Influence of nanotube content on the mechanical and thermo-mechanical behaviour of –COOH functionalized MWNTs/epoxy composites

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MS received 19 April 2016; accepted 21 November 2016; published online 5 August 2017

Abstract. Functionalized multi-wall carbon nanotubes (MWNTs) with carboxylic acid group (–COOH) have been utilized for the preparation of epoxy nanocomposites. Composites were synthesized using three different wt% (0.5, 0.75 and 1) of MWNTs via the solution mixing technique followed by ultrasonication. Mechanical and thermo-mechanical properties of the fabricated composites have been experimented for the suitability of this material in a variety of structural applications. The flexural modulus, strength, hardness, impact strength and storage modulus increased upon increasing MWNTs contents. Best results have been observed in nanocomposites with 0.75 wt% nanotubes loading, which showed 101, 166 and 61% enhancement in the flexural modulus, hardness and storage modulus, respectively, compared to neat epoxy. Achievement of uniform dispersion and hence formation of improved interface between nanotubes and epoxy was the reason behind the maximum enhancement at this wt%, which is further evidenced by the fracture surface morphology obtained from microscopical investigations.

Keywords. Nanocomposites; functionalization; flexural modulus; storage modulus; surface morphology.

1. Introduction

Carbon nanotubes (CNTs) are recently being considered as promising nanoscale fillers for polymer composite materials. Their low density, high aspect ratio and extraordinary mechanical, electrical and thermal properties helps them to be flawless candidates in polymer composites for the application of these materials in aerospace and automotive applications where a weight reduction is extremely crucial [1]. CNTs exhibit tensile strength and elastic modulus in the range of 50–100 GPa and 1.4 TPa, respectively [2], and thus nanocomposites formed by incorporation of CNTs into polymer like epoxy matrix improves the physical properties of the matrix. It is beneficial as there is no significant weight addition; also in addition, the processing equipment required for such nanocomposites is the same as that used for neat resins. Furthermore, CNTs possess diameter-dependent specific surface area that offers available surface for interaction while being incorporated into the polymer. This interaction, in fact, is responsible to modulate the matrix properties in a significant manner.

However, using CNTs as reinforcing agents in epoxy matrix can be a pretty challenging task, because the presence of strong inter-tube interaction offered by the van der Waals' forces creates a genuine difficulty to achieve qualitative dispersion of CNTs into epoxy polymer. Till date, a number

of dispersion techniques are available to disperse CNTs into epoxy. These include mechanical stirring, magnetic stirring, ball milling, calendaring process, stir and extrusion, ultra sonication and high shear mixing, etc. [3,4]. Among all these techniques, the method of sonication has been most commonly used to disperse CNTs in epoxy resin. Now the fact is that like dispersion, interfacial adhesion between the CNTs and epoxy is a vital issue as well, to ensure sufficient stress transfer from the matrix to the CNTs. Hence, a strong interfacial adhesion between the CNTs and epoxy polymer is highly desirable for the effective performance of the resulting composites. On the line of investigation, it has been observed that surface modification, i.e., functionalization of CNTs in an effective way not only improves the interfacial interaction and adhesion, but it rather helps in achieving uniform dispersion of CNTs into polymer [4–6].

Indeed, functionalization is based on the covalent linkage of functional entities onto carbon scaffold of CNTs. These chemically functionalized CNTs can produce strong interfacial bonds with many polymers, allowing CNTs based nanocomposites to possess high mechanical and functional properties. The introduction of tailored chemical groups (e.g., amino, carboxyl or glycidyl groups for epoxies) enables covalent bonding between CNTs and epoxy, improving the interfacial stress transfer and positively affecting the dispersibility of the nanofillers. It has been reported that epoxy polymer

