Influence of Particulate Graphite Additions on the Shear Related Behaviour of Glass Fabric Reinforced Epoxy Composites

N. SAINATHAN, K. PADMANABHAN, S. SASHIDHARA, R. M. V. G. K. RAO** AND KISHORE*

Department of Metallurgy
Indian Institute of Science
Bangalore 560 012
India

ABSTRACT: Glass fabric reinforced composite laminates with two different epoxy formulations as matrix materials were fabricated with discretely varying additions of particulate graphite upto 6 wt%. The influence of these additions on the shear related behaviour of the composite is reported. While the interlaminar shear strength (ILSS) of the composites with both the resin formulations and two different widths exhibited a decreasing set of values for 2 and 4 wt% graphite, those for the 6 wt% additions indicated a trend towards either a saturation or marginal recovery. The compression strengths for the composites fabricated with the two resin formulations showed opposing trends in that the specimens with the room temperature cured resin exhibited an increase upto 4 wt% graphite. The shear strength in compression was observed to be larger than the ILSS values of the abovesaid laminates. The transverse modulus of the composites exhibited an increase upto 4 wt% graphite. Scanning Electron Microscopy (SEM) was carried out on the failed specimens and the observed fracture features are reported.

INTRODUCTION

EPOXY RESINS ARE one of the most common class of materials used in polymer matrix composites. Considering the inherent brittleness of these resins when compared to some of the modern plastics, they are often modified by rubber additions which improved toughness but led to deterioration in some mechanical and thermal properties. Thermoplastic additions have also been made to the epoxy resins to improve the toughness. Inorganic fillers have been successfully incorporated as second phase additions in order to essentially

---

*Author to whom correspondence should be addressed.
**Scientist, FRP Pilot Plant, Materials Science Division, National Aerospace Laboratories, Bangalore-560017, India.
modify the stiffness and strength of engineering plastics [1–4]. Owing to its good lubricating properties, graphite has been added in an epoxy matrix to study its effect on wear properties [5].

A perusal of the available literature points to the paucity of information on the influence of filler additions on the mechanical properties of Fibre Reinforced Plastics under various modes of shear. Incidentally, it has been recognised that the ILSS of laminated composites is a matrix dominated phenomenon [6]. Hence, any addition made to the matrix, is expected to affect the ILSS and other shear related properties of the composite in a beneficial or adverse manner, depending on factors like the interface, the relative hardness and brittleness, the particle size and the weight fraction of the addition, to mention some.

This work highlights the effect of graphite, an important filler material, in discretely varying quantities, on the shear related behaviour of the glass fabric/epoxy composites. Two epoxy resin formulations have been used to fabricate two different glass fabric/epoxy composites, and the influence of graphite content on their shear related behaviour has been studied.

SEM fractography was employed to characterise the fracture features and some corroborative study involving fractography with mechanical test data also reported.

**EXPERIMENTAL**

Two different epoxy resin formulations viz., a room temperature cure (RTC) and a high temperature cure (HTC) were used. The epoxy resin used was diglycidyl ether of bisphenol A (DGEBA) with a trade name MY750 obtained from Hindustan Ciba Geigy Ltd. For room temperature cure the hardener used was an aliphatic amine with a trade name HY951. For the high temperature cured resin, the hardener used was an aromatic amine with a trade name HY972.

The reinforcement used was a 7-mil bidirectional E-glass fabric. The glass fabric used was a four harness satin weave, with a density of 2.57 g/cc. Spectro-grade graphite supplied by Graphite India Ltd., was used as the filler material with an average size of 20 microns. The particles were observed to be flaky in appearance.

