Strengthening in and fracture behaviour of CNT and carbon-fibre-reinforced epoxy–matrix hybrid composite

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Abstract. Advanced materials such as continuous fibre-reinforced polymer matrix composites offer significant enhancements in strength and fracture resistance properties as compared with their bulk, monolithic counterparts. In the present work, mode-I (tensile) fracture behaviour of the neat epoxy (without nano- or hybrid reinforcements), nanocomposite (with amino-functionalized multi-walled carbon nanotube (MWCNT) reinforcement to neat epoxy) and hybrid composite (with amino MWCNT and carbon fibre reinforcements to neat epoxy) along with their flexural strength and interlaminar shear strength has been reported and discussed. Limited topological studies have also been conducted to understand the nature of material fracture and its dependence on the notch orientation. The results thus obtained are analysed and discussed in detail to elucidate: (i) alignment of fibre and its influence on the anisotropy in strength and fracture resistance, (ii) dependence of notch root radii on the apparent fracture toughness and concurrence to strain-controlled fracture and (iii) finally, the nature of J – R curves. The results thus obtained have revealed that the resistance to fracture is significantly increased with the addition of amino-functionalized MWCNTs and carbon fibres. In the hybrid composite, fracture resistance is greater in the longitudinal orientation of fibres than in the transverse orientation and it exhibits a significantly higher strength–fracture toughness combination.

Keywords. Hybrid composite; fracture toughness; flexural strength; interlaminar shear strength (ILSS); J -integral; resistance curve tests.

1. Introduction

The discovery of carbon nanotubes (CNTs) with their remarkable physical and mechanical properties has led to novel approaches of using them as ideal reinforcements in advanced nanocomposites [1, 2]. A homogenous and stable dispersion in polymer matrix is found to be a major difficulty, which most often limits performance of the nanocomposite. Another important issue is the lack of interfacial adhesion between the CNTs and the polymer matrix, which also influences the mechanical performance of the CNT-reinforced polymer nanocomposites [3]. The most common procedure to overcome this problem is to try to get an effective CNT surface grafting, addressing both issues of dispersion and interface stress transfer [4–6]. One of them is based on amino-functionalized CNTs. It is also confirmed that the amino-functionalized CNTs exhibit

higher surface energy and much better wettability with epoxy resin than the pristine CNTs, inhibiting the nanotube re-agglomeration during the curing of the resin [7]. In fact, several works confirm the better thermal and mechanical performance of epoxy matrix composites reinforced with amino-functionalized CNTs when compared with the untreated ones [7–9]. Most of the mechanisms are based on strong interfacial adhesion between CNTs and epoxy matrix to bridge or deflect the propagating cracks.

Contradictory results have been reported on how various techniques of dispersing CNTs in epoxy resin and different types of CNTs affect mode-I fracture toughness (K_{Ic}) of nanocomposites. For instance, some of the researchers used the calendaring technique to disperse CNTs in epoxy resin and used single edge notch bend (SENB) specimen to measure K_{Ic} [10]. According to them the maximum K_{Ic} was obtained for 0.2 wt% of CNTs when the gap between the rolls of calendaring machine was 10 μ m. However, 17%, 24%, 30% and 4% increase in K_{Ic} is reported by adding,

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respectively, 0.1, 0.2, 0.3 and 0.4 wt% of MWCNTs to the epoxy resin using sonication technique [11]. However the effects of functionalization of CNTs on mechanical properties, including K_{Ic} , were investigated in some studies. For example, 1 wt% of pristine and functionalized single-wall CNTs were added to epoxy resin using sonication technique [12]. Fracture toughness enhanced 3% and 18% by addition of pristine and functionalized single-wall CNTs, respectively. Others used 3-glycidoxypolytrimethoxysilane as the functionalization agent for MWCNTs [13]. They used sonication to disperse MWCNTs and the compact tension (CT) specimen to measure K_{Ic} . They added 0.05, 0.1, 0.25 and 0.5 wt% of both pristine and functionalized MWCNTs to epoxy. Fracture toughness decreased 2.5%, 15%, 23% and 24% by addition of untreated MWCNTs and increased 2.5%, 6%, 9% and 10% by addition of functionalized MWCNTs, correspondingly. The interlaminar fracture toughness increased up to 300% by the addition of 5 wt% of cup-stacked CNT to epoxy resin [14].

Among various types of composites, continuous carbon-fibre-reinforced polymer matrix composites (CF-PMCs) offer most significant enhancements in a variety of properties (especially the strength and fracture resistance properties in the direction that is parallel to the fibre/fibre bundle orientation), as compared with their bulk, monolithic counterparts. Particulate reinforcements as well as nano-reinforcements are expected to enhance these strength and fracture resistance properties further. Polymer matrix composites (PMCs) are extensively used in structural applications. They combine high strength and stiffness with low density, which makes them attractive as structural materials not only in the weight-sensitive aerospace industry but also in the automobile, railway, armour, marine, structural engineering and sporting goods industries. The CF-PMCs having high strength and stiffness are generally called as structural grade composites. All structural grade CF-PMCs are invariably made with an epoxy matrix system. This is because epoxy matrix possesses high tensile strength and modulus, low shrinkage on curing, good chemical and corrosion resistance, high adhesion and dimensional stability. The structural performance of a fibre-reinforced composite depends on the fracture resistance to various modes of crack propagation.

The interfacial adhesion (otherwise known as fibre-matrix interface characteristics) plays an important role in dictating the mechanical behaviour of carbon fibre-reinforced composites [15]. However, the smooth and inert characteristics of the carbon fibre surface usually result in a lack of interfacial covalent bonds and low interfacial strength, which in turn affects the ultimate mechanical properties of composites. Therefore a number of studies have been conducted to explore the effects of enhancing interfacial bonding strength by modifying the carbon fibres and applying a toughened matrix [11, 16, 17]. Among all these, CNTs have emerged as an ideal reinforcement for PMCs due to their very high strength, modulus and high aspect ratio [18, 19]. It is well recognized and is a fact that

CNT reinforcements lead to particulate strengthening and toughening [20]. On the other hand, the carbon fibre reinforcements account for fibre strengthening and the toughening occurs by crack bridging mechanism [21–24].