exhibits significantly improved flexural and thermal properties by adding CNTs up to certain percentage loading [7–11]. A number of literatures published earlier demonstrate that chemical functionalization of CNTs, more specifically multi-wall carbon nanotubes (MWNTs), increases the compatibility with the epoxy matrix because of the formation of an interface with stronger interactions [12,13]. Furthermore, carboxylic acid group ($-\text{COOH}$) functionalization assists MWNTs to be soluble in organic solvents in an effective manner, as the hydrophobic nature of MWNTs is changed to a hydrophilic one owing to the attachment of polar groups [4]; and hence, the probability of aggregation of MWNTs' in epoxy polymer reduced. It was experimentally proved that addition of functionalized MWNTs profoundly increased the overall mechanical performances of the epoxy matrix by achieving qualitative dispersion of MWNTs in epoxy [14–21].

The novelty of this work lies not only in the fabrication procedure but also in the curing behaviour, which is different from the conventional techniques used till date. By incorporating $-\text{COOH}$ functionalized MWNTs, we expected to develop the interactions between MWNTs' surface and the epoxy polymer by forming covalent bonds between the nanotubes and the matrix. In addition, obtained mechanical and thermo-mechanical results of all the composites were further supplemented and complemented by a microscopic study. The primary goal of this study is to develop such a novel structural material that can exhibit superior properties.

2. Experimental

2.1 Materials

Carboxylic acid group functionalized MWNTs have been used as reinforcement component and epoxy resin (Ciba-Geigy, araldite LY-556 based on bisphenol A, India) has been selected as the matrix material for synthesis of the nanocomposites. Functionalized MWNTs were commercially purchased from NanoAmour, USA; having diameter of around 20–30 nm and lengths of about 10–30 μm with a carbon purity of $>95\%$. During fabrication epoxy resin ($5.3\text{--}5.4 \text{ equiv kg}^{-1}$) has been cured with an aliphatic primary amine hardener (HY-951) in the wt. ratio 100/12.

2.2 Nanocomposite preparation

A schematic diagram of nanocomposite preparation has been presented in figure 1. A detailed description on the processing of the nanocomposites is given in our earlier work [22]. Prepared composites were designated as follows:

Neat epoxy composite: E_p

Nanocomposite with 0.5 wt% of functionalized MWNT loading: $\text{FC}_{0.5}$

Nanocomposite with 0.75 wt% of functionalized MWNT loading: $\text{FC}_{0.75}$

Nanocomposite with 1 wt% of functionalized MWNT loading: FC_1

Figure 1. Schematic of nanocomposite preparation.

2.3 Characterization details

The covalent functionalization of $-\text{COOH}$ group on CNT surface was confirmed using Fourier transforms infrared spectroscopy (FTIR) on a Perkin Elmer instrument in transmission with a resolution of 2 cm^{-1} (8 scans collected). Flexural tests were accompanied according to ASTM D790–02 ‘Standard Test Methods for Flexural Properties of Un-reinforced and Reinforced Plastics and Electrical Insulating Materials’ on a universal testing machine (Instron 5967, purchased from: United Kingdom, Capacity: 30 kN, test conducted at: NIT Rourkela, Odisha, India). The mode of test was three-point bending and the rate at which the load was imposed was 2.0 mm min^{-1} . The span between two supports, width and thickness of the specimen were 60, 12.5 and 5 mm, respectively. To reproduce the results, five specimens were tested in each group. The hardness of all composite specimens was measured using a micro-hardness tester. The measurement was done by the Vickers hardness test method, which is all about indenting the test material with a diamond indenter. In this method, the hardness is calculated by measuring the load applied and the average diagonal length of the indentation. A total of 10 points on each of the specimens were measured to get the average readings. Izod impact test was performed using Impact tester VEEKAY TL VS4, Pune, India. The impact range of angle was 1500 with the maximum load of about 21.685 J m^2 . The dimension of the specimen for the test was length = 63.5 mm; width = 12.7 mm and thickness = 5 mm. Viscoelastic (thermo-mechanical) properties of composites were analysed using dynamic mechanical analyser (DMA 242E, Germany) in three-point bend mode. Treatment conditions included a temperature range from 40 to 260°C with

Figure 2. FTIR spectra of FC_{0.75} nanocomposite.

