Effect of dispersing CTBN into Diglycidyl Ether of Bisphenol-A on Mixed mode Loading

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Abstract
Delamination of polymer composite is one of the major failure characteristic, in this context the fracture behavior of the tailored composites in combination of opening mode and shearing mode is assessed and its fracture robustness of the glass fiber reinforced laminate are determined experimentally, in this present work by developing a modified Arcan fixture using a single edge notched specimen for characterizing in various loading conditions, The fixture was made of industrial grade Aluminum ingot machined to an outer diameter of 150 mm, having a thickness of 10 mm. The fixture had provision to load the sample at different oblique angles up to 90 degrees in steps of 15 degrees. The samples were attached to the fixture by means of fasteners and were tested in tensile mode using a 40 KN Instron tensile tester at constant displacement and ambient conditions. Further, the resin was strengthened with Carboxyl Terminated Butadiene A纶onitrile (CTBN) and its effect on fracture parameters was studied by varying the loading angles. Results indicate that the fracture parameters vary with loading and at angles greater than 45 degrees, the GFRP sample’s behavior changes from opening mode to shearing mode and the converse is also true. This pattern is similar, with the specimens even after modifying the resin with CTBN however, it was found that stress intensity factor increased corresponding to the increase of CTBN infusion. CTBN was dispersed into the Bisphenol base A (LY566 – A general purpose thermoset epoxy resin) in three different percent: 1%, 3% and 5% by weight. The layup sequence used in this work was cross ply. The effect of varying the loading angles on the stress intensity factors were studied.

Keywords: mixed, mode, modified arcan fixture, CTBN, loading angles

Introduction
Presently the polymeric composite has gained a steady entry in various field from sports industry to space technology. The researchers are always on their toes to seek a better material and contain its growth against crack growth. The failure can occur without warning and can begin with matrix cracking, fiber pull out and debonding of plies. The failure can be sudden and without a fore warning. [1-5]. One simple method to enhance the strength is to add some additives to the thermoset polymer otherwise prone to brittleness and weak in resisting the loads. These fillers are dispersed into the resin and with the addition of these institute deposition filler materials, enhances the strength of the polymer and thereby increases the fracture toughness, particularly the rubbery materials to the thermoset polymer. With the controlled polymerization reaction between the epoxy and CTBN, a phase separation ensues leading to the improved fracture characteristics also bettering thermal and mechanical characteristics. A number of studies [6-10] involved in the modification of the reactive rubber with epoxy resin particularly CTBN. This elastomer when dispersed into the resin, enhances the toughness of the neat resin specimens., while minimal modification led to thermal and mechanical characteristic. [10-12]
The main objective of this paper is: 1. To develop a fixture which can be utilized to determine the mixed mode characteristics. 2. Quantify the fracture parameter with the same sample under various loading angles and hence study the effect of loading angles on the fracture behavior by strengthening the thermoset polymer by CTBN.

Materials and Methods

The diglycidyl ether of bisphenol-A (DGEBA)-based epoxy resin (viscosity: 1000–1500 mPa s at 27 °C) used in all experiments was LY 5566 with an epoxide equivalent weight of 192 g/ equiv, as determined by titration. The curing agent was an aliphatic compound TETA, commercially available from M/S Huntsman, Chennai by the trade name HY951. The elastomer employed for this work was carboxyl terminated butadiene acrylonitrile (CTBN) was obtained from M/S Zibo chemicals, Shandon, China, and it had a viscosity of viscosity: 625,000 mPa s at 27 °C, Figure 1, with a molecular weight of 3500 containing acrylonitrile content 27% and carboxyl content 32%. A 450 GSM stitched woven unidirectional E-Glass mat was supplied by M/S S. T. Composites, Chennai.

