Influence of nanoclay on interlaminar shear strength and fracture toughness of glass fiber reinforced nanocomposites

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Abstract. Multilayer glass fiber reinforced polymer (GFRP) laminates filled with nanoclay was manufactured with compression moulding machine. In the present work, five kinds of nanoclay (Cloisite 25A) loadings viz. 2, 4, 6, 8 and 10% on weight basis of epoxy resin were employed to modify the interlaminar shear strength (ILSS), critical energy release rate (Glc) and impact energy properties of GFRP laminates. Experimental results obtained from ILSS test on clay filled GFRP confirm that the superior strength was attained at low clay content of 155.10 MPa. Furthermore, the mode I interlaminar fracture toughness test conducted on DCB specimens revealed that the commanding improvement of Glc was obtained at 2 wt.% clay content level. On the other hand, both ILSS and fracture toughness was getting reduced at higher clay loadings. At last, the impact strength of the test samples was investigated by using Izod impact test apparatus and observed that the impact energy was increased by 44.39% for 2 wt.% and followed by 24.87% for 4 wt.% clay loadings.

Keywords: Nanoclay; Cloisite 25A; ILSS; Impact strength; Mode I; Interlaminar fracture toughness
1. Introduction
In recent years, lightweight glass fiber reinforced polymer (GFRP) has been widely applied in many engineering components like automobile parts, windmill blade, aerospace parts, toys, ships, marine, armor and sporting goods [1-3]. However, for the GFRP composites panels, the mechanical performance in the in-plane direction is slightly greater than that of the out-of-plane direction, which results in interlaminar delamination in laminates. The interlaminar delamination or fracture is the important failure mode for the GFRP composites, which will reduce the material performances [4-5]. Therefore, many techniques have been used to improve the interlaminar toughness of laminates through toughening the matrix, addition of toughened polymer layers, through-thickness stitching, and three-dimensional weaving. The toughening of the matrix is attained by incorporating the organic and inorganic fillers in the matrix like nanoparticles (like rubber particles, silica particles), nanoclays, nanotubes, nanofibers [3,6,7]. Tsai et al. enhancing the fracture toughness of composites through modifying the epoxy resin by adding the nano silica particles into the rubber and formed a hybrid epoxy matrices. The nano-silica particles had compensated the stiffness reduction caused by the rubber particles [5]. Even though the epoxy is modified with different carbon nanofillers like carboxyl carbon nanotubes, unfunctionalized carbon nanofibers, glycidoxypropyl-trimethoxysilane carbon nanotubes (GPS-CNTs) and nanofibers, the highest improvement of mode I and mode II toughness of 79% and 91% were attained for GPS-CNTs modified glass fiber/epoxy composite [8]. Grimmer and Dharan observed that both critical and sub-critical toughness interlaminar fracture toughness were increased when a small amount multi-walled CNT was added to the matrix of glass fiber composites [9]. Similarly, Gojny et al. investigated the interlaminar shear strength (ILSS) of carbon-based nanoparticles in epoxy resins and observed that a 19% increase of ILSS was attained at low volume fraction [10]. Kasar Iqbal et al. tested the impact resistance of carbon fiber reinforced polymer (CFRP) with nanoclay filled epoxy nanocomposites by low velocity impact test and noticed that the lower value of nanoclay addition less than 3 wt% in the matrix showed low impact resistance than that of the neat epoxy laminates, whereas up to 3 wt% addition proved that both damage resistance and damage tolerance were improved.

High crosslink epoxy resin has commanding heat resistance and good chemical resistance. Therefore, it is majorly employed as a matrix for epoxy based GFRP laminates among various thermosetting polymers [12]. In an attempt to enhance the interlaminar fracture toughness of based GFRP composite laminates, the typical approach is to add a lower amount of nanoclay [13]. Nanoclays are inexpensive natural layered mineral silicates and based on chemical composition, clays are varied as montmorillonite, bentonite, kaolinite, hectorite, and halloysite. However, in the past few decades, many researchers have raised much attention to using 2:1 layered montmorillonite (MMT) nanoclay with a plate structure to toughen matrix [14 - 16]. Generally, if nanofillers dispersed in the matrix as exfoliated manner which provides good mechanical performances than intercalated dispersion [17]. However, due to the hydrophilic nature of the MMT nanoclay, the dispersion in the epoxy resin is generally made as intercalation with low exfoliation. Furthermore, the dispersion of clay/epoxy resin suspension is achieved by improved interfacial interaction and d-spacing between layers, which is attained by high-speed stirring, pressure, and temperature [3, 18 - 20].