Figure 3. Flexural properties of all the composite samples.

a heating rate of $100^{\circ}\text{C min}^{-1}$ in air. Field emission scanning electron microscope (Nova NANOSEM 450, FEI) was used to observe the fracture surface topography of all the composite specimens.

3. Results and discussions

3.1 FTIR analysis

The FTIR spectroscopy of the -COOH functionalized MWNTs/epoxy nanocomposite is shown in figure 2. The spectra showed some intense peaks around $800\text{--}920\text{ cm}^{-1}$. These peaks are commonly for the epoxide groups. The peak around 1765 and 1585 cm^{-1} of the nanocomposite represents the C=O vibration peak that confirms the presence of -COOH group on the carbon skeleton. In addition, the existence of peaks around 1120 and 2900 cm^{-1} are, respectively, represented for the C-O-C vibration peak and C-H vibration peak [23]. Therefore, the nanocomposite specimen exhibits both the peaks corresponding to the epoxy resin as well as -COOH functionalized CNTs.

3.2 Flexural study

Figure 3 illustrates the flexural properties of epoxy and functionalized MWNTs/epoxy composites. The addition of any kind of nanofiller increases the stiffness and strength of the matrix material, as long as a proper impregnation with the matrix and a sufficient adhesion is ensured. Concordantly, in this case, epoxy containing 0.5 and 0.75 wt% of MWNTs, i.e., FC_{0.5} and FC_{0.75} showed 89 and 101% modulus enhancement in comparison to pure epoxy with modulus 4501 MPa, while relatively lower (40%) improvement in the modulus was observed in FC₁. The functionalized nanotubes turned out to be more efficient concerning an improvement of the flexural modulus, thus again proving the relevance of surface functionalization. Good dispersion of MWNTs and cross-linking of functional groups present on the surface of MWNTs with polymer that restricts the mobility of polymer chains in turn enhanced the modulus [16]. In this study, the possible reaction between epoxy and -COOH MWNTs has been estimated and represented in figure 4. Here, -COOH acted as nucleophile, which in reaction with the epoxy polymer opened up the epoxide rings and the anhydrides, facilitating improved MWNT-polymer interactions. This resulted in a high degree of adhesion that could be the prime reason behind superior physical properties of the composites in all respects.

The strength values were in the order of $\text{FC}_1 < \text{FC}_{0.5} < \text{FC}_{0.75}$ with 84, 93, 148 MPa, respectively, in comparison to epoxy having strength of 66 MPa (figure 3). Decrease in strength at higher loading can be attributed to improper dispersion of MWNTs as well as creation of voids and presence of aggregated MWNTs phases in the sample.

Flexural modulus and strength value obtained in this present report has been compared with some previous research reports and presented in table 1. It is clearly visible that significant increment in flexural modulus and strength values occurred in the case of FC_{0.75} sample.

3.3 Micro-hardness test

The hardness of all the composites is studied using a micro-hardness tester. The hardness value is calculated using the Vickers hardness (HV) method, which is given by $\text{HV} = 2F \sin(136^{\circ}/2)/D^2 = 1.854F/D$ (approximately); where, F = load in kgf and D = arithmetic mean of the two diagonals, d_1 and d_2 in mm.

The obtained hardness value of epoxy matrix was 12 MPa while addition of functionalized MWNTs increased it to a great extent. An increment of 75, 166 and 133% hardness values were observed, respectively, for FC_{0.5}, FC_{0.75} and FC₁ nanocomposites with respect to neat epoxy, as shown in figure 5. There may be a number of reasons for which hardness of the nanocomposites can be increased. First, materials having higher crystallinity have greater hardness. Second, the reinforcement effect, which is caused due to the addition of high aspect ratio, high modulus and high strength nanofillers

Figure 4. Possible reaction between carboxylic acid group and epoxy polymer.

