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High-cycle Fatigue Life Extension of Glass Fiber/ Polymer Composites with Carbon Nanotubes

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Abstract: The present work shows that the addition of small volume fractions of multi-walled carbon nanotubes (CNTs) to the matrix results in a significant increase in the high-cycle fatigue life. It is proposed that carbon nanotubes tend to inhibit the formation of large cracks by nucleating nano-scale damage zones. In addition, the contribution to energy absorption from the fracture of nanotubes bridging across nano-scale cracks and from nanotube pull-out from the matrix are mechanisms that can improve the fatigue life. An energy-based model was proposed to estimate the additional strain energy absorbed in fatigue. The distributed nanotubes in the matrix appear to both distribute damage as well as inhibit damage propagation resulting in an overall improvement in the fatigue strength of glass fiber composites.

Key words: glass fiber; composites; carbon nanotubes; fatigue; strain energy

1 Introduction

Glass fiber composites have high strength and low cost, but suffer from poor performance in fatigue. The underlying mechanisms in high-cycle fatigue failure of glass fiber composites are primarily related to matrix-dominated damage accumulation and growth that coalesce and propagate to the fibers resulting in ultimate failure.

Prior fatigue studies of continuous and aligned glass fiber composites have shown that high-cycle fatigue life is dominated by fatigue cracking in the matrix that subsequently propagate and rupture the fibers. Once a significant number of fibers fracture, the composite laminate fails shortly thereafter. Unlike in high modulus carbon fiber composites, the low modulus of the glass fibers results in the imposition of high strains in the matrix leading to matrix fatigue failure[1-3]. In these studies, failure was defined as the number of cycles when a prescribed loss of stiffness is attained. A recent review of fatigue theories is given in the Ref.[4].

Stiffness reduction is an index of damage in composites and has been studied extensively both theoretically and experimentally. However, crack propagation and the resulting loss in stiffness is only a gross overall indicator of damage in composites. Damage can be generated well before microscopic-level crack initiation and microcrack coalescence occurs. Other studies have focused on measuring the fracture energies involved in crack propagation in composites, particularly in delamination fracture, a common failure mode[5]. Such studies show that a single crack that propagates in the matrix or fiber/matrix interface in a composite is associated with a low level of absorbed fracture energy.

In typical composite laminate configurations designed to carry structural loads under cyclic conditions, carbon fiber composites show little degradation with load cycling compared to glass composites. The explanation for the low degradation rates for carbon composites lies in the fact that the higher modulus of carbon fiber results in a low level of cyclic strain imposed on the matrix. A critical strain in the matrix corresponding to the fatigue strain of the matrix at the corresponding applied composite stress was identified as the critical parameter in fatigue failure of the composite[2]. In glass composites, the applied cyclic strain in the matrix exceeds the corresponding fatigue strain in the neat resin, while in higher modulus composites such as carbon fiber composites; the applied cyclic strain in the matrix is below this critical value. Thus carbon composites show little degradation with cycling and are accepted as having good fatigue strength. This explanation has been verified recently on oriented *rope* CNT-reinforced epoxy composites which have high modulus [6].

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Other studies on the effect of CNTs on the fracture of the matrix polymer have shown that small additions of CNTs (0.1wt%-0.2wt%) resulted in a 40% increase in the fracture toughness of the polymer[7]. Microscopy studies show a very high density of nano-scale cracks in the matrix that are attributed to the improvement in the fracture toughness of the matrix polymer.

In this work, the effect of carbon nanotubes on the life of structural composites subjected to static and cyclic loading is studied and a mechanism for the observed behavior is proposed. Damage mechanisms in conventional composite laminates consist of the formation of micro-cracks in the matrix that initiate and propagate under cyclic loading, eventually causing fiber failure and fracture of the composite. The addition of CNTs can be expected to decrease the scale of damage mechanisms by several orders of magnitude resulting in an increase in the absorption of strain energy through the creation of a multitude of fine nano-scale cracks. In addition, fiber bridging at the nanoscale increases energy absorption through the participation of nanotubes in the fracture process. This effect should increase the damage tolerance of the composite and make it more resistant to damage growth under cyclic loading. An energy-based model is proposed that attempts to describe the fatigue behavior of CNT / glass-fiber hybrid composites.

