Interface fracture of sandwich composites: Influence of MWCNT sonicated epoxy resin

Alak Patra, Nilanjan Mitra *

Department of Civil Engineering, Indian Institute of Technology, Kharagpur, India

Abstract

An experimental investigation on sandwich composite materials composed of glass-fiber face sheet and polyvinyl-chloride foam core has been carried out which demonstrates improvement in interface fracture toughness values of samples with addition of a certain percentage by weight of multi-walled carbon nanotubes (MWCNT) in comparison to conventional samples. An easy and cost-effective methodology of MWCNT insertion through sonication of epoxy resin followed by mixing with hardener and thereby using vacuum resin infusion technology for manufacturing of sandwich composites has been prescribed in this study. The study also identifies the optimum weight percentage of MWCNT addition in the resin system for maximum performance gain in interfacial fracture toughness. The results of observations in this study has been supported by high-resolution transmission electron microscope (HRTEM) analysis as well as field emission scanning electron microscope (FESEM) studies.

1. Introduction

The primary advantage of sandwich composite structures is high strength to weight ratio. However, these structures suffer from one major problem: Interfacial debonding between the face sheet and the core, which has limited their applications in different branches of engineering in comparison to monolithic structures. Interfacial debonding may arise during manufacture due to poor resin distribution (which can be controlled by proper quality assurance measures) or during in-service loadings (which are beyond control). Interfacial debonding has thereby been identified as one of the major causes for loss of structural integrity and/or even catastrophic collapse of these structure.

The methodologies that have been proposed to improve the debonding characteristics of sandwich composites can typically be classified as: structural modifications and constituent modifications. Structural modifications typically refers to changes in orientation of the materials in the structure and/or addition of new structural materials to strengthen it and thereby improve the debonding characteristics whereas constituent modifications typically refers to changes in the constituent materials to improve upon the debonding characteristics. Even though structural modifications might offer cost-effective and conceptually easy solution to the problem but there may be issues related to overall weight gain of the component materials (which affects the major advantage of these materials/structures having high strength to weight ratio) when utilizing these techniques for large fabrications. The techniques that have been proposed till now under the heading of structural modifications are

- Z-pinning which involves penetration of metallic or fibrous pins through the thickness of the uncured laminate using an ultrasonic gun [1–6].
- Stitching concept which involves sewing high-tensile-strength yarn through the laminate using an industrial sewing machine [7–10].
- Peel stopper device [11–13] which is based on principle of inserting specially shaped core insert into the core such that the delamination crack front is rerouted along the internal boundary of the peel stopper without further propagation along the face core interface.
- Shear key concept [14,15] which involves grooving of the core region and placing an insert (which may or may not be of the same material as the face-sheet) attached to the face sheet and of the same dimension as that of the foam-core groove.

On the other hand constituent modifications involves changing and/or improving the properties of constituent materials such as the face-sheet, core and/or the resin-hardener system. The primary advantage of this modification over the previous one (structural
modification) is practically no gain in weight. Apart from addition of toughening agents to brittle resin [16,17], primarily the modification of constituents for sandwich composites have been done using single- or multi-walled, functionalyzed or un-functionalyzed carbon nano-tubes (CNT). Literature survey reveals different techniques of addition of CNT’s within the constituents of laminated and/or sandwich composites. CNT’s have been dispersed in the interface of prepreg/plies or in the resin system and GFRP/CFRP and/or sandwich composites. CNT’s have also been grown and aligned on the inter layer of prepreg/plies [31–33] or on the surface of the glass- or carbon fibers [33] constituting laminated and sandwich composites. An excellent treatise on addition of nano particles in CFRP laminated composites can be found in references [34,35].

The approach considered in this manuscript is to disperse multi-walled unfunctionalyzed CNT in epoxy resin using a sonicator. Even though a number of works on determination of mode 1 and/or mixed mode characteristics have been done in this regard for laminated composites; to the best of the authors knowledge there appears to be no work done on influence of sonicated multi-walled CNT dispersed resin system in interface fracture characterization of GFRP/PVC-core sandwich composites. The current work focuses on this issue in which vacuum resin infusion methodology has been utilized for final manufacture of these samples. Close to this topic being addressed in this manuscript there exists related literature on using CNT modified resin system to improve fracture characteristics of laminated composites: a study [18] reported 32% increase in mode 1 fracture toughness on spraying functionalized MWCNT solution on interlayer of CFRP laminates; another study [20] revealed 14% improvement in mode 2 fracture toughness values (through End-Notch flexure tests) by spreading solution of ethanol and MWCNT with an airbrush on surface of prepreg layers; an increase in mode 1 fracture toughness values by 32% was achieved by spraying MWCNT’s on Teflon coated peel clot and subsequently transferring them to the woven prepreg layers [19].