In this research work, Cloisite 25A nanoclay have been employed (viz 0%, 2%, 4%, 6%, 8%, and 10%) to modify the Araldite LY 556 epoxy resin with the advanced processing techniques and HY 951 hardener is used as a curing agent. Based on the above actualities, the nanocomposite laminates are manufactured. The interlaminar shear strength, critical strain energy release rate (Glc) for Mode I fracture toughness and impact energy are calculated.

2. Experiments
2.1. Materials
In the current work, natural Cloisite 25A MMT nanoclay is used to modify Diglycidyl ether of Bisphenol A (DGEBA) based epoxy (trade name: LY 556). This clay is modified with a quaternary ammonium salt (-Hydrogenated tallow alkyl methyl-2-ethylhexyl ammonium salts with bentonite). The clay was purchased from Southern Clay Products, Inc. and mixed with epoxy in the weight of 0 wt.%, 2 wt.%, 4
wt.%, 6 wt.%, 8 wt.%, and 10 wt.%. Tri-ethylene Tetra Amine (TETA) hardener (trade name: Araldite HY 951) is used as curing agent. Both LY 556 resin and HY 951 hardener were supplied by Huntsman Advanced Materials and mixed in the ratio of 10:100 by weight. Furthermore, laboratory grade acetone was used to disperse clay and acting as a solvent. The plain woven E-glass fiber mat (aerial density of 200 g/m²) supplied by Saint-Gobain was used to reinforce in composite laminates.

2.2. Fabrication of nanocomposite laminates

In order to reduce the viscosity of epoxy, initially, it is heated up to 70 °C by using heating mandrel. Then the nanoclay was dispersed in acetone in the weight of 2 wt.%, 4 wt.%, 6 wt.%, 8 wt.%, and 10 wt.% separately. After that, the clay/acetone suspension was poured into heated epoxy and simultaneously by using mechanical stirrer the clay/acetone/epoxy suspension was stirred well. During the entire process, the temperature of the suspension was retained at 70°C. In order to remove the acetone completely, this process is continued for 30 min. Once the acetone removal was ensured, then with the aid of ultrasonicator the nanoclay/epoxy blend was stirred well for 30 min in order to eliminate the agglomeration. During this process, bubbles were formed and these bubbles were removed with help of degasification chamber. After that, the hardener was added to the mixture once the temperature of the matrix was cooled down to normal room temperature. By using compression molding machine the GFRP nanocomposites were manufactured by stacking 14 layers of glass fiber one-by-one and by applying nanoclay/epoxy blend between each layer using a paint brush. The curing process contains 80 °C temperature for 1 h with the pressure of 1500 psi and then followed by post curing at room temperature for 24 h. As per ASTM specification, the specimens were cut for ILSS, impact strength and Mode I interlaminar fracture toughness tests.

3. Material characterization

3.1. Interlaminar shear strength

Interlaminar shear strength was tested by conducting flexural test in three-point bending mode in Kalpak computerized universal testing machine (Model KIC-2-1000C) with a crosshead speed of 2 mm/min and a gauge length of 12 mm. Initially according to ASTM D 2344 standard, five replicate specimens of dimension 20 x 13 x 3 mm were cut from the laminates and ILSS property was derived from the following expression 1. Likewise flexural test setup, the ILSS test specimen was supported on two knife edges as a simply supported beam and the load is applied at its middle point.

\[
\text{Interlaminar shear strength} = \frac{3P}{4bt} \text{ (MPa)}
\]  

where \(P\)–Peak Load (N), \(b\)–Breadth of the specimen (mm), \(t\)–Thickness of the specimen (mm).

3.2. Impact and Mode I Interlaminar Fracture Toughness

Initially, for impact test according to ASTM D 256 standard, the specimens of dimension 62.5 X 12.5 X 3 mm were cut and the test was carried out in Izod impact test apparatus under 0 to 4 J scale. Further, according to ASTM D5528-01 standard, the double cantilever beam (DCB) specimens were cut to the dimension of 125 X 25 X 3 mm from the laminates as shown in Figure 1. The Mode I interlaminar fracture toughness was determined by using Kalpak computerized universal testing machine (Model KIC-2-1000C) with a crosshead speed of 2 mm/min.
A non-adhesive Teflon film of 12.5 µm thickness was inserted in the mid-plane of the laminate for 50 mm length (from the front end) during the manufacturing process of laminates which is used to initiate delamination. The aluminium hinges of 25.4 mm width were pasted as shown in Figure 2 by using epoxy adhesive at each end of DCB specimen arms. Initially, pre-crack is initiated at the end of the DCB specimen surface and after that, the tensile load was applied continuously at each end of the specimen for Mode I test. The Mode I critical strain energy release rate \( (G_{IC}) \) is defined as the amount of strain energy required for initiating a crack and if the load exceeds the critical strain energy, then the crack continues to propagate. During the test, the crack propagation is measured as the pull apart of crack surfaces due to the normal stress which is acting perpendicular to the crack plane. The load versus crack opening displacement curve was taken for analysis and the locations of instantaneous delamination front were marked for different intervals of delamination growth. In the present work, based on linear elastic fracture mechanics and beam mechanics, the fracture toughness is determined by using modified beam theory (MBT) which is based on Irwin-Kies equation 2.

