Effect of nanoclay and nanoscale TiO₂ on carbon/glass fibre reinforced polymer composites

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Abstract
Nanofillers dispersion in polymeric matrix has been identified as a novel method to enhance the mechanical properties of Fibre Reinforced Polymer Nanocomposites (FRPCNs). In general, addition of nanofillers in polymeric resin improves the fracture toughness, tensile and other properties of polymer composites. On the other hand, this inclusion significantly reduces the stiffness, strain at rupture and thermal properties. To overcome these limitations, hybrid nanofillers have been introduced in polymer composites. This work aims to investigate the effect of addition of hybrid nanofillers (Nanoclay-TiO₂) on mode I interlaminar fracture toughness (GIC), tensile as well as flexural characteristics of carbon/glass/epoxy based composites. The pristine epoxy resin was modified with nanoclay and nanoscale TiO₂ nanofillers together with different weight percentages (0.5, 1, 1.5 & 2 wt%) using mechanical stirrer followed by sonication process. The modified epoxy based carbon/glass polymer laminates were fabricated using hand lay-up process. The lay-up sequence considered in this study was (90°C/90°G/0°G)₀, (90°G/90°G/90°C)_³ and (90°G/0°C/90°G)_₀. The mechanical properties of modified laminates were characterized by DCB test, tensile and three point bending test. The experimental results show that the addition of hybrid nanofillers in epoxy resin increased the mode I interlaminar fracture toughness (GIC) by 77% at 1.5 wt%, tensile strength by 31% at 1.5 wt%, and flexural strength by 33% at 2 wt%. Further addition of nanofillers (<2 wt%) decreases the mechanical properties of FRPCNs as a result of matrix embrittlement. The toughening mechanisms such as fibre pull-out, fibre breaking, particles debonding, and crack deflection were identified at the fractured surfaces.

1. Introduction

Fibre Reinforced Polymer Composites (FRPCs) have been largely used as a structural material in marine, aerospace, automobile and nuclear industries, thanks to higher strength-to-weight ratio and greater stiffness. In FRPCs, the epoxy resin is mostly used as a matrix material because it exhibits exemplary mechanical properties such as higher adhesion, low shrinkage and better chemical resistance. In general, the epoxy polymer matrix has low viscosity and facilitates good wetting characteristics with the reinforced fibres resulted larger fibre-matrix interaction. In spite of high strength-to-weight ratio and many other advantages, the epoxy based polymer composites have low interlaminar fracture toughness and offers low crack growth resistance. Delamination is a major failure mechanism in FRPCs and the occurrence of crack results in reduction of stiffness, strain, and other properties [1]. Therefore, numerous attempts have been made by the researchers to improve the mechanical properties of FRPCs without compromising its weight. Dispersion of nanofillers into polymeric matrix has been identified as one of the promising approach for improving the mechanical properties of FRPCs.

The addition of surface-modified silica nanoparticles in epoxy resin improves the fracture toughness and fatigue performance of polymer composites at low concentration [2–4]. The strong and sufficient bonding between epoxy and nanoparticles was responsible for the improved mechanical properties. However, higher
concentration of nanosilica leads to cluster of nanoparticles which eventually increase the brittleness of composites hence reduces the percentage of elongation at break. The carbon nanofibres (CNF) dispersion in epoxy resin enhances the monotonic fracture behavior, and tensile modulus of nanocomposites [5, 6]. Inclusion of small wt% of multi-walled carbon nanotubes (MWCNTs) into epoxy resin increases the tensile strength, elasticity modulus and impact properties of polymer nanocomposites. However, the contact stiffness of the nanocomposites decreases [7]. The functionalized carbon nanotubes (CNTs) inclusion in carbon fibre reinforced polymer nanocomposites (CFRPNCs) offer higher resistance-to-failure under both tension-tension and tension-compression cyclic loading. The formation of large covalent bonds between epoxy and fibre/fabric matrix interfaces was responsible for the improved fatigue resistance [8]. On the other hand, the CNTs inclusion decreases the mode I interlaminar fracture toughness of CFRPNCs. The perlite (Pr) particles incorporation in epoxy significantly enhances the interlaminar shear strength, tensile and flexural properties and decreases the thermal properties of glass fibre reinforced epoxy based nanocomposites [9]. The CTBN rubber particles inclusion in GFRPNCs increased the fatigue life about three to four times, thanks to cavitation and plastic deformation of the surrounding materials, whereas CTBN addition decreases the ultimate tensile strength and tensile modulus of GFRPNCs. In another work, the effect of inclusion of spherical-shaped dry alumina nanoparticles in polymeric resin was reported [10]. This addition improves the overall modulus and strength of CFRPNC, but this addition considerably decreases the strain to failure rate. Nanoclay has been identified as a potential filler material to enhance the mechanical properties of polymer composites [11–13]. The soft nanoclay incorporation in polymeric matrix makes intercalated and exfoliated clay–nanocomposites exhibited exemplary mechanical characteristics [14]. The nanoclay inclusion in epoxy up to 2 wt% improves the interlaminar fracture toughness, flexural strength, and fatigue life of glass/epoxy laminates [15–17]. The titanium dioxide is a well-known material in the field of aerospace and other light weight industries, thanks to its excellent mechanical and corrosion resistant properties. The nanoscale-TiO₂ dispersed epoxy resin shows improved ductility and high strain-to-failure properties on polymer composites. The high cross linking density and higher interfacial interaction among epoxy chains, improves the glass transition temperature and tensile properties of nanocomposites [18, 19].

