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Investigation on Some Matrix-Dominated Properties of Hybrid Multiscale Composites Based on Carbon Fiber/Carbon Nanotube Modified Epoxy

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ABSTRACT: Continuous fiber reinforced polymer-based composites have outstanding fiber-dominated properties but unsatisfactory matrix-dominated performances. In this investigation, carbon fiber reinforced epoxy composites modified with carbon nanotubes (CNTs) were fabricated to evaluate the effects of CNTs on some matrix-dominated properties of the resulting hybrid multiscale composites. Carboxylic acid functionalized multiwalled CNTs were dispersed in epoxy by using high energy sonication, followed by the fabrication of the composites laminates with the epoxy/CNTs dispersion. The dispersion quality of CNTs in epoxy and the capillary infiltration of continuous fiber with the epoxy/CNTs dispersion were characterized using optical microscope and capillary experiment to optimize the processing parameters. A CNTs loading of 1 wt % significantly improved the flexural strength and interlaminar shear strength of the composites containing varying scale reinforcements by 51.8% and 34.2%, respectively, as compared to the control carbon/epoxy composites. Scanning electron microscopy was used to examine the fracture surface of the failed specimens. The moisture absorption behavior of the carbon fiber/epoxy composites with and without CNTs was investigated by comparing the weight gain and shear properties degradation in distilled water and 1.5 wt % brine. The integration of CNTs in composites is found to contribute to the medium-dependent moisture adsorption behavior. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 128: 990–996, 2013

KEYWORDS: carbon nanotubes (CNTs); dispersions; hybrid multiscale; mechanical properties; moisture adsorption

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INTRODUCTION

Continuous fiber reinforced polymer-based composites have earned widespread attention due to their outstanding high strength-to-weight ratio and mechanical performance. With the improvement of our understanding and fabrication technique in the past decade, it is more and more difficult to engineer composites consisting of traditional fiber reinforcement and resin system to cater to a wide variety of requirements. In some sense, we have been approaching the design limit of optimizing composites with traditional micrometer scale fillers/reinforcements and resin matrix, in which macroscopic defects due to regions of high or low volume fraction of filler often lead to materials failure and property tradeoffs. Traditional fiber reinforced composites generally possess good fiber-dominated zmechanical properties capable of suiting the various design requirement and, on the other hand, unsatisfactory matrix-dominated performances such as overall structural integrity, dimensional tolerance, and electrical conductivity. However, the recent advancements in aerospace, automobile, marine, and wind power industries increasingly demand for materials with synergistic properties. Great effort in the research community has been devoted to enhancing the matrix-dominated properties in accordance with the composition- processing- structure-properties relationship. The exceptional physical properties combined with high aspect ratios and low density render carbon nanotubes (CNTs) an attractive candidate for the modification of polymer composites.[1,2] The introduction of CNTs into continuous fiber reinforced composites offers an opportunity for combining potential benefits of nanoscale reinforcement and functionality with well-established fibrous composites to create hybrid multiscale composites. It is possible to develop a new generation multifunctional materials with optimized mechanical, thermal, as well as electrical properties, which represent a good compromise between performance and cost for most applications.

To date, many studies show that the incorporation of CNTs into existing composites to achieve hybridation can be carried out via two routes. One common way is to integrate CNTs into

liquid matrix resin with the help of direct mixing, sonication and high shear mixing via 3-roll milling to accomplish the uniform dispersion of CNTs. The resulting dispersion can be used as nanocomposite matrix to infiltrate fibrous reinforcement. Wichmann et al. reported that the addition of 0.3 wt % CNTs into a resin transfer molded composites could enhance the interlaminar shear strength (ILSS) by 16% and the application of an electrical field in z-direction resulted in an increase in electrical conductivity by more than one order of magnitude, respectively.[3] Seyhan et al. found that 0.1 wt % of CNTs modified laminates exhibited 8% and 11% higher mode II interlaminar fracture toughness and ILSS values as compared to the control laminates and no significant improvement was observed for mode I interlaminar fracture toughness values.[4] Bekyarova et al. demonstrated that the incorporation of CNTs functionalized with carboxylic acid groups produced a 40% improvement of the shear strength at a loading of 0.5 wt %.[5] Kim et al. reported that a combination of Halpin-Tsai equations and woven fiber micromechanics was used in hierarchy to predict the mechanical properties of multiscale composites.[6] Thostenson et al. suggested that CNTs network dispersed in the epoxy matrix as distributed sensor were sensitive to initial stages of matrix-dominated failure and could be used to evaluate the onset and evolution of damage in advanced fibrous composites.[7] Hsiao et al. showed that the spring-in angles of the hybrid composites were effectively restrained and the developed model to predict the spring-in phenomenon agreed with the experimental results reasonably well.[8]

