Structural analysis of sol-gel derived TiO$_2$ nanoparticles: a critical impact of TiO$_2$ nanoparticles on thermo-mechanical mechanism of glass fiber polymer composites

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Abstract
The incorporation of inorganic nanoparticles with thermosetting epoxy polymer is an emerging field of research over the past few years. It is well analyzed that epoxy matrix is brittle in nature that shows rapid crack initiation and rapid propagation without increasing applied stress value. Therefore, researchers are showing their interest in nanoparticles embedded epoxy composites to improve their fracture resistance (brittleness and toughness). In this investigation, the dispersion of TiO$_2$ nanoparticles at different weight fractions (0-2%) with glass fiber reinforced epoxy composites is performed to enhance structural and thermo-mechanical properties. The TiO$_2$ nanoparticles are prepared by sol-gel method and structural analysis of TiO$_2$ nanoparticles shows greater interfacial bond with epoxy matrix and glass fibers due to fine dispersion of nanoparticles. From obtained results, a significant enhancement in their tensile strength (38.56%), flexural strength (30.52%), inter-laminar shear stress (25.22%), impact strength (327.10%), micro-hardness (48.53%) and fracture energy (40.19%) with a minimal detrimental effect on toughness was revealed for GFRP-T1.0 compare to GFRP-T0.0 composite laminates. The stiffness and rigidity also improved up to 52.72% and 34.13% respectively for GFRP-T1.5 compare to GFRP-T0.0 composite laminates. The effects of nanoparticles contents and clustering size on thermal stability and glass transition temperature of developed composites are observed by thermo-gravimetric analysis. The surface morphology of TiO$_2$ nanoparticles is characterized by transmission electron microscope (TEM) while the dispersion of nanoparticles and failure of developed composites were analyzed by scanning electron microscopy (SEM).

Keywords Sol-gel method · TiO$_2$ nanoparticles · Composite laminate · VARIM · Thermo-mechanical properties

Introduction
The advanced composite materials made from continuous fiber polymer matrix composite laminates with different orientation and arrangements comprise a successful structural material due to their less density, better specific strength and stiffness, lower thermal coefficient, high fatigue and damping resistance for various industrial applications like construction, aerospace, marine, automobile and biomedical [1]. Fiber reinforced polymeric composites (FRPCs) such as glass fiber and carbon fiber have attracted much awareness as a substitute for conventional materials like wood, steel and plastics for various structural applications. The replacement of concrete structure with FRPCs gave more flexibility and suitability to the industrial society and has been also highlighted by the American concrete institute (ACI) committee-503 where the adhesion and bonding between fibers and matrix acts a crucial role in the overall performance of the materials [2, 3]. Although, carbon fiber is not available plenty due to its more expensive and low reusability with high design and manufacturing cost, so glass fiber reinforced polymeric composite (GFRP) can be a better alternative material for construction, automotive, marine, aerospace, wind turbine and power plants that also possess excellent chemical, physical and thermo-mechanical properties [4].