\[
G_{IC} = \frac{3P \delta}{2B (a + |\Delta|)}
\]

where \( P \) is applied load, \( \delta \) is crosshead displacement, \( B \) is specimen width, \( a \) is crack length, \( |\Delta| \) is a correction factor needs to be added to crack length to allow crack tip rotation at the root of the cantilever beam and \( |\Delta| \) is the x-axis intercept when the cube root of compliance \( (C^{1/3}) \) is plotted as a function of crack length \( (a) \). The compliance \( C \) is the ratio of crosshead displacement to the applied load \( (\delta/P) \).
As shown in Figure 2, the bridging fibers are used to improve the resistance to delamination and increase the energy release rate with respect to the crack length. This effect is referred as the R-curve (Resistance curve) and in R-curve the values of $G_{IC}$ are plotted as a function of crack length [21].

4. Results and discussion

4.1. Interlaminar shear strength

Figure 3 shows the interlaminar shear strength (ILSS) of unfilled and nanoclay filled GFRP laminates. The graph shows that the unfilled GFRP composite laminates have ILSS of 91.16 MPa and the highest percentage increase of 70% (155.10 MPa) is attained for 2 wt.% content level than unfilled GFRP composite. Generally, the ILSS is a matrix dominant property, and better interfacial adhesion, enhanced bonding nature and unique phase morphology between the epoxy resin and nanoclay have improved the ILSS property greatly for clay filled GFRP composite. Further, it is clear from the graph that for high clay content the percentage increase of ILSS is slowly getting down. Especially at 10 wt.%, the interlaminar shear strength was decreased to 3% (88.43 MPa). This phenomenon is due to more ordered clay particles within this specimen are acted as flaws or crack initiators instead of reinforcements. Lim et al 2006 analysed the effect of nanoparticles with the polymer matrix and observed that the geometry interface may also influence the ILSS by modifying the contact surface of nanoparticles with matrix [22].
4.2. **Impact strength and Mode I interlaminar fracture toughness**

From Table 1, it is observed that the greater impact energy is attained for all nanoclay filled GFRP nanocomposites. Further, for unfilled GFRP laminates, 2.05 J impact strength is attained and the addition of the nanofillers leads to a greater percentage increase of 44.39% for 2 wt.% clay loading is observed. This phenomenon is due to the strong upholding of nanoclay with epoxy and glass fibers which results in strong bonding made between fiber and nanoclay modified matrix. Moreover, during impact test, both clay and glass fiber takes up the impact energy excited on it. Hence, more impact energy is needed for debonding fibers from modified matrix. Thus, commanding increase of impact energy occurs for all nanoclay filled GFRP nanocomposites than unfilled GFRP composite. According to research work of Dorigato et al [23] in laminates, damages occurred during impact test were due to matrix cracking, delamination and fiber failures, and toughening effect due to clay nanoplatelets.

![Figure 3. ILSS of nanoclay filled nanocomposites](image)

**Table 1. Impact energy of GFRP laminates**

| Details of the specimen | Impact Energy (J) | % Gain or Loss |
|------------------------|-------------------|----------------|
| 0 wt.%                 | 2.05              | Nil            |
| 2 wt.%                 | 2.96              | 44.39          |
| 4 wt.%                 | 2.56              | 24.87          |
| 6 wt.%                 | 2.53              | 23.41          |
| 8 wt.%                 | 2.4               | 17.07          |
| 10 wt.%                | 2.29              | 11.71          |
The long-term fatigue life of composites materials are affected by interply delamination and it is considered to be the vital failure mode. Due to the specific stacking sequence, the unfavorable interlaminar stresses may exist at the free edges of composite materials which create interply delamination grows. According to the increasing number of cycles, the delaminated areas may develop firmly and it decreases the effective modulus of the composite. A number of test procedures have been designed to measure the Mode I interlaminar fracture failure by using the critical strain energy release rate ($G_{IC}$). Double-cantilever beam (DCB) is a common method which is used to measure interlaminar fracture toughness. The $G_{IC}$ is used to compare the resistance of different resins against the delamination failure. The image of the front view and top view of DCB specimen is shown in Figure 4 (a) and (b), respectively. In the present work, even though a variety of methods is used to find out $G_{IC}$, the compliance method is employed; due to the ability to reproduce results accurately from the experimental data of DCB test [24, 25].