Table 1. A comparison between our results and some previous reported results on flexural strength and modulus of functionalized MWNTs/epoxy composites.

Systems	Flexural strength, MPa	Flexural modulus, GPa	References
Epoxy/MWNT-COOH 0.3 wt%	91.03	2.71	[16]
Epoxy/MWNT-NH ₂ (0.6 wt%)	58.5	—	[17]
Epoxy/MWNT-NH ₂ (0.6 wt%)	64.5	2.4	[18]
Epoxy/silane-treated MWNT (0.5 wt%)	115–120	3.5–3.6	[19]
Epoxy/Triton X-100 treated MWNT (0.25 wt%)	126.1	3.5	[24]
Epoxy/Teta functionalized MWNT (0.6 wt%)	110.7	2.7	[25]
Epoxy/MWNT-NH ₂ (0.25 wt%)	84.1	3.89	[26]
Epoxy/MWNT-NH ₂ (0.5 wt%)	130	3.5	[27]
Epoxy/MWNT-COOH (0.75 wt%)	148	9.04	Present study

(MWNTs). These reinforced fillers contributed to the increment in hardness value. Third is the homogeneous dispersion of the fillers (MWNTs). Since MWNTs are resilient materials,

homogeneously dispersed MWNTs can add rigidity and hardness via interfacial interaction with the epoxy matrix. Thus, the soft polymer matrix holds together when challenged by

Figure 5. Hardness of all the composite samples.

an applied force and the mechanical properties like modulus and hardness are improved [28]. Fourth is the formation of a long range ordered structure, which can be accomplished by the functionalization of MWNTs. Therefore, all of these said reasons are equally accountable for the dramatic enhancement in hardness values in this case. Hardness results agreed well with flexural test results, with the finding that among the specimens FC_{0.75} showed the maximum improvement. However, for higher concentration in case of FC₁, the hardness value deteriorated greater than FC_{0.75} though it was still higher than other specimens. Reduction in hardness value at FC₁ may be owing to the formation of voids because of the addition of higher nanoparticle contents [29]. In addition, higher concentrated MWNTs may act as a stress concentrator in the composite, which can be the cause behind the decrement in mechanical properties.

3.4 Impact strength measurement

The Izod impact strength of the neat epoxy and all the -COOH functionalized MWNTs/epoxy composites have been determined as shown in figure 6. Usually impact strength signifies the amount of energy a material can sustain before the ultimate fracture. According to the obtained results the impact strength of the neat epoxy was found to be 0.81 J m^{-2} , while the nanocomposites FC_{0.5} and FC_{0.75} showed an enhanced strength having values 0.92 and 0.835 J m^{-2} , respectively. Contribution of low contents of nanotubes provided increased impact strength than that of neat epoxy, i.e., up to $0.75 \text{ wt\%}$ of MWNTs loading. Relative to the flexural test with low loading rate, the impact test applied a high strain rate to the composite. Eventually in high strain rate, stress transfer between MWNT and epoxy is not as effective as flexural tests. This may be the reason behind the trivial increment in impact compared to the neat epoxy. Improvement in impact strength indicates the uniform dispersion of nanotube to epoxy as well as strong

Figure 6. Impact strength measurement of all the composite samples.

adhesion between them, which eventually resists the direction of crack propagation when subjected to applied force. However, at a comparatively higher concentration, i.e., for FC₁ the strength appeared to be decreasing as compared to the neat epoxy. The decrease in impact strength was due to the addition of larger amount of nano-inclusions that finally left the composites highly viscous in nature. Such high viscosity made these materials so brittle that their impact behaviour turns to be infertile [24,30]. The pattern of obtained results has been further analysed and compared with the fracture surface morphology that has been depicted in the microscopical study.

