Polym. Bull. (2010) 65:849–861
DOI 10.1007/s00289-010-0292-z

ORIGINAL PAPER

Effect of amine functionalization of CNF on electrical, thermal, and mechanical properties of epoxy/CNF composites

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Received: 27 June 2009 / Revised: 10 December 2009 / Accepted: 12 May 2010 /

Abstract This paper presents experimental results of the effect of amine functionalization of carbon nanofibers (CNF) on the electrical, thermal, and mechanical properties of CNF/epoxy composites. The functionalized and non-functionalized CNFs (up to 3 wt%) were dispersed into epoxy using twin screw extruder. The specimens were characterized for electrical resistivities, thermal conductivity (K), UTS, and Vicker's microhardness. The properties of the nanocomposites were compared with that of neat epoxy. The volume conductivity of the specimens increased by E12 S/cm and E09 S/cm in f-CNF/epoxy and CNF/epoxy, respectively, at 3 wt% filler loading. The increase in K for former was 106% at 150 °C, while for the latter it was only 64%. Similarly, UTS increased by 61% vs. 45% and hardness 65% vs. 43%. T_g increased with increase in filler content. SEM examinations showed that functionalization resulted in better dispersion of the nanofibers and hence greater improvement in the studied properties of the nanocomposites.

Keywords Amine-functionalized CNF · Extrusion · Electrical conductivity · Thermal conductivity · Mechanical properties

Introduction

Although carbon nano reinforcements such as carbon nanofibers (CNFs) and CNTs have exceptional chemical and physical properties, incorporating them into other materials has been inhibited by the problems such as phase separation, aggregation,

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poor dispersion within a matrix, and poor adhesion to the matrix. The poor dispersion of CNFs lowers their efficiency as reinforcement and the lack of interfacial bonding limits the load transfer capability from matrix to CNF [1–9]. These problems can be overcome by using the functionalized nanofibers, which can provide multiple bonding sites to the organic/inorganic polymer matrix so that the load can be transferred to the nanofibers and thus, inhibiting separation between the surfaces of polymer and nanofibers.

Functionalization of nanofibers is a process of attaching physically or chemically certain molecules or functional groups to their smooth side walls without affecting the desired properties to make them easily dispersible in polymers. The production of robust composite materials requires strong covalent chemical bonding between the filler particles and the polymer matrix, rather than the much weaker van der Waals physical bonds, which occur if the CNFs are not properly functionalized.

Numerous methods for chemical functionalization of carbon nanotubes, either at the tips or sidewalls of CNTs, have already been reported [10, 11]. The chemical covalent bond mechanism has proved to be very useful in maintaining the stable bonds, and significant efforts have been directed towards the establishment of chemical functionalities on the surface of CNTs. Among them, amine-functionalized CNTs have been much researched because amine group has a high reactivity, wealth of chemistry, and can react with many chemicals, and thus can be directly incorporated into epoxy resin. The hydrophobic nature of the as-received MWNT surface becomes more hydrophilic after amine treatments, owing to the creation of amine functional groups, which are reactive with the functional groups in epoxy matrix [12].

Kim et al. [13] showed that the surface modification of CNTs by amine or plasma treatment improved the mechanical and rheological properties of epoxy nanocomposites by the better dispersion and interaction between the CNTs and the epoxy resin. According to Prolongo et al. [14], the amine-functionalized CNF increased the density, glassy storage modulus, and coefficient of thermal expansion of the nanocomposites. Sulong et al. [15] showed that carboxylated- and octadecylated-MWNTs decreased the electrical conductivity of epoxy but the chemical functionalization increased the dispersion quality and strengthens the interfacial bonding with the polymer matrix, which is more important in structural applications. According to Yang et al., the amine functionalization of MWNT improved its homogenous dispersion in epoxy matrix and thereby increased the interfacial interaction between the matrix and the filler. This resulted in better impact property of the nanocomposite [11].

Although several researchers have reported the effect of functionalization of CNTs and CNFs on their dispersion into epoxy and the resulting property improvements in the composites, the same effect on high viscous epoxies has not been reported. Most of the researchers have used ultrasonication for dispersing the nanofillers. Twin-screw extrusion as a dispersion method is yet to be explored. The rotation of the twin screws and the elements of the kneading block develop sufficient shear to enable the nanofillers to disperse in the resin. Also, there is a combined effect of temperature due to the heating coils provided in the barrel and that due to the shear action, which tends to reduce the viscosity of the processing mix.

