J Mater Sci (2008) 43:4487–4492
DOI 10.1007/s10853-008-2651-9

High-cycle fatigue of hybrid carbon nanotube/glass fiber/polymer composites

Christopher S. Grimmer · C. K. H. Dharan

Received: 23 December 2007 / Accepted: 11 April 2008 / Published online: 29 April 2008

Abstract Glass fiber polymer composites have high strength, low cost, but suffer from poor performance in fatigue. Mechanisms for high-cycle (>10^4 cycles) fatigue failure in glass fiber composites consist primarily of matrix-dominated damage accumulation and growth that coalesce and propagate into the fibers resulting in ultimate fatigue failure. This investigation shows that the addition of small volume fractions of multi-walled carbon nanotubes (CNTs) in the matrix results in a significant increase in the high-cycle fatigue life. Cyclic hysteresis measured over each cycle in real time during testing is used as a sensitive indicator of fatigue damage. We show that hysteresis growth with cycling is suppressed when CNTs are present with resulting longer cyclic life. Incorporating CNTs into the matrix tends to inhibit the formation of large cracks since a large density of nucleation sites are provided by the CNTs. In addition, the increase in energy absorption from the fracture of nanotubes bridging across nanoscale cracks and nanotube pull-out from the matrix is thought to contribute to the higher fatigue life of glass composites containing CNTs. High-resolution scanning electron microscopy suggests possible mechanisms for energy absorption including nanotube pull-out and fracture. The distributed nanotubes in the matrix appear to inhibit damage propagation resulting in overall improved fatigue strength and durability.

Introduction

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 since the fibers are the primary load-bearing elements. 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 [4].

Stiffness reduction is now a conventional 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 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,

C. S. Grimmer · C. K. H. Dharan (✉)
Department of Mechanical Engineering, University of California, Mail Code 1740, Berkeley, CA 94720-1740, USA
e-mail: dharan@me.berkeley.edu

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]. The fatigue strength did not change with cycling in a manner similar to conventional carbon fiber composites.

Other studies on the effect of CNTs on the fracture of the matrix polymer have shown that small additions of CNTs (0.1–0.2 wt.%) 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.

There have been no studies on the effect of CNTs on composite strength when subjected to cyclic loading. While the effect on modulus has been shown to be small due to the low volume fraction of the CNT content (0.1–1% range) [8], the presence of CNTs can be significant in restricting damage.

In this work, we investigate the effect of CNTs on the life of structural composites subjected to static and cyclic loading. 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 nano-scale 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.

We have incorporated thermosetting (epoxy) polymers containing uniformly distributed nanofibers (CNTs) into conventional glass fiber polymer (epoxy) composites. Our studies have established that these resins exhibit a relatively uniform distribution of the nanofibers in the polymer with little agglomeration and clumping. This is important for processing our proposed nanofiber-modified composites. The fracture surfaces of the composites and the neat polymer matrix were examined using high-resolution scanning electron microscopy.

Materials, processing, and experimental methods

Materials

The epoxy resin and hardener used in this study was EPON 826 and Epikure 3234, respectively, both manufactured by Hexion Specialty Chemicals, Inc. (Houston, TX, USA). The EPON 826 resin was blended with 1% by weight of multi-walled CNTs by Nanoledge (Clapiers, France). The 1% CNT loading level was selected since it was shown to improve the mechanical behavior of composites in prior work [7, 8]. Higher loadings result in an excessive increase in the viscosity of the polymer making it difficult to impregnate the fibers [9]. The glass fiber woven reinforcement was obtained from Hexcel (Fullerton, CA, USA) designated Type 7500, a 0.28-mm thick plain weave fabric.

Specimen processing

Both the CNT and non-CNT [0/90] fiber-reinforced composites were manufactured by wet lay-up. Eight plies of glass fiber fabric (woven with continuous fibers) were wet with the catalyzed and degassed resin. The residual resin was removed, and the epoxy cured in a heated platen press held at 80 °C and at a pressure of 580 kPa for 1 h. The resin content of the cured laminates was measured and determined to be 44% (resin-to-fiber ratio of 44:56).