Apart from the functionalization effect and uniform dispersion, there is another reason behind the improvement of mechanical properties like modulus, strength and hardness of the composites. It is curing of the fabricated sample at low temperature (4°C). In general, mixing of hardener into the epoxy produces a significant amount of heat in the mixture. This additional heat increases the rate of the curing process and thereby reduces the settlement time of the mixture. This type of faster curing process generally produces voids in the samples and hence, mechanical and physical properties of the composites deteriorated. To avoid this unwanted effect of heat, low temperature curing process has been introduced and experimentally confirmed by our earlier work [22]. This low temperature treatment allows more interaction between hardener and epoxy by delaying settling time to make the composites with proper curing.

3.5 Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was performed to evaluate the viscoelastic properties of the composites such as storage, loss modulus, glass transition temperature, etc. In DMA, a sinusoidal force is applied (or displacement) and the response of the input is recorded. Depending on the nature of

the response, i.e., the output signal behaviour of the material under consideration can be predicted. If the material is not purely elastic the response will be completely out of phase with the input. In this technique, stress is applied as a function of time (temperature) and the relation with the frequency is given by the equation (1) [31];

$$\sigma(t) = \sigma_0 \sin(\omega t + \delta), \quad (1)$$

where, σ_0 is the maximum stress applied, δ the phase angle.

The strain which lags by the phase angle, δ , is given by the equation (2)

$$\varepsilon(t) = \varepsilon_0 \sin \omega t, \quad (2)$$

where ε_0 is the maximum strain amplitude.

Using Hooke's law, the input and the response are related by the dynamic (or complex) modulus. The complex modulus, $E^*(\omega)$ is related to $\sigma(t)$ and $\varepsilon(t)$ as given in equation (3)

$$\sigma(t) = E^*(\omega) \varepsilon(t), \quad (3)$$

The complex modulus has in phase and out of phase components and is given by the equation (4)

$$E^*(\omega) = E'(\omega) + iE''(\omega), \quad (4)$$

where $E' = (\sigma_0/\varepsilon_0)\cos \delta$, is the in-phase portion or real part and characterizes the elastic behaviour of the material and the out of phase or imaginary portion is $E'' = (\sigma_0/\varepsilon_0)\sin \delta$ signifies the viscous behaviour of the material [32]. The storage modulus, E' , is proportional to the energy stored in the material per cycle [33]. The loss modulus on the other hand, E'' , is proportional to the loss or dissipated energy of the material per cycle. Both the elastic and viscous response are exhibited simultaneously by the viscoelastic polymer composite material. The energy dissipation to the energy storage ratio is the tangent of the phase angle, δ , or often called $\tan \delta$, which is given by the equation (5)

$$\tan \delta = E''/E', \quad (5)$$

Figure 7 shows the effect of temperature on the storage modulus of all the composites. It was found that when compared to the neat epoxy composites the value of storage modulus was increased upon increasing MWNTs contents. The value of the storage modulus of neat epoxy composites was found to be around 3.6 GPa. The percentage of increment in modulus was 6, 61 and 44%, respectively, for the FC_{0.5}, FC_{0.75} and FC₁ specimens. FC_{0.75} showed the maximum enhancement in modulus (5.8 GPa) among the nanocomposites. Best result in this wt% may be due to uniform dispersion of reinforcing agents caused by the -COOH functionalization as well as amusing confinement of MWNTs to the epoxy

Figure 7. Storage modulus of neat epoxy and nanocomposite samples.

polymer. However, slightly lower modulus value for FC₁ compared to FC_{0.75} (although greater than neat epoxy and FC_{0.5}) clearly indicates that reinforcement effect of MWNTs was decreased when concentration of MWNTs moved towards higher side attributing to the agglomeration of MWNTs and relatively weak interfacial bonding between MWNTs and epoxy matrix.

The value of storage modulus obtained in this report has been compared with some previous research reports and presented in table 2. It is found that storage modulus of the FC_{0.75} sample in this study is fairly greater than the other reports, whereas there remains one exception. The storage modulus of CNT/basalt/epoxy hybrid composites [21] is slightly greater than the present report. This may be due to the hybrid structure of CNTs and basalt fibres that form a co-supporting network and thereby increasing the overall properties.