Many authors have reported that functionalization improved mechanical properties of the nanocomposites. But, similar studies for electrical and thermal properties are very scarce. The main objective of this research was to study the influence of amine functionalization of the CNF on their dispersion into a high viscous epoxy and the resulting electrical, mechanical, and thermal properties. The nanocomposites are processed using twin-screw extrusion.

Experimental

Materials

Matrix

The resin matrix used in this study consisted of modified DGEBA (Fig. 1) based two component epoxy (AV138M) having viscosity 700 Pa s, modified with butanedioldiglycidyl ether, average molecular weight <700, and density at 25 °C:1.7 g/cc. Formulated polyamine amide (HV998 having viscosity 80 Pa s, density at 25 °C:1.5–1.62 g/cc) shown in Fig. 2 was used as the hardener (supplied by Huntsman, Hindustan Ciba-Geigy Ltd.). The resin hardener ratio was 100:40 by weight as per the manufacturer's recommendations.

CNF and functionalized CNF

The CNF and amine-functionalized carbon nanofiber (f-CNF) used in this study were supplied by Nanovatec Chemapol Industries, Mumbai, India. These nanofibers were synthesized by chemical vapor deposition (CVD) method with yield purity of over 90%.

The amine functionalization process consisted of three stages of treatment, namely, acid treatment, acylation, and amino-functionalization with TETA. The CNFs were treated with a 3:1 (v/v) mixture of concentrated H_2SO_4/HNO_3 under sonication at 40 °C for 10 h. After washing with distilled water, the nanofibers were vacuum dried at 60 °C. The acid-treated CNFs thus obtained were then added to thionyl chloride at 70 °C for 24 h using magnetic stirrer. Surface-acylated CNFs were reacted with TETA at 60 °C for 96 h to get amine-functionalized CNFs [14].

The morphology of the CVD grown CNFs was studied by TEM using JEOL JEM 2000 FX operating at 200 V. The TEM micrographs presented in Fig. 3a shows that

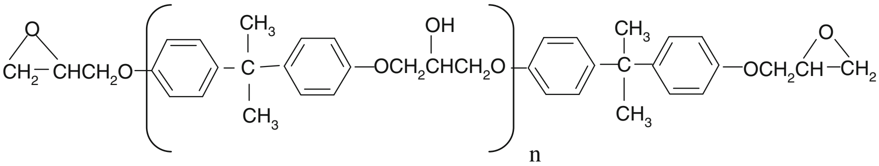


Fig. 1 Structure of diglycidylether bisphenol A (DGEBA) epoxy resin

$$H_2NC_2H_4NHC_2H_4NH\left[COCH_2NHC_2H_4NHC_2H_4NH\right]_n H$$

Fig. 2 Formulated polyamine amide

the mean diameter of the CNFs was 45 nm and the length around 3 μ. The nanofibers are entangled and randomly organized. There are some impurities such as catalyst particles, amorphous carbon, etc.

Figure 3b shows the Raman spectroscopy of CNFs. The Raman spectra obtained in the range 0–2000 cm^{-1} shows a band at 1574.2 cm^{-1} (G band) and another band at 1343.9 cm^{-1} (D band). The width of G band is related to the CNFs size distribution and that of D band to the degree of graphitization. Figure 4 shows the FTIR of amine-functionalized CNF. The peak at 3670 cm^{-1} shows the presence of