Thermoset epoxy resins are commonly used polymeric matrix for fabricating high performance and flexible composites due to their higher durability, better thermal stability
and superior chemical, electrical, and mechanical properties [5, 6]. However, epoxy resins have highly brittle nature that requires high fracture toughness and impact strength. Therefore, to overcome these disadvantages, incorporating or reinforcing fillers into the polymer matrix enhanced the strength and stiffness of the composite without compromising its toughness [7]. To improve the performance and properties of FRPCs, nanoparticles were incorporated to identify as a prospective solution. A broad range of nanoparticles such as silica, clay, calcium carbonate, nickel oxide, layered silicate, titanium dioxide etc. has gained particular interest for inorganic/organic nanocomposites [8]. The impact of nanoparticles on the developed composite has been studied and investigated their performance including TiO₂ spherical nanoparticles [9], carbon oxide dots [10], carbon nanotubes [11], nanoclays [12], dichalcogenides transition metal [13], and graphene [14]. Several researches have been conducted on metallic or inorganic nanoparticles that explained their performance and revealed an excellent candidate to reinforce with polymeric materials mainly thermosetting epoxy resin for better mechanical, thermal and electrical properties [15]. Among various inorganic nanoparticles, TiO₂ has non-toxic, lower in cost, superior refractive index, and chemical inertness that attendant higher interest towards research and have been used for different commercial applications such as antibacterial activities, inhibition, photoelectric and photocatalytic conversion in solar cells as well as utilized in food additives, self-cleaning, corrosion-resistant coating, water and air purification etc [16–18]. Therefore, TiO₂ nanoparticles have been recognized as promising reinforced materials to develop effective composite materials due to their light density, higher mechanical and thermal properties, reduce ultraviolet and thermal degradation [19–21]. Several investigations examined that, the performance and efficiency of the developed composites have been influenced with volume contents, shape and size that enhanced the thermal, mechanical, fatigue and toughness properties [22, 23] while the greater surface area of nanoparticles makes chemically very active to bond with matrix materials [1]. However, these nanoparticles have been agglomerated and incompatible with the polymer matrix due to the large surface area to volume ratio that results in improper bonding and reduces their respective properties [8, 24]. Therefore, hybridization of these nanoparticles with different fiber reinforced materials was identified as a potential solution that enhanced their compatibility and increases the durability of the materials where a low amount of homogeneous dispersion of nanoparticles with GFRP composites demonstrated higher mechanical, thermal, and fracture properties as well as improved their glass transition temperature (Tg) and maximum decomposition temperature [22, 25, 26].

In this context, Researches have observed it extremely difficult to prepare fine TiO₂ particles. Therefore, the sol-gel method was best suited to extract fine particles of TiO₂. The homogeneous dispersion of nanoparticles in fiber reinforced composites has a great challenge and very few studies were reported about good dispersion of TiO₂ nanoparticles with epoxy matrix. Also, according to our knowledge, this is the first study that covers all detailed analyses at a different weight fraction of TiO₂ nanoparticles on tensile, flexural, inter-lamina shear stress impact properties and fracture properties with effects of nanoparticles size on Tg. However, limited investigations reported about the inclusion of fine TiO₂ nanoparticles with glass fiber reinforced composites which may gain an emerging area for industrial applications. Therefore, the current study deals with structural analysis of TiO₂ nanoparticles and the effects of these nanoparticles at different weight fractions on the thermo-mechanical characterization of GFRP composites have been examined. The TiO₂ nanoparticles are prepared by sol-gel methods and GFRP composites laminates are fabricated with vacuum-assisted resin infusion molding techniques (VARIM).

In this study, exceptionally homogeneity dispersion of TiO₂ nanoparticles was achieved using ultrasonic-assisted dispersion method that enhanced the interfacial bonding between fibers and matrix and finally improved their thermo-mechanical properties and glass transition temperature.

Materials and Methods

Materials

The bidirectional E-glass fiber was used for reinforcements that were purchased from Surfland Composites Pvt. Ltd. Bangalore, India. The E-glass fiber was having a density of 180 g/m² with a 5-7micrometre diameter. Araldite LY556 (Diglycidyl either of bisphenol, density-1.15-1.20 g/cc and epoxy content - 5.30-5.45 eq/kg), HY 906 (methylnadic anhydride, density -1.20-1.25 g/cc) and DY 070 (density -0.95-1.05g/cc) were used as resin, hardener and accelerator respectively as a matrix material for fabrication of GFRP composites that were purchased from Huntsman International Pvt. Ltd. Mumbai, India.

For preparation and synthesis of titanium dioxide (TiO₂) by sol-gel method, Titanium Isopropoxide (C₄H₉O₄Ti) having density-0.96 gm/ml, molecular weight-284.22 g/mol and Isopropanol as a liquid precursor were used that purchased from Sisco Research Laboratories Pvt. Ltd. Mumbai, India. TiO₂ nanoparticles were dispersed in resin solution then the solution was prepared with help of proper mixing from proper mechanical stirring then, ultrasonication was done for proper dispersion of nanoparticles in resin solution, then composites were fabricated with VARIM.
Preparation of TiO$_2$ nanoparticles