24 × 200 mm tensile specimens were cut from the cured sheets using a diamond blade wet saw. In all specimens, the warp direction of the fabric was oriented along the loading direction. A 6.4-mm diameter hole was drilled in the center of each specimen to create a stress concentration to localize damage. Aluminum tabs were bonded to the ends of the specimens to facilitate gripping. The specimens were aged for 10 days at 25 °C before testing.

Experimental methods

Specimens were tested to failure using an MTS (Eden Prairie, MN, 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. The Instron controller was connected to a computer via the GPIB bus. A custom program was developed and run using National Instruments (Austin, TX, USA) LabVIEW v7 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% 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.

Results and discussion

Tension testing

Figure 1 shows the stress–strain responses from monotonic tensile tests conducted on the neat resin with and without CNTs. No significant effect was seen in the addition of CNTs on the elastic modulus. This is to be expected since the fraction of CNTs in the resin is only 1% by weight. 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 strain energy-to-fracture in the resin samples containing CNTs. Figures 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 a corroboration of the observed increase in fracture energy.

Figure 4 shows the monotonic tensile fracture surface in the neat resin containing CNTs. While there is generally

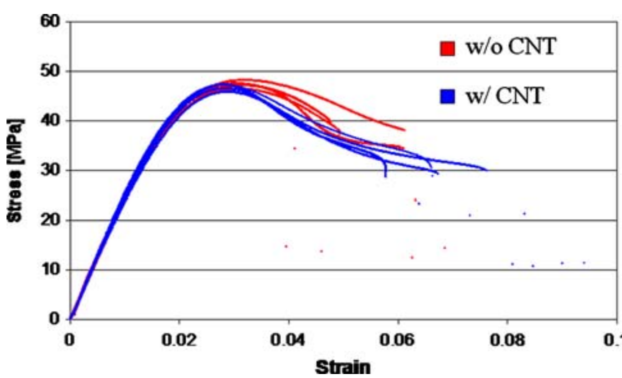

Fig. 1 Tensile stress–strain responses of the neat resin with and without 1% (by weight) of CNTs

