Effect of Carbon Nanofiber Functionalization on the In-Plane Mechanical Properties of Carbon/Epoxy Multiscale Composites

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ABSTRACT: In this work, vapor-grown carbon nanofibers (CNFs) were functionalized using an optimized route and dispersed in the matrix of carbon fabric-reinforced epoxy composites to develop multiscale carbon/epoxy composites. Functionalization was carried out through an oxidative treatment with a mixture of HNO_3/H_2SO_4 (1 : 3) using a combination of ultrasonication and magnetic stirring. Functionalized CNFs (F-CNFs) were characterized for their morphology, length, functional groups, and degradation due to oxidative treatment. The results showed that it was possible to efficiently functionalize CNFs without any degradation through proper selection of treatment dura-tion. F-CNFs were dispersed homogeneously into the epoxy matrix using ultrasonication in combination with high-speed mechanical stirring. The incorporation of 0.1 wt % F-CNFs led to a 65% increase in Young's modulus and a 36% in tensile strength of neat carbon/epoxy composites. The fracture surfaces were studied using scanning electron microscopy to understand the property enhancement due to F-CNFs. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 1951–1958, 2012

Key words: carbon nanofiber; functionalization; multiscale composites; interface; mechanical properties

INTRODUCTION

Advanced fiber-reinforced plastics (FRPs) such as carbon/epoxy composites are a potential candidate for many high-end applications including aerospace, sporting goods, automotive construction, medical equipments, and textile machineries because of their low weight and high strength.[1–3] However, the limi-tations in the matrix-dominated properties such as interlaminar shear strength and fracture toughness have restricted their use in such applications. Efforts were made to improve fracture toughness of epoxy matrix using rubber particles,[4] rigid inorganic fill-ers,[5] and thermoplastic additives.[6] However, these modifiers often reduce modulus, strength, and ther-momechanical properties.[7–9] Recently, attempts have been made to enhance matrix-dominated properties of epoxy-based composites using various nanofillers including carbon nanotubes (CNTs) and carbon nanofibers (CNFs) because of their outstanding mechanical, thermal, and electrical properties.[10–14] These nanoreinforcements open up the possibility of tailoring matrix properties to overcome the draw-backs of existing FRPs with additional improve-ments in other useful properties. The combination of various nanofillers with conventional composites has led to the development of a new class of FRPs known as multiscale hybrid composites. However, the main difficulty in developing these composites arises from nanomaterial agglomeration, especially in the case of nanomaterials with very high aspect ratio such as CNF and CNT. A number of studies covering carbon/epoxy multiscale composites based on various nanofillers such as Al_2O_3, organoclay, and SiC have been reported.[15–17] However, CNT- or CNF-enhanced multiscale composites are new, and a limited number of studies have been reported in this area.[18–21] Dispersion of different varieties of CNT (cup-stacked, double-walled, and multiwalled) was found effective to improve the matrix-dominated properties of carbon/epoxy composites such as frac-ture toughness but not the in-plane properties such as modulus and strength.[18,19] CNFs were found helpful in this regard probably because of better dis-persion of CNFs within the epoxy matrix owing to their larger diameters and lower surface area leading to less agglomeration tendency. The improvement of compressive strength of carbon/epoxy composites by dispersing cup-stacked type CNFs in the matrix has been reported by Iwahori et al.[20] However, they observed no major improvement in tensile and flex-ural properties because of the presence of large CNF clusters and heterogeneity in CNF dispersion.

Vapor-grown (VCNFs) were also found helpful to improve tensile, flexural, and fatigue strength of carbon fabric/epoxy composites significantly when dispersed in the matrix at low concentrations (<2 wt %).[21] However, dispersion of higher concentrations resulted in the reduction of their properties because of improper dispersion and CNF agglomeration.

Therefore, dispersion of CNF has been reported as the key factor for the improvement of in-plane mechanical properties. One of our recent studies demonstrated that in-plane mechanical properties of carbon/epoxy composites can be significantly improved by homogeneously dispersing VCNF and single-walled CNT at very low concentrations (1 and 0.1 wt %, respectively).[22,23] However, apart from CNF dispersion, the interface between CNFs and epoxy matrix may also have significant effect on the mechanical properties of multiscale composites. Therefore, in the current study, an attempt has been made to improve the interfacial bonding between CNF and epoxy matrix through CNF functionalization and to study the effect of CNF functionalization on the tensile properties of multiscale composites. Because the oxidative functionalization process can significantly damage CNFs deteriorating their properties, efforts have been directed in this research toward functionalizing CNFs without degradation by carefully selecting the treatment conditions of oxidative functionalization treatment. The effect of the functionalization process on the morphology, aspect ratio, and degradation behavior of CNF has been thoroughly investigated. Tensile properties of multiscale composites based on very low concentrations (0.1 wt %) of functionalized CNF (F-CNF) have been characterized and compared with that of neat carbon/epoxy and untreated CNF-dispersed multiscale composites. Moreover, the fracture surface of multiscale composites has been studied to understand the effect of CNF functionalization.

