

Unusual fracture surface morphology of fatigued carbon nanofiber/poly(ether ether ketone) composites

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ABSTRACT

Carbon nanofiber/poly(ether ether ketone) composites were prepared in the laboratory via a solvent-based method at 260 °C using benzophenone. After fatigue testing, examination of the fracture surface shows unusual surface morphologies around the nanofibers that appear to be caused by the cyclic testing.

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Fatigue failure is a universal engineering concern and is a common mode of failure for many systems. Materials are constantly tested for their fatigue properties if they are to be used in applications where they could encounter cyclic loading and unloading. While there has been considerable interest in exploiting the mechanical reinforcement of various nanomaterials for enhanced polymer composite mechanical performance [1], only recently have researchers started to study the fatigue performance of these materials. Published results for carbon nanotube polymer composites, and more recently, graphene composites, have shown significantly improved fatigue behavior in comparison to the unfilled matrix material [2–6]. In at least some cases this is attributed to pull-out of nanotube fibers that bridge the crack interface or reinforcement of the fibrils of the craze ahead of the crack tip. Nonetheless, the observation of enhanced fatigue performance of polymer/nanofiller composites could broaden the types of applications for which these materials could be used.

Samples of poly(ether ether ketone) (PEEK) and 1 wt.% carbon nanofibers (CNF) were fabricated in the laboratory with a unique solvent-based method where benzophenone was used as an elevated temperature solvent. The CNFs used were supplied by Pyrograf Products (PR-19XT-PS-AM) with a nominal diameter of 150 nm and tens of microns in length. The PEEK powder was supplied by Solvay Advanced Polymers (KT-820FP). Briefly summarizing the composite fabrication process reported elsewhere [7], the CNFs were first dispersed in the benzophenone solvent with Triton X-100 surfactant at 50 °C using a Misonix XL2020 ultrasonic processor. The suspension was then combined with the PEEK powder, heated

under stirring to 260 °C for 20 min, and then cooled to 180 °C, at which point the composite began to solidify into crumbs. The crumbs were dried for 48 h under vacuum at 190 °C to remove the solvent. The solvent content after drying was found to be always less than 0.4% by weight as measured via thermogravimetric analysis (TGA). The resulting material was compression molded into square pieces at 380 °C under 1000 psi of pressure for 5 min and then machined into compact tension fatigue specimens. The specimens were fatigued in tension in the Paris Law regime [8], $da/dN = C(\Delta K)^m$ (where a is crack length, N is number of load cycles, C and m are material constants and ΔK is the range of the stress intensity factor) at 3 Hz with a stress ratio of $R = 0.1$ (where R is the ratio of the minimum applied stress to the maximum applied stress) and a decreasing ΔK , from $\Delta K = 4$ to $\Delta K = 1$ during each fatigue test.

Fig. 1 shows the deformation cones observed surrounding the carbon nanofibers on the fatigued composite fracture surface. These features were observed at various locations on the fatigued surface. We believe that these unusual deformation cones surrounding the nanofibers were caused by the cyclic loading encountered during the fatigue testing at 3 Hz. To the best of our knowledge, these features in CNF composites have not been reported before in the literature. The oscillation at the advancing crack tip may have caused the nanofibers that were oriented in certain directions and bridging the crack tip to undergo a cyclic semi-circular motion (corresponding to the macroscale applied cyclic loading) and remove polymer in its surrounding area. This could have been aided by a poor interface between the polymer and nanofiber. The stiffer

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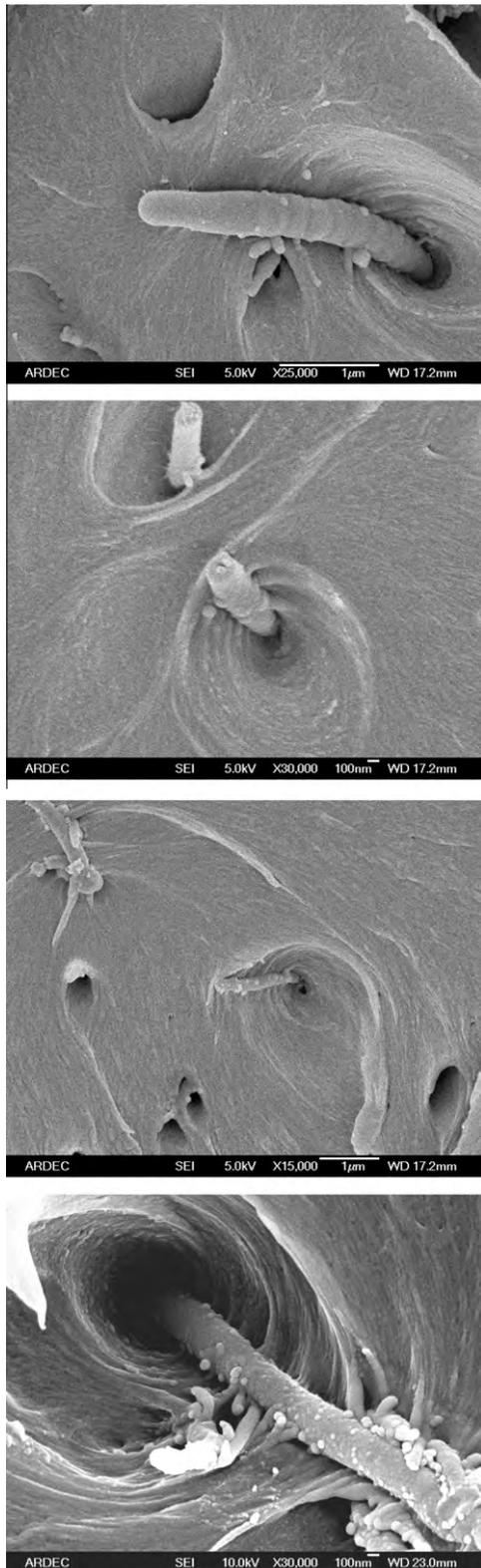