The other route is to deposit or coat CNTs on the fiber surface by using chemical, electrophoresis, chemical vapor deposition (CVD), and spray-up process. The fabricated 2D or 3D woven nanocomposite preform can be suggested for applications in molding and infusion processing. Thostenson et al. prepared a multiscale composites by directly growing CNTs on carbon fiber using CVD and gained selective reinforcement by CNTs at fiber/matrix interface.[9] Bekyarova et al. used electrophoresis processing to develop an engineered multiscale CNTs/carbon fiber reinforced composites and demonstrated 30% enhancement of ILSS and greatly improved out-of-plane electrical conductivity.[10] Zhu et al. improved interfacial shear strength of epoxy composites by overcoating the glass fiber with nanotubes to achieve a multiscale reinforcement.[11] Loyola et al. have proposed an *in situ*strain monitoring technique via CNTs based thin films deposited onto glass fiber weaves.[12]

It has been well recognized that the prerequisites for effective exploitation of potential for CNTs include the degree of dispersion, impregnation with dispersion and interfacial adhesion. Functionalization of CNTs has been successfully employed for the optimization of the polymer/CNTs interface so as to ensure efficient stress transfer.[13] As for hybrid multiscale composites containing microscale fibers and nanoscale CNTs, the dispersion of CNTs in matrix resin and the impregnation of fibrous reinforcement with this dispersion are complicated by thermodynamically unstable suspension and simultaneously existing competitive flow between interbundle and intrabundle. In the current work, we focus on an experimental investigation on the processing and properties of hybrid multiscale composites based on carbon fabric/carboxylic acid-functionalized CNTs modified epoxy. Used as the primary means to achieve CNTs dispersion in epoxy matrix, high energy sonication is evaluated with respect to the effects of sonication parameters on impregnating behavior. The mechanical properties and moisture absorption of the resulting hybrid composites, dominated by resin matrix to a larger degree, are described.

EXPERIMENTAL

Materials

Carboxylic acid functionalized multiwalled CNTs were purchased from Timesnano, China, with an outer diameter of 10 – 20 nm, an inner diameter of ~ 5 nm, and a length of a few microns. The resin used in this study consists of two standard epoxy components: diglycidyl ether of bisphenol A, E-51, supplied by Yueyang Resin Factory, China (epoxy value, 0.51) and diglycidyl ester of aliphatic cyclo, TDE-85, provided by Tianjin Jindong chemical factory, China (epoxy value, 0.85). 2-ethyl-4-methylimidazole (2,4-EMI), obtained from Shanghai Jingchun Reagents, China, was used as the curing agent. The carbon fiber used in the plain fabric was PAN-based T700SC produced by Toray, Japan (filament diameter: 7 μm). The glass fiber used for capillary experiments was manufactured by Nanjing Fiberglass R&D Institute, China (filament diameter: 8 μm).

Fabrication of Hybrid Multiscale Composites

The epoxy matrix was prepared with TDE-85 and E-51 at a ratio of 100 : 30 and the curing agent was 3 phr (parts for 100 parts of resin) of 2,4-EMI. Precalculated amount of CNTs was placed in acetone and agitated by a tip sonication for 15 min. A predetermined amount of epoxy resin matrix was added and the mixture was agitated for certain time. Finally, the beaker containing epoxy, CNTs, and acetone was submerged in a water bath at 60°C and continuously stirred by a magnetic stirrer for 3 h to fully evaporate acetone. The hybrid multiscale composites laminates were produced by compression molding technique. The carbon fiber plain fabrics were initially immersed into a dispersion consisting of epoxy/curing agent/CNTs to obtain prepreg. 8 layers of the prepreg, which gives a 48.9% fiber volume content, were laid up into a 2-mm thick mold cavity coated with mold-releasing agent. The assembly above mentioned was pressed and cured under 4 MPa pressure for 2 h at 80°C, then under 8 MPa pressure for 2 h at 140°C and last under 8 MPa for 2 h at 200°C by a hot-press machine.

Measurements and Characterization

A simple capillary experiment described in literature was performed to explore the CNTs dispersion quality and its effects on the impregnation of fibrous reinforcement.[14] It is easier for glass fiber bundle to observe the rise distance of CNTs dispersions than for carbon fiber bundle, some bundles of glass fiber were aligned and inserted into a transparent polyethylene (PE) pipe with a diameter of 4 mm and then suspended vertically into a 1 wt % CNTs dispersion. The fiber volume content in the PE pipe is very similar to that of compression molded composites.