EXPERIMENTAL

Materials

VCNFs [Pyrograf III PR24 AGLD grade; diameter: 60–150 nm; length: 30–100 μm; density: 1.8 gm/cm^3; Young's modulus: 400 GPa; tensile strength: 2.7 GPa; thermal conductivity: 20 W/(m K); and electrical resistivity: 1×10^{-3} Ω cm] were obtained from Applied Sciences. Carbon fabric with a satin weave pattern, 945 ends and picks per meter, and an areal density of 365 gm/m^2 was used in this study. An epoxy resin based on bisphenol A diglycidyl ether with epoxide equivalent weight of 172–176 was supplied by Sigma Aldrich (India); the resin was cured with a triethylene tetramine hardener (HY 951) supplied by Huntsman India. Concentrated nitric and

sulfuric acids used for the functionalization process were purchased from Merck (India).

Functionalization of CNF

CNFs were functionalized using an oxidative treatment with a 1 : 3 mixture of HNO$_3$/H$_2$SO$_4$ in a bath sonicator (T490DH Transsonic Digital S; Elma) for 1 h followed by magnetic stirring for 15 h. The duration of ultrasonic and mechanical stirring treatment was selected based on a few initial trial and error experiments varying the treatment duration and studying the degradation behavior [as determined by thermogravimetric analysis (TGA)] as well as the dispersion ability of oxidized CNFs in water. Temperature was maintained below 40°C with the help of ice. The CNFs were then separated from the acid mixture by microfiltration using PTFE membrane filter (pore diameter: 0.2 μm). The treated CNFs were then washed with excessive amounts of distilled water and filtered again. The collected CNFs were then dried and ground into fine powder.

Characterization of F-CNFs

The morphology of acid-treated CNFs was studied by transmission electron microscopy (TEM; Phillips C M 12, type of filament: tungsten, accelerating voltage: 100 kV). The functional groups generated during the oxidative treatment were characterized with the help of Fourier transform infrared spectroscopy (FTIR). Thermal stability of treated and untreated CNFs was determined by TGA (Perkin-Elmer TGA-7). The dispersion of acid-treated CNFs in water was characterized with the help of an optical microscope (LEICA DMLP), and the average CNF length was calculated by analyzing the optical micrographs using an image-processing software (ImageJ).

Preparation and characterization of CNF-dispersed matrix

A similar process was used for the preparation and characterization of both untreated and functionalized nanofiber-dispersed epoxy matrix to investigate the effect of functionalization. CNFs were dispersed into the epoxy resin using ultrasonic energy in combination with high-speed mechanical stirring. It was found in our previous study[22] that a combination of 2 h of ultrasonication with 1 h of high-speed mechanical stirring at 2000 rpm can disperse CNFs homogeneously within epoxy matrix without much damage to the nanomaterials. Hence, this process of dispersion has been used in the current study for both untreated CNFs and F-CNFs. Ultrasonication was carried out in an ice-cooled bath sonicator (T490DH Transsonic Digital S; Elma) operated at 40
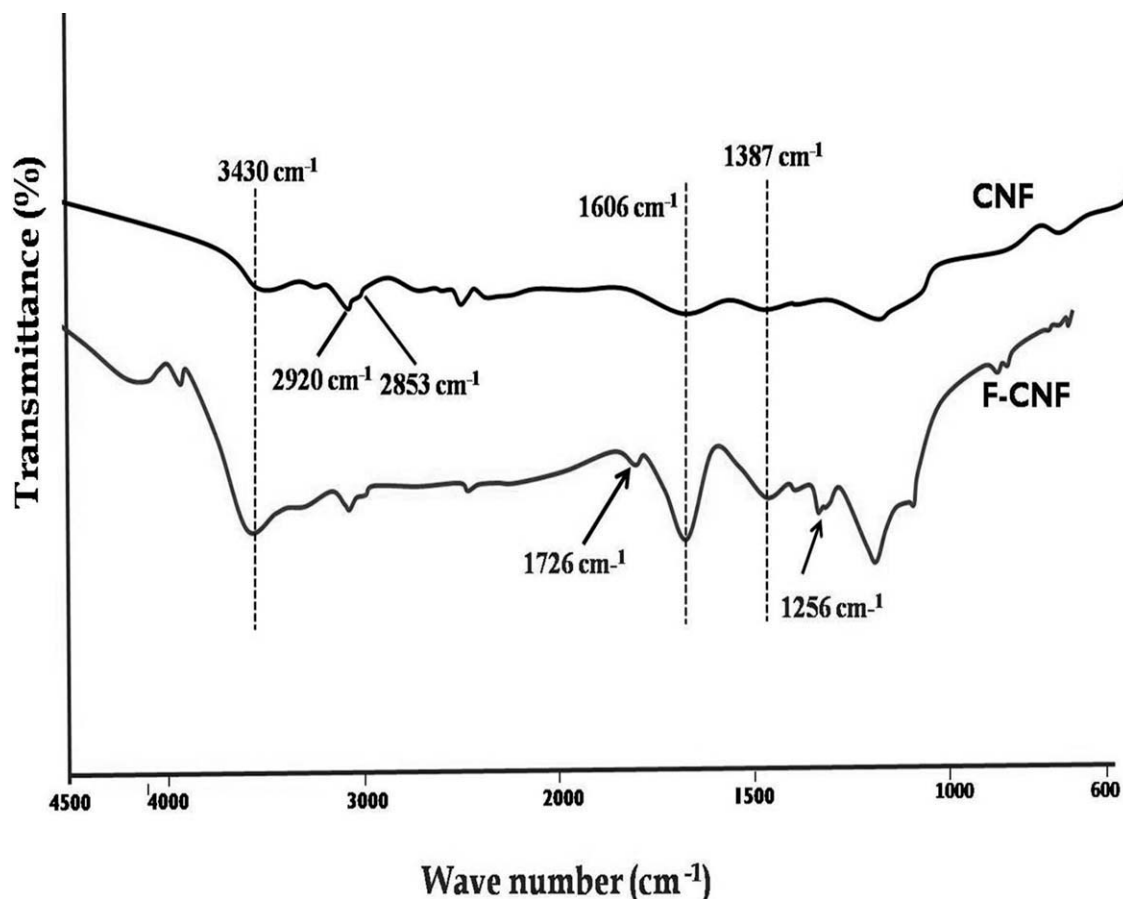
Figure 1 FTIR spectra of untreated and functionalized CNF (F-CNF).

