



## Research paper

# Strengthening and stiffening carbon fiber epoxy composites by halloysite nanotubes, carbon nanotubes and silicon carbide whiskers



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## ABSTRACT

Low-cost natural halloysite (Hal) nanotubes (0.1  $\mu\text{m}$  diameter) were effective for strengthening and stiffening continuous fiber epoxy composites, as shown for cross-ply carbon fiber (5  $\mu\text{m}$  diameter, ~59 vol.%) epoxy nanocomposites under flexure, giving 17% increase in strength, 11% increase in modulus and 21% decrease in ductility. They were less effective than expensive multiwalled carbon nanotubes (0.02  $\mu\text{m}$  diameter), which gave 25% increase in strength, 11% increase in modulus and 14% decrease in ductility. However, they were more effective than expensive silicon carbide whiskers (1  $\mu\text{m}$  diameter), which gave 15% increase in strength, 9% increase in modulus and 20% decrease in ductility. Each filler, at ~2 vol.%, was incorporated in the composite at every interlaminar interface (interface between adjacent fiber laminae) by fiber prepreg surface modification. The flexural strength increase due to Hal nanotubes incorporation corroborated with the interlaminar shear strength increase. The measured values of the composite modulus agreed roughly with the calculated values based on the Rule of Mixtures. The interlaminar interface thickness was higher for the SiC whiskers case than the carbon nanotubes or Hal nanotubes case. The lamina thickness was not affected by the fillers. The composite density was 2% higher for the Hal nanotubes and SiC whiskers cases than the carbon nanotubes case.

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## 1. Introduction

Continuous carbon fiber polymer composites are important lightweight structural materials due to their combination of high elastic modulus, high strength and low density. Lightweight structures using these composites include aircrafts, automobiles, bicycles, ships, wind turbines, bridge decks, offshore platforms, sporting goods, etc.

Continuous carbon fibers are more effective as primary reinforcements than discontinuous carbon fibers, carbon nanofibers and carbon nanotubes, because of the continuous length, good alignment and the consequent high maximum volume fraction of continuous fibers in a composite. However, the discontinuous reinforcement may be used as a secondary reinforcement in composites that involve continuous carbon fibers as the primary reinforcement. Throughout this paper, fiber refers to continuous fiber.

Because the continuous fibers render high modulus and strength to the composite anyway, the stiffening and strengthening of continuous fiber composites are more challenging than those of composites without continuous fibers. For structural performance, high values of both modulus and strength are necessary. Furthermore, stiffening without strengthening tends to cause decrease in the ductility. Thus, simultaneous stiffening and strengthening are desired.

Considerable prior work that incorporated carbon nanotubes in continuous fiber polymer composites had been reported. Increases in

the interlaminar shear strength (the maximum shear stress that can be borne by the interlaminar interface, which is the interface between adjacent laminae, where a lamina refers to a ply of fibers) (Godara et al., 2010; Gojny et al., 2005; Zhu et al., 2007), high-cycle fatigue life (Grimmer and Dharan, 2008) and delamination (local separation of adjacent laminae) fatigue resistance (Grimmer and Dharan, 2010) in glass fiber composites were achieved. In addition, the carbon nanotubes provided electrical conductivity to the glass fiber composite, thus rendering the composite the ability to sense strain and damage through electrical resistance measurement (Alexopoulos et al., 2010; Gao et al., 2009; Rausch and Mader, 2010; Sureeyatanapas and Young, 2009; Thostenson et al., 2009; Zhang et al., 2010) and the ability to shield electromagnetic radiation (Lee et al., 2011). Increases in the interlaminar shear strength (Bekyarova et al., 2007; Cho and Daniel, 2008; F. Zhang et al., 2009; X. Zhang et al., 2009), compressive strength (Cho and Daniel, 2008; Cho et al., 2008), flexural strength and modulus (Kim et al., 2009), fiber–matrix interfacial load transfer effectiveness (Thostenson et al., 2002) and the storage modulus (under dynamic flexure at 1 Hz, increased by 75%) (Kar et al., 2009) were achieved similarly in carbon fiber polymer composites. In spite of the increase in the interlaminar shear strength and flexural strength and modulus, the tensile modulus and strength of carbon fiber epoxy composites were not affected by the incorporation of MWCNT (multiwalled carbon nanotubes) (Bekyarova et al., 2007) or a mixture of CNT (carbon nanotubes) with 1, 2 and 3 walls (Kim et al., 2009), because the tensile properties were dominated by the continuous fibers.