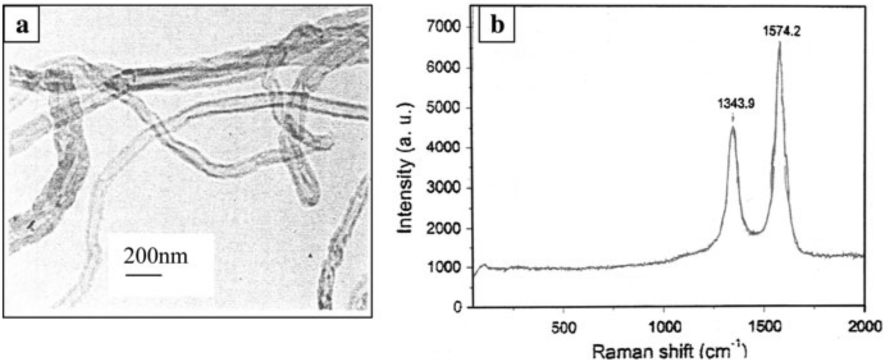


Fig. 3 **a** TEM micrograph of CNF. **b** Raman spectroscopy of CNF

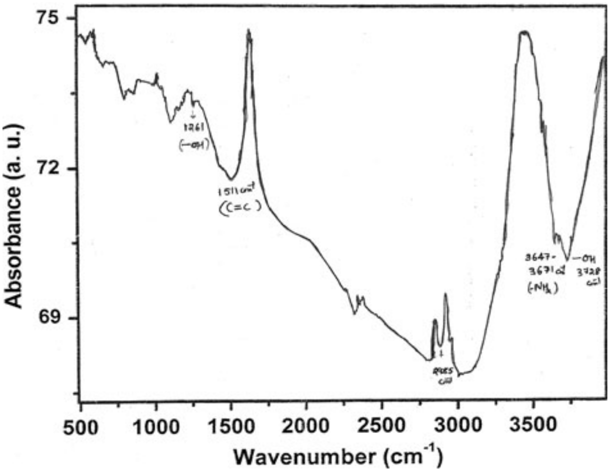


Fig. 4 FTIR spectroscopy of amine-functionalized CNFs

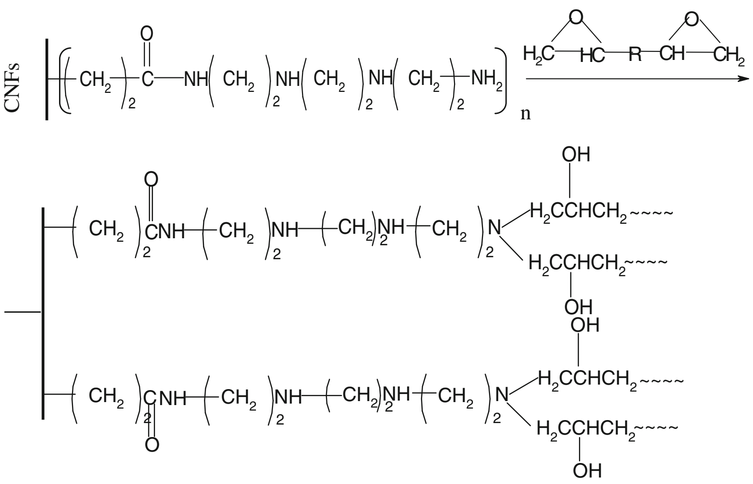


Fig. 5 Chemical reaction between amine-functionalized CNF and epoxy

amine group confirming the functionalization of the CNFs used. The chemical reaction between amine-functionalized CNF and epoxy is shown in Fig. 5.

Preparation of nanocomposites

For dispersing the CNF into a high viscous epoxy, a co-rotating twin-screw extruder (OMEGA 20, M/s STEER Engg, Bangalore) was used. The process parameters for screw extrusion for dispersing CNF into epoxy were evolved based on the viscosity of the resin and initial studies. The same were: speed 200 rpm, temperature 60–75 °C, residence time 2–3 min. The nanofibers with epoxy resin were ultrasonicated for 2 h using tip sonicator (Model VPL-P2 of power 250 watts & dia 1″ supplied by Vibronics Pvt. Ltd., Pune). The predispersed mix was processed using the twin-screw extruder in two passes. The stoichiometric amount of hardener was added to the extruded mix and cured at room temperature. Specimens with CNF loading of 0.5, 1, 2, and 3 wt% were fabricated. The same procedure and loading levels were used for fabricating CNF/epoxy and f-CNF/epoxy specimens for comparative studies.

Morphological characterization of nanocomposites

Scanning Electron Microscope (JEOL JSM 840A, Japan) was used to study the dispersion of CNF/f-CNF in the matrix. The samples were examined with gold-sputtering for SEM characterization.

Electrical resistivity measurement

The volume and surface resistivities of the nanospecimens were measured according to ASTM D257 using Keithley 6517A model 8009. The specimens (3 mm thick, 75 mm diam) were subjected to humidity conditioning at 95% RH and 37 °C and copper plated for better contact with the electrodes. The resistivity values were calculated using the formula

$$\sigma_{\mathrm{v}} = \frac{22.9}{t}R \tag{1}$$

$$\rho_{\mathrm{s}} = 53.4R \tag{2}$$

where σ_{v} and ρ_{s} are the volume and surface resistivities, R the corresponding resistance in ohms (meter reading), 22.9 and 53.4 the apparatus constants.

Thermal conductivity measurement

Thermal conductivity was measured using thermal conductivity instrument (TCI)—2022 SX211 as per ASTM E 1530 under 10^{-5} torr vacuum environment with measurement accuracy of ±3%. The specimens (50 mm diam and 10 mm thick) were used for this study. To ensure good contact between the test samples and the flex meter, the surface finish of the samples were improved by working with a fine emery paper. The experimental results of the thermal conductivity in the temperature range −50 to 150 °C are presented in Fig. 8.