We have incorporated thermosetting (epoxy) polymers containing uniformly distributed nanofibers (CNTs) into conventional glass fiber polymer composites. Our recent studies have established that these resins exhibit a relatively uniform distribution of the nanofibers in the polymer with little agglomeration and clumping[8]. Hybrid composite systems that contain CNTs, both under static and cyclic loading, examined through scanning electron microscopy of the corresponding fracture surfaces exhibit failure modes that suggest the failure mechanism that is proposed here.

2 Experimental

2.1 Materials

The epoxy resin and hardener used was EPON 826 and Epikure 3234, respectively, both manufactured by Hexion Specialty Chemicals, Inc.(Houston, Texas, USA). The EPON 826 resin was blended with 1wt% of multi-walled carbon nanotubes by Nanoledge (Clapiers, France). The current CNT loading level of 1wt% was selected for its promise to be large enough to change the mechanical behavior of the composites[7, 9] and at the same time not reduce manufacturability due to an increase in polymer viscosity[10]. The woven glass fiber was obtained from Hexcel (Fullerton, CA USA) designated Type 7500, a 0.28 mm thick plain weave fabric.

2.2 Specimen processing

Both the CNT and non-CNT [0/90] fiber reinforced composites were manufactured by wet lay-up, cured in a heated platen press held at 80 ℃ and 580 kPa for one hour, with a fiber volume fraction of 0.56. Aligned 24× 200 mm tensile specimens were cut from the cured sheets. A 6.4 mm diameter center hole was drilled in each specimen to localize damage. Aluminum tabs were bonded to the ends of the specimens to facilitate gripping. The specimens were aged for 10 d at 25 ℃ before testing.

2.3 Test methods

Specimens were tested to failure using an MTS (Eden Prairie, Minnesota, USA) 100 kN servo-hydraulic testing machine retrofitted with a variable flow hydraulic supply digitally controlled by an Instron (Norwood, MA USA) Labtronic 8400 controller. National Instruments (Austin, TX USA) LabVIEW v7 was used to command the controller and perform data acquisition. Prior to fatigue testing, the monotonic tensile strengths of both CNT and non-CNT composite samples were obtained.

Both materials were tested in tension-tension fatigue at peak stresses of 70, 60, 45 and 30 percent of their monotonic strengths, all at a stress ratio (R) of 0.15. The loading frequency used was 3 Hz to eliminate sample heating. Representative failed specimens were chosen and their fracture surfaces were excised and sputter-coated with a 2.5 nm layer of platinum using a Bal-Tec (Balzers, Liechtenstein) Med 020 coater. The samples were imaged using a Hitachi (Tokyo, Japan) S-5000 cold field emission SEM with an accelerating voltage of 10 kV.

3 Results and Discussion

3.1 Tension testing

Fig.1 shows the stress-strain responses from monotonic tensile tests conducted on the neat resin with and without CNTs. No significant effect on the elastic modulus was observed. The maximum values of strain to failure, however, were somewhat higher in the CNT-containing resin samples with corresponding slightly lower ultimate tensile strengths when compared with the unmodified resin. These changes in mechanical behavior result in an increased toughness, or energy to fracture, for the neat resin containing CNTs. Figs.2 and 3 show scanning electron micrographs (SEMs) of the fracture surfaces of the two materials. The CNT-containing resin shows a somewhat

rougher fracture surface, which is in line with the increase in the fracture energy discussed above.

Fig.4 shows the monotonic tensile fracture surface in the neat resin containing CNTs. While there is generally uniform distribution of the CNTs in the resin, a few randomly distributed clumps of nanotubes (see insert in Fig.4) were also observed indicating that some agglomeration was present. These agglomerated regions are thought to be detrimental to strength as well as fatigue life[11].