Fixture development

One of the important problems in material testing is to design a fixture and specimens to produce a plane state of stress in all materials and more so for the composite materials, since the composites are often employed as laminates. Perhaps, if a single specimen is available, for off-axis loading, and preferably, if the fibers are oriented at an angle with respect loading angle then plane stress condition ensues. Originally in 1978, Arcan developed this fixture, where the sample had a notch and the fixture can be rotated, [Arcan, 1978]. If the notch of the sample is 90 degrees then the sample is undergoing Mode-I type of loading and if the fibers are parallel to the loading angles, the samples suffer mode-II loading. All fixtures are the successors of the fixture developed by Arcan, Figure 2(a-d). The configuration in figure 2d is the fixture developed for the mixed mode testing of the GFRP samples strengthened with CTBN. An Aluminum block was obtained from M/S Alli Metals, Guindy, Chennai. The block was machined to dimensions having diameter 150 mm with a wall thickness of 10 mm. The machined fixture shown in figure 2d.
A state of pure shear can be obtained by varying the loading angle and a combined stress state is achieved in the test section. Jurf and Pipes (1982) used this Arcan fixture to produce fracture mechanics data for adhesively bonded composite joints but the samples were bonded to the fixture figure. But in this present work the earlier fixture is modified to hold a single edge notched specimen by means of fasteners. The modified fixture had two pairs of 6.4 mm thick aluminum parts. Each pair was equal to one half of the original fixture and was mounted from a circular disk. A 3.2 mm deep trapezoidal cut was machined in each part to host the specimen. As a result, a specimen of up to 6.4 mm thickness could be tested using a fixture. Three holes were drilled at the cut-out section in each part for tightening two parts together with bolts. In addition, the bolts could prevent the specimen from slipping and provide a smooth load transfer.

In each part, several 6.4 mm diameter holes were drilled near the edge along the circumference of the plate. These holes were designed for load application through a pin yoke system and for tightening each pair of fixture plates together. They were located at angles starting from 0 degrees to 90 degrees and the angles were varied in steps of 22.5 degrees, figure 2d.
Sample Fabrication

A known quantity of DEGBA was taken in a borosilicate graduated beaker and was thermally heated to a temperature of 100°C for an hour, also it was constantly agitated, in order to entrap the air bubbles. To his thermoset resin CTBN was added gently by weight in proportion to the resin. The various percent of CTBN was added to the Resin was: 1, 3 and 5 %. The mixture was cooled to the room temperature and then the polymerizing agent TETA was added again the ratio of 100: 100: 10; resin : fiber: hardener. A laminate was demolded from an aluminum mould. Then these samples were post cured at 200°C for 2 hours After that the samples were machined into the required configuration as shown in figure 4. The woven roving mat was utilized in casting the laminate of 9 layers each constituting of cross ply, and the laminate had a thickness of 6.5 mm with a fiber volume fraction of 0.45. Similar procedure was adopted to fabricate the samples after treating the DEGBA with CTBN by varying its percentage of about 1 %, 3 % and 5 % by weight of resin. Figure 3, shows the sample geometry without CTBN modification.

Mathematical formulation and Modeling

Consider a portion of the fixture and the specimen attachment. F is the load applied through the yoke, which transfers the load on the specimen geometry smoothly with the crack width and the farfield angle, the loads on the crack front can have two components., figure 4.

Fig. 3. Sample for mixed mode testing
Fig. 4. Specimen loading geometry

\[ \sigma_x = \sigma \sin \alpha \]  \hspace{1cm} (1)

\[ \tau_x = \sigma \cos \alpha \]  \hspace{1cm} (2)

Where the stress is in terms of load and area of the section where the starter crack is considered with a finite width. Basing on the normal and shear stress components the stress intensity factors for opening mode and the shearing mode can be obtained as:

\[ K_I = \left( \frac{P \sin \alpha}{w \cdot t} \right) f_I \left( \frac{a}{w} \right) \]  \hspace{1cm} (3)

\[ K_{II} = \left( \frac{P \cos \alpha}{w \cdot t} \right) f_{II} \left( \frac{a}{w} \right) \]  \hspace{1cm} (4)

Where \( f_I \) and \( f_{II} \) are the calibration factors and they are obtained by numerical analysis. Numerical analysis was carried out by using the finite element software using Abaqus, the analysis is performed at constant load. The fixture and the specimen were modelled using an eight noded quadrilateral element generating a mesh, figure 5 and refining it at the crack tip, figure 6, with an elemental size of 0.02 mm.
A finite element analysis under plain strain condition was used to determine root square stress field singularity, and to obtain singularity term of the crack tip stress field, the elements around the crack tip and the mid side nodes were moved to a quarter point of each element side. And thus, the calibration factors were obtained as

$$f_I (a/w) = 1.12 - 0.231(a/w) + 10.35 (a/w)^2 - 21.27 (a/w)^3 + 30.39 (a/w)^4$$

and

$$f_{II}(a/w) = (1.122 - 0.56 (a/w) + 0.085 (a/w)^2 + 0.18 (a/w)^3) / (1 - (a/w))^{1/2}$$

From the expression 3 and 4 we can observe that the ratio $a/w$ can be varied to study the its influence on the corresponding stress intensity factor. Also noting that $a$ is the initial length of the starter crack, $w$ being the width of the geometry. Indicating that when $a=w$, the sample has failed completely. While the mixed mode can be obtained by obtaining the ratio of $K_I$ to $K_{II}$.