The moisture absorption behavior of the hybrid multiscale composites was investigated to evaluate the effects of CNTs. Prior to the absorption experiments, all specimens were thoroughly washed and then vacuum dried until a constant weight was

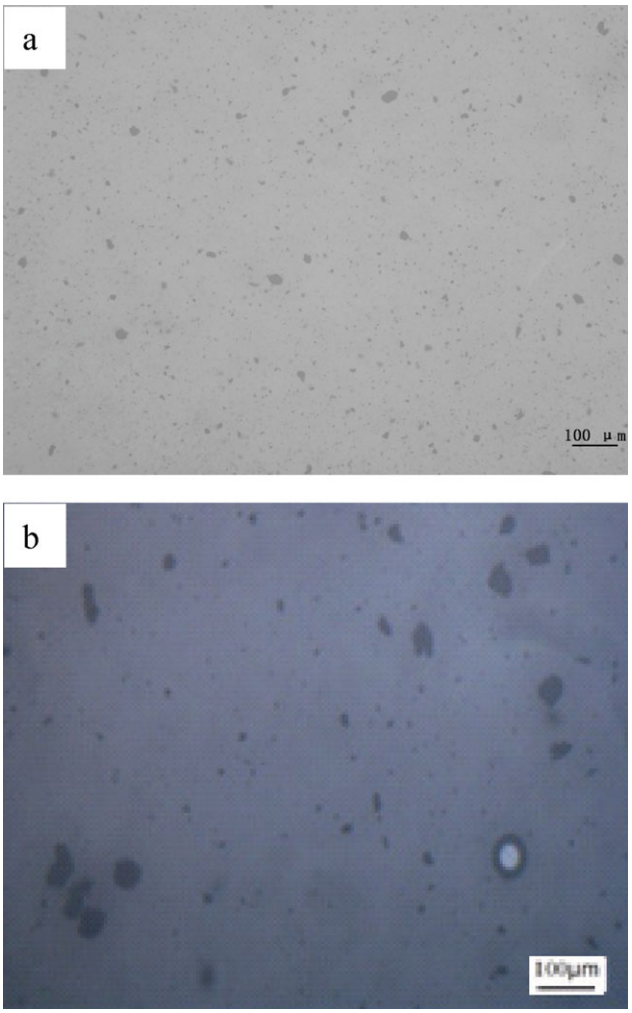

Figure 1. Optical micrographs of CNTs dispersion at different ultrasound frequencies: (a) 20 kHz; (b) 40 kHz. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

obtained. The medium (distilled water and 1.5 wt % brine) temperature was kept at 40°C. At predetermined time intervals, specimens were taken out from the baths, surface dried, and weighed using an analytical balance with a 0.1 mg precision. The weighing was carried out within 30 s to make the error caused by evaporation of water negligible. The moisture absorption process continued until the maximum saturation was achieved. The moisture content at a time point, M_t, was calculated according to

$$M_t = \frac{W_t - W_0}{W_0} \times 100 \quad (1)$$

where W_t and W_0 are the weight of specimens at a time point t and its initial value, respectively.

Flexural strength and ILSS of the composites were tested on RGT-30 I universal testing machine according to National Test Standard GB1449-83 and GB3357-82, respectively. The specimens with the size of 40 mm × 15 mm × 2 mm and 20 mm × 6.5 mm × 2 mm were cut from the resulting composites. Flexural tests were performed under the displace controlled, three-point bending mode at the span length of 32 mm and the cross-head speed of 1 mm min^{-1}. The support span-to-thickness ratio used in ILSS measurement was 5 : 1 at the loading speed of 2 mm min^{-1}. At least five coupons were tested for each sample group from which the mean values were reported. The fracture surfaces of specimen after mechanical testing were examined with Quanta 600 scanning electron microscopy after coating with a thin gold film to increase the conductance. A PMG3 Olympus optical microscopy was used to observe the distribution of CNTs in epoxy resin.