In this study to enhance the dispersion of CNTs in polymer matrix, CNTs are modified with chemical functionalization and processed by ultrasonication process. Amino-functionalized MWCNTs were used in this study. In the past, most of the studies are limited to the evaluation and discussion of the reinforcement effects on the K_{Ic} [3, 25, 26]. In this present research three kinds of materials were studied, namely, neat epoxy, nanocomposite and hybrid composite. The present research is aimed to understand the role of CNTs as additional reinforcement to neat epoxy and the role of carbon fibre as reinforcement to nanocomposite. Thus all the three materials viz., (i) neat epoxy, (ii) nanocomposite and (iii) hybrid composite were tested for the evaluation of strength (flexural strength and ILSS) and fracture toughness (K_{Ic} , J_{Ic} , J_c) properties, in order to bring out the effects in terms of CNT and carbon fibre reinforcements. The tests are also conducted to quantify the effect of directionality (longitudinal and transverse) on strength and fracture toughness properties.

2. Experimental details

The epoxy matrix used in this study consists of a DGEBA-based epoxy resin with diethyl toluene diamine (DETDA) hardener, obtained from M/s Fine Finish organics Pvt. Ltd., Mumbai. The low viscosity of the epoxy matrix makes the dispersion of additives easier. Chemical vapour deposition (CVD)-synthesized amino-functionalized MWCNTs were produced and supplied by M/s Chemapal Industries, Mumbai. They had diameter ranging 20–30 nm and lengths of about 2–4 μm . The amount of amino MWCNTs dispersed in the epoxy resin was kept constant to 0.5 wt%. Initially, an amino MWCNTs-resin mixture is made by mixing 0.5 wt% of amino MWCNTs to epoxy resin. Dispersion of the amino MWCNTs was ensured by sonication with a probe type sonicator (Mesonix-3000, USA) for 45 min followed by ball milling (Insmart Systems, India) for 180 min at 250 rpm. Hardener in the ratio of 1:4 of the resin weight was added to the resin mixture followed by ball milling at the same rpm. To realize nanocomposites, the resin mixture was poured into a die and cured for 2 h at 120°C followed by 3-h curing at 180°C, which is the peak curing temperature of the composition under study. The synthesis process is concluded by the densification and curing process given in three heat treatment cycles in a muffle furnace as shown in figures 1 and 2.

The same matrix resin mixture was used to fabricate the hybrid composite. Neat epoxy specimens were fabricated by simply mixing the curing agent with the resin under stirring and casting the specimens in an oven. The same curing cycle (figure 1) that was employed for curing neat

Figure 1. Heat treatment cycle for the curing of the composite.

epoxy and nanocomposite was followed for curing the hybrid composite [27]. The final material obtained had a thickness of 3.4 mm, and a density of 1.56 g/cc, with a volume fibre fraction of 79%. For the sake of comparison, the density and hardness properties of the composites are included in table 1. The data in table 1 show 30% increase in density for hybrid composite as compared with neat epoxy and nanocomposite. Hardness increased 40% for nanocomposite and 225% for hybrid composite as compared with neat epoxy.

All the three materials were tested to determine the fracture toughness (K_{Ic}) by collecting a minimum of five samples from each of the fabricated composite. A notch

was made at the centre of the specimen and tested as per ASTM D 5045-99 on a universal testing machine (United 50 kN) at a cross-head speed of 0.5 mm/min. Notches of varied length (a) were introduced using diamond wafer blades mounted on a standard Isomet cutting machine equipped with a specially designed jig to introduce straight notches. Nonlinear behaviour of the three materials was also evaluated using the same load–displacement data. In order to substantiate and strengthen the results obtained, which should reflect the material behaviour, for all materials the critical notch root radius was also evaluated, i.e., below the critical notch root radius the notch root radius has no effect on the fracture toughness properties. Flexural and interlaminar shear strength (ILSS) specimens were collected from respective composite sheets and tested following ASTM D 790 and ASTM D 2344, respectively, on the universal testing machine (United 50 kN). Dispersion of amino MWCNTs and fracture mechanisms were studied using a field emission gun-scanning electron microscope (FEG-SEM, model JSM-7600F).

3. Flexural strength properties

Composites used for structural purpose are susceptible to failure in bending and therefore the development of advanced composites with improved flexural properties is essential. Flexural properties are useful for quality control and specification of composites materials. These properties may vary with width of the specimen, temperature, atmospheric conditions and difference in strain rates applied during the evaluation of flexural properties. Flexural tests

Figure 2. Synthesis of the C_f-CNT-reinforced epoxy composite.

Table 1. Density and hardness values.

S.No	Material	Properties		% increase	
		Density (g/cc)	Hardness VHNN	Density	Hardness
1	Neat epoxy	1.2	20	–	–
2	Nanocomposite	1.2	28	~0	40
3	Hybrid composite	1.56	65	30	225

were conducted for all three materials, namely neat epoxy, nanocomposite and hybrid composite, to find out the effect of individual reinforcements.

Short-beam shear test is carried out to study the ILSS properties of the hybrid composite in detail in order to determine the influence of directionality of fibres. ILSS is usually one of the most common limiting design characteristic of continuous-fibre-reinforced PMCs.

3.1 Neat epoxy and nanocomposite

Flexural test in three-point bend loading was conducted on specimens of width 10 mm, thickness of 3.50 mm and length of 75 mm (with an included span length equivalent to 16 times the thickness). Figure 3 shows the typical flexural load–displacement curves for neat epoxy and nanocomposites. Five specimens were tested in each case and here data of only one specimen are being shown for the sake of clarity [28].

