higher applied stress levels, the CNT/matrix interface is believed to be damaged, reducing the load transfer. In addition, nanotubes are less effective in suppressing the rapidly propagating cracks generated at high stress levels. Under these conditions, the fatigue cracks grow at a rapid rate and at several fronts due to the high stress intensity and high strain density, respectively [15].

### Residual Strength and Modulus

Residual modulus is measured under quasi-static loading conditions after subjecting the specimen to cyclic loading. Accordingly, the residual strength is the value of strength required to cause failure of a specimen under quasi-static loading after the specimen is subjected to cyclic loading. Figure 3 shows the residual modulus and tensile strength measured for the neat epoxy and composites after 0, 5000, 15,000, and 25,000 cycles.

Neat epoxy and CNT/epoxy composites retained their quasi-static modulus throughout most of their lives (Fig. 3a). This could be rationalized as follows: damage in the form of cracks or CNT-matrix debonding may initiate

![Residual modulus and tensile strength](image)

**FIG. 3.** (a) Residual modulus and (b) strength of neat epoxy and composites as a function of fatigue cycles. Cycling was performed at a peak stress of 30 MPa.
at a number of favorable sites within the composite. No change in residual modulus during cycling would be detected if these damage zones are too small [16]. If the loading had been continued, the damage zone would grow until reaching a critical size, where failure would initiate. As shown in Fig. 3b, the residual strengths of neat epoxy and composites have similar values. Nevertheless, the values are slightly lower than those obtained during the quasi-static tests of samples not subjected to cyclic loading. We attribute this degradation in tensile strength to the progressive damage accumulation during cyclical loading. Even though this explanation seems to contradict the results obtained for the residual modulus of the composites, it is known that the tensile strength is more sensitive to stress concentration sites, such as CNT agglomerates and damage zones, than the Young’s modulus [17].

Fracture Surface of Specimens After Cyclic Loading

To identify the key mechanisms for the enhancement in fatigue life of epoxy composites reinforced with CNTs, SEM was used. SEM images of the fracture surfaces of the fatigue tested samples are shown in Fig. 4. The neat epoxy (Fig. 4a) exhibited a relatively smooth fracture
surface when compared with the CNT-reinforced composites (Fig. 4b). The obviously greater roughness of the fracture surface reflects the reinforcement effect of CNTs. The formation of such additional surfaces during fracture is indicative of crack deflection [14]. Figure 4c shows a composite cycled until fracture (1146 cycles) at a peak stress of 50 MPa. This image reveals a homogenous dispersion of the CNTs in the epoxy matrix. A magnification of this image (Fig. 4d) shows a CNT pulled out on its two ends, the middle being embedded in the matrix, which indicates a synergistic effect of the CNTs. In Fig. 4e, the fracture surface of a composite tested at a 25 MPa stress peak, with failure after 26,42,497 cycles (more than 10 days) is shown. Again, a homogeneous dispersion of the CNTs is found. A magnification of this image clearly indicates evidence of CNTs bridging growing cracks (rectangles in Fig. 4f). In addition, the pullout of a CNT is highlighted by a circle in the same image.

The quantitative fatigue results and the SEM images clearly show that CNTs enhance the fatigue performance of epoxy. These results confirm that CNTs retard the mechanism of fatigue failure by preventing or minimizing the initiation of catastrophic cracks and by slowing damage accumulation of existing or newly forming cracks [5, 15]. Therefore, the CNTs bridge cracks and reduce the extent of plastic deformation experienced by the matrix, whereas their pullout from the matrix and the separation processes at the crack front dissipates stored strain energy that would otherwise result in damage accumulation and subsequent growth of the fatigue cracks.

CONCLUSIONS

The addition of a small amount of MWCNTs has been shown to significantly improve the fatigue performance of a thermosetting epoxy system. We report an increase in fatigue life of epoxy in the high-cycle, low-stress amplitude regime of 1550%. Micrographs showed that the enhancement in fatigue life is caused by pullout of the CNTs and crack-bridging at the crack interface. This work demonstrates the huge potential of CNTs to improve one of the main structural/dynamic requirements for wind turbine blades, namely fatigue life. Thus, CNT-reinforced thermoset systems can be considered materials of choice to be used in the next generation of wind turbine blades.

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