kHz. Mechanical stirring was performed using a high-speed mechanical stirrer suitable for highly viscous solutions and equipped with a digital speed control unit. The CNF/epoxy dispersions were cured with 15 phr of triethylene tetramine hardener for 12 h at room temperature followed by a postcuring of 2 h at 80°C. Neat epoxy and CNF-dispersed matrix were characterized for tensile properties according to ASTM D-638-03 using a Zwick Z020 Universal Testing Machine with a 1 mm/min crosshead speed. The fracture surface of failed tensile specimens was studied using a scanning electron microscope (SEM; ZEISS Evo 50 with a tungsten filament) using a voltage of 20 kV.

Preparation and characterization of multiscale composites

Carbon fabric was cut into required dimensions and impregnated with the CNF-dispersed resin-hardener mixture and then consolidated to produce prepreg. Multiscale composites were prepared by stacking four sheets of prepreg that were then cured in a compression molding machine using a pressure of 1500 kPa at room temperature for 2 h, followed by a postcure of 2 h at 80°C. Neat carbon/epoxy and

multiscale composites were tested for tensile properties in Zwick Z020 Universal Testing Machine at a crosshead speed of 5 mm/min according to ASTM D-638-03. The fracture surface of failed tensile specimens was studied using a SEM (ZEISS Evo 50) with a tungsten filament and accelerating voltage of 20 kV. Multiscale composites based on both untreated CNFs and F-CNFs were prepared and characterized using similar processes and conditions.

RESULTS AND DISCUSSION

Characterization of F-CNFs

The FTIR spectra of untreated and acid-treated CNFs are shown in Figure 1. The band at 3430 cm^{-1} present in the spectra of untreated CNF is due to the presence of physically absorbed water. A band present at 1387 cm^{-1} corresponds to the in-plane bending of OH group, and the band present at 1606 cm^{-1} corresponds to the stretching mode of a C=C double bond that forms the framework of CNF. The presence of a similar band at 1606 cm^{-1} in the oxidized CNF confirms that the structure of nanofiber backbone is unaffected by the oxidative functionalization treatment. This has also been confirmed by
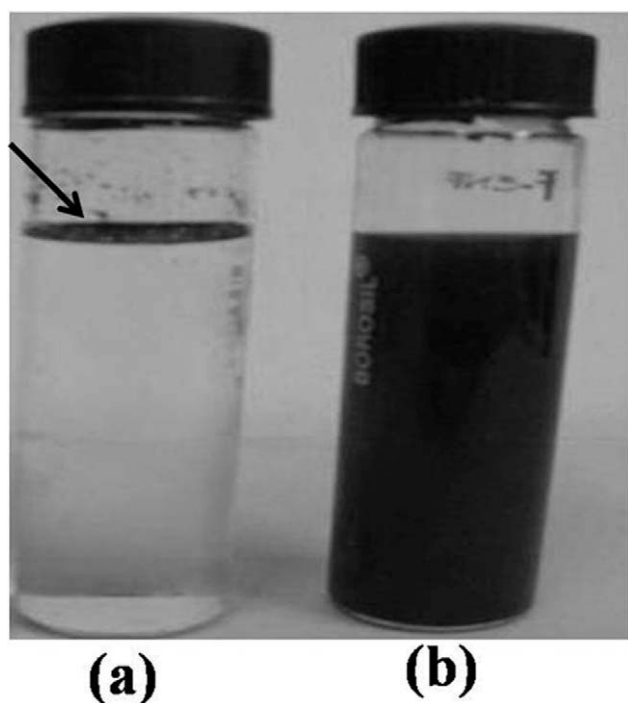
Figure 2 Dispersion of CNF in water: (a) untreated CNF and (b) acid-treated CNF.