The paper has been arranged in the following manner: Section 2 describes the process of manufacture of the samples along with HRTEM investigations for MWCNT dispersion in resin; Section 3 describes experimental investigations carried out with the manufactured samples; Section 4 discusses the results as obtained in experimental investigation (double-cantilever-beam test) and micrograph studies (FESEM) for samples with and without MWCNT; Section 5 provides discussion and conclusion to the manuscript including possibilities of future work.

2. Process of manufacture

MWCNT (supplied by Cheap Tubes of outer diameter less than 8 nm, inside diameter 2–5 nm, length 10–30 μm, specific surface area 500 m²/g, bulk density 0.27 g/cc) was mixed in epoxy resin (Airstone 780E of Dow Chemicals with 1400 mPa·s viscosity and 1.15 g/cc density at 25 °C) using a tip sonicator (500 W Vibracell High Intensity Liquid processor with 20 kHz probe of Sonics and Materials) for 2.5 h intermittently at 60% amplitude. Different percentages of MWCNT by weight of epoxy resin (0.5, 1, 1.5 and 2.0) were utilized in the sonication process. Room temperature (of 25 °C) was maintained throughout the process of sonication. After sonication, hardener (Airstone 785H of Dow Chemicals with 13 mPa·s viscosity and 0.94 g/cc density at 25 °C) was added to the mixture in 30 wt% of epoxy resin and stirred for 15 min at 150 rpm.

HRTEM analysis was done to measure the dispersion of MWCNT in the epoxy resin. Samples of MWCNT sonicated and hardened epoxy resin system were trimmed with LEICA EM trim followed by cutting to 100 nm thickness samples using LEICA EMFCES Ultra-Microtome; which were then eventually placed on copper grids. The samples were examined through JEOL JEM2100 HRTEM operating at 200 kV with 50–500 k magnification. Fig. 1 shows the HRTEM images demonstrating relatively good dispersion for 0.5, 1 and 1.5 wt% of MWCNT. Weight % of MWCNT were taken based on total weight of the epoxy resin used for sample fabrication. Agglomeration could be observed for 2.0 wt% of MWCNT. It should be noted that both dispersion and agglomeration of MWCNT in resin depends on relative van-der Waals forces, curvature, and relative surface energy of MWCNT vs. that of resin. To overcome the attractive forces ultrasonication had been done in this research, but still reagglomeration is possible after discontinuation of external forces [21]. Apart from good dispersion at 0.5–1.5 wt% and reagglomeration at 2 wt%, it cannot be stated clearly from visual observations in Fig. 1 as to which is the optimum wt% of MWCNT in the mix which would give the best values for interfacial fracture toughness. It should be noted that optimum dispersion of MWCNT in resin matrix system is the key parameter to promote better nanofiber–matrix interface properties to reach an efficient load-transfer between the two constituents of the nanocomposite [22]. Fig. 2 shows magnified view of dispersed CNT for 1.5 wt% MWCNT sonicated resin system. In order to resolve the issue of determination of optimum wt% of MWCNT in mix which would give the best improvement in fracture toughness values, sandwich composite samples were manufactured using the resin mix with different wt% of MWCNT and experimentally investigated using a modified double-cantilever-beam test set-up.

Closed cell semi-rigid PVC foam with a density of 100 kg/m³, manufactured by DIAB Inc. and marketed by the trade name of Divinyccell H100, was utilized as core material in this manuscript. The foam-core thickness considered for the experimental investigation is 30 mm and the foam material has a cell size of approximately 400 μm. The foam was sandwiched between two glass-fiber face sheets, each of which is composed of two alternate stitched layers of chopped strand mat (CSM) and woven roving (WR) fiberglass mats. The above prepared resin system was utilized to prepare the sandwich composite panel by vacuum resin infusion methodology. The resin-system-flow through the preform (face sheet and core covered by porous Teflon film and highly

Fig. 1. HRTEM of samples with different weight percentage of multiwalled CNT: (a) 0.5 wt% CNT, (b) 1.0 wt% CNT, (c) 1.5 wt% CNT, and (d) 2.0 wt% CNT.
permeable breather cloth) is primarily assisted through the vacuum alone. Upon complete part wetting, the infusion lines are blocked and is vacuum cured at room temperature for at least 24 h. It should be noted that the resin-system used in vacuum resin infusion methodology consists of resin, hardener and different wt% of MWCNT.