The TiO$_2$ nanoparticles were prepared through hydrolysis and condensation process with help of Sol-gel methods and shown in Fig. 1. Initially, 500ml distilled water having pH 7 was taken in a beaker then, put over a hot plate magnetic stirrer. The stirring process was done at 700 rpm and maintains at 70 °C temperature. Now, 10ml titanium Isopropoxide and 25ml Isopropanol was taken in two separate beakers. Instantly, the titanium Isopropoxide was added to Isopropanol with help of a dropper because titanium Isopropoxide was hazardous it gets react instantly when it comes in contact with moisture and finally mix it properly. The prepared solution was now added dropwise in distilled water beaker. Instantly the gel formation took place in the beaker and the hydrolysis process was started. The desired pH2 of the solution was attained by adding HNO$_3$ or NH$_4$OH. Hydrolysis of the solution produced turbid solution when it was heated at 60-70 °C for 14 h. The process of producing a turbid solution was called peptization. After the peptization process, the decrement in the volume of the solution to 50cm$^3$ was recorded. Depending upon the preparatory conditions, the resultant solution was obtained in white colour with high viscosity. The prepared precipitates were washed with ethanol several times and then filtered with a benchtop centrifuge. The prepared filtrated powders were drying in the oven for 3 h, at 100°C then powders became yellow-white colour. The final obtained powder was coarse in structure, so, mortar and pestle were used to produce fine nanoparticles of TiO$_2$.

Dispersion of nanoparticles

The proper dispersion of nanoparticles in resin solutions was the essential requirement to minimize the scatter and agglomeration in the developed composites. The following techniques such as mechanical stirring, shear mixing, acoustic cavitations, evaporation with solvent, ultrasonic waves, pulsed ultrasound vibration and direct in-situ incorporation with chemical and polymerization methods were used to improve the dispersion process of nanoparticles [25, 27]. In particular, it was observed that the sole gel methods were effective to improve the bonding strength of TiO$_2$ nanoparticles and homogeneous dispersion of nanoparticles played a vital role in improving the thermo-mechanical properties of developed composites [28, 29]. The ultrasonic is a widely used technique to avoid scatter/agglomeration during the mixing of nanoparticles with resin and provide fine quality of filled matrix material [30]. Thus, a fine structure of the matrix enhanced the interfacial bonding strength between fibers and the matrix of developed composites.

For the present study, mechanical stirring and ultrasonication techniques were adopted for superior dispersion of nanoparticles. Initially, the mechanical stirring was done for 15 min to prepare a mixture of TiO$_2$ nanoparticles and resin then finally, the sonication process was used for 30 min to do proper mixing and dispersion to avoid agglomerations.
Preparation of GFRP composite

Glass fiber reinforced TiO₂ nanoparticles with epoxy matrix composite laminates were prepared with VARIM methods and details methodology is showing in Fig. 2. For composite plate fabrication LY556, HY906 and DY090 were used as resin, hardener and accelerator respectively. The weight ratio of resin and hardener is 1:0.95 and the accelerator is taken as 2% of resin weight. An initially adequate amount of resin was taken in hard plastic, then TiO₂ nanoparticles were added then, the whole resin solution (Part A) was taken for mechanical mixing for 15 min. Then slurry of (resin + TiO₂ nanoparticles) was then processed for ultrasonic dual mixing process (UDM) with simultaneous stirring by the impeller for proper dispersion of nanoparticles in a resin solution. After the dispersion of nanoparticles, the hardener and accelerator were added into the solution (Part A) in a stoichiometric ratio. Then the mixture was again put under mechanical stirring action for 10 min for proper mixing. After that, the whole mixture is put inside desiccators to remove the gas or void entrapped into the solution during mixing. The prepared mixture was used for the fabrication of composite plates by the VARIM process.

Vacuum-assisted resin infusion techniques have become popular in the manufacturing of these composites to produce high-quality large-scale products where the process was well controlled, may produce composite plates with less than 1% voids. For this study, the single-side mould surface was taken and then dry release film (or peel ply) were placed on the mould surface. Now, eight layers of glass fiber mats were arranged and cover on both sides with peel ply then mesh was placed over the top surfaces of this arrangement for better flow of resin solution with high permeability inside the composite’s laminates. The vacuum was created over the mould and the resin solution is infused with help of a vacuum pump where the resin solution was spread over the entire surface of the mould. The peel ply was used for superior smoothness and easy removal of composite plates from the mould surface. Finally, the prepared composite plate was taken from the mould and put inside an oven at 120 °C for 2 h called pre-curing and then post-curing of composite plates at 160 °C for 6 h. The prepared composite plates were cut as per ASTM standards for various testing.