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Various methods were used in prior work to incorporate CNT in continuous fiber polymer nanocomposites. These methods included dispersing the nanotubes in the fiber sizing or coating (Godara et al., 2010; Rausch and Mader, 2010; Sureeyatanapas and Young, 2009; Zhang et al., 2010), dispersing the nanotubes in the matrix (Gao et al., 2009; Godara et al., 2010; Grimmer and Dharan, 2008, 2010; Thostenson et al., 2009), applying the nanotubes to the fiber surface or the fiber fabric surface by electrophoretic deposition (Bekyarova et al., 2007; Zhang et al., 2010), and grafting the nanotubes onto the fiber surface by chemical vapor deposition (Kar et al., 2009; Thostenson et al., 2002; F. Zhang et al., 2009).

Much less research was reported on the incorporation of fillers other than carbon nanotubes in continuous fiber polymer composites, in spite of the relatively low cost of other fillers. The incorporation of halloysite (Hal) nanotubes (a natural clay mineral, Brigatti et al., 2006) in the matrix of woven carbon fiber epoxy nanocomposites increased the flexural strength by 14% and the interlaminar shear strength by up to 25%, while the flexural modulus was essentially unaffected (Ye et al., 2011a,b). The incorporation of silicon carbide whiskers at the interlaminar interface of unidirectional carbon fiber composites by spraying the whiskers on the prepreg surface improved the interlaminar fracture toughness, though the strength and modulus were not reported (Wang et al., 2002). The incorporation of montmorillonite (Mt) in the carbon fiber epoxy nanocomposites increased the flexural strength and modulus by 31% and 46% respectively (Chowdhury et al., 2007). Mt was not as effective as alumina particles for increasing the interlaminar shear strength or the transverse flexural strength (Timmerman et al., 2002). The incorporation of alumina particles (25 nm) in carbon fiber epoxy nanocomposites made by filament winding increased the flexural toughness and interlaminar shear strength (Hussain et al., 1996). The incorporation of 48- $\mu\text{m}$   $\text{Al}_2\text{O}_3$  particles in the epoxy matrix of a woven continuous glass fiber composite resulted in 78% increase in flexural modulus and 33% increase in the flexural strength (Asi, 2009). The incorporation of 20–30 nm silica particles to the epoxy matrix of a glass fiber fabric composite increased the interlaminar fracture toughness and the impact resistance (Uddin and Sun, 2008).

Relatively little research was reported on the incorporation of carbon fillers other than carbon nanotubes in continuous fiber polymer composites, in spite of the relatively low cost of these other fillers, such as carbon black and carbon nanofiber. By using carbon black as a filler located at the interlaminar interface of a continuous carbon fiber epoxy composite, the flexural modulus was increased by 6.4% and 11% for unidirectional and cross-ply composites respectively (Han et al., 2008). By incorporating carbon nanofibers (originally known as carbon filaments) in the epoxy matrix of a woven continuous carbon fiber nanocomposite, the flexural strength was increased by 22% while the tensile strength was increased by 11% (Zhou et al., 2006, 2008). However, by using 0.1- $\mu\text{m}$  diameter carbon nanofibers as an interlaminar filler (a filler located at the interlaminar interface) in a continuous carbon fiber epoxy nanocomposite, the tensile modulus and the dynamic flexural modulus were decreased (Hudnut and Chung, 1995; Segiet and Chung, 2000).

The effects of a filler in the absence of continuous fibers (Du et al., 2010; He et al., 2012; Jia et al., 2011; Kong et al., 2011; Lecouvet et al., 2011; Rooj et al., 2011) received more attention than those in the presence of continuous fibers. In spite of the prior work mentioned above on the effects of various fillers in the presence of continuous fibers, comparative evaluation of competing fillers received little or no attention.

The objectives of this paper are (i) to provide a cost-effective method of strengthening and stiffening continuous carbon fiber polymer composites, (ii) to investigate the effectiveness of Hal nanotubes incorporation for strengthening and stiffening carbon fiber polymer composites, (iii) to compare the effects of various high-elastic-modulus fillers, namely an expensive nanofiller (carbon nanotubes), an inexpensive nanofiller (Hal nanotubes) and a microfiller (silicon carbide whiskers

of diameter 1  $\mu\text{m}$ , chosen due to their effectiveness for strengthening polymers (Li and Chung, 1994), aluminum (Lai and Chung, 1996), copper (Yih and Chung, 1996), brass (Yih and Chung, 1999) and silicon nitride (Wang and Chung, 1997)), on the mechanical properties of the composites, and (iv) to correlate the structure and the mechanical properties of these composites.