Fig.5 shows the fracture surface of a hybrid CNT composite showing pull-out of the nanotubes from the matrix (small holes and larger protruding tubes in the figure). Smaller protruding sections of nanotubes seen in this micrograph may indicate that nanotubes were also fractured with the matrix. A single hole (white arrow) corresponds to a tube that was pulled out from this surface. It is this process of nanotube pullout and nanotube fracture that is believed to contribute to the increased fracture resistance as well as significantly improved fatigue life (see below) in the hybrid CNT composites.

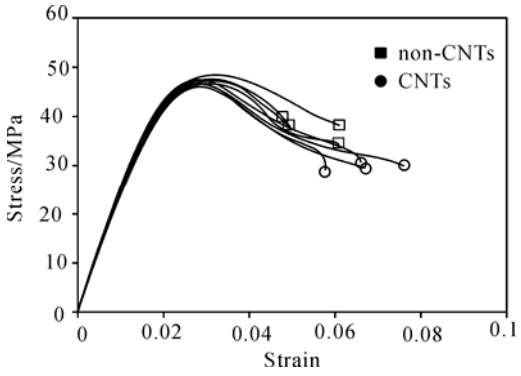

Fig.1 Tensile stress-strain responses of neat resin with and without 1wt% of CNTs

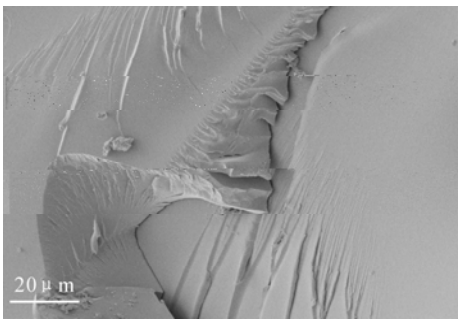

Fig.2 Fracture surface of neat epoxy matrix

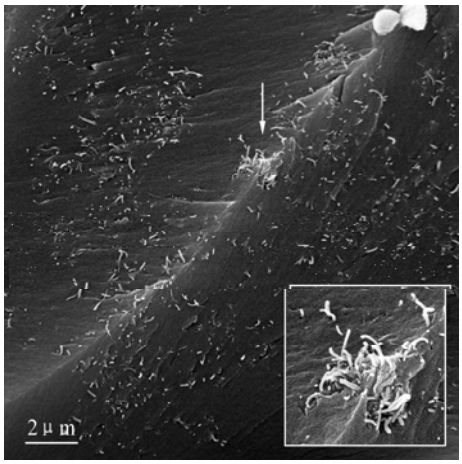

Fig.4 SEM image showing CNT distribution and an agglomerated region containing entangled carbon nanotubes

3.2 Fatigue life

Fatigue life data for glass fiber-epoxy composites (three samples per point) with and without the addition of 1wt% of carbon nanotubes are shown in Fig.6. A significant increase in the number of load cycles to failure for each loading case was observed for the samples that contained the CNTs. The observed increase in life occurs at lifetimes greater than about 104 cycles. In this high cycle regime, much of the load cycles are employed for the nucleation and growth of microcracks[1,2]. Table 1 compares the fatigue lifetimes for glass fiber composites with and without carbon nanotubes (CNTs). The improvement in fatigue life with the addition of CNTs increases as the applied cyclic stress is reduced, making the effect most pronounced at high cycles. At a cyclic stress of 44 MPa, the addition of 1wt% of CNTs results in almost a 3 times improvement in the fatigue life.