Figure 4 TGA curves of untreated and functionalized nanofibers.

TEM morphology study. The peaks at 2920 and 2853 cm^{-1} are assigned to the carbon–hydrogen bonds present as defects in both untreated and treated CNFs. The introduction of new peaks at 1726 and 1256 cm^{-1} in the acid-treated CNFs is a clear evidence of C=O and C—O stretching of carboxylic groups present on the surface of oxidized CNFs.

Furthermore, functionalization is confirmed by dispersing the treated CNFs in water. Figure 2 shows the dispersion of untreated and acid-treated CNFs in water. The untreated CNFs are not miscible with water and float on the surface (indicated by arrow in Fig. 2), whereas the acid-treated CNFs
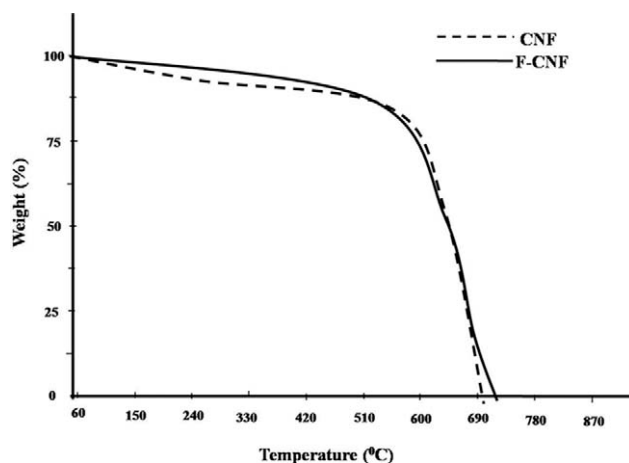
readily disperse in water in a highly stable manner. When the dispersion of F-CNFs in water was observed under an optical microscope in transmission mode, it showed well-separated CNFs (Fig. 3). The average length of these CNFs as measured using the Image J software was 16.5 µm, which is much less than the length of untreated CNFs (>30 µm). This implies that the functionalization treatment led to significant curtailment of CNF length.

Thermal degradation behavior of treated and untreated CNFs as detected by TGA is shown in Figure 4. It can be seen that the oxidized CNFs have slightly higher thermal stability than the untreated nanofibers. This may be attributed to the presence of oxygen on the functionalized nanofiber surface, which stabilized the nanofiber structure. Moreover, the as-received CNFs contain an amorphous phase that could reduce their thermal stability.

TEM micrographs of untreated and treated CNFs are shown in Figure 5. The presence of similar morphology for both types of CNF indicates that CNFs
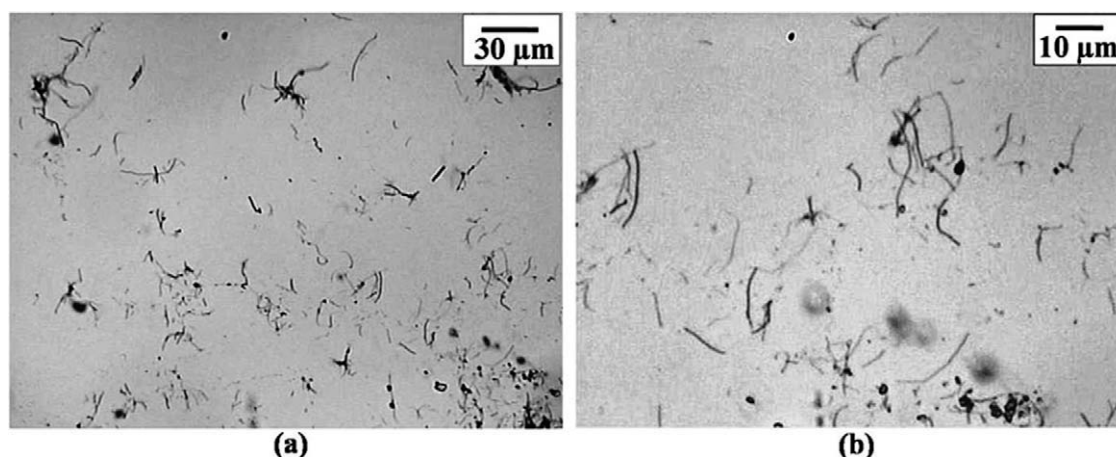