Mechanical property measurement

UTS

Tensile test was performed on the specimens as per ASTM D 3039 at a strain rate of 5 mm per minute using a universal testing machine (M/s Kalpak, Pune). The specimen dimensions were 208 mm × 12.7 mm × 3 mm.

Vicker's hardness test

Hardness of the specimens was measured as per ASTM E 384 using micro-hardness tester (M/s Metatech, Pune). The specimens were polished with sandpaper for getting smooth surfaces for indentation. The indenter used for the test was a 136° square based Vicker's diamond pyramid. Ten measurements at different spots were averaged for each sample. A force of 100 g was applied for 15 s for getting the indentation. The unit and magnitude of the hardness are defined by Vicker's hardness, H_{v} and determined by the equation [16]

$$H_{\mathrm{v}} = 1.854L/d^2 \tag{3}$$

where L is the load applied in grams and d is the diagonal length of diamond impression of the indentation in mm.

Differential scanning calorimetry (DSC)

Glass transition temperature, T_{g}, of the specimens was obtained using DSC (Model—Mettler DSC-823, Temp range: 25–500 °C). The sample weighing 5 mg and sealed in a hermetic aluminum crucible was used for the characterization. For obtaining the curing heat flow pattern of the composite, a dynamic scanning experiment was conducted from room temperature to 150 °C at a heating rate of 20 °C per minute in N_2 atmosphere with a flow rate of 20 mL/min.

Results and discussion

Morphological characterization

Scanning electron microscopy (SEM)

To study the dispersion of CNF in the epoxy matrix, the tensile fracture surfaces of the specimens were observed using SEM. Figure 6a shows the micrograph of 2 wt% f-CNF/epoxy specimens; and in Fig. 6b the marked portion of Fig. 6a is magnified. These micrographs suggest that the CNFs are well dispersed in the matrix due to the functionalization. This reasoning is because CNF/epoxy and f-CNF/epoxy specimens were fabricated using the same processing conditions of twin-screw extrusion.

Carbon nanofiber (CNF) agglomerates are present in the micrograph of 3 wt% CNF/epoxy specimens as shown in Fig. 6c, and the magnified version of the marked portion in Fig. 6d reveals agglomerates of greater scale. Functionalization resulted in strong CNF/epoxy interfacial bonding, which is evident in tube breakage observed in Fig. 6a, b. Non-functionalized CNF specimens showed tube pull out evidencing poor interfacial bonding as observed in Fig. 6c, d.

Electrical conductivity measurement

Room temperature electrical conductivities of CNF/epoxy and f-CNF/epoxy nanocomposites are plotted as a function of filler weight fraction in Fig. 7. Both volume and surface conductivities of the nanocomposites increased with increase in filler content. The volume conductivity of f-CNF/epoxy increased from $6.71 \times {}^{-15}$ (conductivity of neat epoxy) to $2.69 \times {}^{-3}$ S/cm at 3 wt% f-CNF loading. The volume conductivity of CNF/epoxy at 3 wt% loading of CNF was $3.44 \times {}^{-4}$ S/cm. The increase in surface conductivity was also one order higher for f-CNF/epoxy composites compared to non-functionalized CNF/epoxy composites. This indicates that the improved nanofiber dispersion due to functionalization helped the formation of conductive networks with in the polymer matrix giving rise to an increase in the electrical conductivity at a low range of f-CNF content compared to non-functionalized CNF. The presence of nanofiber agglomerates in non-functionalized CNF/epoxy nanocomposites hindered the network formation tending to decrease the extent of conductivity enhancement.

According to percolation theory, there is a critical concentration called percolation threshold at which a conductive path is formed in the composite causing the material to convert from an insulator to a conductor. The volume conductivity data of CNF/epoxy and f-CNF/epoxy samples were fitted to a power