## 2. Experimental methods

### 2.1. Materials

Composite specimens were fabricated by hand lay-up and compression molding of a stack of cross-ply carbon fiber epoxy prepreg sheets. The curing conditions were 90 min at 177 °C and a pressure of 0.5 MPa, unless noted otherwise.

Unless noted otherwise, the carbon fiber prepreg had RS-36 epoxy, with uncured resin density 1.20–1.25 g/cm<sup>3</sup>, resin content (33 ± 2) wt.%, uncured prepreg density 1.394 ± 0.006 g/cm<sup>3</sup> (measured in this work) and fiber volume fraction (obtained from the uncured prepreg density, based on the Rule of Mixtures, i.e., a method of estimating composite properties based on the averaged properties of the components) 0.274 ± 0.010. The prepreg was manufactured by Tencate Advanced Composites USA, Inc., Morgan Hill, CA. Unless noted otherwise, the carbon fibers had designation Torayca M46JB, in the form of 12 K PAN-based fibers, with tensile modulus 436 GPa, tensile strength 4.0 GPa, fiber diameter 5.0 ± 0.3  $\mu\text{m}$  (measured in this work), and elongation at break 1.0%.

For the short-beam shear testing only, the carbon fiber prepreg was from Tencate Advanced Composites USA, Inc., with the carbon fibers designated Pyrofil TR50S 15 K (with diameter 7  $\mu\text{m}$ , density 1.82 g/m<sup>3</sup>, tensile modulus 235 GPa, tensile strength 4.9 GPa and elongation at break 2.1%) and with TC275 epoxy; the resin content of the prepreg was 34 ± 2 %. Curing was conducted at 177 °C and 0.1 MPa for 120 min.

Specimens with and without modification were prepared for comparative evaluation. Two lay-up configurations were studied, namely unidirectional and cross-ply configurations. The cross-ply configuration was symmetrical around the central 90° lamina.

The fillers were MWCNT, silicon carbide whiskers and Hal nanotubes. Unless stated otherwise, the MWCNT was from Nanothinx S.A., Greece, NTX1, with 15–35 nm diameter, 15–35 layers, ≥ 10  $\mu\text{m}$  length, 97% nanotubes purity, 3% metal particles, <1% amorphous carbon, and 1.4 g/cm<sup>3</sup> density. For the short-beam shear testing specimens only, the MWCNT was from ILJIN, S. Korea, as prepared by chemical vapor deposition, with purity above 95%, length exceeding 60  $\mu\text{m}$ , average diameter 50 nm and density 1.4 g/cm<sup>3</sup>. The silicon carbide whiskers (abbreviated SiCw) had a cubic crystal structure, with 1.4  $\mu\text{m}$  mean diameter, 18.6  $\mu\text{m}$  mean length, 99 wt.% SiC, 0.4 wt.% SiO<sub>2</sub> and density 3.21 g/cm<sup>3</sup>, provided by Advanced Refractory Technologies, Inc., Buffalo, NY. The Hal nanotubes were in the form of natural hollow tubes, as provided by NaturalNano, Inc., Rochester, NY. They were heated by NaturalNano at 600 °C (abbreviated HHal). Based on powder x-ray diffraction patterns obtained using CuK $\alpha$  radiation and a Siemens Kristalloflex diffractometer (Fig. 1), HHal was highly disordered, with a basal spacing of 7 Å, indicating that it was unhydrated Hal (Huertas et al., 2004; Wada, 1965). The diameter and length of HHal were roughly 0.1–0.2 and 0.4–0.5  $\mu\text{m}$  respectively, as shown by scanning electron microscopy (Fig. 2); the density was 2.53 g/cm<sup>3</sup>.

The interlaminar interface modification was performed by wet application of the filler on both opposite surfaces of a prepreg sheet. During the wet application, the filler was dispersed in a solvent at a solid content that was low enough for good workability (spreadability) of the dispersion. The content of 2 mass % was used for HHal and SiCw dispersions and the content of 0.8 mass % was used for the MWCNT dispersion. Higher contents were not used in order to maintain low viscosity for effective application on the prepreg surface. Thus, the

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