Characterization of TiO₂ nanoparticles

Structural characterization

The physical structure of the nanoparticles was observed by Brucker D8 focus X-Ray diffraction machine (XRD), operated at a voltage of 30kv/15mA with cu radiation at an angle of 2θ from 5 to 75. The weight loss of nanoparticles at increasing temperature was analyzed by EXSTAR TGA/DTA 6300 Thermo-gravimetric analyzer, where
nanoparticles were heated with a controlled heat flow rate of 10 °C/min at nitrogen environment. To understand the functional groups (chemically) present in nanoparticles, the powder was going through Fourier transform infra-red (FTIR) spectrometer of PerkinElmer Spectrum machine in the range of 500-4000 cm⁻¹ at a resolution of 4 cm⁻¹.

Surface morphological analysis

The surface morphology of TiO₂ nanoparticles was examined by transmission electron microscope (TEM) Philips, CM 200 operating voltages: 20-200kV with resolution:2.4 at room temperature. TEM is a microscopy technique in which a specimen is passed through an electron beam and transmitted in the form of an image. TEM analysis is used for high-resolution imaging compare to light microscopy. The microstructure and dispersion of TiO₂ nanoparticles were characterized with help of field emission scanning electron microscopy (FESEM). FESEM was conducted on Quanta 200 with 15kVvolatege at room temperature. The FESEM analysis was mainly used to characterize the dispersion and scattering of TiO₂ nanoparticles under high magnification of 1000x to 5000x.

Characterization of composite laminates

Mechanical characterization

The tensile testing was performed by using a 50 kN Instron, 8801 universal testing (UTM) machine. The test sample was prepared as per ASTM (D-638) [31] standard with a dimension of 160×15×3mm and testing has been done at 1mm/min of cross speed with a gauge length of 60 mm. The five specimens of each weight fraction were tested and the average value with an error bar has been reported in the graphical representation. The testing was carried under quasi-static tensile loading conditions at room temperature (23 °C), and the modulus of elasticity, yield strength, ultimate tensile strength and strain at failure of specimens at maximum load was measured.

The three-point bending test (also known as the flexural test) was carried out by using a similar universal testing machine, INSTRON, 8801. The five samples of each weight fraction following ASTM D 790 [32] standards with a dimension of 130×14×3mm were tested and the average value was reported. The three-point bending test was conducted at 1mm/min of cross speed and a span length of 60 mm under quasi-static loading conditions at room temperature and the flexural modulus, ultimate flexural strength, maximum deflection before the break of specimens at maximum load were measured.

The micro-hardness testing of the developed composite was done with the help of Vickers micro-hardness tester and following standard ASTM D384-99 [33]. The five different surface positions of each type of sample have been tested and the average value has been presented graphically.

The Charpy impact testing of the developed composite was carried out with the help of a Charpy impact tester made by FIE (Fuel Instruments and Engineers Pvt. Ltd.). The five notch samples of each weight fraction were tested and the average test result was adopted. The ASTM D256-10 [34] standard was followed for preparing the test samples. The dimension of the impact test specimen was 63.5 mm× 12.7 mm×3.2 mm and the depth of the notch was 2.54 mm.

The degree of fiber-matrix interfacial adhesiveness was evaluated by interlamine shear test (also known as short beam shear test). To perform the short beam test, the previously mentioned UTM machine was used and samples were cut as ASTM D2344 [35] standard at room temperature (23 °C). The dimension of the test sample was 37 mm× 9mmx 4.5 mm and the strain rate was maintained at 1mm/min. The five samples of each type of composites were tested and the average result has been reported.

