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Multi-scale reinforcement of CFRPs using carbon nanofibers

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ABSTRACT

In this paper, stacked-cup carbon nanofibers (CNF) were dispersed in the matrix phase of carbon-fiber-reinforced composites based on a high-performance epoxy system with and without modification by an elastomeric triblock copolymer (TCP) for increased toughness. The addition of the TCP provided an enhancement in toughness at the cost of a slight degradation in modulus and strength. The CNFs, on the other hand, provided significantly enhanced strength and stiffness in matrix-dominated configurations, including tension of quasi-isotropic composites and short beam shear strength of both quasi-isotropic and unidirectional composites. Scanning electron microscopy revealed enhanced adhesion between the matrix and carbon fibers with the addition of either TCP or CNFs. However, CNF agglomeration in the studied systems partially offset the energy dissipation processes brought about by the nanofibers, thereby limiting interlaminar fracture toughness enhancements by CNF addition. These results show good promise for CNFs as low-cost reinforcement for composites while offering insight into the codependent morphologies of multi-scale phases and their influence over bulk properties.

1. Introduction

Carbon-fiber-reinforced plastics (CFRP) are characterized by low weight, high strength and stiffness, and low coefficients of thermal expansion in the fiber direction, making them attractive in a wide variety of applications in wind energy, transportation, aerospace design, and sporting equipment, among others. Superior strength-to-weight ratios are a primary motivational factor for the incorporation of CFRPs [1], but these composite materials can also be designed with multifunctionality, replacing non-structural elements while enhancing structural integrity.

High-performance composite systems often incorporate highly crosslinked epoxy adhesives to hold together the load-bearing carbon fibers. These glassy networks offer high creep and corrosion resistance, good adhesion to carbon fibers, and high working temperatures as determined by their high glass transition temperatures (T_g), yet they are also highly brittle and insulating [2]. As a result, CFRPs suffer from poor matrix-dominated mechanical properties such as interlaminar fracture toughness and transverse electrical and thermal conductivity, particularly in matrix-rich interlaminar regions between carbon fibers.

Thus, many studies have focused on toughening the matrix component of CFRPs to improve their mechanical robustness. Rubber-toughening through the addition of discrete rubber particles enhances toughness but also degrades the thermomechanical properties of crosslinked polymer networks [3,4]. Amphiphilic block copolymers undergo reaction induced phase separation (RIPS) during the curing process to yield similar rubbery domains that are anchored into the matrix by epoxy-miscible blocks, providing similar toughening with reduced degradation in thermomechanical properties due to control over morphology [5,6]. The addition of a rigid thermoplastic is another effective method of toughening with low degradation in the thermomechanical properties of the matrix [7–9]. While these approaches have been partially successful, new strategies to improve toughness while maintaining or improving thermal properties and simultaneously addressing additional needs such as transverse electrical conductivity are needed.

In this light, nanoparticles have the potential to toughen the matrix phase and offer the added benefit of multifunctionality for simultaneous enhancements in other properties. For example, clay nanoplatelets offer enhanced flexural modulus and barrier properties [10,11]. Carbon nanotubes (CNT) enable enhanced health monitoring and improved mechanical, electrical and thermal properties in traditional fiber-reinforced systems [12–16]. Cho et al. reported an increase in interlaminar fracture toughness of ~15% with 0.5 wt.% CNTs [16]. Bekyarova et al. grew CNTs on carbon fiber surfaces for enhanced interactions, yielding tensile modulus and strength improvements of ~30% and 15% over the base composites, respectively [15]. Veedu et al. grew CNTs on SiC fiber surfaces by chemical vapor deposition (CVD) and found enhancements in interlaminar fracture toughness of ~386% (CNT

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content unknown) [13]. Unfortunately, CNT growth from carbon fibers often results in non-uniform coverage or damage to the carbon fibers, making this method difficult to optimize for CFRPs [17]. Furthermore, a major limitation of this "hybrid" approach to composites containing both microscale carbon fibers and nanoparticles is the high expense associated with many nanoparticles.

Thus, carbon nanofibers (CNF), which offer a good compromise between performance and cost compared with CNTs [18,19], are an ideal candidate for incorporation into CFRPs. Previous studies have shown good promise, with a 100% increase in mode I interlaminar fracture toughness at only 1 wt.% CNF, as reported by Tsantzalis et al. [20]. An increase of up to ~160% in mode I interlaminar fracture toughness was observed by Yokozeki et al. through a combination of an epoxy phase with 5 wt.% CNFs and a CNF-rich film in the region of crack propagation [21]. Still, there have been limited studies on hybrid composites containing CNFs, particularly on systems incorporating high-performance epoxies ($T_g > 250$ °C), which are particularly difficult to toughen in light of their exceptionally high crosslink densities [22].

CNFs and CNTs are both composed of graphene sheets, yielding similar electrical and thermal properties [23,24]. However, the stacked-cup structure of CNFs entails graphitic stacking of helically coiled graphene sheets or ribbons oriented at an angle with respect to the nanofiber axis (Fig. 1) [25–27]. This unique structure enables failure modes such as unraveling or splaying of the coiled graphitic sheets, which offer new pathways for toughening of nanostructured composite systems [28].