Figure 3 Dispersion of functionalized CNF as observed by optical microscope at ×200 magnification (a) and ×500 magnification (b).
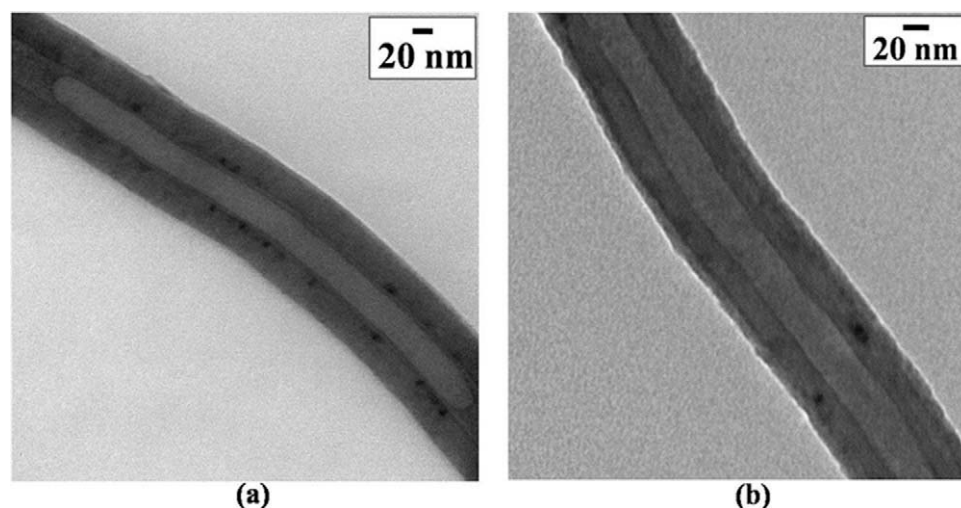
Figure 5 Morphology of CNF as observed by TEM: (a) untreated CNF and (b) F-CNF.

have retained their morphology after the oxidative functionalization process. Therefore, all these characterization techniques revealed that the oxidative functionalization process used in this research allowed the formation of surface functional groups without CNF degradation. However, significant reduction in the CNF aspect ratio was observed.

Tensile properties of CNF-dispersed matrix

Tensile properties of 0.1 wt % F-CNF-dispersed epoxy matrix are listed in Table I and shown graphically in Figure 6 and are compared with neat epoxy and 0.1 wt % untreated CNF-dispersed epoxy matrix. It can be seen that the incorporation of F-CNFs has resulted in a 12% improvement in tensile modulus and a 62% increase in tensile strength of the epoxy matrix. However, in comparison with untreated nanofibers, the tensile modulus was lower; the tensile strength was not significantly influenced by functionalization. Examination of the fracture surface of the tensile specimens (Fig. 7) showed improved interfacial bonding between F-CNF and the epoxy matrix. Significant nanofiber pullouts can be observed in the case of untreated CNF, as indicated by arrows in Figure 7(a), indicating poor bonding

between untreated CNFs and epoxy matrix. Similar nanofiber pullouts were also observed in untreated CNF dispersed multiscale composites, as shown in Figure 7(c). In contrary, fracture surface of F-CNF-dispersed matrix shows good wetting of CNF by epoxy and no nanofiber pullout [Fig. 7(b)]. The surface functional groups probably improved the compatibility between CNFs and epoxy, resulting in chemical bond formation between them. However, in spite of a good interface, the F-CNF-dispersed matrix had a lower elastic modulus, probably due to the reduction of aspect ratio after the functionalization process.

Tensile properties of multiscale composites

Tensile properties of neat carbon/epoxy and multiscale composites based on nonfunctionalized and functionalized nanofibers are listed in Table I and presented graphically in Figure 8. The incorporation of only 0.1 wt % F-CNF resulted in a 65% improvement in Young's modulus and a 36% increase in tensile strength. The improvement in tensile properties was much higher for F-CNFs than that for the 0.1 wt % nonfunctionalized CNF. The fracture surface of F-CNF-incorporated multiscale composites is shown in Figure 9. It can be seen that the matrix strongly

TABLE I
Tensile Properties of Neat Epoxy, CNF-dispersed Epoxy, Neat Carbon/Epoxy and Multiscale Composites