The delamination resistance curve (R-curve) is used to express the relationship between crack length and Mode I interlaminar fracture toughness ($G_{IC}$) as shown in Figure 5. The crack initiation ($G_{IC}$-init) and steady-state crack propagation ($G_{IC}$-prop) values for all nano loadings are summed up in Table 2. The $G_{IC}$-init is defined as the first deviation from linearity and $G_{IC}$-prop is defined by a plateau on the R curve. For all nano loadings, $G_{IC}$-init is referred as the first value in each curve and these values were selected from the load-displacement curves. Moreover, the delamination was visually initiated on the edge and from R curves it was observed that for all nano loadings the initial values of fracture toughness are low. However, the R-curves increased further with the increment of delamination length after initiation.

![Figure 4. (a) Image showing front view of Mode I specimen, Figure 4 (b) Image showing top view of Mode I specimen](image-url)
Figure 5. Resistance curve of Mode I interlaminar fracture toughness

Table 2. Mode I interlaminar fracture toughness

| Nanoclay content | $G_{Ic}$-init (kJ/m²) | $G_{Ic}$-prop (kJ/m²) | Mode I fracture toughness, $G_{Ic}$ (kJ/m²) | % Gain or Loss |
|------------------|-----------------------|-----------------------|---------------------------------------------|---------------|
| 0 wt.%           | 0.94                  | 1.47                  | 1.22                                        | --            |
| 2 wt.%           | 2.04                  | 2.94                  | 2.67                                        | 118.85%       |
| 4 wt.%           | 1.17                  | 1.48                  | 1.33                                        | 9.01%         |
| 6 wt.%           | 1.50                  | 2.13                  | 1.91                                        | 56.55%        |
| 8 wt.%           | 1.15                  | 2.02                  | 1.69                                        | 38.52%        |
| 10 wt.%          | 0.80                  | 0.85                  | 0.77                                        | -36.89%       |

At this point, it is further observed that a rapid increase of $G_{Ic}$ is approximately made within 60 mm of crack growth in the specimens due to the existence of resin rich area in front of Teflon film. The curve almost reaches a plateau for 0 wt.%, 4 wt.% and 10 wt.% and it does not level off for 2 wt.%, 6 wt.% and 8 wt.% nano-filled composites. Further, it is noticed that crack growths for all specimens were entirely unstable with larger scatter. The $G_{Ic}$ values which are shown in Table 2 were taken from the average of plateau region of the R-curves. Moreover, it is observed from the Table 2 that the Mode I interlaminar fracture toughness was commandingly increased by 118.85% for 2 wt.% loaded laminates and followed...
by 6 wt.% loaded GFRP laminates of 56.55% increase. This phenomenon could be due to the fiber bridging effect as noticed in Figure 6 (a) and (b) [21]. Likewise, for 4 wt.% and 10 wt.% nano loadings, the resistance curves are assumed to be a plateau level due to poor insertion of the matrix between layers, which result in decreased adhesion strength between the adjacent layers. This effect, in turn, reduced fracture toughness and the stiffness of specimen is also affected the $G_{tc}$ values.

Figure 6. (a) Image showing initial crack at a distance of 50 mm Figure 6 (b) Image showing propagated crack at a distance of 100 mm

Figure 7 shows the Izod impact strength and Mode I interlaminar fracture toughness of the GFRP nanocomposites with different clay loadings. From both curves, it seems that the tougher matrix improved the impact strength and fracture toughness of the nanoclay filled nanocomposites commandingly at low clay content. Further, both curves look almost similar apart from 4 wt.% and 10 wt.%. 

Figure 7. Impact energy and fracture toughness nanoclay filled nanocomposites
5. Conclusions
The preliminary experimental results of the present study are aiming to assess the influence of the nanoclay loading rate on the interlaminar shear strength, impact energy and interlaminar fracture toughness of GFRP nanocomposites made by compression moulding machine. Based on the experiments conducted on laminates the following conclusions are made:

- The ILSS is found to be higher of 155.10 MPa (70% increase) at 2 wt.% clay loading and then followed by an increase of 64% (149.19 MPa) at 4 wt.% clay loading than unfilled GFRP composite.
- The impact test results showed that greater impact energy is attained for all nanoclay filled GFRP nanocomposites. The highest impact strength was recorded for 2 wt.% clay loaded laminates as 2.96 J with 44.39% increase.
- From the resistance curves for all clay content level is found that the initial values of critical strain energy release rate ($G_{ic}$) are low and it increases further with the increment of delamination length after initiation.
- Further, from the investigation of Mode I test, it is noticed that the $G_{ic}$ is optimally increased by 118.85% for 2 wt.% clay filled GFRP laminates and followed by 56.55% increases for 6 wt.% clay filled GFRP laminates than unfilled GFRP laminates.
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