RESULTS AND DISCUSSION

Dispersion of CNTs in Epoxy

CNTs tend to agglomerate on account of the high aspect ratio and strong van der Waals force between CNTs, so CNTs have to be dispersed with intense shear force or sonication processing. In this study, CNTs were dispersed in the epoxy matrix using a sonicator and the epoxy/CNTs dispersion was used as the nanocomposite matrix of the hybrid multiscale composites. Figure 1(a,b) shows the difference in CNTs/epoxy dispersion processed with 20 kHz and 40 kHz sonication observed under an optical microscope, respectively. A thin layer (10 ∼ 20 μm) of dispersion was cast on a microscope slide. For the same sonication duration, larger CNTs aggregates can be found in the epoxy matrix formed by 40 kHz sonication processing, while 20 kHz is a suitable parameter for CNTs to develop a relatively uniform dispersion. Thermodynamically, the uniform dispersion state of CNTs in epoxy resin is unstable.[15] It is reasonable to assume that the CNTs dispersion is a mixture of both individual CNTs and micro CNTs aggregates connected by CNTs distributed in epoxy resin. Dispersion and agglomeration of CNTs in epoxy can be considered as two competitive processes. The time-dependent reagglomeration of CNTs in epoxy takes place after the applied sonication processing stopped. The attainment of dynamic equilibrium has to be maintained with the help of sonication processing. The structure and performance of CNTs/epoxy dispersion will play a crucial role in the fabrication of the hybrid multiscale composites.

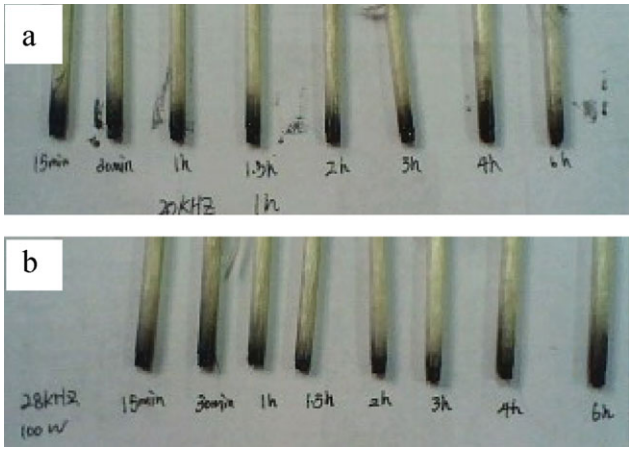

Figure 2. Capillary experiments of CNTs dispersion at different ultrasound frequencies: (a) 20 kHz; (b) 28 kHz. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

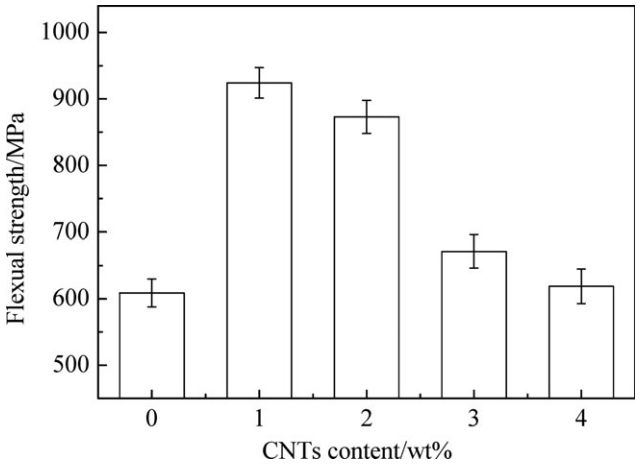

Figure 3. Flexural strength of the hybrid multiscale composites as a function of CNTs content.

Impregnation of Fibrous Reinforcement with Nanocomposite Matrix

The thorough impregnation of fibrous reinforcement with liquid resin matrix is a key step to obtain high performance composites. A simple capillary method was used to characterize the manufacturability of the hybrid multiscale composites consisting of carbon fiber/CNTs modified epoxy. For clarity glass fiber bundle was chosen to replace carbon fiber bundle and inserted into a transparent PE pipe. Thus there simultaneously exist intrabundle and interbundle gaps of the order of 5 nm – 10 μm in the PE pipe, which can be appropriately assumed to represent the assembly of capillary. When this PE pipe touched the CNTs/epoxy dispersion, the capillary force drove the dispersion to rise up. It is well known that the capillary pressure, ΔP_c, in a microchannel is computed as follows:

$$\Delta P_c = \frac{2\gamma_l \cos\theta}{r_e} \quad (2)$$

where r_e is the effective radius of the microchannel. It was hypothesized that the contact angles, θ between glass fiber and

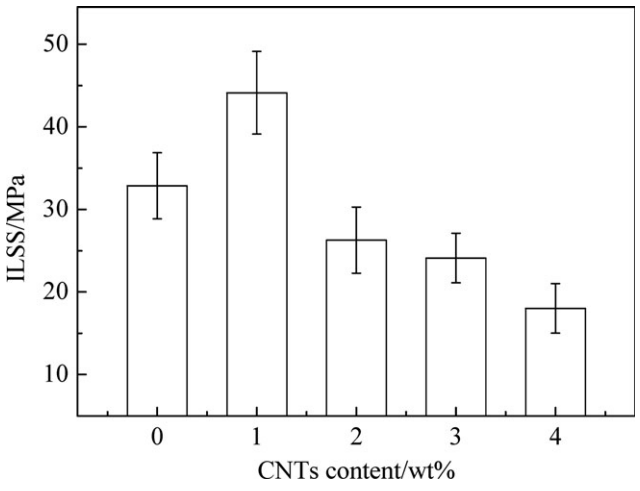

Figure 4. ILSS of the hybrid multiscale composites as a function of CNTs content.