The literatures reveal that the blending of nanofillers in epoxy resin significantly improves the mechanical properties of polymer composites. On the other hand, the nanofillers inclusion reduces the stiffness, strain at rupture and thermal properties. Hybridization of nanocomposites has been identified as a novel method to extend the concept of tailor-made mechanical properties to outfit the property requirements and to overcome the limitations of one component by the addition of other. Tsai et al [20] reported the effect of addition of silica nanoparticles combined with CTBN rubber particles on glass/epoxy based composites. The experimental results show that hybrid nanofillers inclusion significantly enhances the interlaminar fracture toughness, tensile strength as well as strain at rupture properties. Megahed et al [21] studied the impact of silica and carbon black nanoparticles upon GFRP composites. This study discloses that the incorporation of silica nanoparticles improves the tensile properties while the addition of carbon block enhances the impact strength of GFRP composites. Bajpai et al [22] reported the hybridization effect of soft block copolymer combined with rigid TiO₂ nanofillers in epoxy resin. The author reported that, the addition of block copolymer improves the fracture toughness and rigid TiO₂ nanofillers dispersion improves the tensile strength of modified polymer composites. The literature reviews demonstrate that the homogeneous dispersion of highly stiff materials at low weight percentages (0.5, 1, 1.5, and 2 wt%) in softer polymeric matrix improves the mechanical, electrical and chemical properties of polymer composites. These improved mechanical properties entirely depend upon the type, volume/weight fraction, aspect ratio, and orderly/randomly arrangement of nanofillers and size of interface zone [23, 24]. At the same time, further loading of nanofillers (>2 wt%) in epoxy resin significantly reduces the properties of polymer composites.

In recent years, the polymer composites with great diversity in mechanical properties have been developed by reinforcing two or more fibres in polymeric matrix. The reinforcement of carbon fibres in glass/epoxy composite provides greater toughness, good impact resistance, and larger energy absorption characteristics to the polymer composites [25–27]. Further, the strength of the hybrid polymer composites varies along with the stacking sequence, length and orientation of reinforced fibres [28, 29]. Numerous works has been carried out to study the effect of addition of nanofillers on mechanical properties of carbon or glass fibre reinforced epoxy based composites. However, no literature has been published so far on investigating the effect of addition hybrid nanofillers on carbon/glass/epoxy based composites. Hence, to investigate effect of inclusion of hybrid nanofillers on GFRPNCs is of significant importance. The main objective of this research work is to investigate the effect of addition of hybrid nanofillers (Nanoclay-TiO₂) and to analyse the influence of stacking sequence of fibres on mode I interlaminar fracture toughness, tensile as well as flexural properties of unidirectional carbon/glass/epoxy based polymer composites. In order to examine the effect of stacking sequence of carbon and glass fibres on mechanical properties, the carbon fibres are reinforced as exterior, interior and intermediate ply in glass/epoxy based polymer laminates. The FRPNCs were characterized through delamination, tensile and
flexural testing. The toughening mechanisms were analysed through surface morphologies of fractured specimens.

2. Material and methods

2.1. Materials

The highly cross-linked thermoset epoxy resin (Huntsman Advanced Materials Pvt. Limited, India) DGEBA (Diglycidyl ether of Bisphenol A) with density of 1.16 g cm\(^{-3}\) along with Triethylene tetra amine curing agent was used as matrix phase. The unidirectional carbon and glass fibres, procured from Binani industries limited (India) were used as reinforcements. The montmorillonite nanoclay (Cloisite 15A) of 1 nm thickness, 200–300 nm length with high specific surface area (750 g m\(^{-2}\)) and Nanoscale-TiO\(_2\) (<25 nm particle size) were used as nanofillers (Sigma-Aldrich chemicals, India).