Dynamic loss modulus of the neat epoxy and nanocomposites is plotted in figure 8. Even if the change in slope of loss modulus is less pronounced than that of the storage modulus, the loss modulus of the MWNTs/epoxy composite shows a different behaviour with respect to the nanotube loadings. The loss modulus decreased at 0.5 wt% followed by a continuous increase in peak height at increasing MWNTs contents. The increase in modulus is due to the fact that the dispersed MWNTs dissipate energy due to resistance against visco-elastic deformation of the surrounding epoxy matrix [35].

$\tan \delta$ is defined as the ratio of loss to storage modulus of a composite, where δ represents the phase angle. The phase angle is very much sensitive to the structural change of the materials and decreases with increasing filler contents [36]. Figure 9 represents the nature of $\tan \delta$ curves as a function of temperature of all the samples. The essential feature of this plot is the change in peak height of the samples with respect to temperature. A difference of peak height between the neat epoxy and MWNT/epoxy composites is an indication

Table 2. A comparison between our results and some previous reported results on storage modulus of functionalized MWNT/epoxy composites.

Systems	Storage modulus (MPa)	References
Epoxy/MWNT-COOH 0.2 wt%	$2-3 (\times 10^9)$	[16]
Epoxy/silane-treated MWNT (0.5 wt%)	$1-2 (\times 10^9)$	[19]
Epoxy/salt of 6 aminohexanoic acid modified MWNT (0.5 wt%)	10^9	[20]
CNT/basalt/epoxy composites (1 wt%)		[21]
Acid modified (oxidized)	6.5×10^9	
Silane modified (silanized)	7×10^9	
Epoxy/Triton X-100 treated MWNT (0.25 wt%)	$2.5-3.0 (\times 10^9)$	[24]
Epoxy EPI W/-NH ₂ (0.5 wt%)	$3.04 (\times 10^9)$	[9]
Epoxy/MWNT-COOH (1 wt%)	$2-3 (\times 10^9)$	[34]
Epoxy/MWNT-COOH (0.75 wt%)	$5-6 (\times 10^9)$	Present study

Figure 8. Loss modulus of neat epoxy and nanocomposite samples.

of interaction that took place between MWNTs and epoxy polymer at the time of curing.

In addition, the peak of $\tan \delta$ is used to determine the glass transition temperature (T_g) of a material from the onset of the

Figure 9. $\tan \delta$ peak of neat epoxy and nanocomposite samples. **Figure 10.** Glass transition temperature (T_g) of all the composites.

sharp drop in $\tan \delta$ vs. temperature graph. This method of evaluating T_g values for different composite samples are presented in figure 10. It was interesting as well as expected to note that when compared to the neat epoxy all the nanocomposite samples show increment in T_g . An increase of 1–14°C in T_g was recorded for the nanocomposites than the as-received epoxy. T_g is increased due to further addition of -COOH MWNTs, this is because of the fact that mobility of the polymer chain reduced due to the incorporation of MWNTs. In addition, functionalized MWNTs with the surrounding epoxy matrix developed a strong interfacial bonding, which increased thermal stability and hence T_g of the specimen [37]. Apart from these, the strong covalent bonding between -COOH MWNTs and resin-promoted energy dissipation from the matrix to the MWNTs, resulted in greater sustainability in the temperature [20]. Careful observation revealed that the shift in peak height was continuously increasing up to 1 wt% MWNTs loadings. This behaviour is mainly due to the high stiffness of the MWNTs that made the nanocomposite stiffer than the neat epoxy. This stiffness of the material in turn helps in achieving a high degree of T_g [38].

Figure 11. (a) As-received $-COOH$ and (b) ethanol dispersed functionalized MWNTs.

