Effect of electrophoretically deposited carbon nanotubes on the interface of carbon fiber reinforced epoxy composite

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Abstract The interface between reinforcing fiber and matrix is a crucial element in composite performance. Homogeneous and interconnected carbon nanotubes (CNTs) were deposited onto the surface of carbon fibers to produce multiscale reinforcement by electrophoretic deposition (EPD). Single fiber tensile tests showed that the tensile strength and Weibull modulus of the resulting multiscale materials were increased by 16 and 41%, respectively. Compared with as-received carbon fibers, CNTs-deposited carbon fibers provided the decreased surface energy by 20% and the increased adhesion work by 22% using modified Wilhelmy method. Results from single fiber pull-out testing showed that a significant improvement (up to 68.8%) of interfacial shear strength was obtained for the composites containing by CNTs/Carbon fiber multiscale reinforcement. All results strongly suggest that EPD process can provide a feasible platform for improving interface properties of advanced composites.

Introduction

Carbon fiber composites, particularly those with polymeric matrices, have become the dominant advanced composite materials for aerospace, automobile, sporting goods, and other applications because of their high strength, high modulus, low density, and reasonable cost [1, 2]. However, the relatively weak in-plain compressive strength and out-of-plain properties remain as major issues. The main reason is that the conventional reinforcing fibers are difficult to reinforce the matrix-rich regions. The interface between fiber and matrix plays a critical role in the performance and behavior of fiber reinforced composite materials [3].

Extensive researches have been concentrated on carbon nanotubes (CNTs)/carbon fiber multiscale composites, in which nanoscale CNTs are used along with conventional carbon fiber [4, 5]. Two of the most frequently used routes to form CNTs/carbon fiber multiscale reinforcement are growing CNTs on the surface of carbon fiber directly by chemical vapor deposition (CVD), and grafting functional CNTs with carbon fiber through chemical reaction [6–9]. Both methods reported successful attachment of CNTs on the fiber surface. However, the former needed high temperature or predeposited catalysts, and in the latter study, too many chemical treatments and long processing time were necessary, which is less environmentally friendly. In addition, each of them has difficulties in processing large panels and the practical application.

Recently, electrophoretic deposition (EPD) of functionalized carbon nanotubes or nanofibers has been applied successfully to fabricate hybrid composites because of scalability and cost-effectiveness [10]. Bekyarova et al. deposited carboxylic acid-functionalized multi- and single- walled carbon nanotubes (CNTs) on woven carbon fabric [11]. Results showed that interlaminar shear strength and out-of-plain electrical conductivity were significantly improved, compared with those in conventional carbon fiber composites, and it is important to note that they preserved in-plain mechanical properties. Also, different charged CNTs owing to different chemical treatment were deposited onto carbon fabric by anodic or cathodic EPD, respectively [12–14].

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Most studies reported improved properties of composites; however, the effect of electrophoretically deposited CNTs on the interface between reinforcing fibers and matrices has rarely been studied. In this study, EPD was used to deposit carboxylic acid-functionalized CNTs on the surface of carbon fibers. The effects of deposited CNTs on the tensile mechanical properties of carbon fibers were evaluated because these properties determine the in-plain performance of fiber reinforced composites. Contact angle measurements were performed to examine the surface properties of the CNTs deposited fibers, which are relevant to subsequent resin infiltration. The mechanical properties of composites were evaluated by interfacial shear strength (IFSS) using monofilament embedding method.

Experimental

Materials

Polyacrylonitrile-based carbon fibers (Institute of Coal Chemistry, Chinese Academy of Sciences, China) were used as the base material to fabricate the hybrid reinforcement. The multi-walled carbon nanotubes were purchased from Shenzhen Nanotech. Port. Co. Ltd. (Shenzhen, China). These CNTs have an average diameter and length in the ranges of 10–30 nm and 1–2 μm, respectively.

Preparation of CNTs–CF hybrid reinforcement by EPD

Preparation of a stable CNTs dispersion is a prerequisite for successful EPD [15]. Typically, the as-received CNTs (1–2 μm, Shenzhen Nanotech Port Co., Ltd) were refluxed in a 3:1 (v/v) mixture of concentrated sulfuric and nitric acids at 120 °C for 30 min, as reported elsewhere [16]. On cooling, the oxidized nanotubes were washed to pH 7 with distilled water and then vacuum dried at 80 °C for 24 h. The CNTs were dispersed in deionized water by ultrasonication to obtain a dispersion of 0.05 mg/mL. After acid treatment, CNTs can respond to an electric field and move toward the positive pole because they are negatively charged at pH 7 [17]. In this study, carbon fibers were used as the anode and immersed into CNTs dispersion, and a graphite plate was positioned opposite to carbon fibers as the counter electrode. The EPD process was then carried out under a constant voltage of 20 V for 15 min. The distance between electrodes was 2 cm. After deposition, the carbon fibers were washed and dried in air at room temperature.