2.2. Preparation of nanoclay/TiO\(_2\) modified epoxy

Initially, epoxy resin was modified with different weight percentages (0–2 wt%) of hybrid nanofillers by mechanical stirrer for four hours at a speed of 3000 RPM. The nanoclay and nanoscale-TiO\(_2\) particles were added together into the epoxy resin at equal weight proportions. i.e., 0.5 wt% (0.25 wt% TiO\(_2\) + 0.25 wt% Nanoclay), 1 wt% (0.5 wt% TiO\(_2\) + 0.5 wt% Nanoclay), 1.5 wt% (0.75 wt% TiO\(_2\) + 0.75 wt% Nanoclay) and 2 wt% (1 wt% TiO\(_2\) + 1 wt% Nanoclay). Further loading of nanofillers (> 2 wt%) leads to formation of clusters. Triethylene tetra amine was used as a curing agent, added in the ratio of 1:4 into epoxy resin. After mechanical stirring, the modified epoxy resin was exposed to sonication process at a frequency of 50 MHz for 240 min in bath type sonicator without increasing the original temperature. 100% ultrasonic amplitude was applied during this process. The implosion of cavitation bubbles formed during this process helps to obtain uniform dispersion of nanofillers [30]. The nanoclay/TiO\(_2\)/epoxy mixture was collected in a glass tube to ensure the uniform dispersion. After four days at room temperature, the nanofillers were observed to be entirely dispersed and the homogeneous modified epoxy got produced. The homogeneous dispersion of nanoparticles in epoxy resin is required to attain the improved mechanical properties of polymer composites. The molecular structure at the interface between matrix and nanofillers is a vital key factor to maintain the higher modulus and strength.

2.3. Preparation of carbon/glass/modified epoxy based laminates

The carbon/glass/modified epoxy based laminates were fabricated using hand lay-up method at room temperature. In this method, initially a releasing agent was spread over a flat mould to facilitate the easy removal of laminates. Thin layer of nanofillers modified epoxy resin was uniformly applied over the releasing agent. Then unidirectional carbon and glass fibres were stacked alternately. The entrapped air in the laminate was removed by laminate rollers. At room temperature, the laminates were cured while post-curing was performed at 75 °C for about one hour. Three different stacking sequence of laminate were analysed in this study. The stacking sequences and their abbreviated notations, and their constituent fractions of modified laminates are summarized in the table 1.

The carbon and glass fibers were symmetrically arranged in laminates to provide maximum bending stiffness and to avoid the membrane coupling effect. Each laminate consists of six plies, in the thickness range of 4–5 mm. The test specimens were cut from the laminates using water-jet cutting machine. At least six specimens were cut from each lay-up sequence and tested. In order to initiate a crack in DCB specimen, 14 μm thickness Teflon film was inserted along the mid-plane of the laminates. The stacking sequence and orientation of fibres with the detailed fabrication process is illustrated in figure 1.

3. Material characterization

3.1. Double cantilever beam (DCB) test

The resistance of the laminate against the crack propagation was characterized by the interlaminar fracture toughness values (\(G_{IC}\)). This \(G_{IC}\) remains a crucial parameter in the damage tolerant design of polymer composite structure. The Double cantilever beam (DCB) test configuration in accordance with ASTM: D5528-01 standard was used to evaluate the mode I delamination growth of modified Fibre Reinforced Polymer Nanocomposites (FRPNCs). The DCB specimen dimensions are 125 mm × 25 mm × 5 mm. Two aluminium hinges of 25 mm width were fixed at the top and bottom of the specimen, which is used to transmit the applied force to the specimen ends. The surface of aluminum hinges and specimen were polished with sandpaper before fixing. Araldite 420 adhesive was used for fixing hinges. In order to visually observe the crack extension, the sides of each specimen were marked with vertical lines in every 5 mm. Interlaminar fracture toughness of laminate tested by 100 kN Kalpak computerized universal testing machine (Model KIC-2-1000C) with a crosshead speed
of 2 mm min\(^{-1}\) (figure 2). The DCB specimen ends opened by controlling the crosshead movement considered as Crack Opening Displacement (COD) while the load versus COD was recorded. The record of delamination growth was monitored by a digital camera in order to obtain accurate results.

Six samples were tested in each set of laminate. With the use of modified beam theory, the modes I interlaminar fracture toughness values (\(G_{IC}\)) were calculated. The \(G_{IC}\) of DCB specimens was determined using the equation (1)

\[
G_{IC} = \frac{3p\delta}{2B(a + |\Delta|)}
\]
Where, $P$-load applied, $\delta$-cross head displacement, $B$- specimen width, $a$-crack length and $|\Delta|$-correction factor. If one needs to attain the corrected value of $G_{IC}$, the correction factor $|\Delta|$ ought to be inclusive of the crack length. The correction factor was determined through the experimentation from the least square plot of the cube root of compliance $C^{1/3}$.

3.2. Tensile test

With a frame capacity of 250 kN, 100 kN load cell capacity and 0.5 mm min$^{-1}$ cross head speed, the tensile test was performed with the help of servo-controlled hydraulic universal testing machine (UTM). In alignment with the ASTM D3039 standard, the tensile test was conducted at room temperature. The test specimen dimensions are shown in figure 3. The specimen was clamped in the grip of UTM. The tensile load was applied in either direction, until the occurrence of a fracture. The elongation and maximum load were recorded. The tests were repeated thrice and the average value was taken to calculate the tensile strength of the laminate.

3.3. Three point bending test

In order to get an overview of bending resistance of laminates, three-point bending test was conducted at room temperature. The stroke applied at a constant rate of 1 mm min$^{-1}$. The flexural samples were cut from the laminate in accordance with ASTM: D7264 standard is shown in figure 4. In order to ensure the flexural loading,
the specimen is simply supported over two points with 100 mm span length and then load is applied to the top layer of the laminate until the specimen fails. The maximum load before failure is recorded as the flexural strength of specimen. At least six specimens in each set of laminate were tested.

