Original Article

Effect of A-MWCNTs and ETBN toughener on impact, compression and damping properties of carbon fiber reinforced epoxy composites

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1. Introduction

Carbon fiber reinforced epoxy composite (C-epoxy) is a subclass of carbon fiber reinforced plastics (CFRP) which are excessively being used nowadays in the area of aerospace, automotive and underwater applications to replace conventional metallic materials because of their high strength to weight ratio and rigidity [1]. Though C-epoxy composites have high specific strength they are relatively brittle in nature due to high crosslink density with poor resistance to the initiation and growth of cracks [2]. Therefore efforts were made for toughening of these brittle C-epoxy composites through various methods. Among them the most prominent method is the addition of phase separated rubber particles to the matrix system [3]. Various liquid rubber materials such as butadiene acrylonitrile co-polymers containing carboxyl (CTBN), amine terminated butadiene (ATBN) and epoxy

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Abstract

In the present work, epoxy resin is modified with epoxy terminated butadiene acrylonitrile (ETBN) liquid rubber and was used to make carbon fiber reinforced epoxy (C-epoxy) composites with an aim to enhance the impact, compression and damping properties. ETBN added C-epoxy composites were further modified using amino functionalized multi-walled carbon nanotubes (A-MWCNTs) at different weight ratios namely 0.5 wt%, 1.0 wt%, and 1.5 wt% and evaluated impact, compression and damping properties. Results indicate that modification of C-epoxy with ETBN enhances the properties considerably. A-MWCNTs addition to ETBN modified C-epoxy (A-MWCNTs-C-Epoxy-ETBN) further enhances the impact strength (26%), compressive strength (17%) at 1.0 wt% and damping ratio (87%) at 0.5 wt% of A-MWCNTs. The toughening mechanisms contributing to the enhancement of mechanical and damping properties of A-MWCNTs are discussed.

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terminated butadiene (ETBN) reactive end groups [4] are generally added.

The improvement of engineering properties with the use of carboxyl terminated butadiene acrylonitrile (CTBN) [2,5] and amine terminated butadiene acrylonitrile (ATBN) [6,7] particles is well reported. However, ATBN is not compatible with aliphatic amines and the direct addition of CTBN to an epoxy system does not completely separate its phase upon curing leading to the minimum improvement in toughness. This is due to the slow chemical reaction between CTBN rubber and epoxy [8]. Improper phase separation of the rubber particles results in significant reduction in strength and modulus of the C – epoxy system. Hence, for obtaining optimum toughness, butadiene can be modified with the epoxy end group to form ETBN. ETBN interfaces well with the structural grade epoxy resins due to its epoxy end groups thereby providing optimum toughness. However, the improvement in toughness with the addition of rubber particles reduces the strength, stiffness and elastic modulus [4,9]. Hence, the composites modified with reactive liquid polymers show a trade-off between the properties which necessitates an additional reinforcement.

Researchers attempted nanofillers as an additional reinforcement in applications where strength, stiffness and modulus are utmost important [10]. Carbon nanotubes (CNTs) are ideal reinforcing fillers due to their excellent mechanical, electrical and thermal properties [11]. Tang et al., obtained better toughness and electrical conductivity of epoxy composites by combining the multi walled carbon nanotubes (MWCNTs) and spherical rubber particles [12]. Rahman et al., added polyether polyol and amino-functionalized MWCNTs for obtaining the increased fracture toughness without compromising other desired mechanical properties such as strength and stiffness [13]. Ahmed et al., incorporated the reactive rubber particles and nanoclay into the epoxy matrix to obtain balance between toughness and stiffness [14]. However, there is a dearth of information on the composites with light weight, high strength, high stiffness and high damping properties essential for underwater applications.