The composite laminates were prepared by hand lay-up. The inner surfaces of the mould plates were first cleaned with acetone and then coated with a thin layer of wax to facilitate easy removal of the cured laminate. The hardener (12 phr) for RT cure and 27 phr for HT cure) and the required amount of graphite were added to the resin and the mixture vigorously stirred. Alternate layers of this blend and glass cloth were laid onto the mould plate by hand lay-up to a total thickness of 15 plies which by trial and error was found to be adequate to fabricate a laminate of final thickness of 3 mm. The laminates were then compressed between the mould-plates for 24 hours. In the case of HTC laminates, they were compressed between the mould plates and then kept in an oven maintained at 125°C for 24 hours, after which they were cooled. To ensure uniform thickness of the laminate i.e., 3 mm, spacers of 3 mm thickness were placed between the mould plates. In all, eight laminates were made, four of RTC and HTC, each with 0%, 2%, 4%
and 6 wt% graphite. Table 1 gives the volume fraction of glass and graphite in the composites and the values of the void content of the composites. It is seen that the void content of the composites was around 6% irrespective of the graphite content.

The mechanical tests carried out were the ILSS, compressive and the tensile tests. The specimens for the mechanical tests were cut to dimensions specified by the ASTM [7-9]. All the tests were carried out on a 100 kN capacity servo hydraulic type testing machine of Instron make, model 8032. The tests were performed under position control mode and the load-displacement response was recorded in a XY-recorder.

The tests were carried out as per the ASTM standard specifications [7-9]. For ILSS initially, a width of 10 mm was chosen in accordance with the published literature [10,11]. In certain cases, the tests were also conducted with samples having a width of 5 mm. The specimens were centre loaded with the Length: Support span: Thickness ratio as 7:5:1. The cross head velocity was 0.02 mm/sec.

The compression test was conducted to determine the compressive strength and strain at failure. The specimens were loaded under compression in an in-plane configuration [8,12]. The cross head velocity employed was 0.02 mm/sec.

The aim of conducting the tensile tests was to determine the Young's modulus and then the transverse modulus of the composites, as per the ASTM standards specification [9]. The cross head velocity used was 0.02 mm/sec.

The shear strength in compression $\sigma_s$ was calculated by using the formula [13]

$$\sigma_s = \sigma_c \sin \theta \cos \theta$$  

(1)

Where $\sigma_c$ is the compressive strength and $\theta$ is the angle of break. The shear stresses developed in a laminate cause the shear mode of failure under a compressive load as shown by Evins and Ham [14]. It was expected that this value would be similar to the corresponding fibre-matrix interface strength [15]. Further the influence of graphite additions on $\sigma_s$ was a matter of considerable interest especially in the present condition where woven fibres in an in-plane configuration are employed where the sample does not experience free edge effects due to an axial compressive loading.

The fracture features of the failed specimens were examined in a Cambridge Stereoscan 360 SEM after sputter coating the surfaces with Au-Pd alloys.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.58</td>
<td>0.049</td>
<td>0.59</td>
<td>0.067</td>
</tr>
<tr>
<td>2</td>
<td>0.60</td>
<td>0.049</td>
<td>0.61</td>
<td>0.062</td>
</tr>
<tr>
<td>4</td>
<td>0.61</td>
<td>0.055</td>
<td>0.63</td>
<td>0.061</td>
</tr>
<tr>
<td>6</td>
<td>0.63</td>
<td>0.058</td>
<td>0.69</td>
<td>0.065</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

Figures 1 and 2 show the variation of ILSS with the graphite content of the laminates for the RTC and HTC laminates respectively for both specimen widths employed for the testing. From the plots it is observed that the ILSS drops noticeably for all the cases upto 4 wt% graphite addition and then either a saturation in the ILSS values is observed as in the case of RTC laminates or there occurs a slight recovery depending on the material tested. It seems from the plots, that on an average, the ILSS of the 5 mm width specimens is lower than that of the 10 mm width specimens.

Figures 3 and 4 show the variation of deflection at failure with graphite content for the RTC and HTC laminates respectively when tested to determine the ILSS. The plots show the deflection at failure for both the specimen widths employed. As seen from Figure 3 the deflection at failure for the RTC laminates of either width shows a steady rise upto 4 wt% graphite and then decreases. The deflection at failure for the 5 mm width specimen is observed to be smaller than that of the 10 mm width specimens for the range of graphite additions tried in this investigation. It is interesting to note that this difference seems to be rather uniform for all the graphite additions employed in this study.