The flexural stresses \( \sigma_f \) and flexural strain \( \varepsilon_f \) values were calculated using the equations (2) and (3).

\[
\sigma_f = \frac{3PL}{2bt^2} \left[ 1 + 6\left(\frac{D}{L}\right)^2 \right] - 4\left(\frac{d}{L}\right) \left(\frac{D}{L}\right)
\]

and

\[
\varepsilon_f = \frac{L^3}{4bd^3} \frac{\Delta P}{\Delta x}
\]

where, \( P \)—maximum load (N), \( L \)- Span length (m), \( b \)- specimen width (m), \( d \)- specimen depth (m), \( D \)-vertical deflection (m), and \( \Delta P/\Delta x \)—slope of linear region of the force-displacement curve (N m\(^{-1}\)).

### 4. Results and discussion

#### 4.1. Mode I load-displacement curves

Figure 5 summarizes the load curves of DCB test specimens under mode I loading condition. This curve depicts the applied load to the hinges and the corresponding displacement during the crack propagation. Figure 5(a) shows mode I load-displacement curve obtained for FRPNC1, FRPNC2, FRPNC3, FRPNC4 and FRPNC5 specimens with (90 °C/90 °G/0 °G)\(_S\) sequence laminate. In this set of specimens, it was observed that once the crack initiates, the load begins to increase gradually with increasing crack opening displacement. After that, sudden drop in load was recorded with an increase in displacement. The maximum drop denotes the delamination onset at the crack tip, i.e. initiation and growth of the crack in the specimen. The maximum load of 80 N was recorded for FRPNC9 specimen at 1.5 wt% of hybrid nanofillers, which was around 31% higher than neat epoxy (FRPNC1) specimen. Figure 5(b) illustrate the mode I load-displacement curve for FRPNC6, FRPNC7, FRPNC8, FRPNC9, and FRPNC10 specimens with stacking sequence (90 °G/0 °C/90 °G)\(_S\). The maximum load of 88 N was recorded for FRPNC9 specimen at 1.5 wt% loading of nanofillers. The load carrying capability of FRPNC9 specimen got enhanced by 33% in comparison with the pristine epoxy specimen (FRPNC6). Figure 5(c) shows the mode I load-displacement curve for FRPNC11, FRPNC12, FRPNC13, FRPNC14, and FRPNC15 specimens with the stacking sequence (90 °G/0 °G/90 °C)\(_S\). The maximum load of 92 N was observed for FRPNC14 specimen. The load carrying capacity improved by 44% as compared with pristine epoxy specimen (FRPNC11).

The load-displacement curve of all the three laminate follows linear elastic behavior up to the maximum load after that load begin to drop. By comparing the load- displacement curve of FRPNC specimens, the applied load reaches a maximum value in (90 °G/0 °G/90 °C)\(_S\) sequenced laminates at 1.5 wt% of nanofillers. Even at low concentration of nanofillers (0.5 wt%, 1 wt%) the load increases considerably as compared with neat epoxy specimen. The nanofillers inclusion in epoxy resin acts an effective barrier for bifurcation and pinning of the crack advancement offers enhanced load bearing characteristic to modified FRPNCs [31]. In addition, the topographical feature of nanofillers such as valleys, pits, and peaks are allows mechanical interlocking between fibres and modified epoxy matrix provides higher load bearing characteristics to modified FRPNCs [32, 33]. However, at higher weight percentages (> 1.5 wt%), nanofillers aggregation originate local stress concentration, which reduces the load carrying capability of FRPNCs. In view of analyzing the effect of stacking sequence of
laminates on load curves, the maximum load of 92 N was observed in (90 °G/0 °G/90 °C)_S sequence specimen at 1.5 wt% loading of nanofillers (FRPNC14). This load was around 5% and 15% higher than the optimum load of (90 °G/0 °C/90 °G)_S and (90 °C/90 °G/0 °G)_S sequenced laminates at 1.5 wt% of nanofillers. These results confirm that the crack propagates progressively in 90 °C/90 °C interface laminates as compared to 90 °G/90 °G and 0 °G/0 °G interface laminates. This enhanced load carrying capacity of modified FRPNCs demonstrate that the ply stacking sequence and orientation of fibres have a positive effects on the load-displacement behaviour, even the weight fraction of nanofillers remained constant [34].