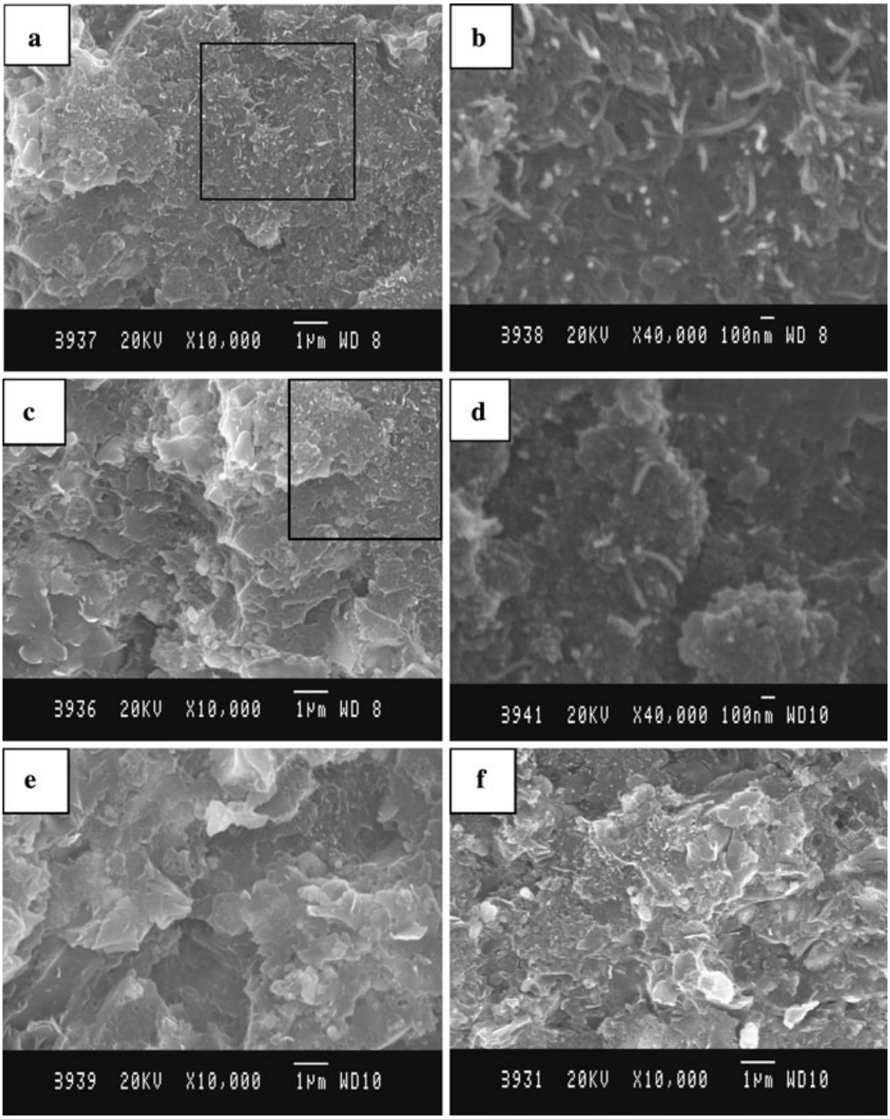


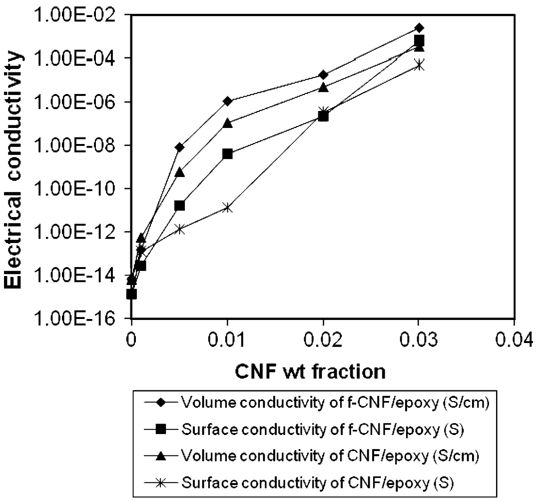
Fig. 6 SEM micrographs of nanocomposites; **a** 2 wt% f-CNF/epoxy and **b** magnified portion from (**a**), **c** 3 wt% CNF/epoxy, **d** magnified portion from (**c**), **e** 2 wt% CNF/epoxy and **f** 3 wt% f-CNF/epoxy

law in terms of weight fraction of nanofibers. The power law is described by the equation [8]

$$\sigma_{pc} = A(w - w_c)^t \tag{4}$$

where σ_{pc} the volume conductivity of the composite, w is the weight fraction of nanofiller in the composite, w_c is the critical volume fraction (percolation threshold), A and t are fitted constants. The geometrical particle anisotropy with a random