Characterization

The carbon fibers were examined using a scanning electron microscope (SEM) (LEO 1530VP) at 10.0 kV and Raman spectroscopy (JY LabRAM HR800) with exaction wavelength of 532 nm. Chemical composition of fiber surface was confirmed by X-ray energy dispersive spectroscopy (EDS). The tension fracture for the fiber-reinforced epoxy composites were observed with JSM 6360LV microscopy at 5 kV. The samples were coated with Au by sputtering.

Single fiber tensile tests were performed using a single fiber electronic tensile strength tester (LLY-06E, China). The tensile specimens were fastened to a paper holder with an instant cyanoacrylate adhesive, as reported elsewhere [18]. A gauge length of 10 mm and crosshead speed of 0.5 mm/min were applied for the tests. At least 20 measurements were tested for each fiber specimen.

Contact angles were performed using a dynamic contact angle meter and tensiometer (DCAT21, Dataphysics Instruments, Germany). Deionized water, diiodomethane (DIM), and E51 epoxy resin ($\gamma^d = 37.71$ mN m^{-1}, $\gamma = 45.78$ mN m^{-1}) were applied to be the test medium. The thermodynamic work of adhesion, WA, between the fibers and the epoxy matrix can be evaluated by the Young-Dupré Eq. 1. Each measurement was repeated four times and the results were averaged.

$$W_A = \gamma_L(1 + \cos\theta) \tag{1}$$

The interfacial shear strength (IFSS) of carbon fiber-reinforced epoxy composites was examined by single fiber pull-out tests as shown in Fig. 1. A carbon fiber monofilament was fixed to a metal holder with adhesive tape and be wetted by resin matrix to form microdroplets due to the function of surface tension. The specimens were cured at 80 °C for 1.5 h, then at 120 °C for 2 h and then finally at 150 °C for 3 h. After curing, the microdroplets with the embedded length of 60–80 μm were selected and tested using an interfacial strength evaluation instrument (Tohei Sayon Corporation, Japan) with a loading rate of 1 μm/s. The values of IFSS were calculated according to Eq. 2 [19],
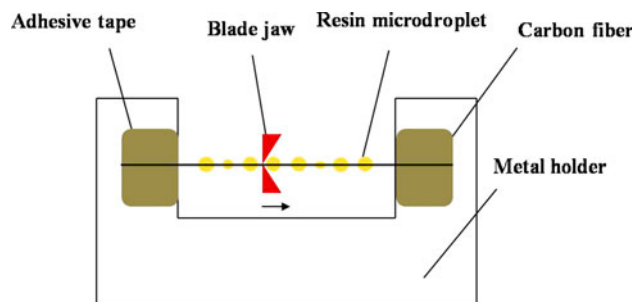

Fig. 1 Schematic of single fiber pull-out test. The *arrow* indicates blade jaw movement direction. Please note that the diagram is not to scale

$$\text{IFSS} = \frac{F_{\max}}{\pi D_{\mathrm{f}} L_{\mathrm{e}}} \qquad (2)$$

where $F_{\max}$ is the maximum load, D_{f} is the carbon fiber diameter, and L_{e} is the embedded length. A minimum of 20 specimens were tested from each set of composites.

Results and discussion

SEM morgraphology of carbon fibers

As shown in Fig. 2, the surface of as-received carbon fiber was rough, and many obvious grooves were uniformly distributed along with the longitudinal direction of the carbon fiber. The morphology of CNTs-deposited carbon fibers changed a lot, compared with that of the untreated one, as shown in Fig. 3. The CNTs were uniformly and densely deposited on the fiber surface at different angles, forming a network of interconnected nanotubes, and the original morphologies can be hardly found. Moreover, deposition of CNTs by electrophoresis provided almost a full carbon hierarchical system, as demonstrated by EDS in Fig. 3b. The observed oxygen may have originated from carbon fiber and carbon nanotubes. This kind of nanotubes feature is different from those of chemical grafting or CVD; the former is relatively sparsely deposition or partly agglomeration [8, 20], and in the latter study, nanotube's

tend to be radial to the fibers [21]. EPD provides a new structure that CNTs internetwork wraps up the whole surface of carbon fibers.