4.2. Resistance curves (R-curves)

Figure 6 shows the R-curves of DCB tested laminates. The delamination resistance curve characterizes the relationship between the crack length and mode I interlaminar fracture toughness (GIC) of polymer laminates. These curves demonstrate that the interlaminar failure energy of polymer laminates depend on the length of propagating crack. In DCB specimen, the initial delamination was located at mid-plane. The crack initiation (GIC-init) values were measured from the first deviation of linearity while the GIC values were calculated from the average of plateau line of the R-curve. The curve shows that almost for all the sequence laminates, the GIC values were lower in the crack initiation region and then GIC increases up to 90 mm crack length due to resistance effect of nanofillers, post which it dropped. The R-curve of (90 °C/90 °G/0 °G)_S sequenced laminate
shown in figure 6(a). The obtained $G_{IC}$ values of FRPNC1, FRPNC2, FRPNC3, FRPNC4, and FRPNC5 specimens were 2.69 kJ m$^{-2}$, 2.91 kJ m$^{-2}$, 3.15 kJ m$^{-2}$, 3.22 kJ m$^{-2}$ and 2.82 kJ m$^{-2}$ respectively. It is clearly observed from the plot that the delamination got opened on the edge and initial fracture toughness values were low at crack initiation ($G_{IC}$-Initial). The crack propagated with advancing crack length between $a = 60$ mm and $a = 90$ mm ($GIC$-Prop) via $90 \degree C/90 \degree G$ ply. After $90$ mm crack length, the $G_{IC}$ values were decreased. The maximum $G_{IC}$ value of 3.22 kJ m$^{-2}$ was obtained corresponding to the crack length $a = 90$ mm (1.5 wt% nano fillers). This might be attributed to the increased adhesion strength between carbon/glass fibres and epoxy matrix in the presence of nano fillers. There was no such observation on the fracture surface of the pristine epoxy specimen. However, different trend was observed in FRPNC5 specimen. Owing to their higher resistance to crack growth, the $G_{IC}$ value of FRPNC5 specimen (2 wt%) increased up to a crack length of $a = 80$ mm, then it dropped due to the agglomeration of nano fillers that act as stress concentration near the crack tip field.

Figure 6(b) shows the R-curve for $(90 \degree G/0 \degree G/90 \degree G)_S$ sequenced laminate. The recorded interlaminar fracture toughness values for FRPNC6, FRPNC7, FRPNC8, FRPNC9, and FRPNC10 specimens are 2.92 kJ m$^{-2}$, 3.38 kJ m$^{-2}$, 3.62 kJ m$^{-2}$, 3.68 kJ m$^{-2}$ and 3.21 kJ m$^{-2}$ respectively. The maximum $G_{IC}$ value of 3.68 kJ m$^{-2}$ was observed for the FRPNC9 specimen at 1.5 wt% nano fillers, which was around 26% greater than pristine epoxy FRPNC6 specimen for the same wt% of nano fillers. The crack length between $a = 50$ mm and $a = 60$ mm, all the specimens (i.e. FRPNC6 - FRPNC10) followed the same trend of increase in the $G_{IC}$ values suggesting higher resistance to start crack propagation. The crack propagates gradually between the crack length of $a = 60$ and $a = 90$ mm via $90 \degree G/90 \degree G$ ply. Figure 6(c) shows the R-curve for $(90 \degree G/0 \degree G/90 \degree C)_S$ sequenced laminate. The obtained $G_{IC}$ values for FRPNC11, FRPNC12, FRPNC13, FRPNC14, and FRPNC15 specimens are 2.98 kJ m$^{-2}$, 3.54 kJ m$^{-2}$, 3.77 kJ m$^{-2}$, 3.85 kJ m$^{-2}$ and 3.33 kJ m$^{-2}$ respectively. The maximum interlaminar
fracture toughness \((G_{IC})\) of 3.85 kJ m\(^{-2}\) was observed for FRPNC14 specimen, which was around 29% higher than unmodified FRPNC11 specimen. This might be attributed to the localization of voids altogether in the entire range of fibre/matrix interface which provides time for the voids to deform plastically, by delaying their coalescence. This led on energy dissipation in huge quantity by void coalescence, resulting increased fracture resistance of laminates\([35]\).

The R-curves disclose that the \(G_{IC}\) values of carbon/glass/modified epoxy based laminates were found to be higher and consistently increased upto 1.5 wt% addition of nanofillers. The \(G_{IC}\) values were increased by 19%, 26%, 29% respectively for \((90^\circ \text{G}/90^\circ \text{G}/0^\circ \text{G})_3\), \((90^\circ \text{G}/0^\circ \text{C}/90^\circ \text{G})_3\) laminates as compared to neat epoxy resin laminate. The curve shows that even for low wt% addition of nanofillers (0.5 wt%, 1 wt%) the fracture toughness value enhances considerably as compared to neat epoxy based specimen. Nanoclay and nanoscale-TiO\(_2\) particles are highly stiffer material and possess large intrinsic strength, which makes plasticity-induced crack closure in front of the crack tip results improved interlaminar fracture toughness\([36]\). The interfacial adhesion strength between epoxy and nanofillers depends on physical, chemical and molecular nature of epoxy resin and nanofillers. In addition, higher specific surface area nanofillers, matrix/particle adhesion strength and random obstacles of the nanofillers may responsible for increase in the interlaminar fracture toughness of the modified epoxy resin \([37, 38]\). Especially the exfoliated structure of nanoclay increased the fibre surface roughness. This increased surface roughness of fibres significantly hindered the crack growth rate and deflect the crack in the propagation region. This provides additional energy absorption mechanism, making the modified FRPNCs composites tougher. However, further loading of nanofillers introduces unexfoliated aggregates in polymeric matrix may act as a stress concentration point lead to reduced \(G_{IC}\) values.