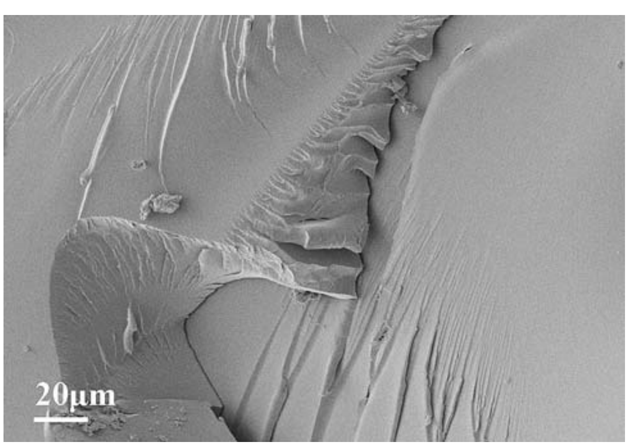

Fig. 2 Fracture surface of neat epoxy matrix

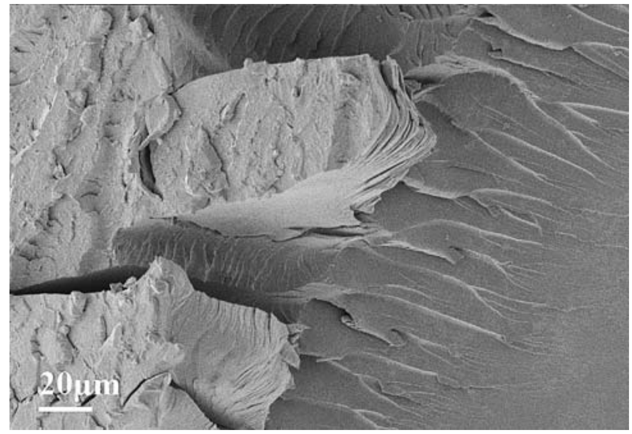

Fig. 3 Fracture surface of the CNT-modified epoxy matrix

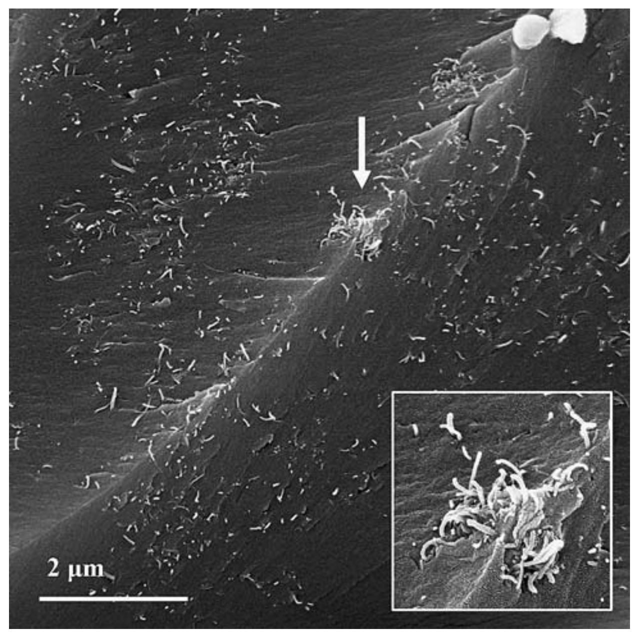

Fig. 4 Scanning electron micrograph showing CNT distribution and an agglomerated region containing entangled CNTs

uniform distribution of the CNTs in the resin, a few randomly distributed clumps of nanotubes (see inset in Fig. 4) was also observed indicating that some agglomeration was present. These agglomerated regions are thought to be detrimental to strength as well as fatigue life [10].

Figure 5 shows a high magnification view of the fracture surface of a CNT composite specimen that failed in a monotonic tensile test showing pull-out of the nanotubes from the matrix (small holes and protruding carbon nanotubes 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

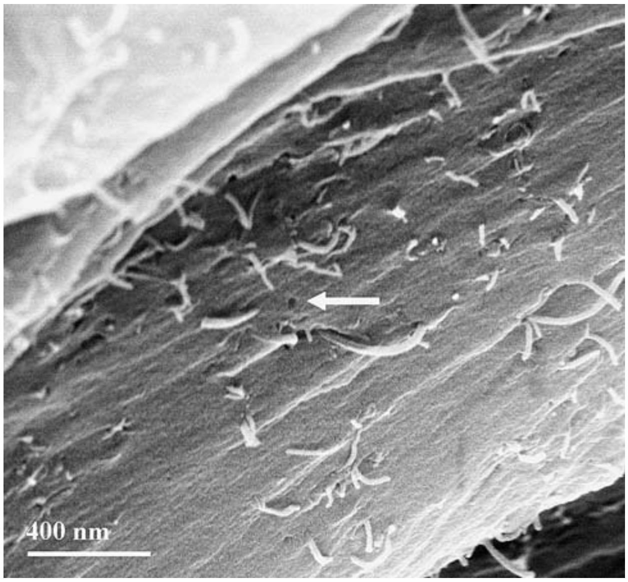

Fig. 5 Scanning electron micrograph of fracture surface of glass fiber composite containing CNTs showing fractured and pulled-out CNTs; the arrow points at a hole from which a nanotube was pulled out

that is believed to contribute to the increased fracture resistance as well as significantly improved fatigue life (see below) of the CNT composites.