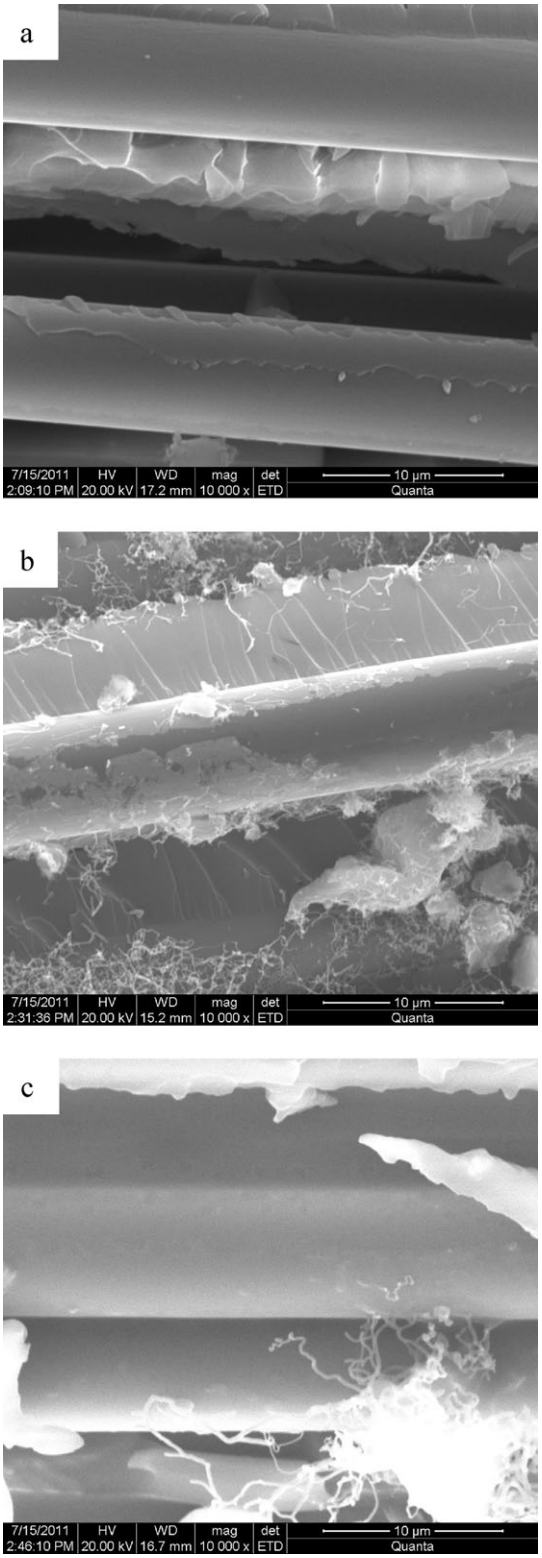

Figure 5. SEM micrographs of fracture surfaces of the hybrid multiscale composites, showing that (a) the failure are at fiber–matrix interface at the CNTs content of 0 wt %; (b) crack-bridging caused by CNTs network is responsible for ILSS increase at the CNTs content of 1 wt % and (c) large agglomerates adversely affect the impregnation of continuous fiber reinforcement at the CNTs content of 4 wt %.

Table I. Effects of Moisture Absorption on Mechanical Properties of 1 wt % CNTs Hybrid Composites

	Flexuaral strength (MPa)		ILSS (MPa)	
Time (h)	Distilled water	Brine	Distilled water	Brine
0	924.2 ± 24.7	924.2 ± 24.7	44.1 ± 4.9	44.1 ± 4.9
50	475.1 ± 12.2	645.9 ± 22.1	33.5 ± 9.1	37.8 ± 8.3
150	327.6 ± 13.4	553.1 ± 15.3	22.9 ± 0.3.5	27.1 ± 0.6.8
400	295.5 ± 19.5	482.5 ± 17.3	18.1 ± 0.2.9	24.6 ± 2.4

