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Enhancement of fatigue life of polyurethane composites containing carbon nanotubes

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ABSTRACT

The effects of carbon nanotube (CNT) inclusion on cyclic fatigue behavior and the tensile properties of polyurethane (PU) composites have been studied. Tension–tension cyclic fatigue tests were conducted at various load levels (30–50 MPa) to establish the relationship between stress and the number of cycles to failure (S–N curves). The tensile energy to break PU composites was enhanced up to 38% by using a low amount of CNTs. In addition, the incorporation of CNTs increased the fatigue life of PU in the high-stress amplitude, low-cycle regime by up to 248%. Micrographs show highly dispersed CNTs and indicate the key mechanisms for enhancement in fatigue life such as CNT crack-bridging and pull-out. The tensile-tensile fatigue properties obtained in this work show that PU systems can outperform epoxy systems widely used in structural applications.

1. Introduction

Due to their exceptional mechanical properties such as Young's moduli that can exceed 1TPa [1], tensile strengths of up to 200 GPa [2], and up to 15% elongation at break [3], carbon nanotubes are considered to be among the most promising candidates for the reinforcement of polymer matrices [4]. Nevertheless, the transfer of the exceptional properties of CNTs to polymer composites has been hampered by the difficulty in obtaining homogeneous dispersions of CNTs and the lack of compatibility between filler and matrices [4]. Of extreme importance is also the stability of the CNT dispersion in liquid systems, such as in the case of thermoset resins [5]. The preparation of long-term stable CNTs suspensions, i.e. master batches, would increase the attractiveness of CNTs to industrial applications.

Chemical functionalization of CNTs has been shown to aid in the dispersion and nanotube–matrix compatibility [6]. One approach for the non-covalent modification of CNTs is the use of block copolymers [7–9]. In this case, it is expected that CNTs will undergo less damage to their structure than in methods using strong acids. Furthermore, block copolymers can be added to the system during the dispersion of the CNTs which eliminates extra processing steps, as would be the case for acid treatments.

Polyurethane (PU) is an important class of polymer materials for a variety of applications in coatings, structural foams, and composites, due to their excellent abrasion resistance, toughness, low temperature flexibility, chemical and corrosion resistance, and a wide range of mechanical strength [10]. Polyurethanes are thermoset systems obtained from the reaction between polyisocyanates and polyols. Such systems are especially attractive because they offer flexibility in formulation, which enables the creation of materials with tailored end-use properties. PU resins are potential alternatives for use in composite materials for wind-blade applications. An understanding of the long-term performance of CNT reinforced PU composites under repeated mechanical loads will enable the potential of both PU and CNTs to be better realized for long term structural applications, such as wind turbine blades.

In the present study, we show that carbon nanotubes are a promising filler for reinforcement of PU systems. We observed increase in the toughness and fatigue life of PU composites prepared with low amounts of CNTs.

2. Experimental

2.1. Materials

The MWCNTs and PU system used in this study were supplied by Bayer MaterialScience. The Baytubes® C150P multiwall carbon

Abbreviations: CNT, carbon nanotube; PU, polyurethane; SEM, scanning electron microscope; TEB, tensile energy to break.

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nanotubes exhibit an average diameter of 13 nm and a length larger than 1 μm. The isocyanate is a polymeric MDI. The polyol component is a mixture of polyether polyols. A dispersing agent, B60H consisting of a polyvinyl butyral (Kuraray) was used to aid the dispersion of CNTs in the PU system. We have tested the potential of eight different dispersing agents for the dispersion of CNTs and their stabilization in the PU system following our recently reported method [5,11]. B60H turned out to be the most appropriate option. All the materials were used as received.

2.2. Experimental methods

PU composites have been prepared via different routes for mechanical characterization. For the preparation of the test samples, MWCNTs (0.3 wt.% in relation to polyol) and 1 × B60H were dispersed in polyol using a high shear Ross mixer. The suspension of MWCNTs was then degassed by applying vacuum until no bubbles were observed coming out of the system. Further, the suspension was mixed with the isocyanate for 3 min by stirring and the mixture was allowed to cure at room temperature overnight and finally post-cured at 90 °C for 6 h. Reference samples of neat resin and resin containing B60H were also prepared following the same route. The influence of the processing route on the tensile and fatigue properties of the composites has also been analyzed.