As discussed earlier, proper dispersion of MWNTs in the epoxy is a very difficult task. Strong van der Waals' force between the nanotubes resists them from dispersing well. In addition, as epoxy possesses high viscosity, nanotubes get agglomerated during the time of mixing. Functionalization of MWNTs overcomes the problem of dispersion as functional groups, being polar in nature, help in dispersion. Apart from this, the process of functionalization endows MWNTs a special mechanism of reinforcement. The functional groups attached on the surface of MWNTs form a soft layer, interconnecting the MWNTs and epoxy polymer. This way, when some external load is applied to the material most of the part of the load is been carried out by MWNTs, as it exhibits extraordinary Young's modulus and strength and thereby acts as a load bearer. As a result, ultimate strength and impact energy of the materials were enhanced. Interfacial adhesion between MWNTs and epoxy is an essential parameter in order to improve the mechanical properties of composites. For the enhancement of mechanical and thermo-mechanical properties of MWNTs/epoxy composites interfacial engineering has been extensively applied by Gojny *et al* and Chen *et al* [10,15]. According to the report, development of strong covalent bonding between functionalized MWNTs and epoxy matrix enhanced the mechanical and thermal properties of the composites via limiting the mobility of the matrix backbone and more effective stress transfer from matrix to nanotube.

The flexural strength, flexural modulus and storage modulus of the nanocomposites obtained in this study has been further compared with previously obtained results by several researchers. It has been noticed that use of $-COOH$ functionalized MWNT in this study has significantly improved the flexural strength in 0.75 wt% MWNT loading along with a dramatic increment in flexural modulus and storage modulus of all the nanocomposite samples.

Apart from functionalization effect and uniform dispersion, there is another reason behind the improvement of mechanical properties like modulus, strength and hardness

of the composites. It is the curing of the fabricated sample at low temperature ($4^{\circ}C$). In general, mixing of hardener into the epoxy produces significant amount of heat in the mixture. This additional heat increases the rate of curing process and thereby reduces the settlement time of the mixture. This type of faster curing process generally produces voids in the samples and hence, mechanical and physical properties of the composites deteriorated. To avoid this unwanted effect of heat, low temperature curing process has been introduced and experimentally confirmed by our earlier work [22]. This low temperature treatment allows more interaction between hardener and epoxy by delaying the settling time in order to make composites with proper curing.

3.6 Fracture surface study

It is well known that CNTs are highly prone to agglomeration that generally occurs due to the van der Waals' forces between the tube walls. Though surface functionalized MWNTs have been used to reduce this effect, yet a finite probability remains for CNTs' aggregation in the viscous epoxy mixture. Here, in figure 11a, the image of, as received, $-COOH$ functionalized MWNTs are shown where entanglement of nanotubes are visible. To overcome this difficulty, i.e., for the effective isolation of nanotubes, at the time of fabrication, nanotubes were manually stirred with an organic solution named ethanol. The presence of polar groups ($-COOH$) assisted the nanotubes to disperse nicely with the ethanol solution, evidenced from figure 11b. The brighter spots in both the figures represent the $-COOH$ group, which is attached to the end of the nanotubes.

The fracture surfaces of composites give first information about fracture mechanisms and the influence of particle modification on the fracture behaviour. To investigate the failure mechanism of epoxy as well as functionalized MWNTs/epoxy composites, the fracture surfaces of failed specimens were examined. The micrograph of neat epoxy in

Figure 12. Comparison of fracture surfaces between (a) neat epoxy, (b) nanocomposites $FC_{0.5}$ and (c) $FC_{0.75}$.

figure 12a demonstrates a typical feature of brittle fracture behaviour, thus accounting for the low fracture toughness of the unfilled epoxy. The surface is smooth, with highly directional deformation lines, which means that the crack propagated is not interrupted. However, the fracture surfaces of composites in figure 12b and c seem to be comparatively rougher. The ridge patterns and river marks in figure 12b and c indicate that the composites presented a more ductile fracture. This means that the energy required for the propagation of the crack increased [39]. This is in accordance with the obtained impact results (figure 6), where it was concluded that compared to the neat epoxy the nanocomposites $FC_{0.5}$ and $FC_{0.75}$ showed greater impact strength.