As illustrated in figure 3, the two specimens exhibited linear flexural behaviour before load reached its maximum level. Figure 3 shows in the neat epoxy specimen a brittle failure that is indicated by the sudden drop in the load from the peak loads, while stable crack growth was observed before failure for a nanocomposite specimen. Assuming that the specimen dimensions are similar the nonlinear extension (an index of permanent damage/deformation that the material sustains) before fracture is more than 6 times higher in case of nanocomposite as compared with matrix neat epoxy. Such enhancements in damage tolerance (in the absence of any microcrack) show that the nanocomposite exhibits significant capability for toughening; this is reflected in the toughness values of the two materials. One

Figure 3. Load–displacement data.

such toughness property is the total area under the load–displacement curve. The computation of total area under the load–displacement curve (which can be referred to as “deformation toughness” of the material once the area under the load–displacement curve is normalized with the width of the specimen) is more than 100% higher in case of the nanocomposite (117.4 MJ/m^3) as compared with the neat epoxy (56.3 MJ/m^3).

The flexural property enhancements that accrue due to amino MWCNT reinforcements to the neat epoxy are shown in figure 4 in terms of (a) nominal flexural modulus, (b) flexural strength, (c) extent of nonlinear deformation/damage and (d) total flexural toughness. The data in figure 4 clearly show that the most dominant enhancement in the property level is in case of nonlinear flexural extension. However all the enhancements from the three other properties are reflected in the total flexural toughness. Hence the order of property enhancement is around 100%, not 600% in case of nonlinear extension or 15% and 25% property enhancement in cases of flexural modulus and flexural strength, respectively. Such enhancement in the total energy absorbing capability as reflected by total flexural toughness shows that the composite has more resilience and more importantly it is amenable to toughness mechanisms such as nanoparticle fracture, microcracking and/or decohesion/cracking at the particle–matrix interface.

SEM images from fracture surfaces were used to observe the morphology of the neat epoxy and nanocomposites in detail. As shown in figure 5, the morphology of nanocomposite sample considerably changed in comparison with the respective neat epoxy (figure 5a and b). The smooth fracture surfaces of the neat epoxy became rough after attendance of nanotubes. The surface roughness increases with amino MWCNT contents, suggesting that the crack propagation in the nanocomposites was opposed by rigid and stiff amino MWCNTs.

3.2 Hybrid composite

Flexural tests in three-point bend loading were conducted on specimens of width 10 mm, thickness of 3.4 mm and length of 75 mm (with an included span length equivalent to 16 times the thickness). A total of 10 specimens were tested and here only one specimen is being shown for the sake of clarity in each case, i.e., longitudinal and transverse orientations [27].

3.2a Longitudinal orientation: It can be clearly seen that the material possesses excellent flexural strength in the longitudinal direction with an average value of 1084 MPa. This can be attributed to the presence of the light weight carbon fibres and also the particulate reinforcement by the CNT. The typical loads vs. displacement curve as in figure 6 for one of the specimens explains the exceptional behaviour of

Figure 4. Flexural properties of the nanocomposite/neat epoxy.

the material. The plot exhibits a gradual increase in the load along with increase in displacement up to a peak point and then shows a steep decrease with falling slope. The gradual increase in the elastic zone is due to the presence of fibres perpendicular to the direction of crack propagation and also due to the CNTs, which take up the load completely (Region I). This is followed by Region II consisting of a sharp and steep fall in the stress value at approximately constant displacement. This stage is largely dominated by shear mode of failure. This is followed by a small increase in the load after this steep decrease, which can be assumed to be the building up of resistance by the surrounding fibres or contribution of CNT. The mechanism of the stress distribution in the hybrid composite can be explained in the following way: firstly, a group of fibres (at the surface), experience the maximum stress initially by taking up the load completely. This is the elastic stresses zone (Region I).

On further increase in the load, the surface fibre bundle breakage starts, leading to crack initiation and instant propagation and with participation of other fibres beneath the surface. With the failure of these fibres, the other fibres start experiencing the stress and further crack propagation occurs (marked by the rise in the plot in Region II). The crack propagation and breakage of fibres are clearly shown in figure 7a and b, respectively.

3.2b Transverse orientation: Load vs. displacement data were plotted for the transverse loading for one of the specimens tested. Here, it was observed that the flexural strength is significantly lesser (3–4%) when compared with the longitudinal direction. The average flexural strength obtained in this orientation is 38 MPa approximately. This phenomenon is because of the fibres that are aligned parallel to the propagation of the crack and thus their participation is largely neglected. The crack path is largely straight enough to justify this statement (figure 8). The matrix takes up the entire load and the maximum load values exhibited here is the load taken by the matrix (epoxy and CNT) alone. Perhaps, the values would degrade even more in the absence of CNTs in the resin mixture, which hinder the crack propagation.

The graph plotted for the transverse alignment of fibres under three-point bend loading exhibits a similar behaviour when compared to the longitudinal orientation except for the fact that the load bearing capacity is very low here. It is interesting to note the scale of both the axes. In this plot in figure 9 “Region I” exhibits the elastic nature of the material and the load increases with increase in displacement. Mild serrations can be observed in this region, which could have resulted due to the presence of CNT. The poor strength properties of matrix are being compensated by the CNT in the matrix mixture. “Region II” shows a more steep and large fall in load and then attains near saturation in load, with an increase in displacement. It can be noted that there is an even more severe serrations region formed in the load displacement data after the steep load drop,

Figure 5. Fracture surface of the flexure samples: (a) neat epoxy and (b) nanocomposite.

Figure 6. Load vs. displacement data for flexural strength (three-point bend loading) test in longitudinal orientation).

which can be attributed to the presence of CNT in the matrix. This could be assumed to be a resistance build-up with a large displacement until the total fracture of the specimen. In this orientation, with a small increase in load/stress, there is a large increase in displacement owing to the poor strength of the matrix mixture. It is observed that the maximum average load level of this composite in transverse orientation is 58 N approximately, which corresponds to a flexural strength of 38 MPa.

