Title: *In-situ bending performance of nanostructured carbon fiber reinforced polymer composites* Proceedings of the **American Society for Composites—Thirty-seventh Technical Conference**

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ABSTRACT

Depositing carbon nanotubes (CNTs) into carbon fiber reinforced polymer composites (CFRPs) is challenging because of the need for complicated lab-scale processes and toxic chemical dispersants that makes conventional means of processing less compatible with existing industrial procedures for large-scale applications. In this work, a scalable supercritical CO_2-assisted atomization technique is used to effectively deposit hybrid CNTs in CFRPs allowing them to boost their functionality and tailor the microstructure. Cellulose nanocrystals (CNCs) are utilized to create hybrid nanostructures with CNTs (CNC bonded CNT) that enables stabilization of CNTs in nontoxic media, i.e., water, and this promotes the scalability of the process. According to Zeta potential values, CNCs successfully stabilize CNTs in water suspension. Scanning electron microscopy (SEM) micrographs show hybrid CNC bonded CNTs are homogeneously dispersed on the carbon fiber surface. According to the *in-situ* bending test under the optical microscope, crack propagation is hindered by engineered hybrid CNT nanostructures in the modified CFRP whereas neat CFRP exhibits low crack growth resistance due to the uninterrupted crack propagation in the continuous epoxy matrix. Our results imply that this strategy probes the importance of new controlled manufacturing of hybrid nanostructures through evaporation-induced self-assembly of nanocolloidal droplets, and allows for tailoring of the desired properties of nanostructured composites.

INTRODUCTION

Carbon fiber reinforced polymer (CFRP) composites have been developed as an engineering material for high-performance applications owing to their lightweight and high specific mechanical performance [1]. The overall performance of CFRP composites is closely related to the interfacial properties because of the weak interfacial interactions between the carbon fibers and bulk polymer matrix [2-5]. The approaches to enhance the interphase of CFRPs can be categorized into two major branches: (*i*) the surface treatment of carbon fibers such as fiber sizing, electrochemical oxidation [6], liquid-phase chemical oxidation, high energy beam irradiation plasma treatment, etc., [7] and (*ii*) the modification of the interface [8, 9]. The interface reinforcement with nanomaterials allows tuning the properties of composite materials with chosen nanofillers, such as fullerene, silica nanoparticles, and carbon nanotubes.

Depositing nanostructures on carbon surfaces by coating is an effective, economical, scalable, and adaptable approach to transferring them to CFRPs. Especially, the spraying method enables to control of the amount of nanomaterial deposited and yields a homogeneous dispersion by controlling the nanocolloidal droplet

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sizes [10]. In this light, Srivastava *et al*. [11] prepared graphene nanoplatelets (GNPs) suspensions dispersing them in an ethanol solution by a probe sonicator and transferring them onto carbon fiber using the spray coating technique. They reported 23 % and 20% improvements in flexural strength and modulus, respectively, due to the enhanced interfacial adhesion with GNPs at the interface. In another study [12], silver (Ag) nanoparticles were deposited on carbon fiber fabrics by spray coating to improve the electromagnetic shielding efficiency; the results show that well-dispersed Ag nanoparticles on carbon fiber surface images as well as achieved exceptional high electromagnetic interference (EMI) shielding performance. These studies suggest that depositing nanomaterials through droplets is not only an effective and scalable approach for manufacturing fabrics but also highly adaptable to various nanomaterials and solution types, and different application purposes.

Self-assembly in colloidal droplets that are created using spraying is the result of a balance between the attractive, repulsive, and directional intermolecular forces [13]. Intermolecular forces should be weak enough for the system to achieve the optimum configuration with minimum free energy. As opposed to the strong chemical bonds i.e., covalent bond, the weak attractive Van der Waals, $\pi - \pi$ stacking, and repulsive electric double layer are the intermolecular forces that contribute to the nanomaterial self-assembly process [14]. In addition, the directional forces such as hydrogen bonds and coordination bonds facilitate the positioning of the final self-assembled nanostructure [15]. These interactions and their balance allow us to engineer the result of the self-assembled nanomaterial process.