2.3. Characterization

The tensile properties of the composites were investigated according to 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 mm^3 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 employed frequency 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. Fracture surfaces of the composite samples were observed using a scanning electron microscope (SEM) (JEOL JSM-6510LV) with an operating voltage of 30 kV.

3. Results and discussion

3.1. Tensile properties of CNT/PU composites

Table 1 lists the tensile properties of the neat polyurethane and PU composites containing 0.1 and 0.3 wt.% CNTs with block copolymers. Samples prepared using B60H without CNTs were also prepared as reference. The tensile energy to break (TEB), i.e. the total energy absorbed per unit volume of specimen tested up to the point of rupture, was also measured. The TEB is indicative of material toughness [12].

Table 1
Tensile properties of neat polyurethane and PU based nanocomposites.

CNTs (wt.%)	B60H (wt.%)	E_t (GPa)	S_M (MPa)	ε_B (%)	TEB (MJ/m^3)
–	–	1.65 ± 0.13	70.29 ± 1.57	7.82 ± 1.14	3.41 ± 0.60
–	0.1	1.81 ± 0.054	69.54 ± 1.55	7.43 ± 0.82	3.26 ± 0.51
0.1	0.1	1.74 ± 0.075	70.90 ± 1.14	8.48 ± 0.51	3.83 ± 0.32
–	0.3	1.72 ± 0.085	71.60 ± 0.82	8.57 ± 1.00	4.04 ± 0.53
0.3	0.3	1.67 ± 0.11	74.03 ± 0.85	9.95 ± 1.76	4.70 ± 0.73

E_t:Young's modulus; S_M: Tensile strength; ε_B: Elongation at break.
TEB: tensile energy to break.

The addition of 0.1 wt.% CNTs with the aid of B60H resulted in composites with improved ductility and toughness. The best results are obtained with the addition of 0.3 wt.% of CNTs and 0.3 wt.% B60H where the TEB increases from 3.41 to 4.70 MJ/m^3 (an increase of 38%), which is most likely due to appropriate dispersion of the CNTs and improved interactions between filler and matrix. The overall enhancement in the tensile behavior of the composites prepared using 0.3 wt.% CNTs and B60H can be better observed in the representative stress–strain curves (Fig. 1).

3.2. Tension–tension fatigue properties of CNT/PU composites

In order to study the influence of CNTs on the fatigue life of PU systems, neat PU and CNT/PU composites were tested under four different peak loading levels: 30, 40, 45, and 50 MPa. Cyclic stress *vs*. lifetime (S–N) curves are shown in Fig. 2 and the data are listed in Table 2. The fatigue life data were fitted to the log-normal function $S_a = AN^B$, where S_a is the stress amplitude and N is the corresponding fatigue life. High coefficients of determination were obtained (R^2 = 0.90–0.94) for both systems. The fitting parameters used for the curves presented in Fig. 2 are A = 98.11 Mpa and B = −0.087 for the neat PU and A = 161.43 Mpa and B = −0.13 for the CNT/PU composites. It is noteworthy that these values for A and B are in agreement with reported values for CNT/thermoset composites [5,13,14].

Under identical loading conditions in the low-cycle, high-stress amplitude regime, composites have longer fatigue lives than those of the neat PU systems. This finding is quite surprising since CNTs are known to usually enhance the fatigue life of composites in the high-cycle, low-stress amplitude regime rather than in the low-cycle regime [13–15]. Testing at 50 MPa peak stress showed the median fatigue life of CNT composites increased by 248% over the neat PU. It has been demonstrated that CNTs can suppress failure in polymers via crack-bridging and a frictional pull-out mechanism [13]. Crack-bridging has been shown as the dominant mechanism for energy dissipation during crack propagation [16]. As the fillers are in nano-scale, the chance that a propagating crack encounters them is statistically higher than in composites with micro-sized fillers.