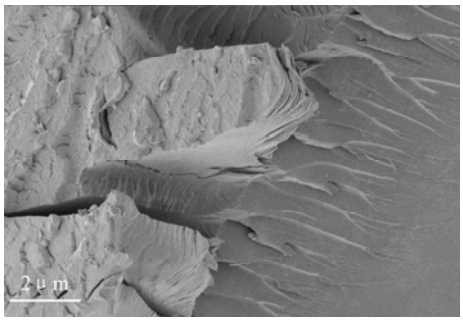

Fig.3 Fracture surface of the CNT-modified epoxy matrix

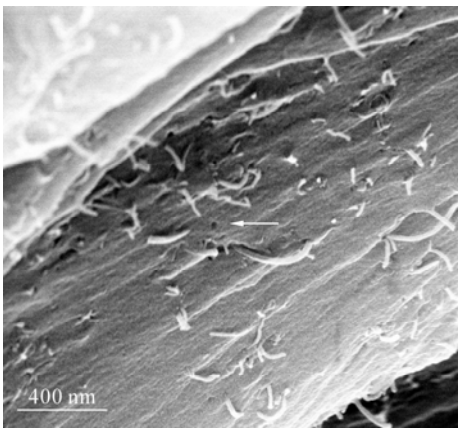

Fig.5 SEM image of fracture surface of glass fiber composite containing carbon nanotubes showing fractured and pulled-out CNTs; the arrow points at a hole from which a nanotube was pulled out

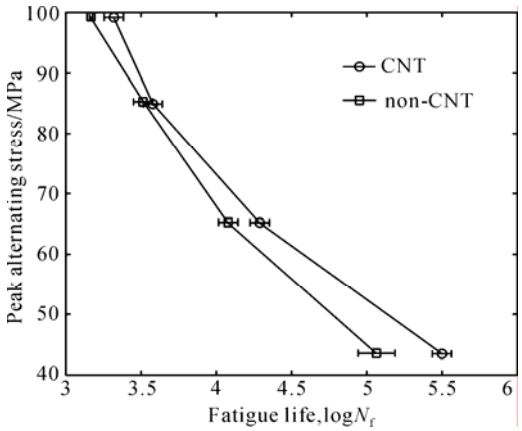

Fig.6 Applied cyclic stress versus the number of cycles to failure of glass fiber-epoxy laminates with and without the addition of 1wt% of carbon nanotubes

In the composites containing nanotubes, it is believed their presence results in a very large number of nucleating sites for cracks to be initiated and grow. Furthermore, it is believed for a given level of strain energy, a large density of nanoscale cracks will grow more slowly than the lower density of microcracks present in composites not containing CNTs. The result is an increase in the number of cycles required for growth and coalescence which means that high-cycle fatigue life is enhanced. In addition, nanoscale crack bridging by nanotubes will result in participation of the nanofibers in the fracture process thereby increasing the fracture energy required for crack propagation, further delaying failure.

3.2.1 Fracture surface analysis

High resolution scanning electron micrographs of the fracture surface of a glass fiber composite sample containing CNTs are shown in Fig.7. Both micrographs are from the same location; the micrograph on the right shows the scale of the carbon nanotubes relative to the fractured glass fiber on the left. Pull-out and fracture of carbon nanotubes were observed in the hybrid composite similar to the mechanisms observed in the neat resin/CNTs fracture surface (Fig.5). Additionally, Fig.7 demonstrates the ability of the CNTs to penetrate between glass fibers, further validating the proper dispersion of CNTs in the polymer [12].

3.3 Differential energy model

A study of the electron micrographs of the fracture surfaces indicates that the primary difference in the fracture behavior of the traditional glass-fiber composites and the behavior of the CNT/glass-fiber hybrid composites from a mechanistic standpoint is the existence of broken and pulled-out nanotubes at the fracture surfaces within the hybrid epoxy matrix. It is proposed that these nano-scale processes in the hybrid composites results in an absorption and dissipation of strain energy which retards the growth of matrix microcracks thereby extending the fatigue life.