The plane strain fracture toughness of the developed composites was investigated by using the previously mentioned UTM machine and following ASTM standard ASTM D5045-99b. The five specimens of each weight fraction composites with single edge notched were tested with a crosshead speed of 10mm/min and the average date has been reported. The fracture energy of each type of composite was found by using Eq. (1) mentioned below [36].

\[ G_{IC} = \frac{U}{B \cdot W \cdot \phi} \]  

(1)

Where \( G_{IC} \) = fracture energy, \( U \) = corrected energy, \( B \) = thickness of the specimen, \( W \) = width of the specimen and \( \phi \) = energy calibration factor.

Thermal stability

To understand the thermal stability and degradation behaviour with glass transition temperature of the developed composites, Thermogravimetric analysis (TGA) and Differential thermal analysis (DTA) were performed. The weight loss of the composites under the influence of temperature and maximum degradation temperature was characterized with help of the EXSTAR TGA/DTA 6300 Thermo-gravimetric analyzer. The test was carried out at a heating rate of 10 °C/min from 30 °C (room temperature) to 900 °C in a nitrogen gas environment.

Morphology analysis of fracture surface

The morphology behaviour of developed composites laminates at fracture surface is characterized with the scanning
electron microscope (SEM). SEM is conducted on Sigma 300 with the voltage of 5 kV at room temperature and used to magnify the microstructure and morphology behaviour of composites in which a high electron beam is an incident on the surfaces of the specimens. To pass the electron smoothly, developed composite specimens are well coated with gold/silver coating for better electrical conductivity.

Result and discussion

Characterization of TiO$_2$ nanoparticles

The structural analysis of prepared TiO$_2$ nanoparticles is characterized by performing XRD, FTIR, TEM, FESEM and TGA. Figure 3a showed the XRD results of prepared TiO$_2$ nanoparticles. The diffraction peak observed at 25.43º, 37.88º, 47.94º, 53.94º, 54.94º, 62.58º and 69.87º with corresponding to the crystalline plane of (101), (004), (200), (105), (211), (204), (116) and (220) of tetragonal anatase TiO$_2$ nanoparticles. The result confirmed that the prepared TiO$_2$ nanoparticles with sol-gel methods are more adequate and fine to enhance the dispersion qualities in the matrix materials [37]. From this diffraction pattern, the Debye-Scherrer equation is used to calculate the average crystallite (grain) size of TiO$_2$ nanoparticles [38].

\[
d = \frac{K \lambda}{\beta \cos \theta}
\]

Where $K=0.89$ (Scherrer constant), $\lambda=0.15406$ nm (the wavelength of the x-ray source), $\beta =$ full width of the diffraction peak (radian) [39]. The average grain size of TiO$_2$ nanoparticles is found as $8.12 \pm 0.21$ nm.

The existence of chemical structure and functional group of TiO$_2$ nanoparticles has been examined with FTIR and measure the intensity of the TiO$_2$ nanoparticles as shown in Fig. 3b. The broad intensity was observed at 3420 and 1630 cm$^{-1}$ due to the stretching vibration of O-H bonding.
due to the presence of moisture [40]. The peak at 515 and 660 cm\(^{-1}\) has been observed due to vibration of Ti-O-Ti bond and minor peaks at 775 and 565 cm\(^{-1}\) has been observed due to Ti-O bonding of Titanium dioxide [41]. Based on the FTIR spectra, the analysis has been made that the TiO\(_2\) nanoparticles can be the better inclusion for preparing composites laminates with better interfacial bonding and strength.

To identify the water content (H\(_2\)O) and weight loss in prepared TiO\(_2\) nanoparticles, thermo-gravimetric analysis (TGA) and derivative thermo-gravimetric (DTG) have been performed. Two types of H\(_2\)O desorption has been observed. First, H\(_2\)O which is absorbed physically made a weak chemical bond with TiO\(_2\) and evaporate at 120 °C. Second, chemically absorbed H\(_2\)O (also called crystallographic water). These types of H\(_2\)O made a comparatively strong bond with TiO\(_2\) and evaporate at 300 °C [42]. The weight loss and derivative weight loss of TiO\(_2\) nanoparticles with the influence of temperature are shown in Fig. 3c. From the DTG plot, one can find the points that showed the maximum weight loss rate at 118 °C to 120 °C and 298 °C to 301 °C. These two peaks are due to the evaporation of physically and chemically absorbed H\(_2\)O. The percentages of physically and chemically absorbed H\(_2\)O are 13.8 % and 9.88 % respectively in prepared TiO\(_2\) nanoparticles.