In the present paper, we use self-assembled hybrid CNTs into CFRP structures using the supercritical CO_2 assisted atomization (SAA) technique, which is an advanced spraying technique, to deposit nanoparticles on the carbon fiber surface, and their effect on bending properties and crack propagation. Along with the Zeta-potential and dynamic light scattering (DLS) measurement and surface characterization by SEM micrographs, the real-time *in-situ* bending test is implemented to exploit the crack propagation pattern of nanostructured CFRPs. The results show that the neat CFRP exhibits low crack growth resistance due to the uninterrupted crack propagation in the continuous epoxy matrix whereas crack propagation is hindered by engineered hybrid nanostructures in the nanostructured CFRP. The reason behind this is attributed to (*i*) the controlled morphology of CNC–CNT droplets on carbon fiber created through SAA and (*ii*) the enlarged interfacial span between carbon fiber and epoxy, which facilitates an efficient stress transfer from epoxy to carbon fiber due to the favorable synergy of CNC with CNT.

MATERIALS AND METHODS

Commercially available unidirectional Hexcel IM7 Intermediate Modulus carbon fibers are used as received in this work. Epoxy INF-114 and INF-211 hardeners are supplied from Pro Set, USA. NCV-100 CNCs (CelluForce, QC, Canada) with a diameter of 2.3-4.5 nm and length of 44-108 nm are used as received. The pristine multi-walled CNTs are purchased from USNano (USA) and produced via catalytic CVD with 95% carbon purity, average outer and inner diameter of 5-15 nm and 3-5 nm, respectively, length of 50 μm and the number of walls of 12 with 1.62. A wall spacing is measured by transmission electron microscopy (TEM).

The nanomaterials are integrated by using a custom-made supercritical CO_2-assisted atomization (SAA) system. CNCs and CNC-CNTs are sprayed onto unidirectional carbon fiber fabrics as per conditions given in Fig. 1. The CNC and CNC–CNT suspensions are prepared with a total mass of 0.4 wt. % concentration. CNCs and CNC–CNT nanomaterials are dispersed in 500 mL of deionized water (DI-H_2O) using probe sonication (Qsonica Q125 equipped with a sonotrode of 25.4 mm) for 2 hours at a frequency of 20 kHz and 75% intensity in an ice bath. The suspensions are filled in the 80 ml volumetric capacity spray gun to deposit the CNC and CNC–CNT onto both sides of the carbon fiber fabric (12 × 12 in.) at room temperature. After the coating process, the carbon fibers are dried at room temperature overnight followed by drying in an oven (Across International AT09) at 60°C for 48 hours. The drying time is determined based on the thermogravimetric analysis (TGA) confirming that there is no water on carbon fiber. Ten layers of the spray-coated carbon fiber fabrics were then cut into 6 × 6 in and used for manufacturing the composite laminates.

Zeta potential and particle size distribution of 0.01 wt% aqueous CNC and CNC–CNT suspensions were measured at room temperature using a Malvern Zetasizer Nano ZS. Suspensions were probe sonicated for 15 min before the measurements to make sure samples were taken from a homogenously dispersed solution. The same instrument was used to measure the hydrodynamic diameter of CNC–CNT at a fixed angle of 90°. All experiments were carried out for at least 10 samples and the average zeta potential and hydrodynamic diameter values are reported. Scanning Electron Microscopy (SEM) (Tescan FERA-3 Model GMH Focused Ion Beam Microscope with an acceleration of 10 kV) was used to visualize the surface properties of the CNC–CNT spray-coated carbon fibers. The *in-situ* bending test is conducted under the optical microscope by using Kammrath Weiss 10 kN bending stage. At least 5 samples with the dimensions of 10 × 50 × 2.1 mm are tested at a cross-head speed of 1 mm/min. The span length is 38 mm.