3.2c Directionality in strength properties: From the above tests conducted and results obtained, it is clear that a

hybrid composite such as C_f (unidirectional) and CNT-reinforced epoxy matrix composite possesses significantly higher flexural strength in the longitudinal orientation, when compared with the transverse orientation. This can be clearly seen in the load vs. displacement curve (figure 10) plotted for both orientations. Though a similarity can be observed in the curve behaviour, there is a huge disparity in the stress-bearing capacities in both the orientations. The hybrid composite showed an isotropic behaviour in Young's modulus, but there is a definite directionality influence on strength properties. This arises from the presence of unidirectionally wound fibres, whose Young's modulus is approximately the same (17 GPa) in the longitudinal orientation and (16 GPa) in the transverse orientation. Fibres have a dominant effect in this orientation resisting the crack propagation. The matrix fails in resisting the crack propagation when load is applied in the transverse orientation. The deformation toughness in longitudinal orientation (130 MJ/m^3) is significantly greater as compared with transverse orientation (4.26 MJ/m^3).

3.3 Interlaminar shear strength (ILSS)

All the ILSS tests were conducted as per ASTM D 2344 using the universal testing machine (United, Model STM 50 KN, USA) with the help of a self-articulating three-point bend fixture. The tests were conducted at ambient temperature and in laboratory air atmosphere. ILSS tests were carried out under ramp control speed of 2 mm/min. For a beam of rectangular cross section loaded in three-point bending, the maximum ILSS occurs at the mid-thickness of the beam between the centre and end supports and it is given as

Figure 7. (a) Crack path observation after flexural testing in longitudinal orientation and (b) bending and breakage of surface fibres observed after the test.

Figure 8. Crack path observation after flexural testing in transverse orientation (a) at low (100 $\times$) magnification and (b) at high (500 $\times$) magnification.

Figure 9. Load vs. displacement data for flexural strength (three-point bend loading) test in transverse orientation.

$$\text{ILSS} = 0.75 \left(\frac{P_b}{wt} \right) \quad (1)$$

where P_b is the breaking load; w and t are width and thickness of the specimens, respectively. A minimum of five specimens were tested in each orientation and for the sake of clarity, only one typical specimen load–displacement data set is shown in each of the cases, i.e., longitudinal and transverse orientations.

The ILSS of the hybrid composite is significantly higher (10 times or nearly 1000%) in longitudinal orientation as

compared with the same in transverse orientation. Based on the results obtained for the present study, the hybrid composite material should be designed so that the major stress axis is in the longitudinal orientation and loading in the transverse orientation should be avoided as much as possible. If the design is based on lowest ILSS values the true potential of hybrid composite cannot be achieved. This is because the transverse ILSS is an order of magnitude lower. With these properties obtained from the hybrid composite, it is clearly suitable for structural applications in the aeronautical and aerospace industry, where the exceptionally high values of longitudinal ILSS can be exploited. Hence the present hybrid composite possesses high anisotropic ILSS properties [29].

4. Fracture toughness properties

4.1 Effect of notch root radius on mode-I apparent fracture toughness

Determination of notch root radius effect is one of the primary requisite before finding out the fracture toughness. The accurate measurement of notch root radius and introducing notch of appropriate root radius are very much essential to use specimens with machined notch instead of fatigue precracking to evaluate the fracture behaviour. The fracture toughness of all the three materials was evaluated and analysed by investigating the influence of varying notch root radii. The actual fracture toughness of the material leads to overestimation if the notch root radius is too large. Determination of notch radii is unavoidable and in order to obtain consistent results the notch radius should be below a critical value.

All composite materials were machined and cut as per ASTM D 5045-99. Single edge notch bend (SENB)

Figure 10. Load vs. displacement data for flexural strength (three-point bend loading) test for longitudinal and transverse orientations.

specimens were used to determine the critical notch root radius and plane strain fracture toughness. Notches of varied crack length were introduced using 150 μm or/and 300 μm thick diamond wafer blades mounted on a standard Isomet cutting machine equipped with a specially designed jig to introduce straight notches. In the study of critical notch root radius (ρ_o) notches with higher notch root radius were introduced by progressive cutting. All the specimen dimensions were accurately measured using a Deta 35 TM x-y profile projector.

Notches of fixed length maintaining a crack length to width ratio of 0.45–0.55 and varying notch root radius (ρ) were introduced. The notches thus introduced were found to have finite root radius (ρ) typically of the orders varying from 110 to 750 μm . The variation of ρ for a particular isomet blade cutting was found to be less than 10 μm . The crack lengths were maintained as per ASTM D 5045-99 for the determination of K_{Ic} (when $\rho < \rho_o$) or K_{IQ} (when $\rho > \rho_o$) values.

4.1a Neat epoxy and nanocomposite: The fracture toughness of the materials is evaluated and analysed by investigating the influence of varying notch root radii in both the materials. The apparent fracture toughness of the material normally increases with increase in notch root radius, if the notch root radius is higher than critical value, ρ_o , which is known as the critical notch root radius. It is then necessary to control the notch root radius and to machine it carefully in order to have a notch root radius below ρ_o . It can be clearly seen that specimens with lower notch root radius exhibit lower fracture toughness up to $\rho=110 \mu\text{m}$ and the value of K_{Ic} increases with increase in the notch root radius.

The results of both neat epoxy and nanocomposite show a similar trend. The higher energy absorbed when $\rho > 110 \mu\text{m}$ is due to crack extension from relatively one blunt initial crack.