Table 1 Comparison of fatigue lifetimes for glass fiber composites with and without carbon nanotubes (CNTs)

Cyclic stress amplitude/MPa	Fatigue life of glass fiber composites/cycles	Fatigue life of glass composites with the addition of carbon nanotubes/cycles	Improvement factor in life
98.0	1473	2091	1.4
85.0	3238	3813	1.2
65.0	11488	18517	1.6
44.0	109055	316227	2.9

*The improvement in fatigue life with the addition of CNTs increases as the applied cyclic stress is reduced, making the effect most pronounced at high cycles. At a cyclic stress of 44 MPa, the addition of 1wt% of CNTs results in almost a 3 times improvement in the fatigue life

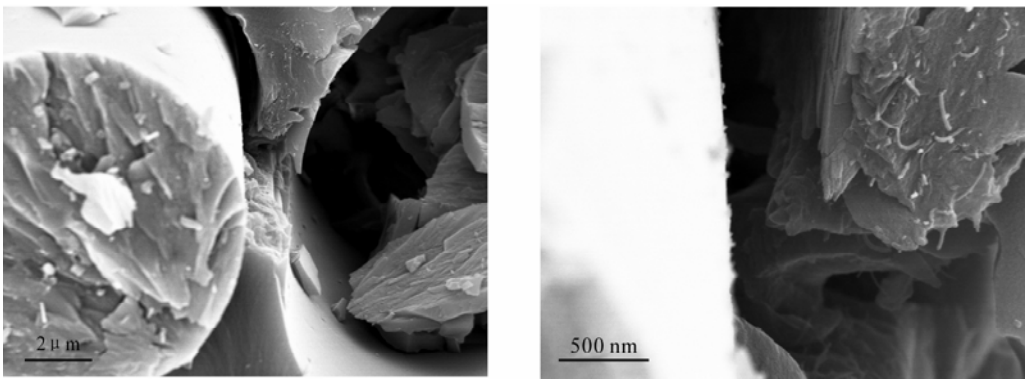

Fig.7 Fatigue fracture surface of glass fiber composite laminate containing 1wt% of carbon nanotubes in the matrix. The higher magnification micrograph on the right shows the carbon nanotubes in the matrix surrounding the fractured glass fiber shown at lower magnification on the left

In the proposed model, individual CNTs are assumed to be evenly distributed and randomly oriented in three dimensions within the epoxy matrix. This assumption facilitates the establishment of the micrometer-scale statistical representative volume element. The bond between the nanotubes and the surrounding epoxy matrix is assumed to consist exclusively of van der Waals forces[13-15]. Due to the lower transverse coefficient of thermal expansion (CTE) in the CNTs relative to the polymer matrix[16], the CTE mismatch following curing at an elevated temperature results in a compressive radial pre-stress on the nanotubes at room temperature. This gives rise to a frictional shear stress, τ_p that resists nanotube pull-out. It is also believed that a certain degree of interlocking between the CNTs and the matrix may contribute to τ_p[11]. Nanotubes are presumed to pull-out from the matrix unless they cross the fracture plane at a critical angle, φ, that causes the tubes to fracture instead of pull out. The angle at which the behavior transitions from pull-out to fracture, φ_c, is presumed to be related to the rate at which the two halves of the fracture surface are separated under cycling. This concept is presented in Fig.8.

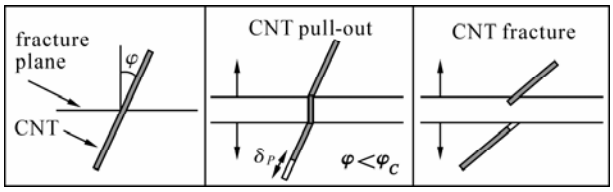

Fig.8 Observed behavior of individual CNTs at the fracture surface

3.3.1 Matrix fracture energy relation

General relations describing the potential energy losses in the elastic matrix of a composite are developed for both the traditional composite and the CNT hybrid composite following the methods used for fracture in reinforced ceramics by Budiansky, *et al*[17]. In the case of the traditional composite, these losses are due to the creation of matrix cracks. Similarly, in the hybrid composite, these losses go toward the creation of matrix cracks, frictional sliding at the CNT/matrix interface during CNT pull-out, and fracture of CNTs. The development of the energy relations for the two cases proceeds in parallel until the inclusion of the terms corresponding to the frictional sliding and fracture of CNTs. Throughout the derivation, symbols corresponding to the traditional composite case will be natural (X, Y), whereas those corresponding to the hybrid composite case will be accented ($\tilde{X}$, $\tilde{Y}$). Fig.9 presents the three states of interest in both cases.