Fig. 7 Variation of electrical conductivity with CNF/f-CNF weight fraction



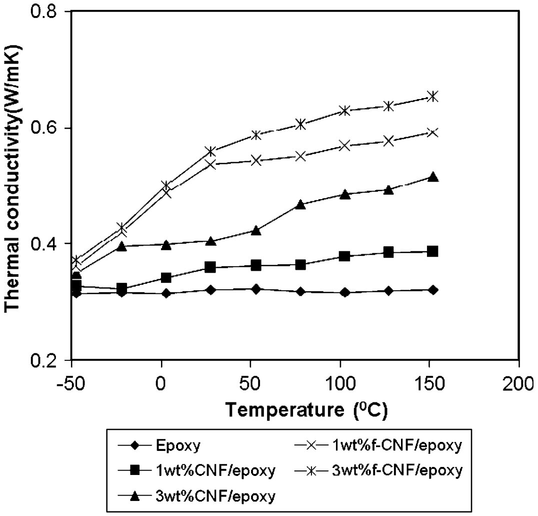
distribution inside the matrix is a key factor for determining the percolation threshold.

The critical volume concentration (percolation threshold where a sharp onset in conductivity occurs) was observed at 0.0025 weight fraction for f-CNF reinforced epoxy samples. The same for CNF/epoxy specimens were at 0.003 weight fraction. The lower percolation threshold for f-CNF/epoxy samples was attributed to the better dispersion of the filler due to the presence of functionalized nanofibers. The value of the percolation threshold is very sensitive to the polymer type, filler, and the dispersion process. The viscosities of the epoxy resins used in similar studies are much lower than that of the epoxy (700 Pa s) used in the present study [3–6]. Higher the viscosity of the resin greater the issues in the dispersion of nanofibers [7]. With the achieved values of volume resistivity, the material becomes suitable for electrostatic discharge (ESD) or electromagnetic interference (EMI) shielding applications. It is reported that electrical resistivity below E08 Ω cm is needed in order to avoid the electrostatic charging of insulating matrix [15].

Thermal conductivity measurement

Both CNF/epoxy and f-CNF/epoxy specimens showed increase in thermal conductivity (K) with increase in temperature in the range −50 °C to 150 °C and the filler loading as shown in Fig. 8. In the testing range, the K-values of the samples increased with increase in filler loadings. The maximum increase in K for f-CNF/epoxy nanocomposite was 106% at 150 °C for 3 wt% f-CNF loading compared to that of neat resin. The corresponding value for CNF/epoxy was 64%. The K-values obtained for f-CNF/epoxy at 1 wt% f-CNF loading were greater than that corresponding to 3 wt% CNF loading for CNF/epoxy in the measured temperature range. The superior K-values for f-CNF/epoxy were attributed to better dispersion due to amine functionalization of CNF thereby making strong interaction between the matrix and the filler. This interaction reduces the phonon scattering at nanofiber–epoxy

Fig. 8 Thermal conductivity of the nanocomposites with different weight fractions of CNF



interface. At a given weight fraction, the functionalization enhances the nanofiber–polymer–nanofiber contacts due to lower levels of agglomeration. This gives rise to increase in thermal conductivity of the f-CNF based composites.

In contrast to the electrical conductivity (σ) behavior, percolation threshold for thermal conductivity (K) was not observed in the specimens. The increase in electrical conductivity achieved was very high, i.e., extents of E12 and E9 for functionalized and non-functionalized CNF/epoxy, respectively, corresponding to nanofiber loading of 3 wt%. But in the thermal transport, the increase in K was only by 74% and 26% for f-CNF/epoxy and CNF/epoxy, respectively, for nanofiber loading of at 3 wt% at room temperature. This is because of the significantly greater values of $\sigma_{\text{filler}}/\sigma_{\text{matrix}}$ (10^{12}–10^{16}) than $K_{\text{filler}}/K_{\text{matrix}}$ (10^4) for epoxy and CNF systems. With high ratios the only effective channel for the electric transport is along the percolation network, but for thermal transport the main channels of heat flow always involve the matrix. In addition, the large thermal interface resistance of matrix to the heat flow at the CNF junctions causes significant reduction in thermal conductivity increase of nanocomposites [3, 5, 9].