The notch sensitivity was extensively studied and reported [30–34]. But similar studies in case of neat epoxy and nanocomposite are not reported to date. In such cases crack extension was found to take place under critical-strain-controlled behaviour; the variation of K_{IQ} with the square root of notch root radius should be linear. This is verified with the data obtained in the present study for both neat epoxy and nanocomposite materials illustrated in figure 11a and b, respectively. The plane strain fracture toughness in nanocomposite was higher than that of the neat epoxy. This is due to the presence of amino MWCNTs, which is evident from the SEM micrographs shown in the figure 12a and b. The increased plane strain fracture toughness could be attributed to the improved dispersion of amino MWCNTs in the epoxy matrix and better interfacial reactions between the functional groups on the carbon nanotube surfaces and the polymer matrix (figure 21a). The fracture surfaces of both the neat epoxy and nanocomposite were observed by the field emission scanning electron microscope in order to study the fracture mechanisms. As shown in figure 12a the fracture surface of neat epoxy is relatively smoother, which shows a low energy fracture as compared with the nanocomposite. Furthermore, the surface roughness increases with amino MWCNT addition, suggesting that the crack propagation in the nanocomposite was opposed by rigid and stiff amino MWCNTs. It can also be seen that a linear relationship between K_Q and ρ is obtained for both the materials, reaching a critical value of notch root radius (ρ_o), below which the value of apparent fracture toughness is invariant (figure 11a and b) and such invariant K_Q is the material fracture toughness (provided the other condition of validity is $B \geq 2.5(K_Q/\sigma_f)^2$, where K_Q is the apparent fracture toughness and σ_f is flexural strength, with an assumption that fracture stress scales with flexural strength). This critical value of notch root radius (ρ_o) thus determined is approximately equal to 340 μm in case of neat epoxy and a marginally lower value (300 μm) in case of nanocomposite. This implies that in both the materials, if the notch root radius is below the critical value then the fracture toughness is solely a material property conditional to the fact that the criteria for linear elastic fracture mechanics (LEFM) and plane strain are satisfied [35].

4.1b Hybrid composite: Similar to the neat and nanocomposite the critical notch root radius of hybrid composite was also evaluated in two orthogonal directions, i.e., longitudinal and transverse orientations. This critical value of the notch root radius (ρ_o) is approximately equal to 270 μm in case of longitudinal orientation and 390 μm in case of transverse orientation [36]. This is shown figure 13a and b.

Figure 11. Variation of apparent fracture toughness with square root of notch root radius for (a) neat epoxy and (b) nanocomposite.

Figure 12. FESEM micrographs of mode-I fracture surfaces for (a) neat epoxy and (b) nanocomposite. Both the materials show quasi-cleavage fracture, with higher energy fracture in the case of nanocomposite.

Using the fracture mechanics approach [37], it is established that the fracture process in all the materials is controlled by strain. The values of critical notch root radius clearly reveal that as the strength of the composite increases the value of critical notch root radius decreases. The fracture toughness value in longitudinal orientation was higher than that of the transverse orientation. This is due to the presence of fibres perpendicular to the loading direction in longitudinal and parallel in case of transverse orientation, which is evident from the SEM photographs shown in figure 14a–d.

4.2 Linear elastic fracture toughness

All the fracture toughness tests were conducted on a universal testing machine using a self-articulating three-point bend fixture. The load–displacement plots thus obtained were analysed to obtain various measures of fracture resistance, and the results are presented and discussed in the following sections. An accurate determination of the plane-strain fracture toughness requires a specimen whose thickness exceeds some critical thickness (B). Testing has shown that plane-strain conditions generally prevail when

Figure 13. Variation of apparent fracture toughness with square root of notch root radius in (a) longitudinal orientation and (b) transverse orientation.

$$B, b \geq 2.5(K_Q/\sigma_y)^2, \quad (1)$$

where $b = W - a$ (W is the width and ' a ' the crack length), B is the minimum thickness that results in insignificant plastic strain at the crack tip, K_Q is the conditional (trial K_{Ic}) value of the material and σ_y is the yield stress of the material.

4.2a Load–displacement data: The load–displacement data for the neat epoxy, nanocomposite, hybrid composite (longitudinal orientation of fibres) and hybrid composite (transverse orientation of fibres) with varying a/W ratio are shown in the figures 15a, 15b, 16a and 16b, respectively. Figure 15a and b shows typical load–displacement curves recorded during fracture toughness evaluation for both neat epoxy and nanocomposite specimens with varying a/W ratio, respectively. The data in figure 15b clearly indicate that maximum load is higher for nanocomposite specimen as compared with neat epoxy specimens when all other conditions such as specimen dimensions and loading rate are maintained to be the same. These observations clearly bring out the fracture resistances between neat epoxy and nanocomposite specimens, thus bringing out the effect of amino MWCNTs reinforcement on the fracture behaviour.

The hybrid composite data in figure 16a and b clearly point to the fact that the maximum load and conditional load are 20 times higher for the longitudinal orientation specimens as compared with the transverse specimens. Apart from such large variation in the magnitudes of loads for fracture, the nature of load displacement data is also too indispensably different for the two orientations. Though the load was initially found to increase linearly with the displacement for both longitudinal and transverse orientations (figure 16a and b) corresponding to a stage where the specimens are elastically loaded, crack extension takes place over a narrower displacement range (0–1 mm) in

transverse specimens as compared with those longitudinal orientation specimens (0–3 mm). Secondly, the crack arrest loads (the load corresponds to plateau in load–displacement curves) are significantly higher and also the extents of such crack arrest displacements are higher for longitudinal oriented specimens. Lastly, the load drop following the attainment of P_{max} is significantly steeper in case of the transversely oriented specimen.

4.2b Plane strain fracture toughness: Fracture toughness of neat epoxy, nanocomposite and hybrid composite specimens was determined according to ASTM standard D 5045 under a static three-point test of the SENB specimens. In the data in all the cases the values of P_{max}/P_Q are found to be less than 1.1 and also the thickness validity criterion is found to be satisfied. Hence the results obtained are valid and the values can be termed as K_{Ic} . The values of K_{Ic} thus determined for neat epoxy, nanocomposite and hybrid composite specimens (longitudinal and transverse) are given in table 2. As per ASTM D 5045, only the specimens with a/w values in the range of 0.45–0.55 are used to arrive at K_{Ic} .

The nanocomposite exhibits a higher fracture toughness value with an absolute value of 2.02 MPa√m, which is more than 18% higher as compared with the same for the neat epoxy specimen (1.72 MPa√m). The ratio of fracture toughness to flexural strength epoxy is found to remain the same for both neat and nanocomposite specimens. This also clearly reveals that enhancement in fracture toughness is almost due to the LEFM-controlled fracture. This is because the fracture toughness scales with strength in both neat epoxy as well as nanocomposite [38].