Fatigue behavior

Fatigue life

Fatigue life data for glass fiber-epoxy composites (three specimens per point) with and without the addition of 1% by weight 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 CNT-blended resin. The observed increase in life occurs at lifetimes greater than about 10^4 cycles. In this high-cycle regime (or lower stress levels), the effect of CNTs is even more pronounced in improving life. At the lowest stress levels tested, the CNT-modified composite samples showed fatigue lives that were more than 2.5 times that of the unmodified composites. These are significant improvements in the high-cycle fatigue life of glass fiber polymer composites, and represent an opportunity to utilize glass composites in high-cycle fatigue applications by adding small fractions of CNTs to the matrix resin.

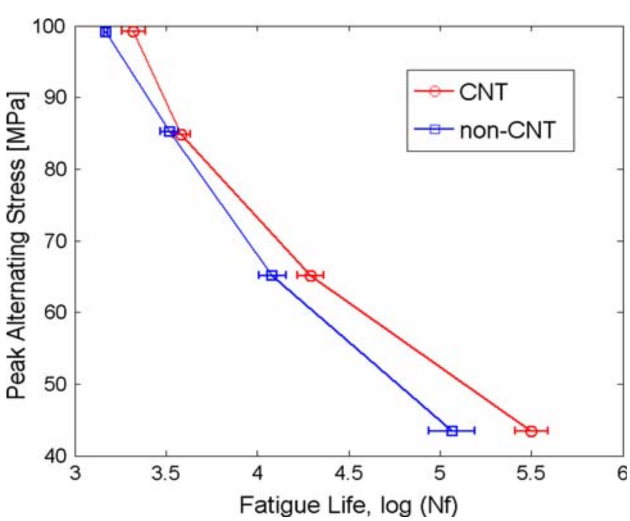

Fig. 6 Applied cyclic stress versus the number of cycles to failure of glass fiber-epoxy laminates with and without the addition of 1% by weight of CNTs

The larger effect that the addition of CNTs has on fatigue life at low cyclic stress levels may be explained by first considering the observed failure mechanisms in glass fiber composites subjected to cyclic loading. Dharan showed that the fatigue life of glass fiber composites is related to the nucleation and growth of damage in the polymer matrix, and that damage in the matrix was found to be an accurate measure of the fatigue strength of the composite [1]. At high cyclic stress amplitudes, significant and extensive matrix damage is created in a few cycles. With continued cycling, damage in the form of relatively closely spaced cracks, propagates rapidly on several fronts until failure results. At low stress levels, damage in the matrix is limited; with continued cycling, a few cracks widely spaced propagate slowly until eventually, failure occurs.

Corroborating evidence of these mechanisms has been presented by other investigators who studied the fatigue response of both short and continuous glass fiber polymer composites [11–13]. For example, in the fatigue of sheet-molding compound, a randomly oriented short fiber polymer composite, high crack densities were observed at high cyclic stresses, while much fewer cracks, which propagated slowly, were seen at low cyclic stress levels [11]. Short fiber composites, such as sheet-molding compound, may be considered to be analogous to dispersed CNTs in the polymer matrix, albeit at much higher fiber volume fractions.

The relative effectiveness of CNTs at low cyclic stress levels relative to high stress levels can be explained by strain energy considerations and the fatigue failure mechanisms described above. At high stress levels, the applied strain energy density is high and damage propagation occurs at several fronts and at a rapid rate. Under such conditions, obstacles, such as inclusions or, in this case, CNTs , in the path of the damage are not very effective in slowing damage propagation, since the high stress intensities at the crack tips can overcome these obstacles in a few cycles. At low stress levels, however, damage propagation is slower and at a few widely spaced crack fronts, these can be slowed relatively effectively since a larger fraction of the strain energy must be dissipated in overcoming the obstacles. Thus, at low cyclic stress levels, the addition of CNTs is more likely to be effective in improving fatigue life than at high cyclic stress levels.