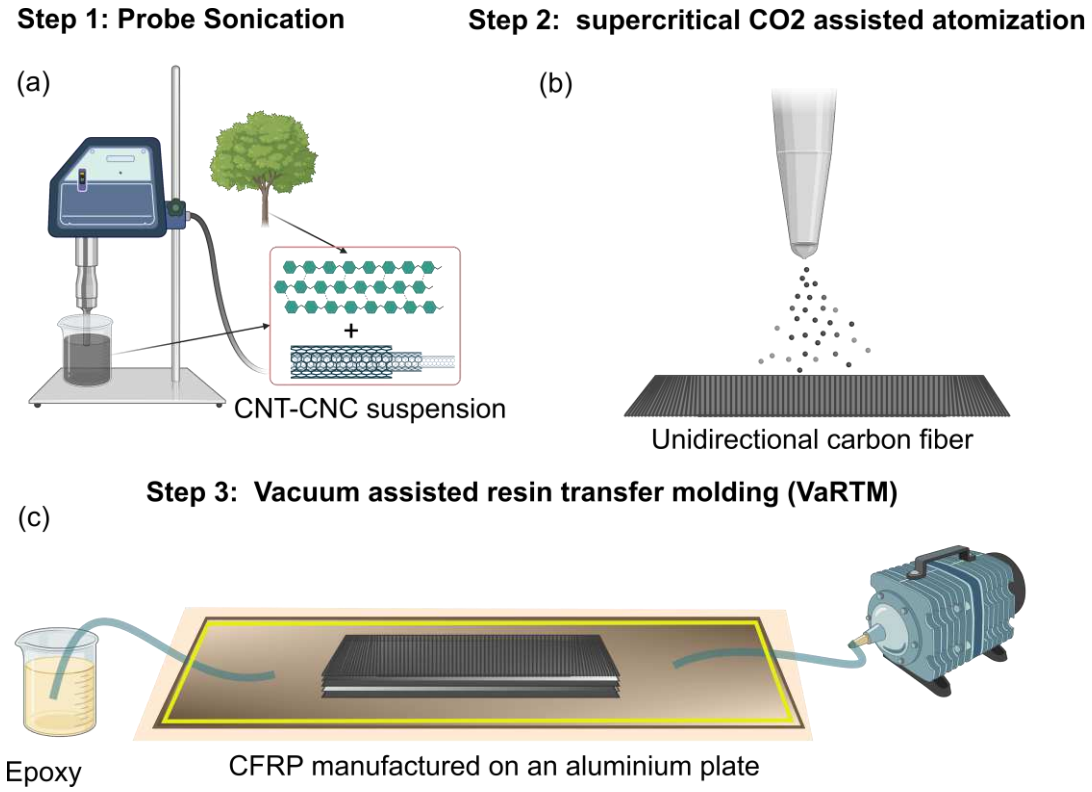

Figure 1. Schematic of composite preparation technique. (a) Probe sonication of CNC–CNT suspensions. (b) CNC–CNT deposition onto carbon fiber surface using SAA technique. (c) VaRTM technique of nanostructured CFRP.

RESULTS AND DISCUSSIONS

Dispersing nanomaterials in water suspension allows to maintain inherent nanomaterial in an environmentally friendly processing approach. However, transferring CNTs' outstanding properties is a challenge because they cannot be dissolved in a polar solvent (i.e., water) due to the strong Van der Waals attraction between them. To overcome this issue, CNCs are utilized to stabilize CNTs in water due to their highly negatively charged surface.

Table 1 demonstrates Zeta potential and DLS measurements of the CNC–CNT hybrid by changing the ratio of CNC to CNT. A higher zeta potential value and lower hydrodynamic diameter indicate higher hydrophilicity of CNC–CNT and better dispersion in water, respectively. According to Table 1, the Zeta potential value of CNC is almost -53.43 mV, and that of CNC–CNT ranges between -20.39 and -54 mV. The highest zeta potential, which is an indication of the hydrophilicity degree, is achieved for CNC–GNP 4:1 ratio at -54.91 mV which is higher than the neat CNC's -53.53 mV Zeta potential value. Table 1 also presents the DLS values, which are the hydrodynamic diameter of nanoparticles. The addition of CNTs increases the hydrodynamic diameter of nanoparticles which is in the range of 278 nm for CNC–CNT 4:1. Unsurprisingly, DLS values experience a slight decrease with changing the ratio (increasing the CNC content) which implies that CNCs and CNTs attach. Overall, we conclude that the best dispersion ratio is CNC–CNT 10:1 and we used the ratio to characterize the *in-situ* bending performance of the composites.

TABLE I. ZETA-POTENTIAL AND DLS OF CNC–CNT SUSPENSIONS

Suspension	Zeta-Potential -mV	DLS nm
CNC	53.43±0.66	75.79±7.83
CNC–CNT 4:1	20.39±0.33	278.03±9.76
CNC–CNT 6:1	40.10±2.50	246.06±8.48
CNC–CNT 8:1	52.14±0.43	231.83±1.24
CNC–CNT 10:1	54.91±0.36	233.17±2.90
CNC–CNT 12:1	52.73±0.96	244.76±4.15