The epoxy hybrid composite exhibits a significantly higher fracture toughness value in the longitudinal

Figure 14. SEM photographs of fracture-toughness-tested specimens in longitudinal [(a) low magnification and (b) high magnification] and transverse orientation [(c) low magnification and (d) high magnification].

Figure 15. Load vs. displacement graph for (a) neat epoxy and (b) nanocomposite.

Figure 16. Load vs. displacement graph for the hybrid composite: (a) longitudinal orientation of fibres and (b) transverse orientation of fibres.

orientation with an absolute value of K_{Ic} (22.15 MPa $\sqrt{m}$) that is more than 20 times higher than the value obtained for the transverse direction (0.94 MPa $\sqrt{m}$). Such a large variation in the fracture resistance in the test direction in these hybrid composites is directly attributed to unidirectional weaving of the carbon fibre, which essentially results in gross fracture resistance anisotropy.

4.3 Nonlinear fracture behaviour

4.3a Elastic–plastic fracture toughness (J_{Ic}): The procedure proposed by Landes and Begley [39] and the ASTM standard E-813 furnish details of the standard practice for the evaluation of elastic–plastic fracture toughness, J_{Ic} . Alternatively, another widely accepted methodology, again proposed by Begley and Landes [40], can also be employed for J_{Ic} determination. Both these procedures are based on Rice-proposed J -integral [41]. The later procedure principally involves the determination of fracture energy (J_Q) from the energy absorbed in the fracture process (E , area under the load–displacement, usually the displacement considered here corresponds to the load line) by specimens with different crack lengths, up to either a constant displacement or a constant load. In the present case, the load–

displacement data obtained from the three-point bend test are used to calculate the energy for the crack initiation (E_{ini}), which is assumed to occur at the displacements corresponding to the peak load. E values thus determined are used to calculate the fracture energy J_Q as [40, 41] follows:

$$J_Q = \frac{\Delta E}{\Delta a} \frac{1}{B} \quad (2)$$

where (ΔE) is the difference in the fracture energies when the ΔE corresponds to peak loads in the load displacement curves of two specimens with different initial crack lengths (their difference is Δa). The J_Q value obtained will represent J_{Ic} , the elastic–plastic fracture toughness corresponding to crack initiation. The values of J_Q , determined from the load–displacement curves for neat epoxy, nanocomposite and hybrid composite are shown in figures 17a, 17b and 18, respectively, as a function of crack length. It is to be predicted that the hybrid composite shows constant values of J_Q in the longitudinal and transverse orientations. However, all these values were found to satisfy the validity conditions and hence J_Q value can be termed as the elastic–plastic fracture toughness J_{Ic} of the respective composites.

As stated above, the J_{Ic} corresponds to the peak load (assumed to correspond to the crack initiation) and hence would comprise only those fracture events that occur in the hybrid composite material before or up to the event that the material undergoes first fibre bundle fracture. Hence, the J_{Ic} values evaluated and reported in the present section are valid materials' fracture resistance properties; however, they are conservative in nature.

The elastic–plastic fracture toughness (J_{Ic}) is calculated as 184 J/m² for neat epoxy and 505 J/m² for nanocomposite. The higher value of J_{Ic} is due to better bonding

Table 2. Fracture toughness for neat epoxy, nanocomposite and hybrid composite.

Composite	Fracture toughness (K_{Ic}) (MPa $\sqrt{m}$)
Neat epoxy	1.72
Nanocomposite	2.02
Hybrid composite (longitudinal orientation)	22.15
Hybrid composite (transverse orientation)	0.94

Figure 17. Variation of fracture energy with the crack length for the (a) neat epoxy and (b) nanocomposite.

between amino MWCNTs and the matrix, crack bridging and increased fracture surface area. The same is calculated as 46.6 kJ/mm^2 (or 46.6 GJ/m^2) for longitudinal orientation of the hybrid composite, which is approximately 100 times higher than the J_{Ic} value in the transverse orientation (0.48 kJ/mm^2 or 0.48 GJ/m^2). It is to be noted here that in case of hybrid composite the disparity in fracture resistance in two test orientation increases drastically when the nonlinearity in load–displacement curves (indication of fracture processes involving relative motion between carbon fibre and epoxy matrix) is considered. The J_{Ic} is much higher as compared with that of the nanocomposite; this is due to high strength carbon fibres and strong interface between carbon fibres and the matrix.

4.3b Total fracture energy release rate (J_c): The total fracture energy release rate, J_c , comprises different stages of fracture events in the “fracture zone”. In case of homogeneous materials, fracture processes ahead of or at the crack tip predominantly contribute to the overall fracture resistance. Hence, the energy release rate at the crack tip (termed as ' J_{tip} ') predominates the values of J_c . Therefore, in all such cases the overall energy release rate J_c essentially includes fracture energy corresponding to wake zone effects and the contributions from the crack tip processes or crack tip fracture zone (J_{tip}) are only marginal. Further, the total fracture energy release rate (J_c , or sometimes referred to as G_c) is the most commonly used parameter when a fracture process involves two or more different components of fracture. This is the case in the

present hybrid composite material. As we know, the increasing contributions from mode II (occurs at higher crack lengths) in-plane shear fracture during mode-I fracture toughness evaluation using specimens of varied crack length require the adoption of such an energy concept. Hashida *et al* [42] have clearly shown that the total fracture energy release rate (they referred to this parameter as the global or over-all fracture energy release rate, J_c , the critical) is given as

$$J_c = J_b + J_{tip} \quad (3)$$

where J_b is the energy consumed by the development of fracture process zone and J_{tip} can be obtained from the stress intensity factor at the crack tip, K_{tip} , using the equation

$$J_{tip} = K_{tip}^2 (1 - \nu^2) / E. \quad (4)$$

The overall fracture energy release rate (J_c) could be obtained from the relation [43]

$$J_c = \left\{ - \left(\frac{\Delta E_{fr}}{\Delta a} \right) \right\} / B \quad (5)$$

$\Delta E_{fr} / \Delta a$ is the slope of the linear regression curve fit between the total energy for fracture (E_{fr}) and the crack length (a). The Δa here is actually the difference in the crack lengths (such as $a_2 - a_1$ or $a_3 - a_1$, where a_1 , a_2 and a_3 correspond to the initial crack lengths of different specimens) but not crack extension. Once the two terms J_c and J_{tip} are

Figure 18. Fracture energy vs. crack length for (a) longitudinal orientation and (b) transverse orientation of fibres.

calculated individually, the third term J_c can be computed from Eq. (3). Specimens of varied crack length (five in longitudinal and six in transverse orientation) are subjected to three-point bend test. The procedure involved for the evaluation of J_c can be obtained from references [44, 45].