State (0) corresponds to a free body of volume V and surface ST, not subjected to any external loads, and exhibiting no displacements or strains, containing some internal stress distribution σ_0. State (1) corresponds to the same body, with applied tractions T, which result in a stress distribution σ_1, displacements u_1, and corresponding strains ε_1. With no change in the surface

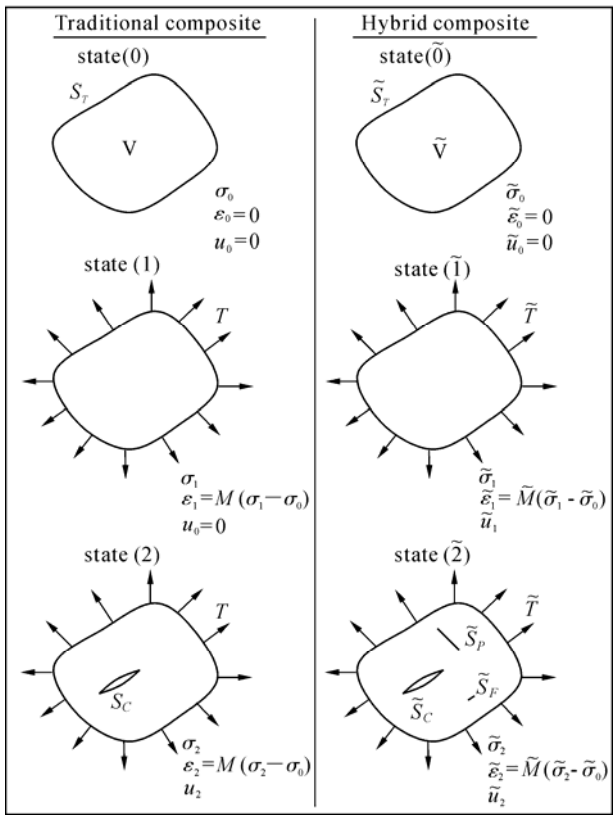

Fig.9 The three states of the body for traditional and hybrid composites

tractions T, state (2) has undergone some internal cracking resulting in crack surface SC, and new values of stress distribution σ_2, displacements u_2, and strains ε_2.

Similarly, for the case of the hybrid composite matrix, state (0̃) corresponds to a free body of volume $\tilde{V}$ and surface S̃T, not subjected to any external loads, exhibiting no displacements or strains, containing some internal stress distribution $\tilde{\sigma}_0$. State (1̃) corresponds to the same body, with applied tractions $\tilde{T}$, which result in a stress distribution $\tilde{\sigma}_1$, displacements $\tilde{u}_1$, and corresponding strains $\tilde{\varepsilon}_1$. With no change in the surface tractions $\tilde{T}$, state (2̃) has undergone some internal cracking resulting in new crack surface S̃C, frictional sliding due to pull-out at the new CNT / matrix interfacial surface S̃P, fracture of CNTs creating new CNT surface S̃F, and new values of stress distribution $\tilde{\sigma}_2$, displacements $\tilde{u}_2$, and strains $\tilde{\varepsilon}_2$.

The constitutive relations relating stress to strain in the two cases are

$$\varepsilon = M(\sigma - \sigma_0) \tag{1}$$

for the traditional glass-fiber composite and:

$$\tilde{\varepsilon} = \tilde{M}(\tilde{\sigma} - \tilde{\sigma}_0) \tag{2}$$

for the CNT/glass-fiber hybrid composite, where M and $\tilde{M}$ are the elastic compliances for the two cases.