Raman characterization

As shown in Fig. 4, two characteristic broad bands, D (nearly 1350 cm^{-1}) and G (nearly 1580 cm^{-1}) modes were detected from the carbon fibers. After the electrophoretic
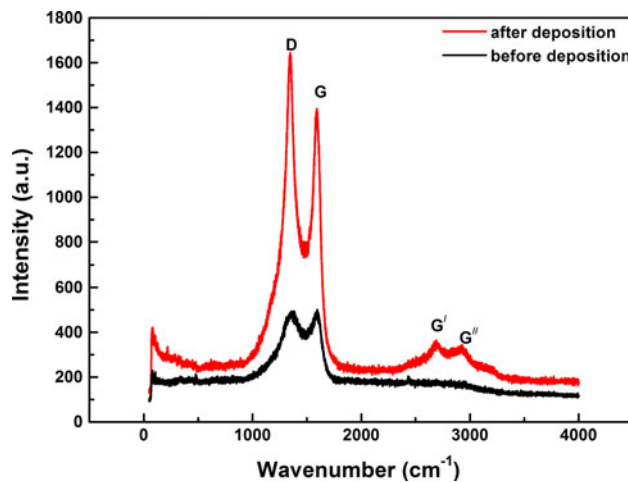

Fig. 4 Raman spectra of carbon fiber before (the *lower curve*) and after (the *upper one*) the deposition of CNTs

Fig. 2 SEM images of as-received carbon fibers: **a** low magnification, and **b** high magnification
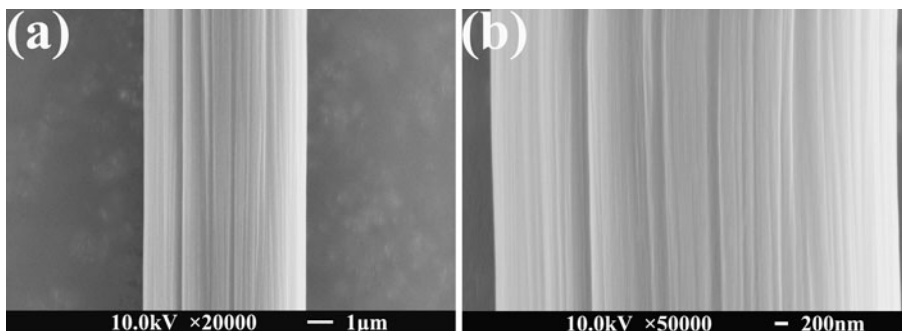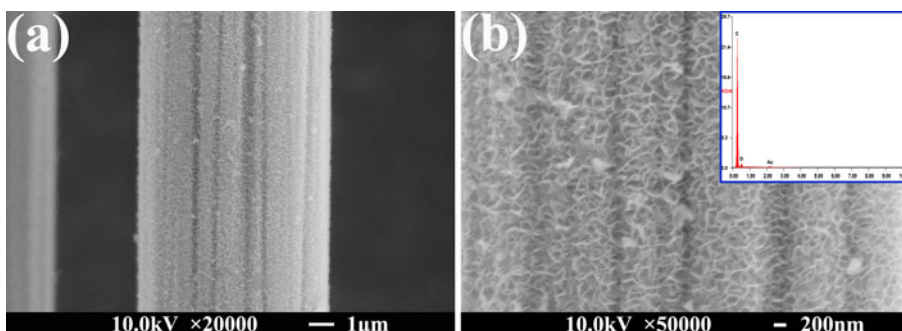

Fig. 3 SEM images of CNTs-deposited carbon fibers: **a** low magnification, and **b** high magnification with inset showing EDS of fiber surface

deposition of CNTs, the characteristic signals of CNTs appeared, as indicated by the narrower band width of the D and G modes and the presence of the G′band (nearly 2720 cm^{-1}). In this case, both the signals from carbon fibers and CNT-depositing were detected, leading to convolution exhibited in the spectra.