The variation of fracture energy (E_{fr}) determined is shown as a function of crack length in figures 17a, 17b and 18, respectively, for neat epoxy, nanocomposite and hybrid composite. The increase in slope of the linear curve fit with increasing displacement indicates the increase in the value of total fracture energy release rate with crack extension. No displacements are considered for the J_c evaluation in the present study, which are in excess of this δ_{max} value, which corresponds to 0.15 mm for neat epoxy, 0.25 mm for nanocomposite, 2.5 mm for hybrid composite (longitudinal orientation of fibres) and 0.8 mm for hybrid composite (transverse orientation of fibres). Further, in the displacement region where shear fracture is dominant, any further crack extension (i.e., increase in the displacement, δ) does not significantly increase the total fracture energy release rate (J_c). It is also observed that in case of hybrid composite, soon after the event of first fibre bundle fracture, the crack front becomes unstable; however, the specimen regains stability (shown as the increase in the load with crack extension) after crack extension of a few tens of microns (figure 16a and b). The displacement value at which such an unstable/stable crack extension occurs has been chosen as the critical displacement value δ_c . This δ_c is taken as the one corresponding to the average δ at peak load of the three or four specimens that are tested with different initial crack lengths. The δ_c values for neat epoxy and nanocomposite are taken arbitrarily, which are 0.1 mm and

Figure 19. Variation of total fracture energy release rate with normalized displacement in case of neat epoxy and amino-MWCNT-reinforced epoxy nanocomposite.

0.2 mm, respectively. A δ_c value of 0.80 mm for longitudinal orientation and 0.2 mm for transverse orientation is found to be appropriate for hybrid composite. The derived values of total fracture energy release rate at varied displacements (given as displacements normalized by the δ_c) are shown in figure 19 for the present neat epoxy and nanocomposite and in figure 20 for the hybrid composite material in both orientations. The nanocomposite exhibits

Figure 20. Total fracture energy release rate vs. normalized displacement (J - R curve) for (a) longitudinal orientation and (b) transverse orientation of fibres.

Figure 21. FEG SEM images of nanocomposite: (a) arrows indicate some degree of pullout and well-dispersed AMWCNTs in the matrix and (b) arrows showing step-like morphology.

120% higher J_c when compared with the neat epoxy. This can be attributed to the various energy absorbing mechanisms involved in the presence of amino MWCNTs during the fracture test. The amino MWCNTs need extra energy in order to be pulled out and for crack deflection, and that extra energy contributes to higher J_c value [46].

The data in figure 20a and 20b show the R -curve behaviour (variation of fracture resistance in terms of total fracture energy release rate, J_c with normalized displacement (δ/δ_c)) for the epoxy hybrid composite, respectively, for longitudinal and transverse orientation. The nature of these fracture resistance curves is grossly similar. The

hybrid composite in both test orientations exhibits rising R -curve behaviour with a slight sign of saturation in longitudinal orientation and it is highly risen with no sign of saturation in transverse orientation. But it should be noted here that the absolute values of J_c are more than two orders of magnitude higher in longitudinal orientation as compared with the values in transverse orientation. Further, the two orders fit of the R -curve data is much better in longitudinal orientation as compared with the transverse orientation; the J_c values show significant variation especially in the stages of crack extension. However, the kind of scatter in fracture resistance data observed for transverse

Figure 22. SEM micrograph of neat epoxy.

orientation is indeed what is normally observed for engineering materials. The longitudinal orientation data set is exceptionally well fitted for a two orders polynomial regression.

It is also to be noted here that the total energy fracture E_{fr} values, especially those corresponding to transverse orientation, show large variation when they are determined for varied crack length. This is because the transversely oriented specimens used in the present study are found to have significantly varied width, while the standard test procedure calls for use of specimens with nearly same width and thickness with only intended variation in crack length. Such variation in specimen width also results in varied extents of crack tip extension processes and varied extent of carbon fibre epoxy–matrix interface interactions (varied degree of crack bridging), leading to variation in the E_{fr} values at any normalized displacements. The hybrid composite shows significantly higher J_c as compared with the nanocomposite. This is due to the reinforcement of high-strength carbon fibres into the matrix (epoxy loaded with amino MWCNTs).

5. Fractography

In order to determine the reasons for the above trend the fracture mechanisms in mode-I loading were investigated. The fracture surfaces of all the specimens were studied using FEG-SEM. Figure 21a shows well-dispersed amino MWCNTs on the fracture surface of nanocomposite. Diameter of CNTs in the as-received form was around 30 nm, while in the present image they show a slightly higher diameter due to matrix coating on their surface. This indicates better bonding between CNTs and matrix [47]. This better bonding in turn is due to amino-functionalized groups present on the surface of CNTs, which covalently bond with the epoxy matrix. Amino MWCNTs showed some degree of pull-out during the fracture. During the pull-out, they bridge the surfaces that were undergoing cleavage, thereby increasing the energy for fracture. Fracture surfaces were observed to show step-like morphology as shown in figure 21b. More steps on the fracture surfaces result in improved toughness. This is because each step corresponds to different cleavage zones during fracture. Less number of cleavage zones gives a glassy surface (figure 22), which results in lower toughness as there is no resistance to crack propagation. On the other hand nanocomposite has shown multiple steps during fracture. This is because when the crack propagates, amino MWCNTs resist the propagating crack, thereby forcing the crack front to either split into two different crack fronts or they deflect its path. Both result in generation of more fracture area, which leads to higher toughness for the composite.