Fig. 2a demonstrates the evaporation of particle-laden droplets and self-assembly of CNC–CNT on carbon fiber surface using the SAA technique. In evaporative particle-laden droplets, an outward capillary flow moves the nanoparticles' mass loss along the periphery that is positioned on the carbon fiber substrate [16]. In hydrophilic samples, which is in this case, this movement shuffles the CNC–CNT particles that are uniformly dispersed in water (with a zeta potential of ~ 55 mV shown in Table 1) and allows them to position in a ring-shaped pattern. Their strong attraction to water molecules and their small hydrodynamic diameter (~ 240 nm shown in DLS measurement in Table 1) accommodates this movement. After the evaporation, homogenously dispersed CNC-CNTs orient themselves throughout the carbon fiber surface (Fig. 2b). Fig. 2c shows the CNC–CNT is successfully deposited via nanocolloidal droplets after the evaporation.

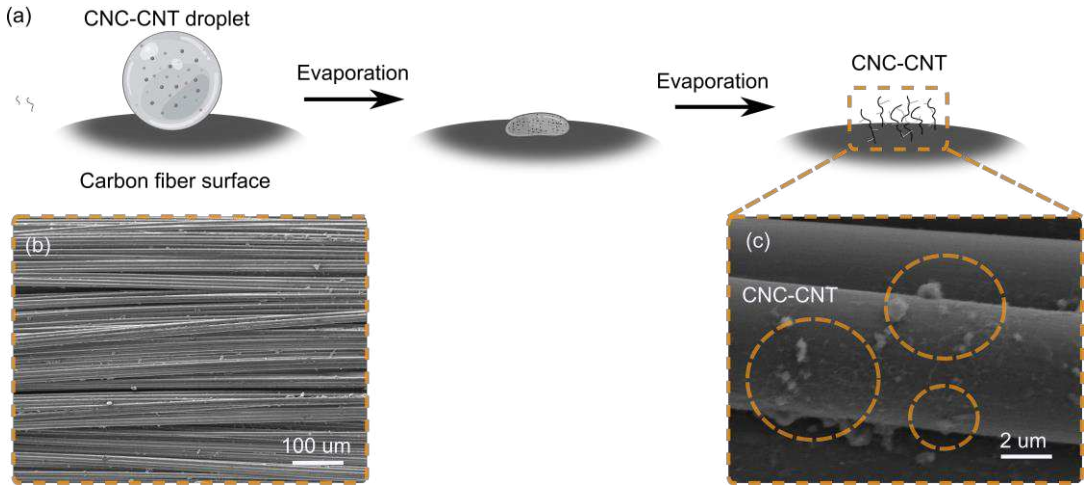

Figure 2. (a) Self-assembly of CNC-CNTs on carbon fiber substrate created through evaporative particle-laden droplets. SEM images of CNC–CNT (b) distributed, and (c) deposited on carbon fiber.

The *in-situ* bending test consists of a small-scale bending stage and optical microscope as shown in Fig. 3a. From the top view of the stage, the cross-section of CFRPs is monitored from the optical microscope during the test simultaneously. The *in-situ* bending stress-strain plot is revealed in Fig. 3b and demonstrates that neat CFRP fails at 450 MPa. In contrast, CNC–CNT deposited CFRP resists until 590 MPa, which indicates that CNC–CNT integration improves crack resistance. To visualize the crack resistance, optical micrographs of crack failure in neat and CNC–CNT spray-coated

CFRPs are displayed in Fig. 3c-d. Neat composite (Fig. 3c) experiences sudden delamination once it reaches 450 MPa. This indicates an uninterrupted crack propagation in the continuous epoxy matrix in neat CFRPs due to their low crack growth resistance [11]. According to the *in-situ* bending performance of CNC–CNT deposited CFRPs shown in Fig. 4d, matrix cracking occurs with the crack propagation, which indicates that CNC–CNT nanostructures successfully resist crack propagation that leads to altering the cracking path. Nevertheless, in CNC–CNT deposited CFRPs, retardation in crack propagation is promoted by the synergetic effect of CNCs and CNTs. Their effectiveness in bridging cracks is strongly dependent on the distribution of hybrid CNC-CNTs in the polymers and the efficiency of load transfer between CNTs and the surrounding epoxy matrix [11]. It is seen that hybrid CNC-CNTs act as obstacles in crack propagation; hence, the cracks prefer to propagate around CNC-CNTs, instead of passing through them. In other words, unlike neat CFRP, crack propagation is hindered by engineered hybrid nanostructures in the CNC–CNT nanostructured CFRP. The reason behind this is attributed to (*i*) the controlled morphology of CNC–CNT droplets on carbon fiber created through SAA and (*ii*) the enlarged interfacial span between carbon fiber and epoxy, which facilitates an efficient stress transfer from epoxy to carbon fiber due to the favorable synergy of CNC with CNT [8].

