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Application of continuously-monitored single fiber fragmentation tests to carbon nanotube/carbon microfiber hybrid composites

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ABSTRACT

To assess the effect of carbon nanotube (CNT) grafting on interfacial stress transfer in fiber composites, CNTs were grown upon individual carbon T-300 fibers by chemical vapor deposition. Continuously-monitored single fiber composite (SFC) fragmentation tests were performed on both pristine and CNT-decorated fibers embedded in epoxy. The critical fragment length, fiber tensile strength at critical length, and interfacial shear strength were evaluated. Despite the fiber strength degradation resulting from the harsh CNT growth conditions, the CNT-modified fibers lead to a twofold increase in interfacial shear strength which correlates with the nearly threefold increase in apparent fiber diameter resulting from CNT grafting. These observations corroborate recently published studies with other CNT-grafted fibers. An analysis of the relative contributions to the interfacial strength of the fiber diameter and strength due to surface treatment is presented. It is concluded that the common view whereby an experimentally observed shorter average fragment length leads to a stronger interfacial adhesion is not necessarily correct, if the treatment has changed the fiber tensile strength or its diameter.

1. Introduction

The discovery of carbon nanotubes (CNTs) in the 1990s almost immediately triggered the exploration of their potential use in composites. Indeed, nano-reinforcements, especially CNTs, were found to exhibit exceptional mechanical properties including very high elastic modulus and strength combined with high flexibility, low density and negligible thermal expansion [1–8]. Moreover, since nano-scale objects have a great deal more surface area (thus, for the case of composites, significantly more interfacial area) massive stress transfer and energy dissipation was expected to potentially lead to very high strength and toughness in these materials [9]. Indeed, it was observed that the addition of tiny amounts of CNTs to polymer matrices could result in improved mechanical properties [10–13]. Unfortunately, the improvements are almost always limited by a 'critical mixing threshold' of particle content, above which severe particle aggregation and drastic viscosity increases arose. As a result, it is currently impossible to manufacture CNT-based composites with CNT loadings that would be comparable to those of microfibers used in conventional composites (60–70% or so). This current state of affairs also contrasts with the existence in nature of nanocomposites with very high nanofiller content, up to 95 wt.% and sometimes even more [14,15]. Faced with such a challenge, composite material scientists are thus attempting to develop simple preparation techniques leading to high-content nanocomposites with superior mechanical properties.

The road to high-performance synthetic nanocomposites requires that a fourfold set of structural parameters be optimized. These include (1) the particle aspect ratio, (2) particle dispersion, (3) particle packing (i.e. alignment), and (4) polymer-to-particle interfacial stress [9]. A recent review by Qian et al. [16] suggests two different routes for combining CNTs with conventional fiber-reinforcements in polymer composites: either by dispersing CNTs throughout the composite matrix or by attaching CNTs directly onto primary reinforcing fibers (see Fig. 1 in Ref. [16]) using either chemical vapor deposition (CVD) [16–18] or electrophoretic deposition (EPD) [19,20]. By focusing here on the second route and using CVD to grow CNTs directly on the surface of fibers, we deal mainly with points 3 and 4 above while avoiding the problems of controlling the CNT dispersion in the bulk of the matrix as well as the CNT aspect ratio (a non-trivial task). Such an approach, wherein CNTs are vertically grown over specific fibers or over fabric layers, might lead to well-controlled, high CNT content, high toughness nanocomposites [15]. Perhaps more importantly, the presence of well-ordered CNTs at the fiber–matrix interface might enhance interfacial adhesion and stress transfer, and positively affect the mechanical properties of such hierarchical composites.

In the present work, CNTs were synthesized and grown on carbon fibers by chemical vapor deposition (CVD). Single-fiber

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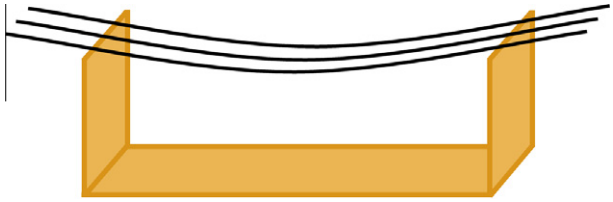

Fig. 1. Custom-made support bridge ensuring full CNT-coating of the individual fibers when held horizontally in the growth environment during synthesis.

fragmentation tests, of the continuously-monitored type [21,22], were then performed on both the CNT-grafted and reference (pristine) single fiber composites using a relatively soft epoxy matrix. The fragmentation phenomenon, in its continuously-monitored version, is a rich source of micromechanical information [21,22] as it simultaneously enables the rapid measurement of (i) the Weibull shape and scale parameters of the single fiber (within the matrix), (ii) the effect of fiber length on strength and thus the strength of fiber fragments having reached the saturation length, and (iii) the interfacial shear strength, a crucial factor in determining the strength and toughness of a composite.