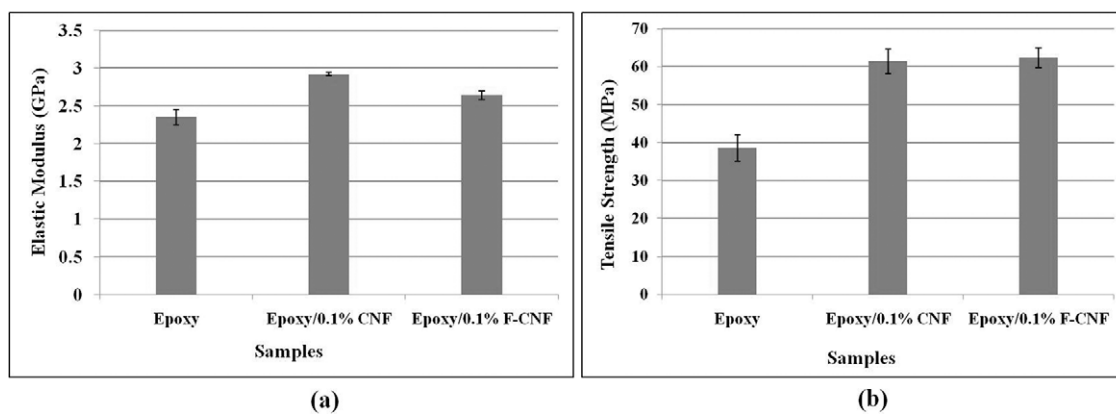| Samples	Tensile modulus (GPa)	Improvement (%)	Tensile strength (MPa)	Improvement (%)
Neat epoxy	2.35 ± 0.10	–	38.5 ± 3.5	–
Epoxy/0.1% CNF	2.92 ± 0.02	24	61.4 ± 3.2	59
Epoxy/0.1% F-CNF	2.64 ± 0.06	12	62.4 ± 2.6	62
Neat carbon/epoxy	48.3 ± 2.2	–	665.7 ± 10.5	–
Carbon/epoxy/0.1% CNF	65.1 ± 4.4	35	737.0 ± 69.5	11
Carbon/epoxy/0.1% F-CNF	79.7 ± 2.9	65	905.5 ± 11.3	36

Figure 6 Comparison of tensile properties of neat epoxy and CNF-dispersed epoxy matrices: (a) modulus and (b) tensile strength.

adhered to the carbon fibers. This indicates the formation of a very strong interface between carbon fibers and epoxy matrix in the presence of functionalized

nanofibers. It was previously reported by the authors that neat carbon/epoxy composites show much lower mechanical properties than predicted due to the weak
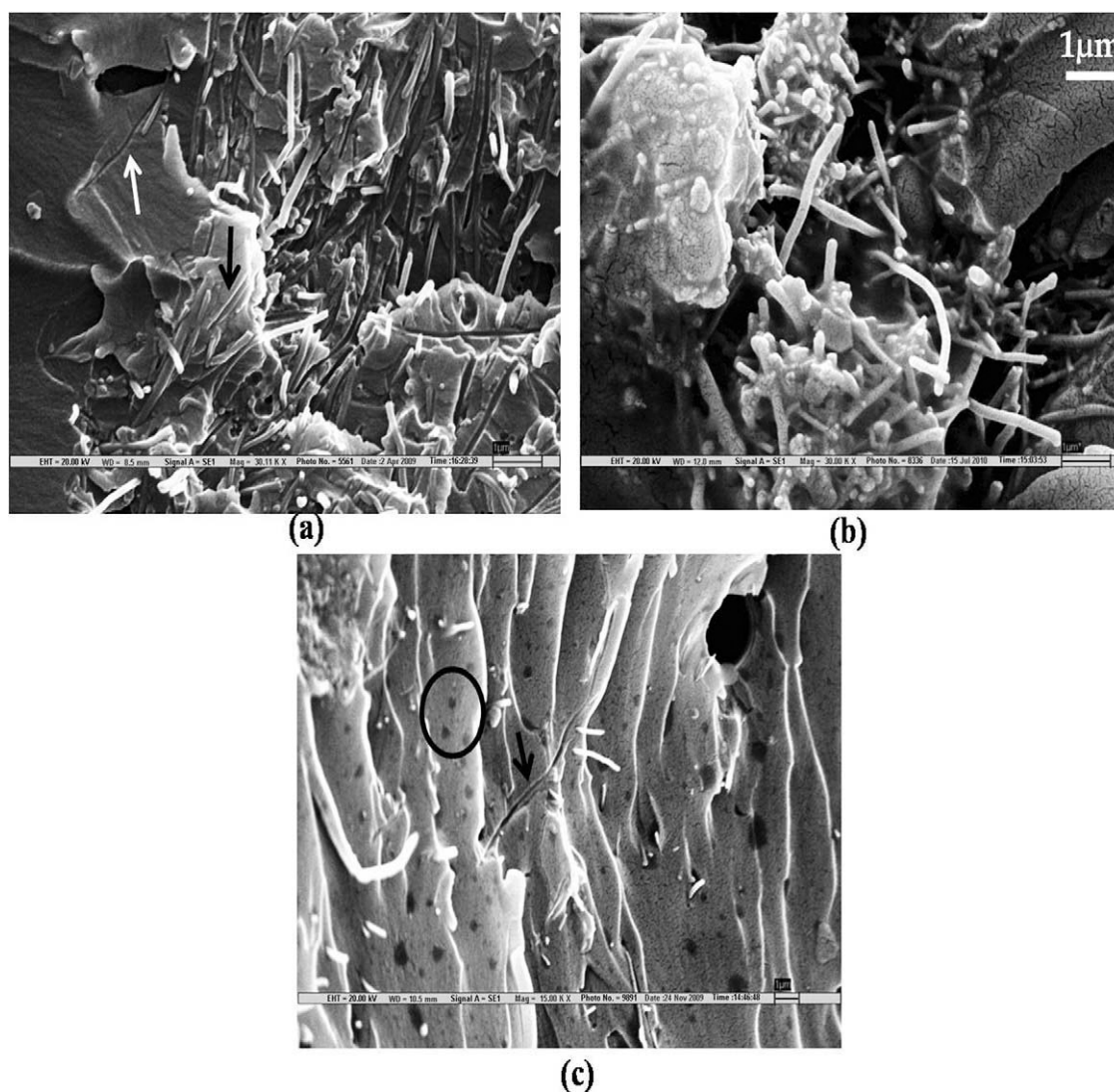