The main interest of the present work is to develop a multi-phase composite material with unique properties to suit the underwater applications such as shells and other mechanical systems. The underwater mechanical systems such as weapon systems experiences shock loads when entering into the water during launching. So the materials should have high impact strength to overcome these shock loads. Damping is also critical for the materials used in underwater applications as its improvement will reduce the noise levels and enhances stealth properties. Apart from damping characteristics higher compressive strength is also essential to withstand external hydrostatic pressures. The present investigation is therefore aimed at studying the effect of addition of ETBN and A-MWCNTs to C-epoxy composites on their impact, compression and damping properties. To the best of the authors’ knowledge, not much work is reported on a multi-phase composite of MWCNTs and rubbery particles added CFRP system with a focus on the above combination of properties.

2. Experiments

2.1. Raw materials

Epoxy resin and the hardener used in this matrix system are diglycidyl ether of bisphenol-A (DGEBA) and diethyl toluene diamine (DETDA) respectively. Polyacrylonitrile based T-300 carbon fabric having 8-H satin weave (woven with 3K tows) was used as the main reinforcement. MWCNTs synthesized by the chemical vapor deposition method having 99% purity, diameter in the range of 20–30 nm and lengths of 2–4 μm were used. One of the authors of this paper, I. Srikanth et al., studied the effect of amino functionalized MWCNTs on toughness and other mechanical properties of CFRPs. Amino functionalization of MWCNTs is reported as the suitable functionalization method to ensure better bonding with the epoxy matrix and it also enhances the fracture toughness of the matrix [15,16]. A-MWCNTs can invariably increase the degree of crosslinking of epoxy due to participation of amino groups in crosslinking. Amine functional groups on CNTs are reported to show high reactivity and ability to incorporate directly in to the epoxy resin system [17,18]. In the present investigation amino functionalization of MWCNTs prepared through thionyl chloride route are reported to have increased degree of cross linking of epoxy due to participation of amino groups of MWCNTs in cross linking [19]. This gives positive reinforcement effect up to certain critical concentration. In the present work and here after these MWCNTs are referred as A-MWCNTs. ETBN toughener of 5 wt% was added to DGEBA for all the tested components. The amount of rubber particles was selected based on the past literature [5,20].

2.2. Fabrication of A-MWCNTs – ETBN – C-epoxy multi-phase composite

To fabricate A-MWCNTs – ETBN – C-epoxy laminated composites, initially MWCNTs were dispersed in epoxy resin system. This involves adding required weight % MWCNTs to epoxy resin at room temperature. Probe type sonicator, (Mesonix 3000) was used for the sonication of mixture to ensure uniform dispersion of A-MWCNTs for 15 min, followed by ball milling for 120 min at 250 rpm using a planetary ball mill. ETBN toughener (5 wt%) was added to resin having A-MWCNTs and continued the ball milling at the same speed for 15mins. Required quantity of hardener was added to the MWCNTs resin mixture and continued the ball milling at the same speed. Carbon fabric was cut into pre-decided specific dimensions impregnated with A-MWCNTs – ETBN – C-epoxy hardener mixture. Impregnated fabric layers were stacked and compressed in a suitable size metallic die by using compression molding process. Volume fraction (Vf) of the composite was controlled by varying the number of fabric layers as per pre-decided thickness of approximately 6.3, 3 and 4 mm for impact, compression and damping specimens respectively to obtain fiber Vf close to 60% (±1%), which is equivalent to 68% weight fraction of fiber. Higher fiber volume fraction generally increases the strength up to some extent beyond that strength may decrease due to improper wetting of fiber. At the same
Table 1 - Identification codes of the composite samples.

<table>
<thead>
<tr>
<th>Sample ID no.</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ID-1</td>
<td>Carbon fiber + Epoxy – (C-Epoxy)</td>
</tr>
<tr>
<td>ID-2</td>
<td>Carbon fiber + Epoxy + ETBN</td>
</tr>
<tr>
<td></td>
<td>toughener + 0% CNT – (Blank)</td>
</tr>
<tr>
<td>ID-3</td>
<td>Carbon fiber + Epoxy + ETBN</td>
</tr>
<tr>
<td></td>
<td>toughener + 0.5% CNT</td>
</tr>
<tr>
<td>ID-4</td>
<td>Carbon fiber + Epoxy + ETBN</td>
</tr>
<tr>
<td></td>
<td>toughener + 1.0% CNT</td>
</tr>
<tr>
<td>ID-5</td>
<td>Carbon fiber + Epoxy + ETBN</td>
</tr>
<tr>
<td></td>
<td>toughener + 1.5% CNT</td>
</tr>
</tbody>
</table>

Fig. 2 - Compression strength test samples prepared with end tabs.