Amino MWCNTs are known to strengthen the interface between carbon filament and matrix, which results in enhanced mechanical properties. Figure 23a shows strong bonding between carbon filament and matrix at the interface. CNTs were observed to strengthen the matrix, thereby

Figure 23. FEG-SEM images of the hybrid composite: (a) carbon filament and its interface and (b) magnified view of the encircled zone of (a) showing well-dispersed CNTs in the matrix (indicted by arrows).

increasing the overall strength of the matrix. A magnified image of the encircled zone (figure 23a) is shown in figure 23b, where well-dispersed amino MWCNTs are shown.

6. Conclusions

- (i) A nanocomposite was successfully fabricated using the ultrasonication technique followed by the ball milling process. The combination of amino functionalization of MWCNTs and ultrasonication is a useful approach to improve the dispersion state of the MWCNTs and the interfacial interactions to the matrix epoxy. The hybrid composite was successfully manufactured by a hand layup technique. Materials processed in the most optimized condition have been evaluated for flexural strength and fracture toughness properties in order to bring out the effects of CNT and carbon fibre reinforcements.
- (ii) The neat epoxy and the two composites, namely nanocomposite and hybrid composite, were tested for their density and hardness properties in order to bring out the effects of the reinforcement on these properties. The results obtain from the present study show that the CNT as well as CNT plus carbon fibre reinforcements hardly change the density of neat epoxy, while the hardness properties are enhanced by 40 % and 225 %, respectively.
- (iii) Flexural strength of the epoxy composite incorporating 0.5 wt% amino MWCNTs showed 25% improvement in strength, 15% improvement in flexural modulus and improvement of 600% in nonlinear extension in comparison with neat epoxy. Unlike the above three property enhancements the most appropriate property enhancement for material design is proposed to be the *total flexural toughness*. Based on this parameter the amino MWCNTs reinforcement of 0.5 wt% is found to enhance the strain energy sustaining capability by slightly more than 100%.
- (iv) The flexural strength of the hybrid composite is significantly higher in longitudinal orientation (1084 MPa) as compared with the same in transverse orientation (38 MPa). ILSS is also significantly higher in longitudinal orientation (56 MPa) as compared with the same in transverse orientation (5 MPa). Thus, the composite showed an appreciable influence of fibre orientation. With these properties obtained from the hybrid composite, it is clearly suitable for structural applications in the aeronautical and aerospace industry, where the exceptionally high values of longitudinal flexural strength can be exploited.
- (v) The fracture toughness is independent of the ρ below the ρ_o of 300 μm for neat epoxy and increases linearly with the square root of notch root radius for ρ greater than 300 μm . Similarly, the ρ_o for nanocomposite is 340 μm , hybrid composite (longitudinal orientation) is 270 μm and for hybrid composite (transverse orientation) is 390 μm . An analysis of the variation in apparent fracture toughness with notch root radius has revealed that the fracture behaviour in all the three materials is controlled by the critical strain.
- (vi) The K_{Ic} of the neat epoxy is determined to be 1.71 $\text{MPa}\sqrt{\text{m}}$, whereas it is nearly 2.02 $\text{MPa}\sqrt{\text{m}}$ for the nanocomposite. The increase ($\approx 20\%$) in fracture resistance is due to the presence of amino MWCNTs and toughening mechanisms in the neat epoxy. The hybrid composite exhibits a significantly higher K_{Ic} value in the longitudinal orientation. A representative/characteristic K_{Ic} value of 22.15 $\text{MPa}\sqrt{\text{m}}$ obtained for the longitudinal orientation is more than 20 times higher than the value obtained for the transverse orientation (0.94 $\text{MPa}\sqrt{\text{m}}$). In all the three materials the ratio K_{Ic}/σ_f is found to be the same. This clearly reveals that, the fracture behaviour is controlled by LEFM.
- (vii) Elastic-plastic fracture toughness (J_{Ic}) for the nanocomposite (505 J/m^2) is more than 2 times larger as compared with the neat epoxy (184 J/m^2). In case of hybrid composite, for the longitudinal orientation (46.6 KJ/mm^2) it is more than 2 orders of magnitude higher. However the J_{Ic} of hybrid composite in transverse orientation (0.48 KJ/mm^2) is much lower and found to be comparable with that of the nanocomposite. Though the values of total fracture energy release rate (J_c) are higher than corresponding J_{Ic} values of experimental materials namely the neat epoxy, nanocomposite and hybrid composite, the relative enhancements in either J_{Ic} or J_c values due to amino MWCNT and carbon fibre reinforcements are similar.
- (viii) The variation of J_c with normalized displacement (δ/δ_c), designated as the *R-curve*, was found to be rising in case of nanocomposite as well hybrid composite. However, the absolute values of J_c are greater than two orders of magnitude greater in longitudinal orientation compared with transverse orientation in hybrid composite. This is principally due to unidirectional weaving of the carbon fibres in epoxy matrix and effects of such weaving on the fracture behaviour.
- (ix) Based on the fractured morphologies of materials one can conclude that the enhanced properties, both flexural strength and fracture toughness, are due to homogenous distribution of amino MWCNTs in epoxy, pull-out of amino MWCNTs and ability of strongly bonded amino MWCNTs to deflect the matrix cracks, forcing the advancing crack front to follow torturous paths. This has been amply reflected

in the higher extent of fracture surface roughness of the predominant quasi-cleavage fracture facets.

- (x) Additional and much more significant property improvements in hybrid composites as compared with neat epoxy and nanocomposite are due to optimum interface bonding characteristics, which is well reflected in the large extents of carbon fibre pull-out and extensive and gradual fibre bundle fracture.

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