As seen from Figure 4, the deflection at failure observed in the case of HTC composites shows a complete reversal of trend from that observed in the case of RTC composites. Here, the deflection at failure decreases gradually upto 4 wt% graphite and then shows a steady rise. Here again the 5 mm width specimens showed a lower deflection than the 10 mm width specimens over the range of graphite additions as emphasized earlier.

Figure 5 shows the variation of the transverse modulus with graphite content for the RTC and HTC laminates. The RTC laminates show an increase in the transverse modulus reaching a peak in the range 2-4 wt% graphite after which it decreases. The HTC laminates show a steady increase in the transverse modulus upto 4 wt% graphite after which the decrement is less rapid.

![Graph](image-url)

Figure 1. ILSS of room temperature cured composite laminate with varying graphite content.
DISCUSSION

The ILSS with the graphite content of the specimens was found to be highest for both specimen widths employed. It is observed that the ILSS drops with the addition of graphite and then either a saturation of RTC laminates or there occurs a slight increase. It seems from the plots, that the ILSS of the 10 mm specimens is lower than that of the 5 mm specimens.

The deflection at failure with graphite content when tested to determine the ILSS for both specimen widths employed. The deflection for the RTC laminates of either width increases and then decreases. The deflection observed to be smaller than that of graphite additions tried in this investigation, seems to be rather failed in this study.

The failure observed in the case of HTC and from that observed in the case of RTC decreases gradually up to 4 wt% graphite and then again the 5 mm width specimens over the range of 6 to 8 wt% graphite.

Figure 2. ILSS of high temperature cured composite laminate with varying graphite content.

The transverse modulus with graphite content of the RTC laminates show an increase in the range 2–4 wt% graphite after which there is a steady increase in the transverse modulus, the decrement is less rapid.

Figure 3. Midspan deflection for RTC laminates, in an ILSS test.

Figure 4. Midspan deflection for HTC laminates, in an ILSS test.
Figure 5. Transverse modulus in tension for RTC and HTC laminates.

Figure 6 shows the variation of compression strength with graphite additions for the RTC and HTC laminates. The compressive strength of the RTC laminates shows an increase up to 4 wt% graphite and then a drop for 6 wt% graphite, while the compressive strength of the HTC laminates shows a decrease up to 4 wt% graphite followed by a substantial increase. This aspect is discussed later.

Figure 7 shows the variation of compressive strain at failure with graphite additions for the RTC and HTC laminates. The compressive strain at failure for the RTC laminates shows a steep increase up to 4 wt% graphite after which it decreases while the same at failure for the HTC laminate shows a slight fall up to 4 wt% graphite and then a small increase occurs for 6 wt% graphite. By comparing the compressive strain at failure and deflection at failure for ILSS it is seen that the trends observed by the RTC and HTC laminates are identical.

Figure 6. Compression strength vs. graphite content for RTC and HTC laminates.
As is seen in Figure 8, graphite forms a weak interface with the epoxy resin. It is also known that graphite has a higher modulus compared to the epoxy resin and is also harder. Here, we have a situation wherein the two different epoxy resins have hard particles uniformly distributed in them and having a weak interface. It is also known that the HTC epoxy resin is more cross-linked than the room temperature cured epoxy resin for the same degree of cure and is hence more brittle [16].

It has been suggested that if a matrix is ductile, void or hole generation owing to separation of a particle from the matrix will generate inhomogeneous deformation in it in the form of shear bands or plastic deformation in the matrix [17]. This region, called the modified zone around the hard particle, will not make its presence felt in the more brittle HTC resin as much as in the case of RTC resin. Ye and Pearson [18] found that epoxy resins possessing lower cross-link density were easily toughened. Based on these grounds, it is argued that toughen-

Figure 7. Compression strain vs. graphite content for RTC and HTC laminates.

Figure 8. SEM photograph showing the graphite-epoxy weak interface.
ing from hard particles is possible only in inherently ductile matrices. In brittle matrices, it is generally believed that the presence of hard particles with inadequate adhesion with the matrix will form voids that will generate a crack due to stress concentration, and a premature failure in the brittle matrix will occur.

