



A biomimetic approach to improve the dispersibility, interfacial interactions and toughening effects of carbon nanofibers in epoxy composites



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ABSTRACT

In this work, the surface of stacked-cup carbon nanofibers (CNFs) was coated with polydopamine (PDA) via a facile biomimetic method based on catecholic chemistry. The modified CNFs (D-CNFs) were incorporated into an epoxy resin in a solvent-free manner. In addition to hydrogen bonding, covalent bonding is also present between amino groups in PDA and epoxy, as verified by Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS). Owing to the strong interfacial interactions brought by PDA, D-CNFs show significantly improved dispersibility in epoxy matrix. Consequently, the reinforcing effects of D-CNFs clearly outperform those of pristine CNFs (P-CNFs), especially in terms of fracture toughness. Dynamic thermo-mechanical studies show that the addition of D-CNFs can increase storage modulus more effectively without deteriorating the thermal stability of epoxy matrix. This study confirms that enhancing interfacial interactions in polymer composites by coating nanofillers with PDA is a useful strategy to obtain simultaneous stiffening and toughening in rigid thermoset polymers.

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1. Introduction

Continuous fiber-reinforced polymer composites (CFRPs) are increasingly used for applications that require high-performance light-weight structural materials [1,2]. For example, in 2013, BMW marketed its revolutionary i3 electric car with the whole body being made from carbon fiber reinforced composites. Likewise, the content of advanced composites in Boeing's new 787 Dreamliner amazingly reaches over 50 wt percent. For modern high-performance CFRPs, epoxy resins are the most commonly used thermosetting matrix materials due to their good mechanical strength, dimensional stability, adhesive properties, chemical resistance and cost-performance ratio [3,4]. However, the

mechanical properties of epoxy resins, especially their strength and toughness, still need to be further enhanced in order to increase the lifetime and application range of the composites. To address this issue, a great deal of research works have been undertaken, among which the incorporation of nanometer-sized fillers such as particles, fibers and sheets, is a popular strategy to reinforce and toughen epoxy resins [5].

Carbon nanofibers (CNFs) are highly graphitic carbon nano-materials with hollow cylindrical morphology. CNFs typically have an outer diameter in the range 50–500 nm and length in the order of 50–100 μm with tensile strength of ~ 3 GPa and tensile modulus of ~ 250 GPa [6,7]. Although the mechanical properties of the CNFs are in general inferior to those of carbon nanotubes (CNTs) due to their less ordered structures, they have much lower production cost than CNTs [8], which makes CNFs an ideal candidate for reinforcing epoxy resins for high-volume applications, as well as simultaneous reinforcing and toughening rigid polymers owing to their abundant

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sacrificial bonds [9]. Like most nanofillers, the reinforcing efficiency of CNFs depends heavily on their dispersion states and interfacial interactions between CNFs and polymer matrices. Unmodified CNFs are difficult to be uniformly dispersed in epoxy resins even after treatment by high shear mixing, three-roll milling, ultrasonication or solvent dilution [9–11]. To improve the compatibility between CNFs and epoxy resins, one common strategy is to functionalize carbon atoms on CNF surface. For example, triazole-functionalized CNFs have been prepared by arylation with in-situ generated diazonium salts in our previous work [12]. Surface modification can also promote load transfer from polymer matrices to CNFs. However, the reported methods to covalently functionalize CNFs generally involve the usage of corrosive chemicals or tedious synthesis procedures [12–15]. Therefore, a simple, eco-friendly method to modify the surface of CNFs is highly desired.

Polydopamine (PDA), a biomimetic synthetic polymer based on catecholic chemistry, has attracted great interests recently because of its amazing adhesion to a variety of material surfaces [16]. It has been reported that polydopamine can be facily coated on various nanofillers by self-polymerization of dopamine in basic aqueous solutions [17–22], and the catechol groups in PDA are capable of forming hydrogen bonds with polar groups in epoxy and polyurethane [17,18]. In addition, the possibility of interfacial covalent bonding between PDA and epoxy cannot be completely rolled out because the primary and secondary amine groups in PDA may react with epoxy groups and the amine hardener may react with PDA via Schiff base reaction or Michael addition [23,24]. Therefore, this simple bio-inspired method for surface modification may have the potential to improve the dispersibility of CNFs in epoxy and the interfacial interactions between epoxy and CNFs, facilitating interfacial stress transfer and sacrificial bond-induced toughening. To verify this hypothesis, PDA-modified CNFs (D-CNFs) were dispersed in an epoxy resin using a solvent-free method and the dispersion state of D-CNFs were investigated by various microscope observations. Presence of chemical interactions between the coated PDA and epoxy were confirmed by Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) measurements. Mechanical properties of the D-CNFs/epoxy composites, including tensile properties and fracture toughness, were systematically studied. Finally, the effects of addition of D-CNFs on the thermo-mechanical properties of epoxy matrix were investigated by dynamic mechanical analysis (DMA).