Induction of initial delamination in the sample, which are required for carrying out interfacial fracture toughness tests, was done by implanting a 80 μm thick non-stick impermeable Teflon sheet between the face sheet and the core during vacuum resin infusion process for sample fabrication.

3. Experimental investigation

A schematic diagram of the test setup along with sample dimensions are shown in Fig. 3. Samples of dimensions 180 mm × 25 mm × 35 mm (where \( L = 180 \text{ mm} \) and \( b = 25 \text{ mm} \) as per Fig. 3) were cut from the initially manufactured panel. The length of initially delaminated region for the cut samples was kept as 50 mm. Aluminium hinges were then glued (using DP 460 adhesive) on either sides of the face sheet in the initially delaminated region. Dimension of \( a \) (as shown in Fig. 3) was kept at 25 ± 1 mm. Similar experimental investigations on sandwich composites to determine fracture toughness values can be found in literature [36–39]. It should be mentioned in this context that at continuum level the interface between the glass-fiber face-sheets and foam-core is a smeared-layer of chopped strand mats within the glass-fiber face-sheets, the resin system and the PVC foam-core. Thereby, there does not exist a distinct interface layer of resin system separating the face-sheet and the foam-core.

The hinge tabs were fitted to the pneumatic grips of INSTRON ElectroPulse 1000. A 1 kN loadcell at constant cross head speed of 0.5 mm/min was then utilized to provide tensile loading to the samples as shown in Fig. 4 till the point where the crack has advanced more than 20 mm from the initial point of delamination. Atleast 10 samples (which yielded results in between mean to 2 times the standard deviation) were investigated to arrive at any conclusion from experimental investigations. The experimental investigation results shown in the manuscript represent mean of the results obtained.

As tension is applied to the grips, the initial face-core delamination length increases and crack slowly propagates in the face/core interlayer regions. The load vs. deflection plot of the cross-heads were obtained from the computer whereas the crack lengths were observed through camera attachments and were taken at discrete load points along the entire span of load vs. displacement plots. Fig. 5 shows final deflected shape of the sample. Apart from changes in stiffness, load capacity and ductility, no significant behavioral difference was observed between samples with and without MWCNT. At a later stage of crack propagation, the crack kinked downward into the core in a large number of samples. Typically the explanation to this behavior can be derived from previous analytical study [40] in which it was demonstrated that the
direction of crack propagation depends upon the fracture toughness of the associated components (interface region as well as the two materials on either side of the crack).

The interface fracture toughness calculated from modified double cantilever beam tests (as done in this manuscript) typically involves contributions from both mode I and II. In fact, there are standard specifications (ASTM D5528-01) for carrying out DCB tests for laminated composites. However, in this case where the properties of material above and below the initial delamination are significantly different, it is considered as a bimaterial interface region. For similar homogeneous material on both sides of the interface, it has been demonstrated analytically [41,42] that if the crack travels in a plane without kinking up or down then it reveals a pure mode I type of failure mechanism. However, no such similar analogous analytical/numerical conclusions exist which shows pure mode I behavior for interfacial crack between two dissimilar materials. Conclusions by various previous researches [40] suggest that the kinking of a crack does not demonstrate observance of initiation of mixed mode crack for bimaterial interfaces; infact a crack can be perfectly straight within the interface region demonstrating mixed mode behavior. It has been identified that observance of kinking in bimaterial interfaces typically depends upon stiffness and strength of the associated materials at the interface as well as the interface itself [40,43]. Thereby it can be expected in this experimental investigation that both modes contribute to interfacial fracture propagation even though the contribution of mode I might be higher typically when the crack initiates.