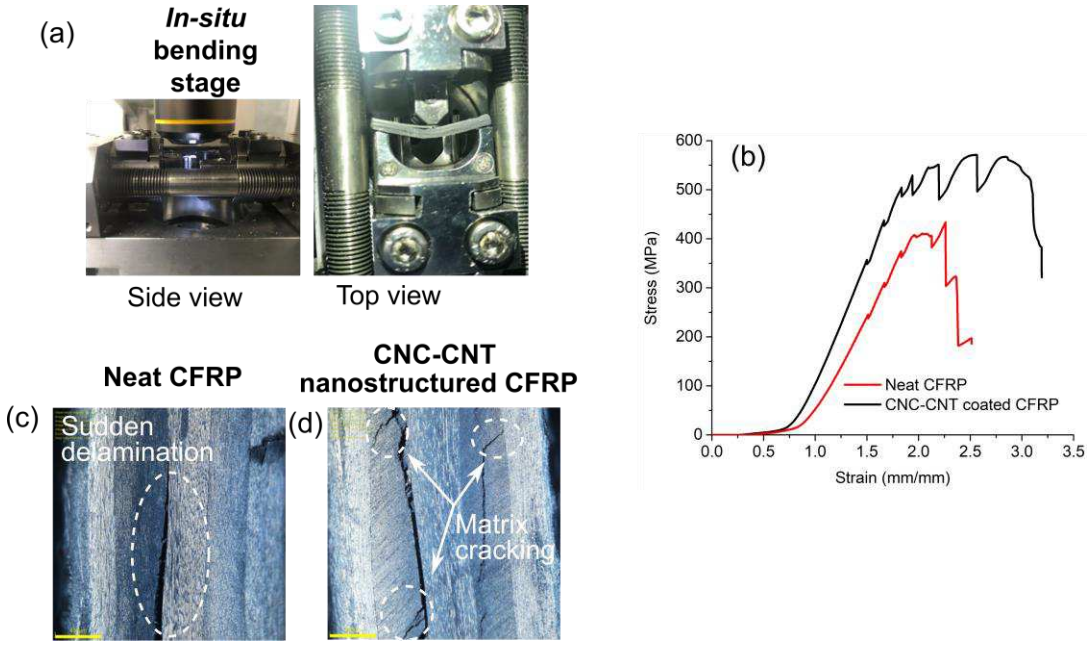

Figure 3 (a) *In-situ* bending stage under the optical microscope from the side and top views. (b) The bending plot of neat and CNC-CNT deposited CFRPs and their post-optical microscope images of (c) neat and (d) CNC-CNT deposited CFRPs.

CONCLUSION

In this study, we investigate the scalable manufacturing of CNT nanostructured CFRPs and monitor their nano-structural contribution to CFRPs under an *in-situ* bending test. We use a novel supercritical CO2-assisted atomization (SAA) system to create fine hybrid nanostructure droplets that are homogeneously distributed on a carbon fiber substrate. According to *in-situ* bending results, the neat CFRP delaminates at 450

MPa, while CNC–CNT integration in CFRPs leads to retardation of the delamination up to 590 MPa. The role of CNC–CNT nanostructures in CFRP is much clear in the crack propagation patterns revealed by optical microscope images that were taken during the test. The neat CFRP exhibits low crack growth resistance due to the uninterrupted crack propagation in the continuous epoxy matrix whereas crack propagation is hindered by hybrid nanostructures in the modified CFRP. The reason behind this is attributed to the controlled morphology of CNC–CNT droplets on carbon fiber created through SAA and the enlarged interfacial span between carbon fiber and epoxy, that facilitates efficient stress transfer from epoxy to carbon fiber. It is concluded that self-assembled hybrid CNC–CNT nanostructures effectively enhance the structural properties of CFRPs due to the synergistic effect of the nanostructures and homogenous distribution through evaporation-induced self-assembly of nanocolloidal droplets. This strategy provides new possibilities to precisely control the material microstructure and enables the bottom-up manufacturing of hybrid nanostructured composites.

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