During the cyclic loading at low-stress levels, the CNT/matrix interface integrity is expected to be preserved and the load effectively transferred from the matrix to the CNTs. Damage propagation is slow and few widely spaced crack fronts generated can be slowed by CNTs bridging across nano-scale cracks and nanotube pull-out from the matrix. At high-applied stress levels the CNT/matrix interface could be damaged, reducing effectiveness of the load transfer. Damage propagation occurs at several fronts and at a rapid rate. Many reports have shown that under such conditions CNTs in the path of the damage are not very effective in slowing damage propagation [13,14,17,18]. Our results are conflicting with the aforementioned rational. In fact, our results show that CNTs can effectively suppress crack propagation generated under high-stress loading. We believe the enhancement of fatigue life at high-stress loads observed in this study can be explained in terms of an efficient CNT/matrix load transfer in the PU composites, suggesting little damage of the CNT/PU interface at high-stress amplitude. The reason why CNTs did not improve the fatigue life of the composites at high-cycle, low-stress amplitude regime is not clear at this time.

Noteworthy is the comparison between the tensile–tensile fatigue properties of the neat PU and CNT/PU composites with the properties of epoxy systems widely used in the wind-energy

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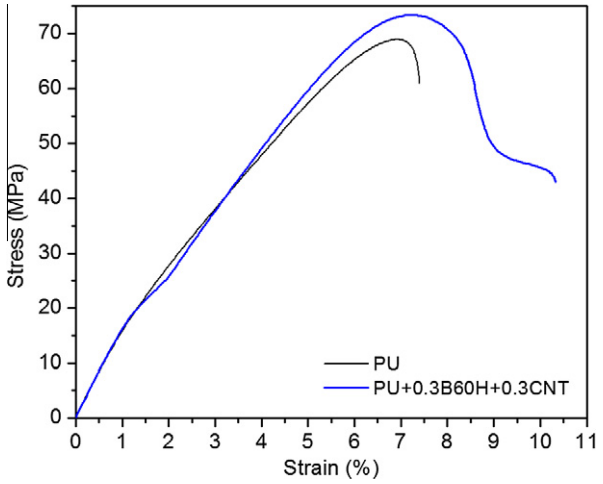

Fig. 1. Representative stress–strain curves for the neat polyurethane and the PU based composite containing 0.3 wt.% CNTs and 1x B60H.

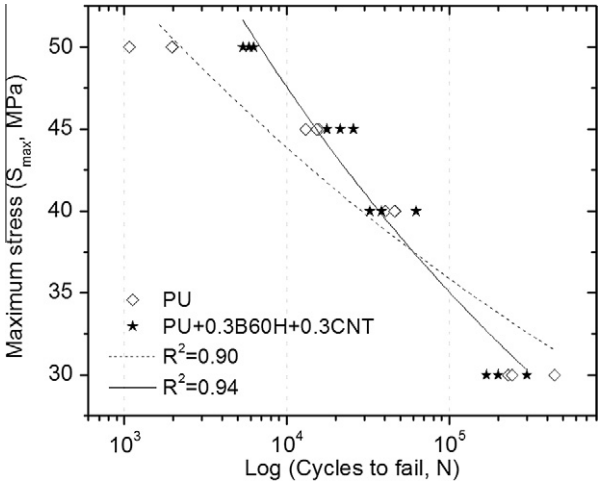

Fig. 2. S–N curves for the neat PU and PU/CNT composites.

Table 2
Fatigue loading and cycles to failure (N) of neat polyurethane and CNT/PU composites.

PU			PU + CNTs		
S_{max} (MPa)	N	Average N	S_{max} (MPa)	N	Average N
50	1986		50	5376	
50	1962		50	6245	
50	1075	1674 ± 520	50	5844	5822 ± 435
45	13,090		45	25,755	
45	15,726		45	17,676	
45	15,269	14,695 ± 1409	45	21,313	21,581 ± 4046
40	40,571		40	32,523	
40	46,393		40	38,337	
40	46,041	44,335 ± 3264	40	62,660	44,507 ± 15,988
30	230,395		30	299,916	
30	244,589		30	168,997	
30	443,401	306,128 ± 119,093	30	199,821	222,911 ± 68,446