In this work, the specimen dimensions were chosen to be 120 mm long. For that purpose, various types of composite laminates were manufactured. The specimens were cut into various sizes using a CNC milling and water jet machine tool for performing the above tests. For each type of sample three specimens were tested and its average was noted. Environmental scanning electron microscopy (ESEM-FEI Quanta 400) was used for analyzing the dispersion of A-MWCNTs, interface of A-MWCNT-ETBN-C-epoxy and microstructure of the samples.

3. Results and discussion

3.1. Impact strength

The results of impact strength of all the composite samples listed in Table 1 is shown in Fig. 3. The addition of ETBN
toughener to the C-epoxy shows a significant improvement of 14% on the impact strength. Maximum impact strength was obtained at 1.0 wt% MWCNT loading corresponding to an increase of 26% as compared to C-epoxy. Reasons for improvement in the impact strength with the addition of toughener can be understood from the fact that, during the impact loads when a sudden pointed load is impinged on a composite specimen, the load is centered at the point of impact. Faster the impact energy is dissipated away from the point of impact, better will be the impact resistance of the composite as it ensures harnessing of a maximum area of composite against the impacted loads. In case of C-epoxy, due to the weak interface strength they give away cracks. The impact strength of the C-epoxy composites is lower. The resistance to impact will be more if the Mode II delamination resistance is high. This is due to the fact that the laminates can resist formation of sub critical crack generation and propagation [22]. This ultimately leads to harnessing larger area of composite to resist impact loads. When a toughener is added, delamination resistance increases because toughener preferentially settles along the fiber-matrix interface during the phase separation of ETBN toughener from the main resin system DGEBA. Preferential deposition of toughener at the interface is due to the ability of active zones of fibers to act as nucleating sites for the cross linking reaction between the toughener and the hardener. Moreover epoxy group in ETBN is a bulky/high molecular weight side chain. This makes it difficult to diffuse to longer distances during curing. Hence it preferentially settles on the surface of C-fibers and participates in crosslinking. Due to the presence of toughener phase, interface acquires ability to undergo more elastic deformation while dissipating the impact energy. Thus better cushioning of impact energy across the interface without forming interface cracks takes place due to the toughener phase in C-epoxy as shown in Fig. 4. This leads to the improved impact strength for the ETBN added C-epoxy composite.

On the other hand, when A-MWCNTs are added, they act as additional strengthening sites at the interface due to their superior properties with large aspect ratio, which enables them to bridge the interface between the filaments thereby improving the interfacial fracture behavior of CFRPs [23]. Besides their ability to strengthen the interface, MWCNTs can also act as a better energy dissipating medium due to their high stiffness. This results in enhanced impact energy dissipation across the interface to larger areas. Through the crack bridging and crack deflection, these A-MWCNTs offer more resistance for the crack propagation. The breakage and pull out of A-MWCNTs as observed in Fig. 5 at 1.0 wt% loading of A-MWCNTs indicates that more amount of energy was absorbed during impact which resulted in improved impact resistance of A-MWCNT-ETBN-C-epoxy as compared to ETBN-C-epoxy. The improved impact strength observed with the addition of nano fillers is in line with the past literature [24]. However, beyond 1.0 wt% addition of A-MWCNTs, they are known to agglomerate as shown in Fig. 6 which results in deterioration of the interface properties of CFRPs which resulted in reduction of impact strength.