Single fiber tensile testing

It is generally accepted that CNTs grafted on carbon fiber through CVD or chemical grafting is accompanied by a decrease in the tensile strength due to surface etching [22, 23]. Thus, we need to investigate the effect of depositing CNTs by EPD on the mechanical properties of carbon fibers. The tensile strength and Weibull modulus were summarized in Table 1. The results showed that the average tensile strength of CNTs-deposited carbon fiber was 4.14 ± 1.02 GPa, which is 16% higher than that in the as-received state (3.57 ± 0.80 GPa). The Weibull modulus increased from 4.55 for the as-received carbon fibers to 6.40 for CNTs-deposited carbon fibers i.e., by 41%. The tensile modulus of CNTs deposited on carbon fiber increased to 232 ± 28 GPa from 230 ± 13 GPa in the as-received state. In addition, the ductility of CNTs deposited on carbon fiber was measured to be 1.53 ± 0.44%, which is slightly higher than that in the as-received state (1.48 ± 0.42%). The theoretical strength of carbon fiber is 180 GPa; however, we cannot achieve this value because of many defects existing in the fibers, especially the surface defects. Now the deposition of dense CNTs network on carbon fibers makes up some of the surface flaws of carbon fiber during manufacturing and reduces the strength-limiting defects, which, in turn, improve the tensile strength and Weibull modulus [7].

Table 1 Tensile strengths and Weibull moduli of carbon fibers before and after depositing CNTs

Fiber	As-received	CNTs deposited
Tensile strength (GPa)	3.57 (0.80)	4.14 (1.02)
Tensile modulus (GPa)	230 (13)	232 (28)
Failure strain	1.48 (0.42)	1.53 (0.44)
Weibull modulus	4.55	6.40

Bracket indicate standard deviations

Dynamic contact angles analysis

The changes of chemical environment and topography of carbon fiber surfaces affect the fiber surface properties. The contact angles (θ), dispersive (γ^d) and polar component (γ^p) of surface energy (γ), and the adhesion work (W_A) were summarized in Table 2. The results showed that obvious increasing trends of contact angels were observed from the as-received carbon fibers to CNTs-deposited fibers for both the polar water and non-polar DIM. As can be seen in Table 2, the surface energy decreased from 52.11 mN m^{-1} for the as-received to 41.76 mN m^{-1} for CNTs-deposited carbon fibers by 20%. In Addition, the dispersive component of surface energy increased from 32.81 to 34.42 mN m^{-1},whereas the polar component decreased from 19.31 to 7.34 mN m^{-1} after deposition on the carbon fibers with CNTs, which are relatively hydrophobic. Thus, the CNTs deposition has a strong effect on the wettability of carbon fibers in polar liquids. It can be also found that the contact angles for epoxy resin decreased from 70.80° to 51.38° after CNTs deposition. The adhesion work (W_A) significantly increased from 60.82 mN m^{-1} for the as-received to 74.34 mN m^{-1} for CNTs deposited carbon fibers by 22%. The increased adhesion work indicated the better wettability for resin and stronger interfacial adhesion strength. Possible reasons can be attributed to two aspects: (1) the deposition of CNTs improves the dispersive ratio of fiber surface energy, which is basically equal to that of epoxy resin (0.82); and (2) the network structure formed by CNTs on fiber surface is beneficial to the spreadability of epoxy resin.

Single fiber pull-out testing

The interfacial shear strength (IFSS) results of epoxy composites reinforced by the as-received and the CNTs-deposited carbon fibers were shown in Fig. 5. The results showed that the IFSS increased from 67.3 MPa for the as-received carbon fibers to 113.6 MPa for the CNTs-deposited fibers by 68.8%. It is generally accepted that IFSS improvement is partly due to the increased surface energy [23]. However, the surface energy decreased by 20% in this study. Our study demonstrated that the improvement of IFSS was more dependent on the fiber surface structure and polarity match with resin matrix rather than on surface
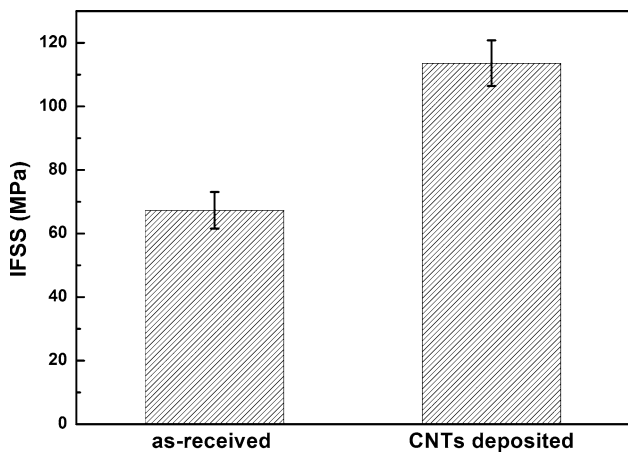
Table 2 Contact angles, surface energy, and adhesion work of carbon fibers measured by modified Wilhelmy technique

Fibers	θ/deg			γ^d/mN m^{-1}	γ^p/mN m^{-1}	γ/mN m^{-1}	W_A/mN m^{-1}
	Water	DIM	Epoxy				
As-received	55.13	33.61	70.80	32.81	19.31	52.11	60.82
CNTs deposited	72.23	39.61	51.38	34.42	7.34	41.76	74.34

Fig. 5 Interfacial shear strength of the composites reinforced by the as-received and CNTs-deposited carbon fibers

energy, as mentioned above. Depositing CNTs onto fiber surfaces is an effective approach to improve fiber surface roughness, creating mechanical interlocking, and/or local stiffening at fiber/matrix interface, all of which may improve stress transfer and interfacial properties [6]. In Addition, the chemical bond between the CNTs and the epoxy resin played a very important role in improving IFSS.