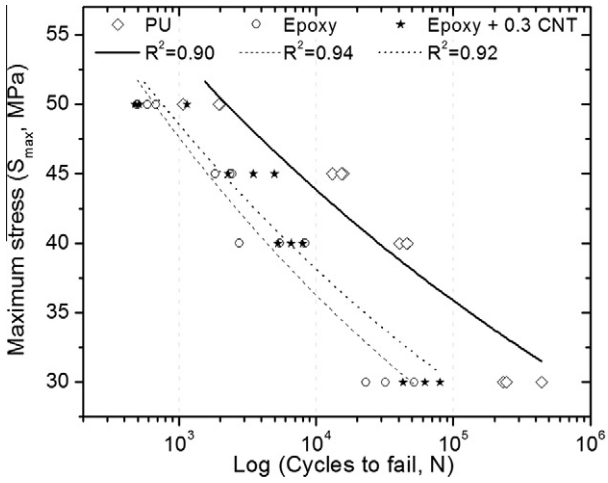

Fig. 3. Comparison between the S–N curves for the neat PU in tension–tension cyclic fatigue obtained in this study and the S–N curves for neat epoxy and epoxy reinforced with CNTs from Reference [13].

industries (Fig. 3). The data for the neat epoxy and CNT/epoxy composites used in the comparison were obtained in our previous work [13]. The comparison shows that the neat PU outperforms the neat epoxy, as well as the CNT/epoxy composites. This comparison emphasizes the significant potential of carbon nanotube reinforced PU systems for use in the next generation of wind turbine blades.

3.3. Morphology of CNT/PU composites

The fracture surfaces of the fatigue tested samples have been analyzed by SEM. The surface of the neat PU is presented in Fig. 4a while the fracture surfaces of the composites are shown in Fig. 4b-f. The neat PU (Fig. 4a) exhibits a relatively smooth fracture surface when compared to the CNT reinforced composites (Fig. 4b). The noticeable greater roughness of the fracture surface is indicative of the reinforcement effect of CNTs. The formation of such additional surfaces during fracture is evocative of crack deflection [13]. Fig. 4c shows the fracture of a composite cycled until fracture (6245 cycles) at a peak stress of 50 MPa. This image reveals a homogenous dispersion of the CNTs in the PU matrix. A magnification of this image (Fig. 4d) shows individual CNTs pulled out of the PU matrix, suggesting an energy absorbing mechanism responsible for the increase in the fatigue life. In Fig. 4e the fracture surface of a composite tested at a 30 MPa stress peak, with failure after 167,921 cycles is shown. Again highly dispersed CNTs are found. A magnification of this image clearly pinpoints to CNTs bridging the growing cracks (arrows in Fig. 4f). The quantitative fatigue results and the SEM images undoubtedly show that CNTs enhance the fatigue performance of PU systems. CNTs retard the fatigue failure by preventing the formation of large, catastrophic cracks due to the large number of interfaces provided by the CNTs [13,18]. CNTs can also bridge cracks and reduce the extent of plastic deformation experienced by the matrix whereas their pull-out 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 fatigue damage.

4. Conclusions

PU composites containing highly dispersed carbon nanotubes have been successfully prepared. Composites containing 0.3 wt.% MWCNTs and B60H showed an increase of up to 38% in tensile energy to break. The incorporation of CNTs increased the fatigue life of PU in the high-stress amplitude, low-cycle regime by up to 248%. Micrographs indicate the key mechanisms for enhancement in fatigue life such as CNT crack-bridging and pull-out. The effective enhancement in the properties of PU obtained in this study is attributed to successful dispersion of the CNTs and improved interaction between filler and matrix, which in turn, assures an efficient