CNTs/epoxy dispersion and the surface tension, γ_l, are constant throughout the capillary experiment. The CNTs/epoxy dispersion treated by sonication is a mixture composed of separate CNTs and CNTs aggregate linked by CNTs. If these aggregates have a larger radius than r_e, they would block the capillaries in the PE pipe and the dispersion rise will be arrested prematurely. The level to which the dispersion treated under different sonication processing conditions rises within the glass fiber bundles are shown in Figure 2(a,b). The size and number of the CNTs aggregate in 20 kHz specimens are reasonably considered to be smaller than those in 28 kHz specimens. Economically, 20 kHz/30 min have been found to be the optimized sonication parameters. Damages imposed on CNTs by long duration sonication significantly reduces the aspect ratio of CNTs and thereby the entanglement in epoxy,[16] which results in the higher level to which the dispersion treated at 28 kHz/6 h rise as suggested in Figure 2(b). This experiment confirms that only under the sway of capillary force can CNTs/epoxy dispersion processed with the sonication parameters used in this study infiltrate into the interbundle and intrabundle gaps. The level to which the dispersion rise is restricted by the inevitable increase in viscosity resulted from the addition of CNTs. As can be seen in eq. (2), despite the differences in surface free energy of carbon fiber and glass fiber, thus the difference in contact angle between them and CNTs/epoxy dispersion, capillary experiment can be used as a qualitative method to characterize the dispersion of CNTs in polymer and impregnation of fibrous reinforcement with CNTs/polymer dispersion. The capillary apparatus used in this study is, to a certain extent, analogous to a quasi one-dimensional liquid composites molding equipment. The model system we have chosen provides baseline information on impregnation process.

Effects of CNTs on the Shear Properties of Composites

ILSS and flexural strength are the most interesting through-thickness properties for composite laminates. The results from the flexural strength and ILSS tests of the composites differing in CNTs content are summarized in Figures 3 and 4, respectively. All data include statistical deviation. In comparison to the control composite specimen, the CNTs hybrid multiscale composits exhibit significantly improved flexural strength of 924.2 MPa and ILSS of 44.1 MPa for 1 wt % CNTs content, corresponding to the improvements by 51.8% and 34.2 %, respectively. The presence of carboxylic acid functional groups on CNTs surface used in this study facilitates the formation of the covalent bond between the CNTs and epoxy upon curing. The incorporation of CNTs into epoxy, which can be used as nanocomposite matrix, provides a significant improvement in mechanical properties of the neat matrix. The resulting hybrid multiscale composites could benefit from an increase in nanocomposite matrix properties. To some degree, the increase in flexural strength and ILSS of composites at the CNTs loading of 1 wt % are ascribed to the transferability of enhanced matrix properties into hybrid multiscale composites. Figure 3 and 4 also suggest that the system with 1 wt % loading is the best system, the flexural strength and ILSS begin to degrade beyond

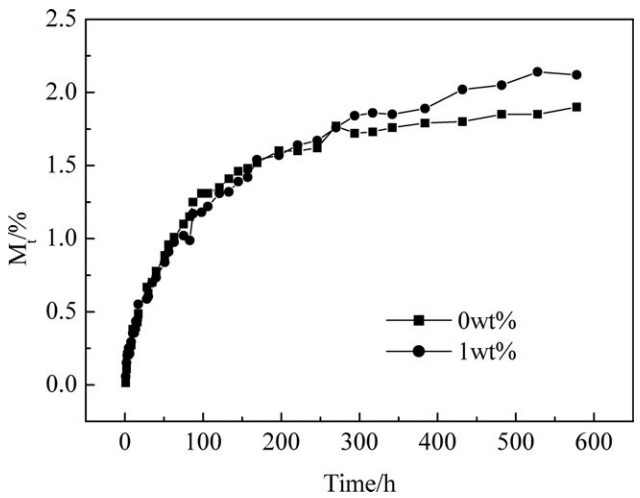

Figure 6. Moisture content, M_t, of the hybrid multiscale composites in distilled water as a function of time.

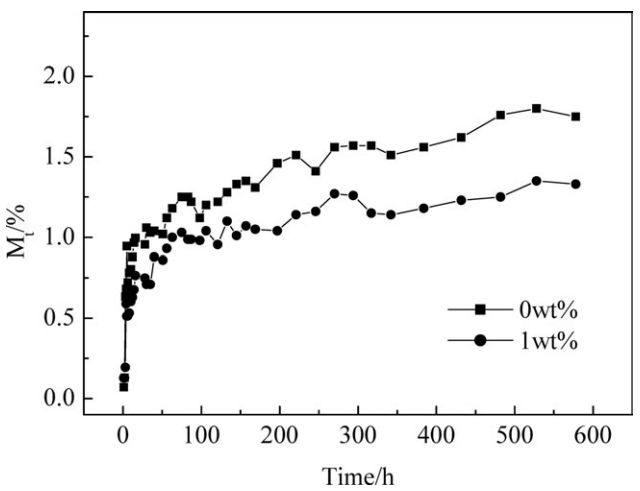

Figure 7. Moisture content, M_t, of the hybrid multiscale composites in 1.5 wt % brine as a function of time.