**Test procedures**

Prior to the sample preparation, reactivity test and thermal analysis were conducted the reactivity was performed to assess the gel and cure time, gel and cure temperature because the addition of CTBN into the thermoset resin will alter performance of the virgin resin. A known quantity of DGEBA and CTBN were mixed in a glass beaker and put in a water bath with a temperature of 70°C. A thermocouple was used to measure the temperature and the other parameters. Perkin Elmer differential scanning calorimeter was employed to determine the $T_g$ of both untreated and treated samples. Samples of about 8–10 mg were heated at a rate 10°C min $^{-1}$ in a nitrogen atmosphere over the temperature range from 30°C–100°C.

In fracture mechanics testing all the fracture modes are related to the loading either opening, shear and out of plane load conditions. A safe assumption the flaw propagates at the pre-existing crack plane, hence initially the loads at which the failure occurs were determined using the tensile tests and were noted for each layup sequence, these tests were repeated thrice and average values were used in determining the stress intensity factors. All test was done with open loop servo hydraulic universal testing machine with a constant cross head speed of 0.25 mm/min. From the test data the stress intensity factors were determined for pure opening mode, sliding mode and combination of both the modes.

**Results and Discussions**

The following properties like gel time, cure time, gel temperature and cure temperature were the object of the tests. It was found that the gel time and cure time increased with the CTBN content in the thermoset polymer, can perhaps be attributed due to the fact that movement of the reactive molecules. While the gel temperature and cure temperature were higher for all values of CTBN content, which was relatively higher than those of the untreated resin content, figure 7.
Fig 7. Effect of CTBN percent on gel time and temperature, cure time & temperature

The $T_g$ values for all of the CTBN-modified epoxy samples are lower than those of the unmodified epoxy are. This decrease in $T_g$ values can be attributed to the fact that a chemical interaction occurred between the CTBN and the polymer phase. This implies that a larger amount of CTBN led to better interaction with epoxy and hence better crosslinking, Figure 8. In other words, the amine reactions formation of hydrogen bonds stabilizes the transition state while the reaction rates are accelerated. Larger addition of CTBN might have accelerated the curing rate. The carboxyl content present in the co-polymer has influenced the curing rate.

Fig. 8 Effect of CTBN percent on transition temperature

The relationship between the non-dimensional stress intensity factors and the loading angle is shown in figure 9 for a/w ratio of 0.8. It can be seen that for loading angles less than 60 degree, the mode-I fracture is dominant and as the mode-II loading contribution increases, the mode-I stress
intensity factor decreases and the mode-II stress intensity factor increases. For loading angles greater than 60-degree mode-II fracture becomes dominant. This pattern is true for the laminates enhanced with CTBN.

![Figure 9 Effect of the calibration parameters on the loading angle](image)

All the samples for different stacking sequence were mounted on to the fixture and were tested on an open loop servo Universal test machine, with constant displacement mode. Gradually the fixture was rotated the samples were tested for different loading angles. Peak loads were obtained in static mode and were used to determine the stress intensity factors using equations 3 and 4. The mixed mode results are obtained by considering the natural logarithms of the ratio of $K_I/K_{II}$. The stacking sequences were considered along with various CTBN percent. The result is presented for mode-I, mode-II and mixed mode for various CTBN infusion and for each stacking mode. Fracture tests were carried out on UTM in tensile mode, the samples were fastened to the fixture and tested under constant displacement at the rate of 0.5 mm/min. The tests were repeated for consistency. The average values were utilized for determining the stress intensity factors. The laminate was loaded under pure mode-I loading, in mode-II. The mixed mode behavior was exhibited by the samples when the loading angles were between 55 and 65 degrees. All the graphs were plotted for the stacking sequence of 0°/90° with 9 layers and at a CTBN dispersion percent of 1, 3 and 5 by weight. It can be noticed that the stress intensity behavior was same irrespective of the percent CTBN diffusion. The calibration factors helped in understanding the fracture behavior. Then the mode-I stress intensity factors were obtained by fitting a polynomial inclusive of the critical loading. The mode-II stress intensity factors increased.
Fig. 10. Unmodified stress intensity factors for Mode-I