2. Materials and specimen preparation

The substrate fiber used in this work was an intermediate-modulus PAN-based carbon, T-300 from Cytex, untreated and sized. Its Young's modulus is 157 GPa and its nominal diameter is 7 μm. For the CNT growth, a well-documented vapor-phase chemical vapor deposition (CVD) synthesis procedure [18] was employed, using xylene and ferrocene as the carbon and catalyst precursors, respectively. Individual fibers were loaded into a custom-made support bridge (Fig. 1) which held the suspended fibers horizontally in the growth environment during synthesis. The CNTs grow normal to the surface, thus suspension was necessary to keep the individual fibers separated and to prevent them from disturbing each other's radial, "pipe-cleaner-like" structure during synthesis. The copper foil bridge suspended individual fibers across two slits separated by a distance of ~50 mm, while excess fiber length hung over the outside of the bridge support to help prevent excessive drooping. Many slits were made for the possibility of loading multiple fibers in parallel. The fiber-loaded bridge was placed into a 50 mm-in-diameter quartz tube to act as the transfer boat, which was then positioned at the center of the 70 mm-in-diameter quartz tube which served as the growth environment. The chamber was held at atmospheric pressure conditions and set to a temperature of 780 °C, while at the same time Ar flowed at a rate of 1.00 L/min to purge the growth environment. A 1 mm-in-diameter quartz tube was used as a nozzle tip to transport the precursor solution into the reaction zone, and was positioned into the furnace at ~300 °C. When the synthesis temperature was achieved, the carrier gas was changed to a gas mix (15% H_2/balance Ar) and was set to a flow rate of 4.00 L/min. A 3 mm-in-diameter steel tube concentric to the 1 mm-in-diameter quartz tube carried the identical gas mix at a rate of .64 L/min to promote the nozzle tip spray pyrolysis of the chemical precursor. A 5 min synthesis time resulted in ~10 μm-long MWCNTs grown outwardly from the fiber surface. Typical CNT grafting results can be seen in Fig. 2.

Epoxy films containing a single fiber were prepared according to a procedure now routinely used in our laboratory and described in our previous works [21,22]. The matrix was EP-502 from Polymer Gvulot, a bisphenol-A based (DGEBA) liquid epoxy resin, mixed with the curing agent EPC-9, triethylenetetramine (TETA). The Young's modulus of the cured matrix is 1.34 GPa. Curing, film forming and sample cutting were performed according to the procedure described in previous work [9]. The resulting single fiber composite samples had typical cross-sectional dimensions of 3.1 × 0.15 mm^2, and a gauge length of 12 mm.

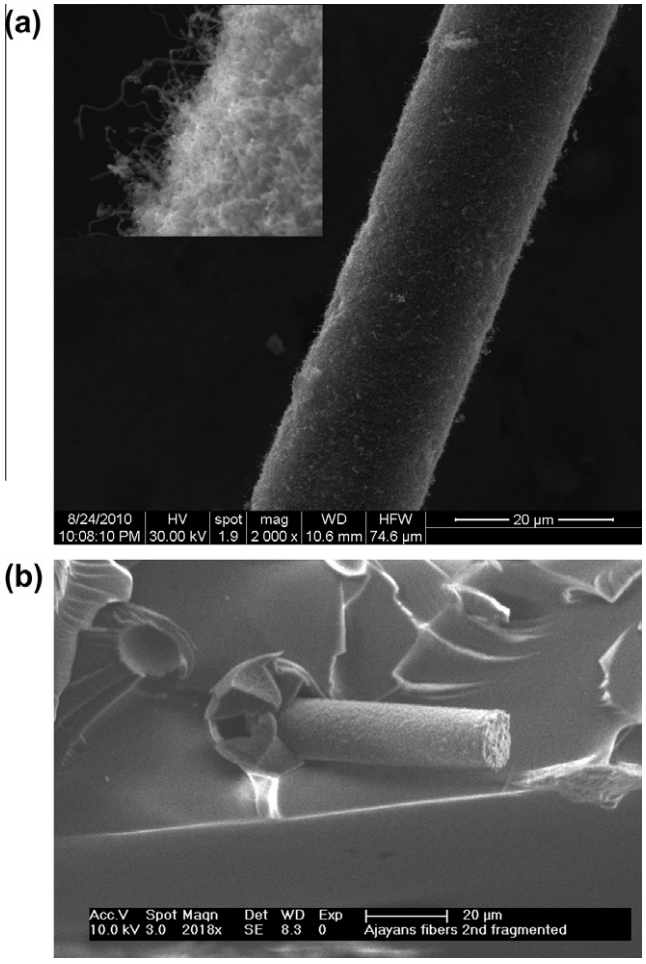

Fig. 2. SEM views of (a) CNT-grafted fibers prior to embedment in epoxy. Inset: High magnification (5000×). (b) pulled-out CNT-grafted fibers from the epoxy specimens following final rupture of the fragmentation test specimen. The fiber diameter is approximately 17 μm before and after pull-out (Table 1), an indication of the strength of the fiber-CNT interface.

3. Continuously monitored single-fiber fragmentation tests

Mechanical testing of single fiber composites of each type was carried out using a computer-controlled MiniMat tensile tester fitted to a microscope possessing video recording capability. Four pristine specimens and five CNT-coated specimens were tested at a deformation rate of 50 μm/min. The continuously monitored version of the single filament composite test (CM-SFC) developed in our laboratory [21,22] and further validated along the years [23,24] was used. During a fragmentation test, under increasing levels of applied stress the fiber gradually breaks into shorter and shorter fragments. The rising stress–strain curve, as well as a magnified digital version of both the stress and the strain, was recorded simultaneously with the individual fracture events which were counted sequentially from real-time color video monitoring. Birefringent gaps under polarized light helped identify the fiber break sites while the specimen was under load, see Fig. 3. When a break occurred, the corresponding stress was recorded, and the average length of the fragments present was calculated by dividing the initial gauge length by the number of breaks plus one. The