Figure 7 Fracture surface of untreated CNF-dispersed epoxy matrix (a), F-CNF-dispersed epoxy matrix (b), and multi-scale composites (c).
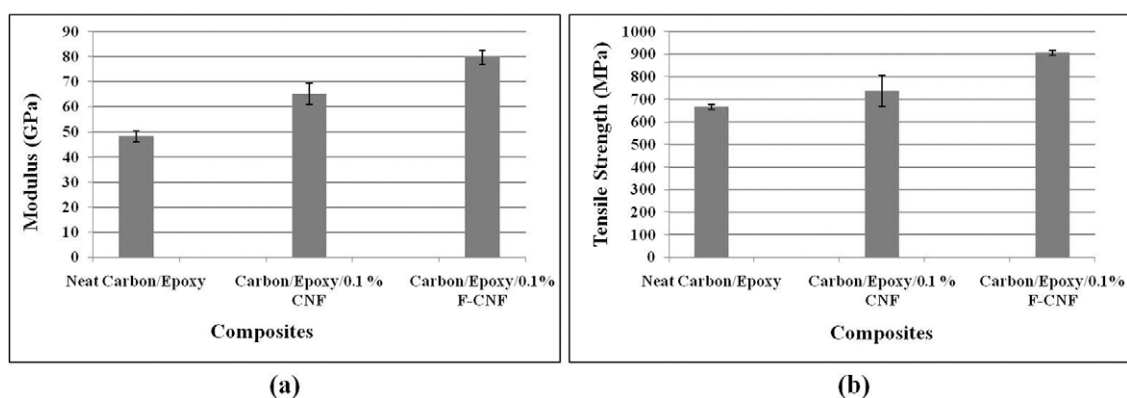
Figure 8 Comparison of tensile properties of neat carbon/epoxy and multiscale composites: (a) modulus and (b) tensile strength.