Fracture morphology analysis

To explore the nature of their fracture behavior, the fracture surface of the tensile tested composites specimens reinforced by the as-received or CNTs-deposited carbon fibers were examined using SEM (Fig. 6). For the composites without CNTs, there is no residual resin on the fiber surface (Fig. 6a) and the fiber crenulations can be clearly visible (Fig. 6b), indicating debonding along the fiber/matrix interface. However, the fracture surface of the composites with CNTs deposition presents completely different morphologies, with resin adhered on the fiber surface (Fig. 6c), and the pull-out hole is highly wrinkled (Fig. 6d). The CNTs deposition has formed a new interface layer. The powerful mechanical interlocking restricts the slip between the fiber and the matrix and improves the load-transfer ability. It is also found that a large part of the deposited CNTs were completely embedded into the matrix, again demonstrating its excellent wettability by epoxy resin. The adhesive strength between electrophoretically deposited CNTs and carbon fibers may be relatively weaker compared with the one between CVD-deposited CNTs and fibers, because the failure is at or near the root of the CNTs in the latter study [24].

Conclusion

Uniform CNT networks were deposited on carbon fibers to improve the interfacial properties between carbon fibers and epoxy matrix by EPD process. Single-fiber tensile tests showed that both the tensile strength and Weibull modulus were improved, which effectively solved the disadvantages of the CVD process and/or chemical grafting. The CNT's deposition decreased the surface energy, while improving the wettability for epoxy resin. Results from single fiber pull-out tests showed an increase in interfacial shear

Fig. 6 SEM images of the fracture surfaces of carbon fibers/epoxy composites (**a**), **b** without; and **c**, **d** with CNTs deposited on the fiber surface. *Scale bar* = 1 μm
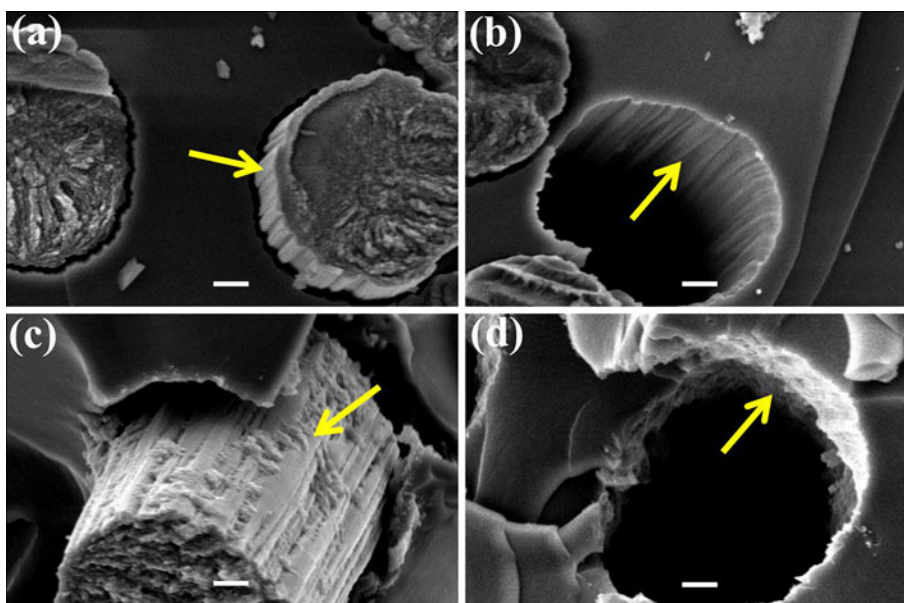
strength (IFSS) of 68.8% for the composites containing CNTs/carbon fiber multiscale reinforcement. Further investigation into the fracture surface showed that new interface formed between carbon fiber and resin matrix formed after CNT's deposition, which can restrict the slip and improve the ability of load transfer. In brief, EPD is a feasible and completive approach for preparing CNT's/carbon fiber multiscale reinforcement and improving composite interface.

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