In this study, we have investigated the influence of various amounts of stacked-cup carbon nanofibers in "hybrid" composite systems containing both micro- and nano-scale carbon fibers. The matrix phase in the composite systems under study consisted of either a "base" high-performance epoxy or the same epoxy "toughened" with 5 phr (parts per hundred resin by weight) of a commercial elastomeric triblock copolymer (TCP) in order to determine the effect of a second polymer phase in the matrix component of these hybrid composites and to take advantage of synergistic toughening of the epoxy matrix. The resultant composites were characterized mechanically and electrically in conjunction with scanning electron microscopy to understand the interactions between the reinforcing phases and their influence on macroscopic properties.

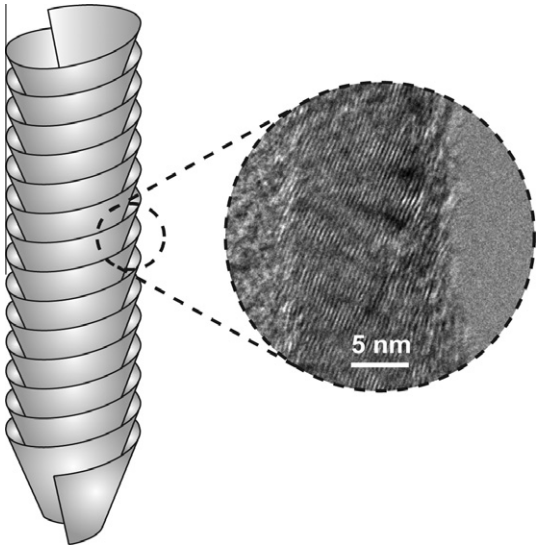

Fig. 1. Schematic stacked-cup carbon nanofiber structure with a TEM image showing the inclined orientation of the stacked graphene sheets with respect to the nanofiber axis.

2. Experimental

2.1. Materials

Two high-performance epoxy systems were used as the matrix phase in CFRPs. The "base" system consisted of a high-viscosity tetrafunctional resin (tetraglycidyl 4,4′-diaminodiphenyl methane, Araldite MY721, Huntsman) cured with a diamine hardener (diaminodiphenyl sulfone, DDS, Aradur 976, Huntsman) at a 100:44 ratio by weight, as recommended by the manufacturer. The cured network results in an exceptionally high crosslink density and thus a low molecular weight between crosslinks ($M_c \sim 175$ g/mol). The 'toughened' epoxy system was prepared with 5 phr (parts per hundred resin by weight) of a commercial triblock copolymer (M52N, Arkema) containing midblocks of *n*-butyl acrylate with symmetrical endblocks of random copolymers of methyl methacrylate and N,N′-dimethylacrylamide. The triblock copolymer molecular weight is 36 kg/mol with 18 kg/mol midblocks. Carbon nanofibers (GANF1, Grupo Antolín Ingeniería) produced by Ni-catalyzed carbon vapor deposition with 20–200 nm diameters, 1–6 μm lengths, and ~35:1 aspect ratio were used as received [25]. CNFs were incorporated at 0, 1, and 3 phr (0, 0.69, and 2.0 wt.%) in the base system and 0 and 1 phr (0 and 0.67 wt.%) in the toughened system, as summarized in Table 1.

2.2. Sample preparation

CNFs were dispersed in the base epoxy systems (*i.e.* composites without TCP) by shear mixing in order to take advantage of the epoxy precursor viscosity in shearing apart CNF bundles. First, the resin was heated to ~135 °C, and the hardener was slowly added while stirring until dissolved. The mixture was allowed to cool to ~80 °C, and the appropriate amount of CNFs were hand mixed. The mixture was mechanically mixed using a shear mixer at 7000 rpm for 2 min, followed by degassing under 29.4″ Hg of vacuum at 80 °C until all gas was removed. The short duration of shear mixing was used in order to minimize shortening of the CNFs [18].

CNFs were dispersed in the toughened epoxy systems (*i.e.* composites with 5 phr TCP) by solution processing, as is commonly employed for composites based on epoxy with block copolymer or CNF reinforcement [6,18,22]. First, the resin, hardener, and triblock copolymer were all dissolved in acetone in a round-bottom flask. The desired amounts of CNFs were suspended in acetone in 40-mL vials at a concentration of 15 mg/mL and were bath sonicated for 1 h to disperse the nanofibers. Following sonication, the CNF suspensions were poured into the epoxy-TCP solution, followed by 1 h of additional bath sonication. Then the solvent was removed by rotary evaporation, followed by degassing under 29.4″ Hg of vacuum at 80 °C until all gas was removed.

These epoxy precursors were used to prepare carbon-fiber prepregs (65 wt.% CF) containing continuous PAN-based carbon fibers with 7 μm diameter (AS4GP, Hexcel) at a fiber areal weight of 190 g/m^2, which were subsequently laid up by hand in both

Table 1
Summary of CNF contents in the matrix phase of CFRPs in parts per hundred resin (by weight) and weight percent.

CFRP matrix	CNF content, phr (wt.%)
Base (pure epoxy)	0 (0) 1 (0.69) 3 (2.0)
Toughenened (epoxy + 5 phr TCP)	0 (0) 1 (0.67)