For the case of the traditional composite, the potential energy in each of the three states respectively can be described as in [17] by:

$$\pi_0 = \frac{1}{2}\int_V \sigma_0 : M(\sigma_0)\mathrm{d}V \tag{3}$$

$$\pi_1 = \frac{1}{2}\int_V \sigma_1 : M(\sigma_1)\mathrm{d}V - \int_{S_T} T \cdot u_1 \mathrm{d}V \tag{4}$$

$$\pi_2 = \frac{1}{2}\int_V \sigma_2 : M(\sigma_2)\mathrm{d}V - \int_{S_T} T \cdot u_2 \mathrm{d}V \tag{5}$$

where, the volume integral describes the stored elastic energy and the surface integral describes the work done at the surface of the body by the applied tractions. Taking the compliance to be a constant,

$$\sigma_1 : M(\sigma_2) = \sigma_2 : M(\sigma_1)$$

The change in potential energy of the body due to the internal cracking is found to be:

$$\pi_1 - \pi_2 = \frac{1}{2}\int_V (\sigma_1 + \sigma_2) :$$

$$M(\sigma_1 - \sigma_2)\mathrm{d}V - \int_{S_T} T \cdot (u_1 - u_2)\mathrm{d}s \tag{6}$$

Equating the external virtual work of the traction T over the displacement $u_1 - u_2$ to the internal virtual work corresponding to the internal stress, σ_2 over the strain $M(\sigma_1 - \sigma_2)$, we have

$$\int_{S_T} T \cdot (u_1 - u_2)\mathrm{d}S = \int_V \sigma_2 : M(\sigma_1 - \sigma_2)\mathrm{d}V \tag{7}$$

Combining Eqs. (1), (6) and (7) gives us the general form for potential energy loss due to matrix cracking, from state (1) to state (2):

$$\pi_1 - \pi_2 = \frac{1}{2}\int_V (\sigma_1 - \sigma_2) : (\varepsilon_1 - \varepsilon_2)\mathrm{d}V \tag{8}$$

Derivation of the potential energy loss in the case of an elastic body containing frictional sliding and fiber breakage, in our case due to nanotube pull-out and the fracture of CNTs, proceeds much the same as before, up until the calculation of the virtual work. For completeness, the potential energy equation for the second case takes the exact form as its predecessor, Eq. (6), but with accented rather than natural notation:

$$\tilde{\pi}_1 - \tilde{\pi}_2 = \frac{1}{2}\int \tilde{V} (\tilde{\sigma}_1 + \tilde{\sigma}_2) :$$

$$\tilde{M}(\tilde{\sigma}_1 - \tilde{\sigma}_2)\mathrm{d}\tilde{V} - \int_{\tilde{S}_T} \tilde{T} \cdot (\tilde{u}_1 - \tilde{u}_2)\mathrm{d}\tilde{S} \tag{9}$$

The difference in the derivation of the energy relations in the hybrid matrix case is the two additional internal virtual work terms corresponding to the frictional sliding and fiber breakage. The frictional sliding term takes the form

$$\int_{\tilde{S}_P} \tau_P \cdot \delta_P \mathrm{d}\tilde{S} \tag{10}$$

where, τ_P is the shear traction applied by the polymer matrix on the nanotube as it slides a distance δ during the pull-out process. Noting that the nature of a frictional shear traction implies that the traction will always be operating in the direction opposite the sliding, we can remove the dot product, simplifying Eq. (10) to

$$-\tau_P \int_{\tilde{S}_P} \delta \mathrm{d}\tilde{S} \tag{11}$$

The fiber breakage internal virtual work term takes the form

$$-\int_{\tilde{S}_F} \int_{l_0}^{\infty} \psi(l)\mathrm{d}l\mathrm{d}\tilde{S} \tag{12}$$

where, $\psi(l)$ is defined here as the cohesive traction corresponding to the inter-atomic forces binding two halves of a nanotube together per unit nanotube cross-sectional area, l is the distance between the two halves, and l_0 is the equilibrium carbon-carbon bond length. Rewriting Eq.(7) with accented notation and adding the terms found in Eqs. (11) and (12) gives the new virtual work equation for the hybrid composite

$$\int_{\tilde{S}_T} \tilde{T} \cdot (\tilde{u}_1 - \tilde{u}_2)\mathrm{d}\tilde{S} = \int_{\tilde{V}} \tilde{\sigma}_2 : \tilde{M}(\tilde{\sigma}_1 - \tilde{\sigma}_2)\mathrm{d}V - \tau_P \int_{\tilde{S}_P} \delta d\tilde{S} -$$

$$\int_{\tilde{S}_F} \int_{l_0}^{\infty} \psi(l)\mathrm{d}l\mathrm{d}\tilde{S} \tag{13}$$