However, some workers have suggested toughening of brittle materials by incorporation of hard particles under certain circumstances [19,20]. According to them, this is achieved through crack pinning or crack deflection [21] at the hard inclusions. This concept is similar to the strengthening of metals from dislocation pinning. The results obtained in the mechanical tests are a manifestation of these various mechanisms.

ILSS has been recognised to be a matrix dominated phenomenon. The portion of the graph up to 4 wt% graphite in Figure 1 and Figure 2 clearly demonstrates this view, wherein even very small additions of a hard particle having a weak interface with the matrix bring down the ILSS drastically. It is known that a weak interface site like that of the graphite/epoxy can generate a few cracks but one such site can blunt or deflect only fewer of such cracks. The statistical aspect of such events in the Graphite/epoxy interfacial sites needs investigation. It is also known that only cracks initiated in the favourable direction can propagate as governed by the state of stress. A large fraction of graphite particles are sandwiched between the glass fabric and are hence in the direction of shear, as a result of which more blunting of the cracks or crack detour takes place. The marginal increase in ILSS observed at 6 wt% graphite may be explained as being the result of increased crack pinning or crack detour occurring at the hard graphite particles. From the foregoing deliberations it may be suggested that ILSS up to 4 wt% graphite is matrix dominated and above that it is influenced more by the graphite/epoxy interface.

The decrease in the observed values of ILSS for the 5 mm width specimens in comparison to the 10 mm width specimens may be explained by studying the fibre

![Figure 9. A typical fibre pull-out on the tension side of an ILSS beam.](Image)
mats. In brittle materials with inadequate particle indentation, a crack due to the matrix will occur. According to the flaw propagation [21] at the hard particles from dislocation and the manifestation of these flaws. The portion clearly demonstrates having a weak interfacial bond, known that a weak few cracks but one statistical aspect of investigation. It is also propagation can propagate as the particles are sandblasted, as a result of shear, as a result of the ILSS between the particles and that ILSS up to 4 mm width specimens in particular studied by observing the fibre

\[ \text{Table 2.} \]

<table>
<thead>
<tr>
<th>Specimen</th>
<th>(1) Pullout µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>RTC (6 wt.% graphite)</td>
<td></td>
</tr>
<tr>
<td>10 mm width</td>
<td>296</td>
</tr>
<tr>
<td>5 mm width</td>
<td>340</td>
</tr>
<tr>
<td>RTC (unfilled)</td>
<td></td>
</tr>
<tr>
<td>10 mm width</td>
<td>300</td>
</tr>
<tr>
<td>5 mm width</td>
<td>340</td>
</tr>
<tr>
<td>HTC (6 wt.% graphite)</td>
<td></td>
</tr>
<tr>
<td>10 mm width</td>
<td>450</td>
</tr>
<tr>
<td>5 mm width</td>
<td>540</td>
</tr>
<tr>
<td>HTC (unfilled)</td>
<td></td>
</tr>
<tr>
<td>10 mm width</td>
<td>420</td>
</tr>
<tr>
<td>5 mm width</td>
<td>490</td>
</tr>
</tbody>
</table>

pull-out from the matrix in SEM and by consideration of the nature of 4 harness satin weave glass fabric used. Thus, examining fracture feature of the failed specimens in the SEM, it was found that the extent of fibre pull-out from the matrix for the 5 mm specimens was greater than those of the 10 mm width specimens. A typical pull-out is shown in Figure 9. The average pull-out distances are tabulated in Table 2.

The four harness satin glass weave used is shown pictorially in Figure 10. The interlacing points determine the integrity of the fabric. Hence, if two specimens are chosen which differ only in their widths, the one that has a smaller width will have lesser number of interlacing points along the width. When mechanically tested (as in the determination of ILSS), the fibres in the specimen of smaller

![Figure 10. A photograph giving details of four harness satin weave.](image)
width will pull-out from the matrix to a greater extent, due to the weaker transverse reinforcements (interlacing points), which are known to be potential locations of load redistribution and shear. The lower values of ILSS for the 5 mm width specimens on an average has been attributed to the ease of fibre pull-out from the matrix.