4. Results and discussions

Load–displacement plots for conventional and MWCNT sonicated samples (1.5 wt% MWCNT) are shown in Fig. 6. Even though...
load–displacement was obtained for all samples with different percentages of MWCNT; only samples with 1.5 wt% MWCNT have been shown in the figure since the samples provide the best results. It can be observed that typical MWCNT sonicated samples improve the stiffness as well as the peak-load carrying capacity by approximately 13.06% and 14.4% respectively in comparison with samples without MWCNT. It can also be observed from the figure that a drop of around 20% from the peak-load carrying capacity in the post-peak regime was also delayed in the MWCNT sonicated samples in comparison to conventional samples without MWCNT thereby indicating an increase in ductility of the samples. The reason for the above mentioned differences in results between samples with and without MWCNT can be attributed due to presence of MWCNT dispersed in the epoxy resin mix which resists the formation and/or propagation of cracks.

Interface fracture toughness, $G_c$, of the DCB sandwich samples is calculated using the compliance calibration (CC) method [44] considering the modification due to shear [45]. Similar methodology
is the compliance (calculated using CC method) of the DCB sandwich
proportion to samples without MWCNT addition. The compliance calibration method typically depends on change in compliance with crack length and is given as

\[ G_C = \frac{P^2}{2b} \frac{dC}{da} \]  

(1)

where \( P \) is the load applied, \( b \) the beam width, \( C = \frac{1}{2} \) is the compliance, \( a \) the crack length and \( d \) the load point displacement. The experimental compliance vs. the crack length data of the sandwich DCB specimen is fitted to a power function of crack length as

\[ C = C_o a^n \]  

(2)

Based on mean of the values utilized for this work, the value of the exponent \( n \) was obtained as 2.22; which is different from the value of 3 as prescribed in ASTM D5528-01 for calculating mode 1 fracture toughness of laminate composites (and is the basis for modified compliance calibration method). Differentiating the value of \( C \) with respect to \( a \) and substituting it in the expression for \( G_C \) provides the value for interface fracture toughness. Mean (and standard deviation) of the interface fracture toughness values for samples without MWCNT was obtained as 0.99 N/mm (11.9%) whereas the corresponding values obtained for samples with 1.5 wt% MWCNT was 1.33 N/mm (8.3%) thereby demonstrating an increase of 34.34% for samples with 1.5 wt% of MWCNT in comparison to samples without MWCNT addition.

It should be mentioned here that values were specified for only 1.5 wt% MWCNT addition, even though calculations were made for other wt% of MWCNT addition as well, since that particular wt% gave the best gain in performance. Fig. 7 shows interface fracture toughness, \( G_C \) (calculated using CC method) of the DCB sandwich samples increases from 0.5 wt% to 1 wt% and attains a maximum value at 1.5 wt% prior to decreasing at 2 wt%. Obviously better the dispersion of MWCNT in the resin, the better is the improvement in fracture toughness values. Failure toughness values for 2 wt% MWCNT addition were observed to be lower than 1.5 wt% addition primarily because of agglomeration of MWCNT (refer Fig. 1) which eventually turns out as zones of localized stress concentration thereby acting as regions of crack initiators. The result on increase of fracture toughness values with addition of CNT has also been demonstrated by previous researchers [18,19] who observed an increase of 32% on using CNT for laminated composites. Apparently in a sandwich composite material (due to presence of two different materials at the interface) it may appear that performance would not be great on addition of MWCNT in comparison to laminated composites (using similar material on the two sides of the interface). However, it was observed from this study on sandwich composites that performance improvement (of 34%) was quite significant compared to earlier studies on laminated composites. Moreover the methodology of addition of MWCNT for performance improvement (as prescribed in this study) was comparatively very simple in comparison to methodologies prescribed by previous researchers. The reason for this improved performance using a very simple methodology is primarily due to random dispersion of MWCNTs across the mid plane of interface between the face and core (methodology process contradictory to complex methodology used by Garcia et al. [31] to achieve improvement of 50% in mode 1 fracture toughness values for laminated composites).