In addition, in composites containing nanotubes, our hypothesis is that their presence also results in a very large number of nucleating sites for cracks to initiate and grow. For a given level of strain energy (a given cyclic load amplitude), a larger density of nanoscale cracks will grow more slowly than the lower density of larger microcracks present in composites not containing CNTs. The result is an increase in the number of cycles required for initiation, growth, and coalescence which means that high-cycle fatigue life is enhanced. In addition, crack bridging will result in participation of the nanotubes in the fracture process, thereby increasing the fracture energy required for crack propagation, which will also result in higher fatigue lifetimes. However, as discussed above, the effect is more pronounced at lower cyclic stress levels and high cycles.

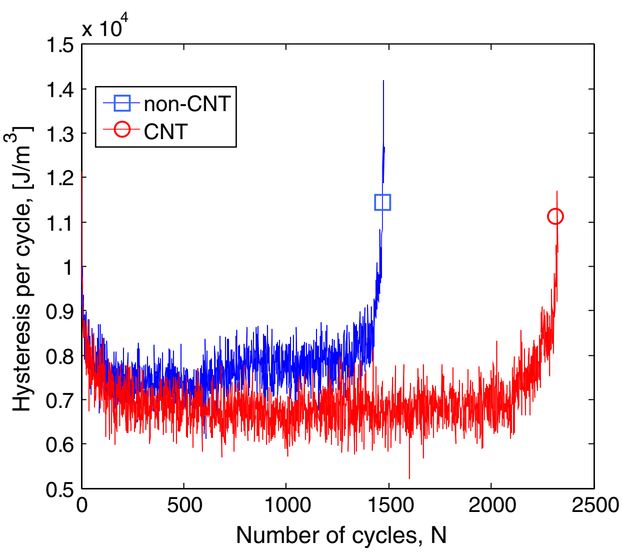

Fig. 7 Hysteresis per cycle as a function of number of applied cycles for representative CNT and non-CNT glass fiber-epoxy composites

Hysteresis

Hysteresis per cycle has recently been shown to be a low-cycle predictor of overall fatigue life in composites [14]. Figure 7 shows hysteresis data on a per-cycle basis for two representative samples that were fatigued at 70% of their monotonic strengths. This data shows that, after an initial phase of decreasing hysteresis per cycle, the hysteresis level is relatively stable until it increases rapidly as failure approaches. The composite not containing CNTs showed an overall hysteresis level that was higher than the composite with CNTs. Failure occurred significantly earlier in the composite without CNTs relative to the CNT-modified material at numbers of cycles-to-failure of 1450 cycles and 2300 cycles, respectively. This represents an improvement in life by almost 60% with only 1% by weight of CNTs incorporated into the matrix.

Fracture surface analysis

High-resolution scanning electron micrographs of the fracture surface of a glass fiber composite sample containing CNTs are shown in Fig. 8. Both micrographs are from the same location; the micrograph on the right shows the scale of the CNTs relative to the fractured glass fiber on the left. Pull-out and fracture of CNTs were observed in the composite similar to the mechanisms observed in the neat resin/CNTs fracture surface (Fig. 5). The presence of CNTs between glass fibers as shown in Fig. 8 demonstrates that dispersion of CNTs is adequate [15].

Summary

The addition of 1% by weight of CNTs to the polymer matrix of glass fiber-epoxy composite laminates improved their high-cycle fatigue strength by 60–250%, depending