As discussed earlier, many properties seem to be matrix dominated up to around 4 wt% graphite and interface influenced for larger additions. Figures 3–7 emphasise the above-said aspect. Deflection at shear failure, transverse modulus in tension and the compressive strength and strain exhibit a change in the trend at 4 wt% graphite. The RTC resin is less brittle, crosslinked to a lesser extent and has a stronger interface with the particulate graphite additions than the HTC resin.

The trends in deflections at failure in the interlaminar mode as shown in Figures 3 and 4 are similar to the strain values in compression tests reported in Figure 7 indicating that the ILSS behaviour is a compression dominated phe-

\[
\text{Table 3.}
\]

<table>
<thead>
<tr>
<th>Graphite Wt. %</th>
<th>Shear Strength in Compression ((\sigma_c)) MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RTC</td>
</tr>
<tr>
<td>0</td>
<td>55.2</td>
</tr>
<tr>
<td>2</td>
<td>50.3</td>
</tr>
<tr>
<td>4</td>
<td>48.8</td>
</tr>
<tr>
<td>6</td>
<td>42.5</td>
</tr>
</tbody>
</table>
The shear related behaviour of glass fabric reinforced epoxy composites

As shown in Figure 5, the shear strength of the composites is lower than the ILSS. This phenomenon is due to the weak interfacial bonding between the matrix and the fibres, which are known to be potential failure points. Lower values of ILSS for the 5 mm width specimens is attributed to the effect of fibre pull-out and matrix crack propagation.

Figure 12. Fibre-bridging observed along the angle of break.

The shear strength of the composites is lower than the ILSS due to the weak interfacial bonding between the matrix and the fibres. This phenomenon is due to the weak interfacial bonding between the matrix and the fibres, which are known to be potential failure points. Lower values of ILSS for the 5 mm width specimens is attributed to the effect of fibre pull-out and matrix crack propagation.

The shear strength in compression was calculated as described in the earlier section. The average angle of break observed, as shown in a representative SEM fractograph in Figure 11, was determined for each parameter. The calculated shear strengths in compression are as tabulated in Table 3.

It is noticed that the shear strength in compression is lower than the ILSS. This difference perhaps can be traced to the material geometry used, test configuration employed and absence of free edge effects in compression where the inplane loading configuration enables an angled break to cause significant fibre bridging as shown in Figure 12. At about 6% graphite addition the shear strength in compression becomes comparable to the ILSS of the unfilled specimens.

CONCLUSIONS

From the results of this study the following important conclusions emerge.

1. The initial decrease in the ILSS which is observed up to 4 wt% graphite in all the cases has been attributed to the formation of more weaker interfaces (graphite/epoxy) within the matrix thereby leading to more crack initiation events. But as the graphite addition is increased, the ILSS improves due to the increase occurrence of crack pinning and crack deflection which occur at the hard graphite particles. In this sense, it may be said that the ILSS test results suggest a transition from matrix dominated mechanical behaviour to an interface controlled one at around 4 wt% graphite additions.

2. The ILSS of the 5 mm width specimens were, on an average, less than those
of the 10 mm specimens because of the role played by the transverse interlacing points on the pull-out characteristics of the axial fibres. It was also seen that the addition of a particulate filler like graphite did not have any influence on the "width effect" noticed in the deflection at failure for the above mentioned specimens.

3. The transverse modulus of both the RTC and HTC laminates show an initial increase and then decrease appreciably in the case of Room Temperature Cured resin but only marginally in the case of High Temperature Cured resin. Above 4 wt% graphite, the influence of the interfaces supercede the effect of the rule of mixtures.

4. The compression strength and strain of the RTC specimen shows an increase up to 4 wt% graphite owing to the increased plasticity of the resin surrounding the graphite particles. The compression strength and strain of the HTC samples show an identical behaviour as in the case of ILSS. For the test condition and material geometry employed the shear stress in compression is seen to be more than the ILSS.

ACKNOWLEDGEMENTS

The authors thank the Chairman, Dept. of Metallurgy for the encouragement and facilities extended. The support and encouragement extended by The Head, Materials Science Division and The Director, National Aerospace Laboratories are greatly appreciated.

REFERENCES

The Shear Related Behaviour of Glass Fabric Reinforced Epoxy Composites