Mechanical properties

UTS results

Tensile tests were performed to evaluate the effect of functionalization of CNF on the mechanical properties of the nanocomposites. Figure 9 shows the tensile strengths of the nanocomposites with increase in nanofiber content. The results reveal that the nanofibers modified the properties of epoxy resin. Amine-functionalized nanocomposites exhibited much better performances than those without functionalization. The f-CNF/epoxy nanocomposites showed 61% increase in tensile strength compared to 45% in the case of CNF/epoxy nanocomposites at 3 wt% nanofiber

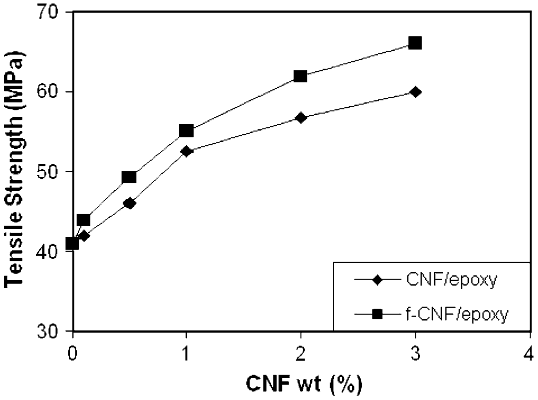


Fig. 9 Tensile strengths of the composite with increase in nanofiber content

loading. The functionalization can modify the fiber surface and improve the adhesion between nanofibers and epoxy matrix [1].

The amine groups stabilize the nanofiber dispersion by stronger interactions with the epoxy matrix. Because of multiple amino groups attached to the CNFs, the resulting composites form a heavily cross-linked structure with a covalent bond between the nanofibers and epoxy matrix. The nanofibers are chemically bonded to the matrix and hence become an integral part of the composite. The covalent bond helped in the effective load transfer between the matrix and the nanofibers [2].

Hardness results

In Fig. 10, the hardness of the nanocomposites with increase in nanofiber weight percentages is plotted. It can be seen that the addition of nanofibers into epoxy increased the hardness for both f-CNF/epoxy and CNF/epoxy nanocomposites. The continuous increase of the nanofiber content resulted in increasing the number of high strength reinforcements inside the composites, thus increasing their hardness property. Specimens with functionalized nanofibers showed 65% increase in hardness compared to 43% with non-functionalized nanofibers at 3 wt% loading.

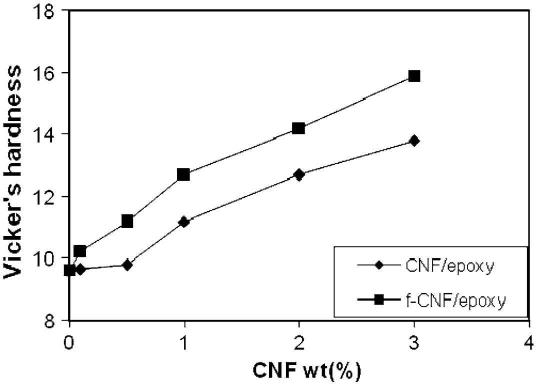
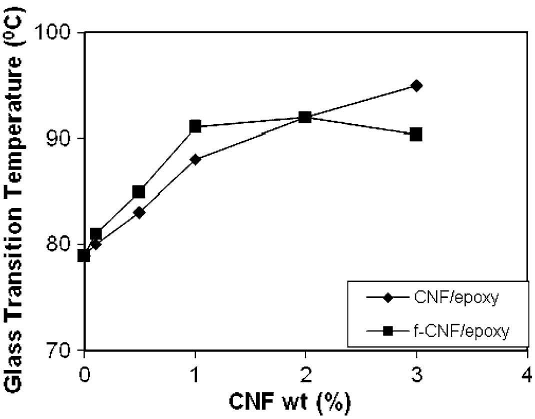


Fig. 10 Variation of Vicker's hardness of the nanocomposite with nanofiber content

Fig. 11 Variation of glass transition temperature (T_g) with nanofiber content



This may be related to the difference in the nanofiber dispersion. Amine functionalization resulted in the formation of covalent bond with the matrix and increased the interfacial bonding between the nanofibers and the matrix and thus caused greater enhancement in hardness compared to CNF/epoxy composites.

DSC

Differential scanning calorimetry was used to determine the T_g of the nanocomposites using the measurement of heat flow versus change in temperature. Figure 11 shows the variation of glass transition temperature with increase in nanofiber loading. The glass transition temperature increases linearly for CNF/epoxy nanocomposites. The gain in thermostability can be interpreted as a reduction in the mobility of epoxy chains around the nanofibers by interfacial interactions. The f-CNF/epoxy nanocomposites showed greater increase in T_g up to 2 wt% nanofiber loading compared to CNF/epoxy nanocomposites. This may be due to the improved interaction between the nanofibers and the epoxy matrix due to the amine functionalization [17].