3.2. Compression strength

One of the aims of the present work is also to improve the compressive strength without sacrificing the toughness. The
results of compression strength of all the composite samples are given in Fig. 7. The compression strength is higher for A-MWCNTs-ETBN-C-Epoxy composites followed by ETBN-C-Epoxy and C-epoxy. A marginal increase in compression strength of 7% was observed for ETBN-C-Epoxy composite when compared to C-epoxy. It is reported that the mechanical strength of the composite may decrease when low modulus rubber particles are added to a high modulus epoxy [25]. However, in the present work, there is an increase in strength with the addition of ETBN rubber particles. This is attributed to the fact that under compressive loads, CFRPs fail by out of plane rotation of fibers followed by interfacial shearing. Fibers which are more favorably aligned to the axis of load experiences more load and thus initiate the out of plane movement. However, if the matrix at the interface having more elongation/toughness, they can resist the interface shearing. This explains the reason for improvement in the compressive strength for C-epoxy due to the addition of ETBN. Uniform dispersion of amine MWCNTs up to 1.0 wt% resulted in improvement in the compressive strength by 17% increases compared to C-epoxy. Increased compressive strength can be attributed to enhanced reinforcement of the matrix by this nano filler material as also reported earlier [26]. In addition to the increased specific energy absorption of CFRPs with the addition of A-MWCNTs effectively prevents the initial formation of micro cracks. Even after the formation of micro cracks the availability of A-MWCNTs absorbs more energy, thereby hindering the macro cracks which results in increased fracture resistance. Beyond 1.0 wt% loading of MWCNTs there is a slight drop in compressive strength probably due to agglomeration of A-MWCNTs. The increase in compressive strength with the addition of CNTs is similar to that reported earlier [27].

The compressive load vs. displacement curves of the composite samples are shown in Fig. 8. The sudden drop in displacement of the ID-1 specimen (C-epoxy) indicates brittle failure. With the increased loading of A-MWCNTs tendency of agglomeration increases. These agglomerated particles act as stress concentrators and hence there is reduction in strength at 1.5 wt% loading of A-MWCNTs. As mentioned earlier, irrespective of dispersion, beyond the optimum loading of A-MWCNTs to CFRPs, mechanical properties of composites tends to deteriorate as higher crosslink densities embrittles the interface [19].

### 3.3. Damping ratio

Though CFRPs have high specific strength and stiffness, poor damping characteristics are the reasons for limited use of CFRPs in structural applications [28]. It can be seen that, addition of ETBN rubber particles and A-MWCNTs to the C-epoxy system enhances the damping characteristics when compared to the C-Epoxy. Table 2 shows the damping ratios and

<table>
<thead>
<tr>
<th>S. no.</th>
<th>ID no.</th>
<th>Modes</th>
<th>Natural frequency</th>
<th>Damping ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ID-1</td>
<td>1</td>
<td>460</td>
<td>1.61</td>
</tr>
<tr>
<td>2</td>
<td>ID-2</td>
<td>1</td>
<td>517</td>
<td>2.12</td>
</tr>
<tr>
<td>3</td>
<td>ID-3</td>
<td>1</td>
<td>540</td>
<td>3.02</td>
</tr>
<tr>
<td>4</td>
<td>ID-4</td>
<td>1</td>
<td>562</td>
<td>2.41</td>
</tr>
<tr>
<td>5</td>
<td>ID-5</td>
<td>1</td>
<td>625</td>
<td>1.10</td>
</tr>
</tbody>
</table>

Fig. 6 – SEM image shows agglomeration of CNTs (1.5 wt%) with ETBN added C-epoxy.

Fig. 7 – Compression strength of the carbon epoxy composite samples.

Fig. 8 – Compressive load vs. displacement curves of the composite samples.
the corresponding natural frequencies for all the composite samples. Figs. 9 and 10 and shows the damping ratios and frequency response function (FRF) of the composite samples. The improvement in damping ratio when compared to C-epoxy is 31% for blank specimen (addition of ETBN toughener alone), 49% at 1.0 wt% and as high as 87% at 0.5 wt%.