2. Experimental section

2.1. Materials

Pyrograf-III carbon nanofibers (PR-24-XT-LHT, 50–200 μm in length, 70–200 nm in diameter) were supplied by Applied Science, Inc. (USA). Hydroxyphenethylamine hydrochloride (dopamine, 98%) and tris-(hydroxy-methyl) aminomethane (TRIS, 99%) were supplied by Sigma-Aldrich Chemicals, Inc. (USA). The epoxy matrix used in this study was epoxy (Epolam 5015) and amine curing agent 5015 purchased from Axson, Inc. (USA).

2.2. Preparation of D-CNFs

Preparation of D-CNFs was similar to the method reported in our earlier publication [17]. In a typical experiment, 1.0 g of pristine CNFs (P-CNFs) was added in a beaker with 100 mL deionized water. The mixture was processed by magnetic stirring for 12 h followed by bath ultrasonic treatment for 15 min. The CNF suspension was slowly poured into 250 mL TRIS buffer solution (10 mM, pH = 8.5) under constant magnetic stirring. After that, 0.55 g of dopamine was added and the suspension was stirred for 2 h at ambient

temperature. The obtained black CNF suspension was treated by vacuum filtration and washing with excess deionized water to remove the unreacted dopamine. Finally, D-CNFs were obtained by freeze drying the filter cake for 48 h.

2.3. Fabrication of CNFs/epoxy composites

First, a calculated amount of D-CNFs was weighed and directly dispersed in epoxy (Epolam 5015). The mixture was then processed by high-speed shear mixing at 9000 rpm for 15 min via a homogenizer, followed by ultrasonic treatment for 20 min. When the mixture cooled to ambient temperature, amine curing agent 5015 (epoxy/curing agent was 100/30 by weight as suggested by the supplier) was weighed and added. Subsequently, the mixture was manually stirred for 10 min and then degassed for 30 min in a vacuum oven at ambient temperature. Finally, the obtained mixture was carefully poured into self-made silicone molds and cured at 25 $^{\circ}\text{C}$ for 24 h, followed by post cure at 80 $^{\circ}\text{C}$ for another 24 h. Neat epoxy and P-CNFs/epoxy composites were also prepared using the same procedure as mentioned above.

2.4. Characterization

FTIR spectroscopy was performed on a Perkin Elmer Instruments Spectrum GX FTIR spectrometer with attenuated total reflection (ATR) attachment. XPS measurement was conducted using Kratos Analytical AXIS His spectrometer. A monochromatized Al Ka X-ray source at 1486.6 eV was adopted to scan the surfaces of CNF samples. DMA was measured on a Q800 Dynamic Mechanical Analyzer (TA Instruments) at 3 $^{\circ}\text{C}/\text{min}$ heating rate and 1 Hz frequency under an air atmosphere. The measurements were performed using a single cantilever beam model and the dimension of the specimens is 40 \times 13.0 \times 2.0 mm³. Tensile properties of neat epoxy and the composites were measured on an Instron Test Machine 5567 following standard ASTM D638 (sample type V). At least six valid values were recorded for each sample. The mode I fracture toughness was measured with three-point-bend configuration on single edge-notch specimens (53 \times 12 \times 6 mm³) following standard ASTM D5045. A sharp notch was accurately machined at the midpoint of each specimen using an automatic notch maker. A pre-crack was introduced by careful tapping a chilled fresh blade (GEM 3 facet) in the notch. The tests were performed on Instron Micro Tester 5848 equipped with a 2 kN load cell and the specimens were loaded to failure at a crosshead speed of 1 mm/min. Critical stress intensity factor (K_{Ic}) and critical strain energy release rate (G_{Ic}) were calculated according the method given in ASTM D5045. At least eight valid specimens were tested for each sample. The states of dispersion for CNFs/epoxy blends were inspected using an optical microscope (Eclipse LV100 POL, Nikon Instruments). Transmission electron microscopy (TEM) was conducted on a JEOL JEM-2010 with 200 kV accelerating voltage. CNFs/epoxy composites specimens were cut in water using a diamond knife on the ultramicrotome. The morphologies of the fractured surfaces were observed with a field emission scanning electron microscope (JEOL FESEM 7600F). Each sample was coated with gold for 90 s.

3. Results and discussion

3.1. Surface modification of P-CNFs

D-CNFs were prepared using a well-established method (Fig. 1a) based on catecholic chemistry and the polymerization mechanism of dopamine has been well studied in previous research [25]. This method of surface modification by PDA is simple, eco-friendly and scalable. The successful coating of PDA on P-CNF surface is verified

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