At higher concentrations of f-CNF (above 2 wt%), the nanocomposite showed decrease in T_g. This may be explained by the fact the presence of amine groups on the functionalized nanofiber surface would lead to non-stoichiometric balance between epoxy monomer and curing agent. Consequently, the extent of crosslinking in the nanocomposites is decreased [14, 18]

Conclusions

Experiments were conducted to evaluate the effect of amine functionalization of CNF on the electrical, thermal, and mechanical properties of epoxy nanocomposites. The specimens were fabricated using twin-screw extrusion process. Functionalized nanofibers were found to be more uniformly dispersed into epoxy as evidenced by SEM and the experimental results. Greater improvements in electrical conductivity, thermal conductivity, UTS, and hardness were observed in f-CNF/epoxy specimens than that of the nanocomposites prepared using non-functionalized nanofibers. The CNF/epoxy nanocomposites showed greater increase in glass transition temperature, which can be due to the stoichiometric imbalance by the amine groups in f-CNF, which increases the mobility of matrix.

References

1. Luyi S, Warren GL, O'Reilly JY, Everett WN, Lee SM, Davis D, Lagoudas D, Sue HJ (2008) Mechanical properties of surface-functionalized SWCNT/epoxy composites. Carbon 46:320–328
2. Gojny FH, Wichmann MHG, Fielder B, Schulte Karl (2005) Influence of different carbon nanotubes on the mechanical properties of epoxy matrix composites-A comparative study. Compos Sci Technol 65:2300–2313
3. Yu A, Itkis ME, Bekyarova E, Haddon RC (2006) Effect of single-walled carbon nanotube purity on the thermal conductivity of carbon nanotube-based composites. Appl Phys Lett 89:133102
4. Moisala A, Li Q, Kinloch IA, Windle AH (2006) Thermal and electrical conductivity of single- and multi-walled carbon nanotube-epoxy composites. Compos Sci Technol 66:1285
5. Song YS, Youn JR (2005) Influence of dispersion states of CNTs on physical properties of epoxy nanocomposites. Carbon 43(7):1378–1385
6. Zhou YX, Wu PX, Cheng ZY, Ingram J, Jeelani S (2008) Improvement in electrical, thermal properties of epoxy by filling carbon nanotube. eXPRESS Poly Lett 2(1):40–48
7. Choi Y-K, Sugimoto K-I, Song S-M, Gotoh Y, Ohkoshi Y, Endo M (2005) Mechanical and physical properties of epoxy composites reinforced by vapor grown carbon nanofibers. Carbon 43:2199–2208
8. Ounaies Z, Park C, Wise KE, Siochi EJ, Harrison JS (2003) Electrical properties of single wall carbon nanotube reinforced polyimide composites. Compos Sci Technol 63:1637–1646
9. Shenogina N, Shenogin S, Xue L, Keblinski P (2005) On the lack of thermal percolation in carbon nanotube composites. Appl Phys Lett 87:133106
10. Abdalla M, Dean D, Robinson P, Nyairo E (2008) Cure behavior of epoxy/MWCNT nanocomposites: the effect of nanotube surface modification. Polymer 49:3310–3317
11. Yang K, Gu M, Guo Y, Pan X, Mu G (2009) Effects of carbon nanotube functionalization on the mechanical and thermal properties of epoxy composites. Carbon 47:1723–1737
12. Shen J, Huang W, Wu L, Hu Y, Ye M (2007) The reinforcement role of different amine-functionalized multi-walled carbon nanotubes in epoxy nanocomposites. Compos Sci Technol 67:3041–3050
13. Kim JA, Seong DG, Kang TJ, Youn JR (2006) Effects of surface modification on rheological and mechanical properties of CNT/epoxy composites. Carbon 44:1898–1905
14. Prolongo SG, Campo M, Gude MR, Chaos-Moran R, Urena A (2009) Thermo-physical characterization of epoxy resin reinforced by amine-functionalized carbon nanofibers. Compos Sci Technol 69:349–357
15. Sulong AB, Muhamad N, Sahari J, Ramli R, Deros BMd, Park J (2009) Electrical conductivity behaviour of chemical functionalized MWNTs epoxy nanocomposites. Eur J Sci Res 1:13–21 (ISSN 1450–216X 29)
16. Lau K-T, Shi S-Q, Zhou L-M, Cheng H-M (2003) Micro-hardness and flexural properties of randomly-oriented carbon nanotube composites. J Compos Mater 37(4):365–376
17. Samal SS (2009) Role of temperature and nanotube reinforcement on epoxy based nanocomposites. J Mater Mater Charact Eng 8(1):25–36
18. Luqi Lui H, Wagner D (2005) Rubbery and glassy epoxy resins reinforced with carbon nanotubes. Compos Sci Technol 65:1861–1868