Delamination occurs due to the interlaminar stresses being developed at the interfaces in the laminates. The alternate stacking sequence and orientation of carbon/glass fibres effectively changed the delamination path which results improved interlaminar fracture toughness of modified laminates. The crack propagation was slower in \((90^\circ \text{G}/0^\circ \text{G}/90^\circ \text{C})_5\) sequenced laminates as compared to \((90^\circ \text{C}/90^\circ \text{G}/0^\circ \text{G})_5\), \((90^\circ \text{G}/0^\circ \text{C}/90^\circ \text{G})_5\) laminates. The laminate with \([90^\circ \text{C}/90^\circ \text{G}]\) interface exhibits higher interlaminar fracture toughness of 3.85 kJ m\(^{-2}\) at 1.5 wt%, which was around 20% higher than \((90^\circ \text{G}/0^\circ \text{C}/90^\circ \text{G})_5\) sequenced laminates, 5% higher than \((90^\circ \text{G}/0^\circ \text{C}/90^\circ \text{G})_3\) sequenced laminates for same wt% of nanofillers. This increased \(G_{IC}\) value might be due to the bridging of high stiffness carbon fibres in fibre region and restriction of chains not to break the released energy in the matrix region. The bridging effect between the reinforced fibres and epoxy matrix in the presence of nanofillers may be responsible for the improved interlaminar fracture properties. The fibre bridging interconnect the crack faces, consequently it reduces the stress concentration near the crack tip \([39, 40]\). The \(G_{IC}\) values were decreased in \((90^\circ \text{C}/90^\circ \text{G}/0^\circ \text{G})_5\), and \((90^\circ \text{G}/0^\circ \text{C}/90^\circ \text{G})_5\) sequenced laminates disclose that the fibre bridging effect was lower in \([90^\circ \text{G}/90^\circ \text{G}]\) and \([0^\circ \text{G}/0^\circ \text{G}]\) ply interface.

### 4.3. Tensile strength

Figure 7 shows the variation of tensile stress of carbon/glass/modified epoxy based composite with increased weight fraction of nanofillers with different stacking sequences of fibres. The tensile stress is a measure of resistance to longitudinal pull of laminates. The carbon fibre has good load bearing capacity and the tensile strength of carbon fibres is higher than glass fibres. The reinforcement of both carbon/glass fibres and addition of nanofillers in epoxy based composites improve the tensile strength of modified laminates. Figure 7(a) shows the tensile stress values for FRPNC1, FRPNC2, FRPNC3, FRPNC4 and FRPNC5 specimens with \((90^\circ \text{G}/0^\circ \text{G}/90^\circ \text{C})_5\) sequenced laminate are 242 MPa, 278 MPa, 284 MPa, 298 MPa and 274 MPa respectively. The ultimate tensile stress of modified FRPNC is gradually increased with the addition of nanofillers upto 1.5 wt% and then decrement in tensile strength was observed at 2 wt%. The maximum tensile stress of 298 MPa was recorded for FRPNC4 specimen, which is 23% higher than the pristine epoxy specimen. The tensile stress turn down to 274 MPa at 2 wt% addition of nanofillers as compared to modified FRPNCs (0.5–1.5 wt%), but this is 13% higher than unmodified FRPNC (0 wt%). The tensile stress values of 254 MPa, 292 MPa, 304 MPa, 326 MPa and 288 MPa were recorded for FRPNC6, FRPNC7, FRPNC8, FRPNC9 and FRPNC10 specimens with \((90^\circ \text{G}/0^\circ \text{C}/90^\circ \text{G})_5\) sequenced laminate shown in figure 7(b). The maximum tensile stress of 326 MPa was observed for FRPNC9 specimen at 1.5 wt%, which is 27% higher than pristine epoxy specimen (FRPNC6). Further addition of nanofillers, the tensile strength of laminates got decreased to 288 MPa however this is 13% higher than pristine epoxy based specimen. The tensile stress of 268 MPa, 316 MPa, 330 MPa, 362 MPa and 296 MPa were observed for FRPNC11, FRPNC12, FRPNC13, FRPNC14 and FRPNC15 specimens with \((90^\circ \text{G}/0^\circ \text{G}/90^\circ \text{C})_5\) sequenced laminates shown in figure 7(c). The maximum tensile stress of 362 MPa was observed for FRPNC14 specimen at 1.5 wt% of nanofillers, which was 31% higher than the pristine epoxy specimen (FRPNC11). For 2 wt% addition of nanofillers, the tensile stress value reduced from 362 MPa to 296 MPa, despite that it was around 10% higher than FRPNC11. According to the experimental results, the
addition of nanofillers (Nanoclay-TiO$_2$) into epoxy resin increases the tensile strength of modified FRPNCs with increase in wt% of nanofillers. The modified epoxy laminates with 1.5 wt% loading of nanofillers (i.e. FRPNC4, FRPNC9, FRPNC14) shows an average tensile strength in the range of 298–362 MPa, which was around 23%–50% higher than pristine epoxy specimen. In dispersion strengthened fibre reinforced polymer composites, the fibre is a primary load carrying material and modified epoxy matrix accept the larger load over their surface area and transfer it to the reinforced fibres. In particular, the incorporation of nanoscale-TiO$_2$ in epoxy resin provides strong interfacial adhesion at fibre and fibre/matrix interfaces results higher resistance to deformation under tensile loading [41]. However, 2 wt% addition of nanofillers lead to agglomeration it decreased the inter-particle spacing which results micro void nucleation and accordingly the tensile properties got reduced.