interface between the carbon fibers and the epoxy matrix.[22] The fracture surface showed less matrix adherence to the carbon fiber surface, indicating weak interfacial interactions [Fig. 9(c)]. Moreover, it was also found that the fiber/matrix interface in the case of untreated CNF-dispersed multiscale composites is much stronger than that in neat carbon/epoxy composites. This is probably due to increased residual stresses or interface pressure on the surface of carbon fibers by epoxy matrix in the presence of CNFs. The residual stresses were generated due to the change in thermal shrinkage of epoxy matrix during curing. Similar observations were also made by other researchers in case of nano-Al_2O_3 and other
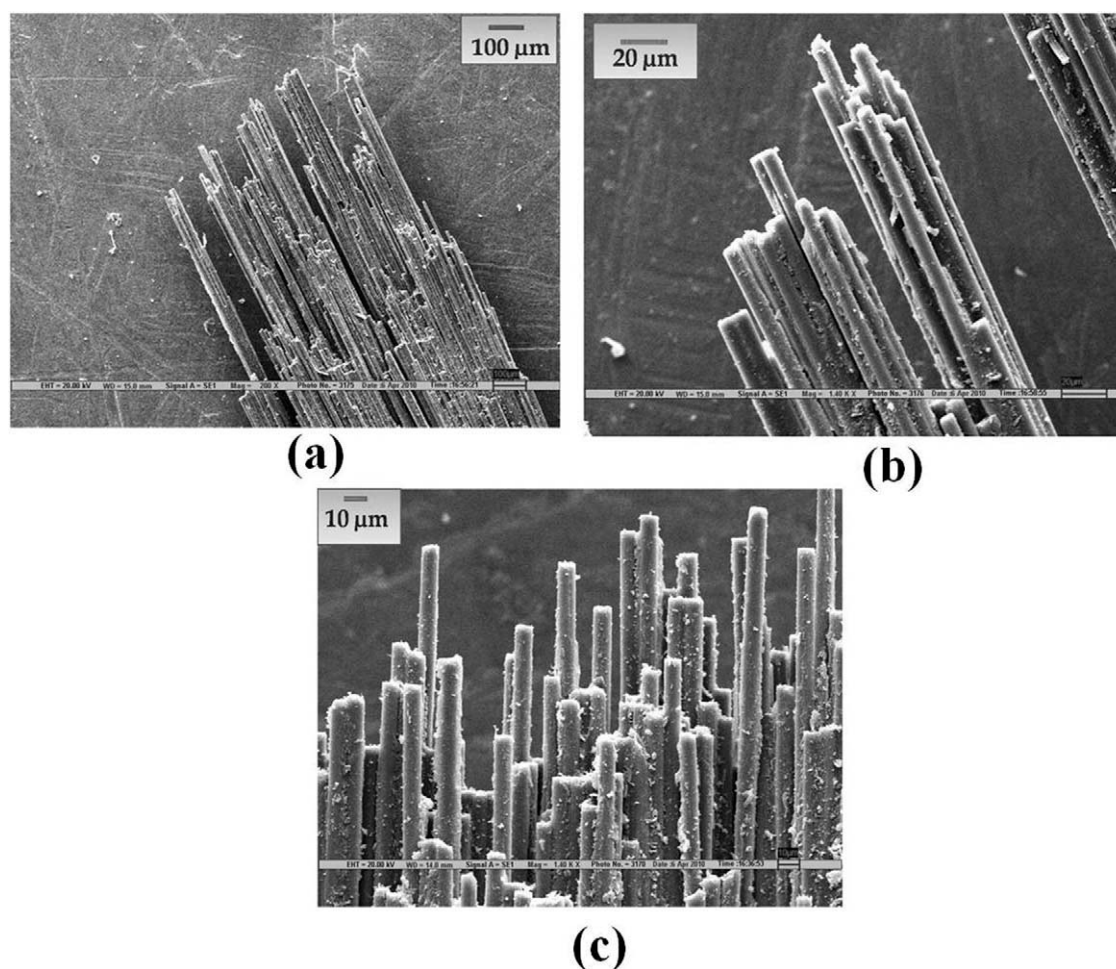

Figure 9 Fracture surface of F-CNF-dispersed multiscale composites at different magnifications (a) and (b); neat carbon/epoxy composites (c).

nanofillers.[15] However, this effect is more pronounced in the case of F-CNF-dispersed matrix due to the presence of strong bonding between F-CNFs and the matrix. Therefore, the strong improvement in tensile properties is mainly attributed to the formation of a very strong interface between carbon fibers and epoxy matrix in the presence of F-CNFs. As a result, although functionalization led to a slight reduction in the mechanical properties of the CNF-dispersed matrix, it proved very effective in improving the mechanical properties of multiscale composites.

CONCLUSION

VCNFs were successfully functionalized through an oxidative treatment with a 1 : 3 mixture of HNO_3/H_2SO_4 using 1 h of ultrasonication followed by 15 h of magnetic stirring. F-CNFs indicated the presence of carbonyl and keto groups as a result of oxidation and became readily soluble in water. Moreover, they demonstrated similar morphology and degradation behavior when compared with that of untreated CNFs, indicating no degradation as a result of functionalization treatment. However, the CNF aspect ratio reduced significantly after functionalization, and as a result, tensile properties of the CNF-dispersed matrix deteriorated slightly in spite of strong bonding between F-CNFs and epoxy matrix. The in-plane mechanical properties of multiscale composites were mainly influenced by the interface between carbon fibers and the epoxy matrix. The formation of a much stronger interface in the case of F-CNF-dispersed multiscale composites resulted in significantly higher tensile properties than that of neat carbon/epoxy and untreated CNF-dispersed multiscale composites. The incorporation of only 0.1 wt % of functionalized nanofibers led to 65% and 36% improvements in the Young's modulus and the tensile strength, respectively. Therefore, multiscale composites based on F-CNFs, as developed in this research, have immense potential to replace conventional carbon/epoxy composites.

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