Fig. 1 – Carbon nanofibers protruding from the fatigued surface surrounded by deformation cones. Images were taken from various locations on a fracture surface after a fatigue test from a ΔK of 4 to 1. At a high ΔK , there were approximately 2000 cycles/0.25 mm of crack growth and at the low ΔK there was approximately 8000 cycles/0.25 mm of crack growth.

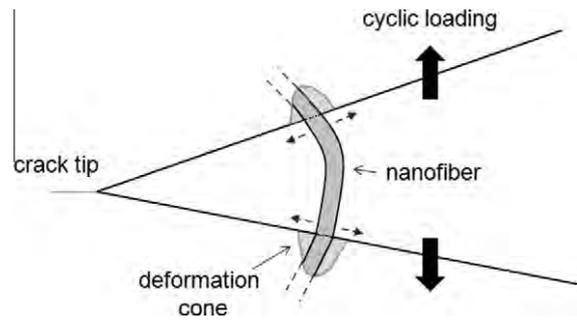


Fig. 2 – Schematic of proposed mechanism for formation of deformation cone around nanofiber during fatigue.

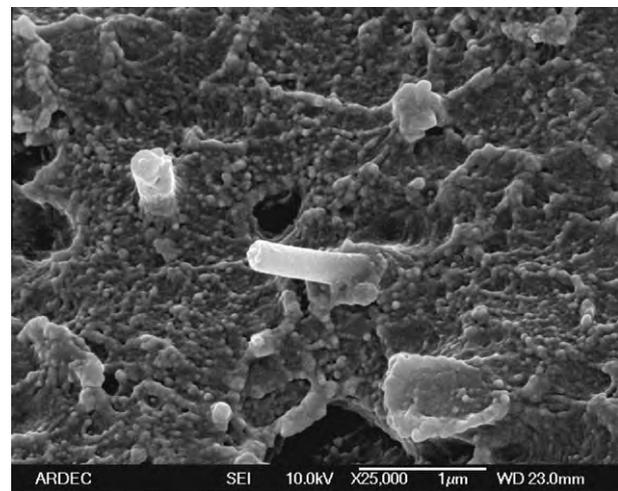


Fig. 3 – Cryo-fracture surface of nanofiber composite that has not been fatigued. Deformation cones around the nanofibers are not seen.

nanofiber would then cause local deformation in the surrounding softer matrix [9]. Closer examination of the nanofiber shows possible balling-up of polymer beads that have been scraped from the matrix as the nanofiber interacts with the surrounding surface. Balling-up of polymer on carbon nanotubes has been reported previously [10]. The stacked cone structure of the nanofiber can also be seen in the micrograph and may contribute to the removal of polymer material around the fiber. A schematic of the proposed mechanism by which the deformation is formed is shown in Fig. 2. It is likely that the formation of the deformation cone is occurring during fatigue testing given the fact that they are not observed in samples that were not fatigued, as seen in the cryo-fractured fracture surface image in Fig. 3. Deformation cones were also not seen in samples fractured at room temperature.

In order to establish a relationship between the deformation cone feature size and the magnitude of ΔK or dN (number of cycles), we measured approximately 30 deformations cones throughout the fatigued fracture surface. The features that were observed in this study were approximately 1–2 μm in diameter on average and they did not have a statistically significant difference in size (confirmed by a Student's *t*-test

analysis) between the high ΔK and the low ΔK regions of the test sample. The high ΔK portion of the sample would experience a lower number of cycles, dN , per given distance of crack growth, while the low ΔK region of the sample would experience a higher number of cycles per given distance of crack growth. If the nanofiber crack bridging zone is larger for a low ΔK [2], one would expect to see a larger number of the deformation cones at a small ΔK . While we do not see a statistically significant difference in cone size or frequency in our samples between high ΔK and low ΔK regions, it may just be a result of sampling too small a range of ΔK values. The feature morphology may also be dependent upon other factors such as nanofiber diameter and length as well as processing parameters and will be the subject of further study to be reported elsewhere.

From a statistical perspective, the nanofibers surrounded by a deformation cone were a minority (estimated to be less than 20% based on our extensive SEM imaging of these surfaces). When observed under SEM the fatigued sample surface was consistently found to contain: (1) nanofibers surrounded by the deformation cone, (2) some empty holes which are attributed to nanofibers that were pulled out of the mating surface, and (3) what appear to be rigid CNFs that appear well-adhered to the PEEK matrix and do not have a deformation cone. It is likely that certain conditions needed to be met in order for the deformation cone phenomenon to occur. These conditions likely include (1) a stiff nanofiber in a softer surrounding matrix under cyclic loading, (2) a nanofiber that bridges the advancing crack tip, and (3) a nanofiber oriented at an angle that can cause the deformation cone to form while the nanofiber moves during cyclic loading. Studying these features could provide further insight into how nanofibers interact with crack tips during fatigue analysis and are currently ongoing in our group.

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