The degree of functionalization has a certain influence on the mechanical properties of this resulting composite. The presence of $-COOH$ on the surface enables a better dispersion of MWNTs and reduces the amount of impurities. Higher magnification images in figure 13a and b show that in $FC_{0.5}$ and $FC_{0.75}$ system nanotubes were well separated and uniformly embedded in the epoxy resin. Stronger adhesion at the MWNTs/epoxy interface was obtained due to the prolonged reaction among carboxyl group, polymer and DGEBA (hardener used in this study) at low temperature curing. Another important aspect is that cracks were spanned by the nanotubes due to the bridge formation, shown in figure 13c and d. This phenomenon highly signifies that MWNTs greatly prevented the composites to be fractured during the application

Figure 13. Dispersion behaviour of (a) FC_{0.5} and (b) FC_{0.75}, and bridging mechanism in (c) FC_{0.5} and (d) FC_{0.75}.

Figure 14. (a) Fracture surface of FC₁ and (b) dispersion of FC₁ showing agglomeration.

of load [25]. This is why overall mechanical and thermo-mechanical properties of the nanocomposites increased significantly at this wt%. Although, several debonded interfaces were observed in figure 13a and b, superior adhesion at the functionalized MWNTs/epoxy interface resulted in the failure of nanotubes without pulling out from epoxy matrix.

A spatial bonding of the reactive groups at the interface enables a partial debonding of the interface, but allows a crack bridging.

When MWNTs loading increased to 1 wt%, the failure mode of nanocomposite changed. Microscopic examination reveals agglomeration of several nanotubes and formation

of voids in various areas of the FC₁ specimen, shown in figure 14a and b. These lead to crack initiation in the composites, shown by circular marks in figure 14a, due to the stress concentration [40,41]. In addition, in some locations, crack damage started easily from the interface due to the applied external force that compels MWNTs to come out from the smooth resin matrix [42], shown by a big circular mark in figure 14b. This type of pulling out of MWNTs displays weak interfacial bonding between CNTs and the epoxy matrix at higher loading. As a result, mechanical and thermo-mechanical performances at this higher wt% reduced.

4. Conclusion

Due to the low temperature curing and incorporation of –COOH functionalized MWNTs into the epoxy an improved dispersion as well as strong interfacial bonding was realised in the final composites. This facilitates significant improvement in mechanical and thermo-mechanical behaviour of the nanocomposites. The value of the storage modulus of the neat epoxy composites was found to be around 3.6 GPa. The increment percentage in the modulus was 6, 61 and 44%, respectively, for the FC_{0.5}, FC_{0.75} and FC₁ specimens. According to the flexural data FC_{0.5} and FC_{0.75} showed 89 and 101% modulus enhancement in comparison to neat epoxy, while relatively lower (40%) improvement in modulus was observed in FC₁. The strength values were in the order of FC₁, < FC_{0.5} and < FC_{0.75} with the values 84, 93 and 148 MPa, respectively, compared to neat epoxy having strength of 66 MPa. Nanocomposites FC_{0.5}, FC_{0.75} and FC₁ demonstrated an increment of 75, 166 and 133% hardness values, respectively, with respect to neat epoxy. In addition, contribution of low contents of nanotubes provided increased impact strength than that of pure epoxy. Finally, microscopical analysis confirmed better dispersion and adhesion in FC_{0.75}, which is the cause behind the maximum enhancement in flexural properties and found agglomerated in FC₁ that is responsible for lowering the overall mechanical performance of the nanocomposites. Therefore, by analysing and correlating the obtained results, it can be concluded by saying that addition of very low wt% of MWNTs in epoxy yields an excellent mechanical and thermo-mechanical behaviour that can be used as structural parts in various applications.

Acknowledgements

We cordially thank the Naval Research Board, New Delhi, for providing the financial support for this research work.

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