Combining Eqs. (2), (9) and (13) gives the final form for potential energy loss in an elastic body due to matrix cracking, frictional sliding and fracture of nanotubes

$$\pi_1 - \pi_2 = \frac{1}{2}\int_{\tilde{V}} (\tilde{\sigma}_1 - \tilde{\sigma}_2) : (\tilde{\varepsilon}_1 - \tilde{\varepsilon}_2)\mathrm{d}\tilde{V} +$$

$$\tau_P \int_{\tilde{S}_P} \delta \mathrm{d}\tilde{S} + \int_{\tilde{S}_F} \int_{l_0}^{\infty} \psi(l)\mathrm{d}l\mathrm{d}\tilde{S} \tag{14}$$

The next section will take these two potential energy Eqs. (8) and (14), and make a direct comparison across the two materials they are based on to create the differential energy model capable of predicting the change in potential energy loss that is expected when one moves from a traditional glass-fiber composite to a CNT/glass-fiber hybrid composite of otherwise identical makeup operating under similar conditions.

3.3.2 Comparison of energy relation

In this section, a direct comparison is made of the two potential energy loss equations previously developed, or more specifically, the potential energy difference between state (2) and state ($\tilde{2}$). While the two relations, represented by Eq.(8) in the case of the traditional composite, and Eq.(14) in the case of the hybrid composite, have a similar form, they are derived for two different materials and as such, steps need to be taken before a direct comparison is valid. This crucial necessary step is to recognize that while the two materials are in fact different, the outward, macro-scale elastic mechanical behavior of the two materials is argued here to be equivalent. Returning to Fig.2, we can see that the difference in the elastic modulus and the yield strength of the CNT and non-CNT epoxy samples, corresponding to the polymers used in the subsequent composites, is small. The change in strain-to-failure observed in the CNT-epoxy system is not relevant in this context since the polymer matrix experiences low strains as a component in the composite. In light of this established symmetry in material properties,

$$M = \tilde{M} \tag{15}$$

recognizing that state (1) and state ($\tilde{1}$) are energetically equivalent, namely that $\pi_1 = \tilde{\pi}_1$, setting the external tractions T and $\tilde{T}$ and the associated internal stresses to be

equal, and making use of Eq. (15), we find the difference between Eqs. (14) and (8) to be:

$$\pi_2 - \tilde{\pi}_2 = \tau_P \int_{\tilde{S}p} \delta_P \mathrm{d}\tilde{S} + \int_{\tilde{S}_F} \int_{l_0}^{\infty} \psi(l) \mathrm{d}l \mathrm{d}\tilde{S} \qquad (16)$$

Eq.(16) represents the difference in lost potential energy between the two bodies required to reach the damaged states (2) and ($\tilde{2}$). More simply put, the right hand side of Eq.(16) represents the amount of strain energy that is absorbed by the two damage processes unique to the hybrid composite, during the formation of a unit area of matrix cracks. It is this absorption of strain energy in a way that does not promote the growth and coalescence of matrix microcracks that has been proposed here as the means by which the hybrid composites are able to significantly outperform traditional composites in fatigue applications.

5 Conclusion

The addition of 1wt% of CNTs to the polymer matrix of glass fiber-epoxy composite laminates improved their high-cycle fatigue lifetimes significantly.

Tensile tests on neat resin (without glass fibers) specimens showed no effect on the elastic modulus when CNTs were added. However, ther