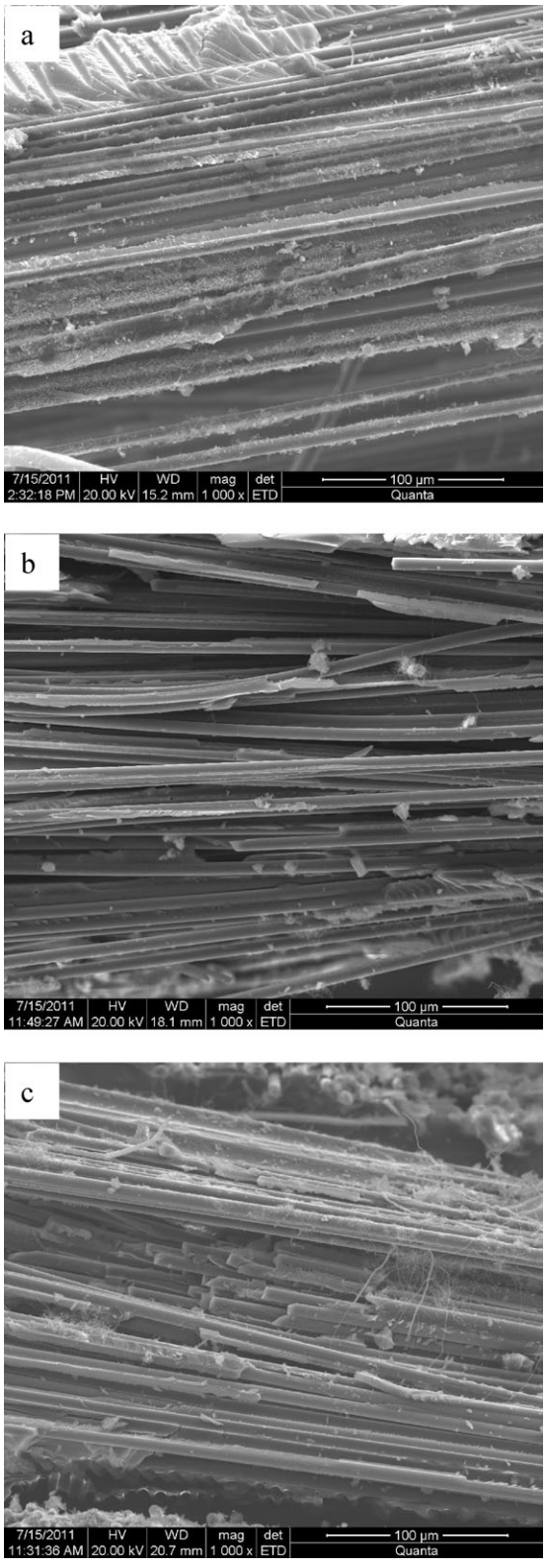

Figure 8. SEM micrographs of fracture surfaces of the 1 wt % CNTs composites hygrothermally treated in different medium for 406 h: (a) untreated; (b) distilled water; (c) brine.

1 wt % content. The likely explanation is that the higher content of CNTs can not be uniformly distributed in epoxy and dramatically increase the viscosity of resin matrix. As the concentration increases, the space between CNTs decreases and CNTs tend to develop entangling aggregates. It is reasonable to assume that the number and size of CNTs aggregates in epoxy increase. It is expected that such a nanocomposite matrix containing higher concentration of CNTs will adversely affect the impregnation of continuous fiber reinforcement by blocking the microflow channel in fiber bundle and thereby the mechanical properties of the composites.