Field emission scanning electron microscope (FESEM) studies were also done for the cracked interfacial surface between the PVC foam core and the GFRP face sheet. After completion of the experiment, the interface between the PVC foam-core and the GFRP face-sheet were separated; small samples were cut at different regions as shown in Fig. 6a. These samples were gold coated in Sputter Couter machine to prevent charge buildup by electron absorbed by the specimen. A 15 kV accelerating voltage was applied to achieve desired magnification. FESEM of the prepared samples were done using Carl Zeiss SUPRA 40 machine. At 65 k magnification (refer Fig. 8b) MWCNT filaments were observed to be dispersed at the surface of the resin system. This feature may lead to enhanced void reduction in the fabricated samples. Zoomed in region (Fig. 8c) shows a single MWCNT in the resin system at a magnification of 229 k. Fig. 8d obtained at a magnification of 27 k shows MWCNT dispersed in the resin system between two glass fibers as well as on the surface of the glass fiber. This demonstrates a better fiber–matrix bond, achieved as a result of high aspect ratio of the MWCNT, in comparison to the conventional glass-fiber matrix bond in samples without MWCNT. The MWCNT act as mechanical interlocking mechanism between glass fibers and the matrix (between the glass fibers and the PVC foam core) which eventually results in high friction coefficients. Bridging between two resin-system blocks by a MWCNT is shown in Fig. 8e at a magnification of 119 k. This bridging effect prevents crack generation and increases crack propagation resistance. The above figures may indicate that the pre-peak nonlinear behavior for the MWCNT system (observed in Fig. 6) is due to delamination of the MWCNT from the resin system. Fig. 8f shows pulled out ends of the MWCNT at a magnification of 186 k. Typically when load is applied to the composite system, the matrix (epoxy resin system) starts to crack first and stress is transferred from the lower modulus matrix (epoxy resin system) to the MWCNT by bridging effect. MWCNT anchored in the resin system matrix prevents propagation of these cracks. Apart from that, the MWCNT anchored to both resin system and glass fiber promotes better interfacial bonding between the resin system matrix and glass fiber which eventually enhances the interface fracture toughness as well as load carrying capacity of the composite.

After the initiation of the crack, the crack typically tends to propagate along the interface. The experimental investigation was stopped momentarily and values of crack length (expression a in Eq. (11)) were recorded using a travelling microscope along with the load (P) and load point displacement (\( \delta \)). Fig. 9 shows that as the crack length increases the fracture energy values (G) decreases. The justification for this plot can be obtained from studies made by Cantwell et al. [37]. Using a different experimental setup it was demonstrated by Cantwell et al. [37] that as crack length increases \( \frac{G}{a} \) decreases. It was also stated by them that typically for sandwich composites with glass fiber face-sheet and balsa wood core (having relatively similar stiffness and strength as that of pvc foam core used in this study) fracture toughness of mode 1
is almost 10 times that of the fracture toughness of mode 2. So obviously it can be expected that as crack length increase interfacial fracture toughness (containing components of both fracture modes) will decrease, as has been observed from experimental investigations carried out in this study.

It should be pointed out that the rate of decrease (measured by the tangent to the curves shown in Fig. 9) of fracture energy values for samples without MWCNT are higher than those with MWCNT. Out of the different weight % of MWCNT samples investigated, 1.5 wt% gave the lowest rate of decrease of fracture energy values thereby demonstrating increase in ductility of the samples with addition of MWCNT. Even though it has been mentioned that nanotube doping can speed up the damage especially in pure shear loaded laminates [47], no such effect was observed in this study dealing with interface fracture involving mode mixity for sandwich composites.

5. Conclusions

The manuscript highlights differences in experimentally observed response of interface fracture toughness of samples with and without MWCNT. Out of the different process of addition of MWCNT in the PVC-core/glass-fiber/epoxy-resin sandwich (as can be obtained from literature), a simple method of sonating the MWCNT in epoxy resin has been chosen in this research to demonstrate significant improvement in mechanical performance of samples against interfacial delamination. The research demonstrates an improvement of 14.4% in peak load carrying capacity for samples with 1.5 wt% MWCNT (weight % being taken with respect to amount of epoxy resin used for sample fabrication) in comparison to samples without MWCNT. Good dispersion of MWCNT was also observed with 1.5 wt% MWCNT addition in comparison to other percentages of addition of MWCNT by weight.

Samples with 1.5 wt% MWCNT recorded an increase in fracture toughness values of 34.34% in comparison to samples without. Fracture micrographs also demonstrated good dispersion and fiber bridging of MWCNT in the epoxy resin system. Ductility was also observed to be higher for samples with MWCNT in comparison to samples without from fracture energy vs. crack length plots of the samples.

Acknowledgements

This work was supported by Department of Science and Technology, India under Award No. SR/S3/ERC-035/2010. The first author would like to thank many students and technicians who had helped him for carrying out the experiments. Any opinions, findings and conclusions or recommendations expressed in this manuscript are those of the writers and do not necessarily reflect those of the Department of Science and Technology, India.

References