Figure 8 shows the effect of stacking sequences of carbon/glass fibres on tensile properties of FRPNCs. The carbon/glass fibre reinforced laminates exhibits more yielding strength when compared to glass fibre composites. The stacking sequence and orientations of fibres were significantly affect the ultimate tensile strength of carbon/glass/modified epoxy composites. Further, it was observed that the tensile properties of hybrid composite were extremely sensitive to inter-ply sequence of carbon/glass fibres even the weight fraction of nanofillers is constant. The 90 °C/90 °C oriented carbon fibre in mid-plane has maximum tensile strength of 362 MPa which was around 21% higher than 0 °G/0 °G mid-ply laminates and 11% higher than 90 °G/90 °G sequenced laminates. This might be due to the inclusion of high stiffness carbon fibre in the mid-plane [42, 43]. The primary observation of the this work is that one can achieve higher tensile strength when placing unidirectional glass fibres in exterior and unidirectional carbon fibres in interior surface.
4.4. Flexural strength

Figure 9 shows the variation of flexural strength of FRPNCs with increased weight fraction of nanofillers with different stacking sequence. The higher surface energy absorption behaviour of hybrid nanofillers considerably increased the flexural strength of carbon/glass/epoxy polymer composites. According to the test results, the localized compressive load applied in the three-point bend led to tensile failure at the bottom surface, while at the same time, there was a complete crush observed in the compression side. The flexural strength of FRPNCs increases linearly with increasing wt% of nanofillers. The flexural strength of 251 MPa, 288 MPa, 314 MPa, and 454 MPa were observed for FRPNC1, FRPNC2, FRPNC3, FRPNC4 and FRPNC5 specimens respectively is shown in the figure 9(a). The flexural strength got improved by 14%, 25%, 53%, and 81% correspondingly at 0.5 wt%, 1 wt%, 1.5 wt%, and 2 wt% nanofillers. The maximum flexural strength of 454 MPa was observed for FRPNC5 specimen at 2 wt% nanofillers loading, which was around 81% higher than FRPNC1 specimen (pristine epoxy). Figure 9(b) shows the flexural strength for FRPNC6, FRPNC7, FRPNC8, FRPNC9 and FRPNC10 specimens with (90°/0°/90°)S sequenced laminate. The values of 341 MPa, 384 MPa, 412 MPa, 471 MPa, 502 MPa were observed at 0.5 wt%, 1 wt%, 1.5 wt%, and 2 wt% nanofillers loading. The flexural stress reaches to a maximum of 502 MPa (FRPNC10) at 2 wt% nanofillers loading which was 47% much higher than the FRPNC6 specimen (pristine epoxy). Figure 9(c) shows the flexural strength of FRPNC11, FRPNC12, FRPNC13, FRPNC14 and FRPNC15 specimens with (90°/0°/90°)S sequenced laminates. The flexural strength got improved by 10%, 21%, 35%, and 43% correspondingly at 0.5 wt%, 1 wt%, 1.5 wt%, and 2 wt% loading of nanofillers. The maximum flexural strength of 545 MPa was recorded for FRPNC15 specimen, which was 43% higher as compared to unmodified specimen. From the experimental results, it can be observed that the addition of small wt% of hybrid nanofillers into epoxy resin, increases the flexural strength of FRPNCs to maximum of 545 MPa at 2 wt% loading of nanofillers. This enhancement in flexural strength was mainly due to the presence of highly exfoliated nanoclay structure. The larger interfacial interaction between epoxy and nanoclay provides higher resistance to localized compressive load at top surface and localized tensile load at the bottom surface of specimen [44]. In addition, the larger surface-to-volume ratio of nanoclay offers excellent interlocking mechanism with the matrix led to the higher energy absorption behaviour and improves the stress transfer properties of modified matrix. However, higher concentration of nanofillers addition (>2 wt%) results weak interfacial adhesion strength between fibre and modified matrix which reduces the flexural strength of FRPNCs [45].