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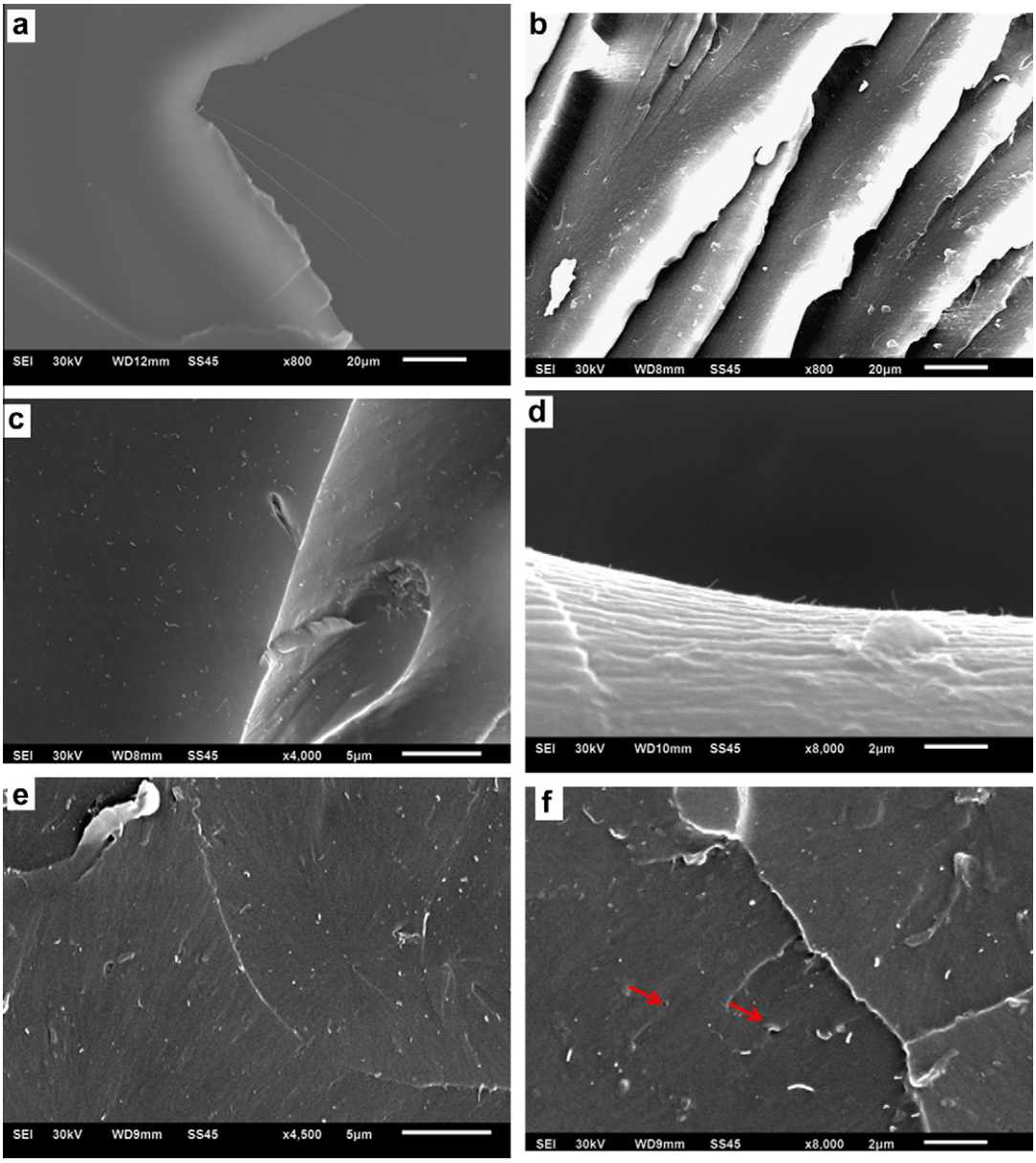

Fig. 4. Scanning electron micrographs of the fatigue fracture surface of the neat PU and composites: (a) neat PU, S_{max} = 50 MPa, N = 1962; (b–d) composite, S_{max} = 50 MPa, N = 6245; (e, f) Composite, S_{max} = 30 MPa, N = 167,921. The arrows in (f) pinpoints to individual CNTs bridging growing cracks.

load transfer from the CNTs to the PU matrix phase. The tensile-tensile fatigue properties obtained in this work show that PU systems can outperform epoxy systems widely used in structural applications. This emphasizes the huge potential of carbon nanotube reinforced polyurethane systems for use in the next generation of wind turbine blades.

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