SEM Analysis of Fracture Surface of Composites

The fracture surfaces of hybrid composites that failed in shear test were examined by scanning electron microscopy (SEM) to understand the reinforcement mechanism for CNTs. SEM image in Figure 5(a) shows the fracture surface of typical carbon fiber/epoxy laminates and the failure is at a fiber–matrix interface. The matrix detached from the fiber surface due to a weak adhesion evidenced by the smooth fiber surface. Interfactial debonding of matrix from the fiber can be considered as the dominant mechanism for shear failure of composites without CNTs. In comparison, the laminate specimen containing CNTs loading of 1 wt % presents a significantly different fracture surface. It can be seen in Figure 5(b) that carbon fiber as continuous reinforcement were impressively covered with a thin layer of matrix. Interconnecting CNTs network was observed between neighboring carbon fibers, which greatly improved the matrix toughness. Nanocomposite interfacial layer developed on carbon fiber surface due to the presence of CNTs. Toughening effect by CNTs appears to be supported by comparing Figure 5(a,b). CNTs network acting as microcrack arrester can enhance the composites toughness through the bridging mechanism in resin-rich region. More energy absorption of laminate specimen subjected to shear failure was attributed to the pull-out of more functionalized CNTs from epoxy. The hierarchical microstructure of the hybrid multiscale composites seems to be responsible for the increase in flexural strength and ILSS. It is difficult for carbon fiber reinforcement to be impregnated with 4 wt % CNTs nanocomposite matrix on account of the presence of large CNTs aggregates shown in Figure 5(c). In comparison to flexural properties, the ILSS of the hybrid multiscale composites, which is mainly dominated by the matrix, is more sensitive to CNTs content in epoxy. SEM observation is in agreement with mechanical test results.

Effect of CNTs on the Moisture Absorption of Composites

In order to evaluate the behavior of CNTs hybrid composites in moisture conditions, to predict their performance in service as engineering marine composites applications, and thus to make full use of them, an insight into hygrothermal aging behavior is required. The specific objective of the present study is, therefore, to understand the moisture uptake behavior of the CNTs hybrid multiscale composites, to determine the effect of CNTs. As is seen from Table I, the mechanical properties of 1 wt % CNTs hybrid composites consistently degrade by hygrothermal aging. However, it can be notified in Figures 6 and 7 that the moisture absorption versus time curves of the specimens with and without CNTs at a temperature of 40°C display a totally different hygrothermal behavior depending upon their medium, distilled

water or brine. Especially, the value of M_t in equilibrium state for CNTs hybrid composites in brine was obviously lower than that of specimen without CNTs. This implies that the existence of CNTs exerted a noticeable effect on moisture uptake of composites. Moisture absorption behavior of composites is matrix-dominated and interface-sensitive. Generally, moisture absorption involves several absorption mechanisms. The water molecules diffuse through matrix microcrack and transport along fiber-matrix interface because of capillary effect, making the matrix swell.[17] As a result of the difference in expansion of fiber and polymer matrix, internal stresses developed at interface are expected to weaken the interfacial bonding. In distilled water, as shown in Figure 6, covalently bonded CNTs network in hybrid composites is considered to force water molecules to follow a tortuous path and thus reduce water wicking of the specimen immersed for 200 h. The hybrid multiscale composites containing microscale fibers and nanoscale CNTs bear more surface area for polymer/CNTs and polymer/carbon fiber interaction. As absorption progresses, more interface debonded. Eventually, the quantity of water absorbed in the hybrid composites is more than that of the control composite specimen. Interestingly, not only the values of M_t in equilibrium state for composites containing CNTs in brine observed in Figure 7 was lower than that of specimen without CNTs in brine, but also it is significantly lower than that of the specimen containing CNTs in distilled water. According to the results reported in literature,[18] it is understandable that the specific adsorption of Na^+ and/or Cl^- onto carboxylic acid functionalized CNTs surface prevents moisture penetration through blocking the matrix microcrack and pores. The interface-sensitivity and the medium-dependence of moisture absorption for CNTs hybrid composites can be examined by comparing Figure 8(a–c). The serious interface failure as revealed in Figure 8(b) may be sufficient to confirm that the larger content of absorbed water is responsible for the faster reduction in shear properties in the case of the hybrid composites hygrothermally treated in the distilled water.

CONCLUSION

In this study, the usage of CNTs in carbon fiber/epoxy composites was investigated to evaluate its effects on some matrix-dominated properties of composites. The study mainly focused on characterization of the state of dispersion of CNTs, analysis of the impregnation of continuous fiber reinforcement with CNTs/epoxy dispersion and assessment of shear properties of the resulting hybrid composites. The sonication process was optimized to achieve the CNTs/epoxy dispersion amenable to be used to impregnate carbon fiber reinforcement. In sequence, the flexural strength and ILSS values at a CNTs concentration of 1 wt % are found to be 51.8% and 34.2% higher with respect to those of the control laminate, respectively. The microscopy pictures of the fracture surfaces confirm that there were no large CNTs aggregates between the adjacent carbon fibers and carbon fiber reinforcement can be impregnated with 1 wt % CNTs nanocomposite matrix. Hygrothermal experimental results suggest a totally different moisture absorption behavior depending upon their medium, distilled water or brine. It is identified that the lower weight gain of the hybrid composites in brine is attributed to the use of CNTs. Further investigation on enhancing the processing-structure-property relationships of the hybrid multiscale composites will be conducted in the future.

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