Figure 10 shows the effect of stacking sequences of carbon/glass fibres on the flexural properties of FRPNC composites. The flexural strength values of FRPNC1, FRPNC5 and FRPNC10 specimens (0 wt%) showed that, by varying the stacking sequences of carbon and glass fibres, the flexural strength of laminates can be increased up to 35%–52%. Incorporation of 2 wt% of hybrid nanofillers (i.e. FRPNC5, FRPNC10, FRPNC15 specimen), an average of 43%–80% of flexural strength can be increased as compared with pristine epoxy specimen. In all the sequence laminates, the weaker fibre got failed first while the weaker fibre lay-up angle played a vital role in flexural properties [46]. From the plot, it can be observed that the flexural strength of (90°/0°/90°)S sequenced laminates got improved by 20% when compared to (90°/0°/90°)S laminates and 9% in comparison with (90°/0°/90°)S sequenced laminates. This may be due to the mechanism behind the hybrid effect and the inclusion of high stiffness carbon fibre in the mid-plane. The results demonstrate that, even
Figure 9. Flexural stress of (a) (90 °C/90 °G/0 °G/0 °G)₃, (b) (90 °G/0 °C/90 °G), (c) (90 °G/0 °C/90 °C), sequenced laminates.

Figure 10. Flexural stress comparison.
though the reinforcement material and wt fraction of nanofillers is constant in the laminates, the flexural strength got changed according to the stacking sequence and orientation of carbon and glass fibres.

5. Morphology study

The post failure surfaces of the delaminated DCB specimens were examined by the scanning electron microscope images around the crack front region are shown in figure 11. The SEM images of the fractured specimen show the toughening mechanisms can be operative during the crack propagation. This might be attributed to the fracture failure mode that got changed from an interface failure between epoxy and carbon/glass fibre to a combination of interface failure and matrix failure in the presence of nanofillers. The predominant toughening mechanisms such as fibre pull-out, fibre breaking, particles debonding, and crack deflection can be active in the fractured surfaces. Figure 11(a) shows the pull-out of fibres, demonstrating that the poor adhesive strength between rough fibre surface and modified matrix owing to local shear at the fibre interface. The fibre pull-out direction is parallel to the crack propagation direction. The nanofillers also confine the unlocking of plies due to the frictional energy that got dissipated at the time of pullout that bridges the interlaminar crack. During crack propagation, the fibres at interfaces were break at excessive applied load. Figure 11(b) shows the fibre breaking mechanism, which was observed in the fibre region. The broken fibres show different inclining angles relative to the crack propagation direction. One more toughening mechanism, particles debonding were also observed in the fractured surface shown in figure 11(c). The debonding mechanism behaves like plastic void growth and may responsible for the improved interlaminar fracture toughness. The interaction between the reinforcement and crack front is promoted by extrinsic toughening mechanism causes deflected crack. Figure 11(d) shows the crack deflection, exhibit that the crack front goes around the nanofillers and then the crack propagates. The path of the crack at the interfaces provides highly tortuous path which improves toughness of the modified composite. The primary purpose of the crack deflection is to prevent the crack tip from the far-field driving forces results crack slowed down. These toughening mechanisms may responsible for the improved fracture toughness of FRPNCs.
6. Conclusion

The pristine epoxy resin was successfully modified by hybrid nano-fillers (TiO$_2$–Nanoclay) and tested for its impact on mode I interlaminar strength, tensile strength and the flexural strength of unidirectional carbon/glass/epoxy based polymer laminates after being fabricated. The experimental results demonstrate that variations in the mechanical properties of constituent fibres, interfacial bond strength between the matrix and nano-fillers, and hybridization effect improves the stiffness, flexural strength and fracture toughness to the modified polymer laminates. The following conclusions were drawn based on the experimental results.

- Addition of small wt% of hybrid nano-fillers (0.5, 1, 1.5 & 2 wt%) increases the mode I interlaminar fracture toughness to a maximum of 3.85 kJ m$^{-2}$ and makes the laminates stronger due to near-molecular blend of nano-fillers, higher matrix/nanoparticles adhesion strength, and mechanical interlocking.

- The mode I interlaminar fracture toughness and tensile strength values of FRPNCs attain a maximum value at 1.5 wt% loading of nano-fillers. The flexural strength seems to be optimum at 2 wt% loading of nano-fillers.

- Addition of nanoscale-TiO$_2$ apparently stiffened the laminates and increases the tensile strength to a maximum of 362 MPa at 1.5 wt% nano-fillers.

- Network structure of the nanoclay, increased the flexural strength of FRPNCs to a maximum of 345 MPa at 2 wt% loading of nano-fillers.

- The stacking sequences and orientation of carbon/glass fibre are highly influence in mechanical properties of FRPNCs. Laminate with 90 °C/90 °C interface exhibits highest delamination resistance, and increased tensile as well flexural strength due to bridging effect of high stiffness carbon fibres.

- The toughening mechanisms such as fibre pull-out, fibre breaking, particles debonding, and crack deflection were identified at the fractured surfaces.

- Incorporation of nanoclay in epoxy increases the mode I interlaminar fracture toughness and flexural properties, whereas nanoscale-TiO$_2$ addition improves the tensile strength of modified laminates.

- The enhanced delamination, tensile and flexural properties of modified FRPNCs prove that the nanoclay and nanoscale-TiO$_2$ particles may be used as excellent nano-fillers to improve the overall mechanical properties of epoxy based polymer composites.

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