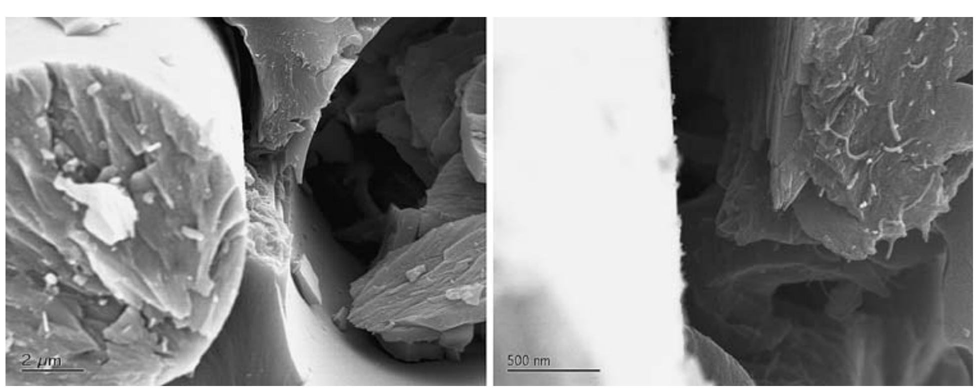

Fig. 8 Fatigue fracture surface of glass fiber composite laminate containing 1% by weight of CNTs in the matrix. The higher magnification micrograph on the right shows the CNTs in the matrix surrounding the fractured glass fiber shown at lower magnification on the left

on the loading condition. In addition, real-time monitoring of the hysteresis per cycle during loading showed that the overall hysteresis level was lower than unmodified glass fiber composites.

Tensile tests on neat resin (without glass fibers) specimens showed no effect on the elastic modulus when CNTs were added. However, there was a slight increase in the strain-to-failure and corresponding higher toughness relative to the unmodified resin. High-resolution scanning electron microscopy of the neat resin specimens after tensile fracture revealed somewhat higher surface roughness in the CNT-modified resin.

Inspection of the composite specimens tested in fatigue showed CNTs that were either pulled out of the resin matrix or fractured, suggesting energy-absorbing mechanisms that may be responsible for the increase in the fatigue life observed. These include the creation of a much larger density of nucleation sites for fatigue crack initiation in the epoxy matrix as well as possible crack bridging by the CNTs. Both mechanisms can result in a significant increase in crack energy absorption during fatigue crack initiation, coalescence, and propagation, resulting in the observed increase in the fatigue life when CNTs are added.

This study shows that the addition of small fractions of CNTs to glass fiber composites can result in a significant increase in their fatigue life, making glass fiber composites more useful in applications involving high-cycle fatigue.

Acknowledgement This work was supported in part by a grant from Entropy Research Laboratories, San Francisco, California, USA.

References

1. Dharan CKH (1975) ASTM Spec Tech Publ 569:171
2. Dharan CKH (1975) J Mater Sci 10:1655. doi:10.1007/BF00554927
3. Hahn HT, Kim RY (1976) J Compos Mater 10:156. doi:10.1177/002199837601000205
4. Degrieck J, Van Paepegem W (2001) Appl Mech Rev 54(4):279. doi:10.1115/1.1381395
5. Saghizadeh H, Dharan CKH (1986) J Eng Mater Technol: Trans ASME 108(4):290
6. Ren Y, Li F, Cheng HM, Liao K (2003) Adv Compos Lett 12(1):19
7. Ganguli S, Aglan H (2006) J Reinforc Plast Compos 25(2):175. doi:10.1177/0731684405056425
8. Gojny FH, Wichmann MHG, Fiedler B, Bauhofer W, Schulte K (2005) Composites A 36:1525. doi:10.1016/j.compositesa.2005.02.007
9. Kim JA, Seong DG, Kang TJ, Youn JR (2006) Carbon 44:1898. doi:10.1016/j.carbon.2006.02.026
10. Wong M, Paramsothy M, Xu XJ, Ren Y, Li S, Liao K (2003) Polymer 44(25):7757. doi:10.1016/j.polymer.2003.10.011
11. Wang SS, Chim ES-M (1983) J Compos Mater 17:114. doi:10.1177/002199838301700203
12. Stinchcomb WW, Reifsnider KL (1979) ASTM Spec Tech Publ 675:782
13. Owen MJ, Howe RJ (1972) J Phys D App Phys 5(9):1637
14. Dharan CKH, Tan TF (2007) J Mater Sci 42(6):2204. doi:10.1007/s10853-007-1498-9
15. Fan Z, Hsiao KT, Advani SG (2004) Carbon 42:871. doi:10.1016/j.carbon.2004.01.067