The addition of ETBN rubber particles into the C-epoxy system increases the damping characteristics. A sound wave in general propagates through series of compression and rarefaction. When, sound wave propagates in composite samples, the matrix and fiber experiences differential expansion and contraction as they possess different modulus values. This results in interfacial shearing which acts as a source for damping the propagating sound wave. Thus CFRPs are better in damping efficiency as compared to the metals. However, due to the high crosslink density of the conventional DGEBA based epoxy which possess higher modulus as compared to rubber counterparts, damping is not efficient as compared to the rubbers/or rubberized epoxies. In the present study, when ETBN is added, large improvement in damping was observed as compared to the C-Epoxy sample. This is because of the presence of rubber phase at the interface which increases modulus mismatch between the fiber and the matrix to higher extent leading to more localized shear which consumes higher sound energy. When series of sound waves pass through a composite interface, it will produce cycles of shearing which is generally referred as stick-slip cycles. Apart from this, even within the matrix phase heterogeneity is introduced in the form of elastic rubbery phase encased in a stiff and highly cross linked DGEBA epoxy phase. This new interface also consumes sound energy due to interfacial shearing across the rubbery phase to the DGEBA epoxy matrix. In case of A-MWCNTs addition, they assume interface position between the fiber and matrix and anchor it. Hence, in the presence of A-MWCNTs, shearing during stick-slip cycles will consume more energy leading to more damping. This increase in damping ratio with the increase in loading of A-MWCNTs is observed in earlier works [29]. However, it can be seen that, damping ratio is more at 0.5 wt% than at the higher loading of A-MWCNTs i.e., at 1.0 and 1.5 wt%. This can be explained by the fact that, with increased loading of A-MWCNTs stick slip mechanism may cease to operate as the interface has become strong due to the anchoring of higher amount of A-MWCNTs, so applied sound energy is not able to initiate shearing at the strong interface. Moreover A-MWCNTs which are having high modulus may bridge adjacent filaments of a carbon tow like a stiff rod, which can act as a medium for energy transmission from one filament to the other filament with minimal involvement of matrix at the interface. Matrix regions by virtue of their anchoring with the high concentration of A-MWCNTs have to start vibrating at the same phase as that of the main reinforcement that is carbon fibers. As this mechanism starts to predominate against the stick slip mechanism, damping efficiency of the composite starts to come down. This explains the higher damping ratio at 0.5 wt% when compared to 1.0 and 1.5 wt%.

4. Conclusions

C-Epoxy composites were modified with ETBN and A-MWCNT and evaluated for their impact, compression and damping properties. Following are the salient observations.

(a) The phase separated ETBN rubber particles preferentially settled along the interface which facilitated the faster dissipation of energy, thus improving the impact strength, whereas weak interfacial strength in carbon – epoxy gave away the cracks which hindered the transmission of energy by localizing the impact.

(b) The addition of A-MWCNTs to C-epoxy-ETBN became additional strengthening sites and these fillers act as an energy transmitting medium resulting in further improvement of impact strength. Loading of A-MWCNTs beyond optimum point (1.0 wt%) tends to agglomerate, which deteriorate the interface properties and thus impact resistance.

![Damping ratios of the composite samples.](image1)

![Frequency response function (FRF) of composite samples.](image2)
(c) In spite of low modulus of rubber particles, an increase in compressive strength is observed with the addition of ETBN toughener due to their ability to cushion interfacial shearing and out of plane rotation of C-fibers. Increased energy absorption of CFRPs with the addition of A-MWCNTs effectively resisted the initial formation of micro cracks and conversion of these micro cracks into macro cracks, thereby increasing compression strength. Beyond 1.0 wt% A-MWCNTs makes the matrix embrittle at the interface due to the formation of high crosslink densities leading to reduction in compression strength.

(d) The phase separated ETBN rubber particles created high degree of modulus mismatch resulting in differential expansion and contraction of the interface leading to increased interfacial shearing hence improved damping performance for ETBN modified C-epoxy as compared to C-epoxy. In the presence of limited quantities of A-MWCNTs (0.5 wt% in present study) stick slip cycles consumes energy at the interface and hence increases the damping characteristics, whereas with the increased loading of A-MWCNTs beyond 0.5 wt%, these stick slip cycles cease to operate and brings down damping.

Conflicts of interest

The authors declare no conflicts of interest.

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