Fig. 11. Mode II- Unmodified stress intensity factors

Fig. 12. Mode-I Stress intensity factors for 1% CTBN dispersion

Fig. 13. Mode -II stress intensity factors for 1% CTBN dispersion

Fig. 14. Stress intensity factors for 3% CTBN dispersion for Mode-I

Fig. 15. Mode-II stress intensity factors for 3% CTBN dispersion.
Fig. 16. Mode-I Stress intensity factors for 5% CTBN

Fig. 17. Mode-II stress intensity factors for 5% CTBN

Fig. 18. Mixed mode stress intensity factors

Fig. 19. Mixed mode factors for 1% CTBN

Fig. 20. Mixed mode factors for 3% CTBN

Fig. 21. Mixed mode factors for 5% CTBN
The data presented in figures 9-10 show the variation of the non-dimensional stress intensity factors against the loading angles by rotating the fixture and the effect of varying a/w. Series of curves are obtained. As the loading varies the opening mode values decrease, while the shearing mode values increase. Figures 11, 13 and 15 represent the variation of the non-dimensional stress intensity factors for mode-I for different CTBN infusion into the resin system, comparing the figures the stress intensity factors increase against the unmodified thermoset resins. While the figure 12, 14 and 16 represent the sliding mode stress intensity factors for different CTBN dispersion at 1%, 3% and 5% respectively. Again, as expected the fracture parameters improved significantly. The mixed mode parameters are presented in figure 17, indicating that beyond the angle 65 degrees the mode-I behavior changes to Mode-I, the figures 18-20 represent the non-dimensional mixed mode stress intensity factors. Curing of the resins is one major contribution to forming crosslinking with the reactive agents, and mechanical properties are dependent on the level of curing. And lowering the Tg which is an established fact. Improving the mechanical properties can be achieved by the addition of the fillers to the resin systems, the size, topology of the fillers varies in size and shape, another requirement is that the filler must dissolve in the resin and participate in the curing process. Carbaryl terminated butadiene acrylonitrile satisfies the both requirements. The addition of CTBN reduces the Tg, figure, stiffness, increases CTE and plasticizes the resin system, and increases the fracture toughness. These particles yield, tear, stretch, bifurcate, crack bridging, debonding, crack path deflection and pinning, thus crack tip bluntness ensues and leading to increase in the fracture toughness. [12], all these phenomena are represented schematically in figure 21.

![Fig. 22 Crack propagation model](image)

The unmodified values and the modified stress intensity factors in opening and sliding mode is presented in table 1.
Table 1 Mixed mode stress intensity factors

| Loading Angles | KI 0.5 MPa m | KII 0.5 MPa m |
|----------------|--------------|--------------|
|               | UM 1% 3% 5%  | UM 1% 3% 5%  |
| 0             | 7.09 22.79 25.911 39.86 | 0 0 0 0 |
| 22.5          | 6.589 21.055 21.316 38.29 | 0.5500 1.650 2.0633 2.887 |
| 45            | 5.3686 16.114 20.301 28.286 | 1.0100 3.01 3.789 5.311 |
| 67.5          | 2.89 9.634 12.01 15.288 | 1.321 3.974 5.113 6.952 |
| 90            | 0 0 0 0 | 1.428 4.30 5.556 7.499 |

Conclusions

The mixed mode fracture mechanics parameters were determined for CTBN enhanced GFRP samples using the modified Arcan test specimen. Various percent of CTBN was infused into the brittle epoxy to toughen it. Finite element analysis is used to evaluate the effect of crack length on fracture criterion. The geometric calibration factors were obtained for both the modes of loading. The same calibration parameters were used for both modified and unmodified coupons. CTBN enhanced the fracture parameters but did decrease the Tg, and the particles provided a meandering path for the crack to propagate, ensuing the crack tip bluntness and hence the increase in fracture toughness.

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