The shape of the prepared TiO\(_2\) nanoparticles has been observed with the help of a field emission scanning electron microscope (FESEM). Figure 3d showed the microstructure behaviour of TiO\(_2\) nanoparticles and analyzed that, the microscopic view of nanoparticles tends to spherical shape. The spherical shapes of nanoparticles have a positive impact on the thermo-mechanical properties of developed nanocomposites and also help to enhance the interfacial bond between reinforcement and matrix materials [43, 44].

The high-resolution transmission electron microscope (TEM) was performed to analyze the micrographic view of TiO\(_2\) nanoparticles shown in Fig. 4a. It was observed that the nano-ceramic particle forms dense aggregates made by crystallites whose sizes were varied from 10 to 20 nanometers. Figure 4b showed the selected area electron diffraction (SAED) ring pattern with the mark of Miller indices of TiO\(_2\) nanoparticles. The SAED is the crystallographic experimental method to examine the crystal structure pattern of TiO\(_2\) nanoparticles [25]. The ring pattern of TiO\(_2\) nanoparticles confirmed that the granular appearances of the ring are well balanced with polycrystalline where sizes of the ingredient crystallites ranged between 10 to 20nm.

**Characterization of composite laminates**

**Tensile properties**

For the design and development of new composite materials, it is very essential to identify the tensile properties. To find out the tensile strength, tensile modulus and elongation at break of the developed
composites, tensile testing has been performed. The maximum tensile strength identifies the ability of a material to resist failure, whereas, the ability of the material to resist deformation or plastic deformation is characterized by tensile modulus also called the stiffness of the materials and elongation at break identifies the ability of elongation of the material before it goes through fracture and failure [45]. Figure 5a showed the typical engineering stress-strain graph and Fig. 5b showed the comparative analysis of tensile properties with the influence of different weight fractions of TiO₂ nanoparticles for developed composite laminates.

The addition of TiO₂ nanoparticles up to certain percentages along with glass fiber showed an increment in tensile strength and tensile modulus for developed composites. This may be due to the addition of fine and well dispersion of nanoparticles along with glass fibers that improve the interfacial bonding strength between matrix and fiber. The better interfacial bonding helps to transmit higher load and stress from matrix to reinforced materials [30]. From the results, it was observed that the tensile strength of the developed composites was recorded maximum for GFRP-T1.0 (341.53 MPa) which was 38.56% higher than GFRP-T0.0. Furthermore, the tensile modulus was recorded highest for GFRP-T1.5 (12.89 GPa) which was 52.72% greater than the GFRP-T0.0 composite laminates due to rigidity and stiffness provided by the nanoparticles. Further increments of nanoparticles loading (More than 1.5%) showed, decrement in tensile properties due to agglomeration/clustering effects of TiO₂ nanoparticles with epoxy matrix while, the presence of excessive nanoparticles in developed composites may also obstacles the matrix continuity, which may result in the decrements of tensile properties [8, 30].

**Flexural properties**

To find the flexural properties of developed composite laminates such as flexural strength, flexural modulus and maximum deflection, the three-point bending test has been performed. Figure 6a showed the flexural stress-strain plot and Fig. 6b showed the comparative analysis of flexural properties with the influence of different weight fractions of TiO₂ nanoparticles for developed composite laminates. As similar to tensile properties, the addition of TiO₂ nanoparticles up to 1% by weight along with glass fiber showed an increment in flexural strength while maximum flexural modulus was recorded for GFRP-T1.5 composite laminates. The maximum flexural strength was observed for the GFRP-T1.0 (421.26 MPa) which was 30.52% greater than GFRP-T0.0 composite laminates. This increment may be due to the dispersion of TiO₂ surface area and the adhesive bond between matrix and reinforcement at the lower weight of TiO₂ nanoparticles. The maximum flexural modulus was observed for GFRP-T1.5 (16.19 GPa) which was 34.13% greater than GFRP-T0.0 composite laminates. This increment happened due to a greater adhesion bond between fiber and matrix with fine dispersion of TiO₂ nanoparticles while the orientation of fibers also enhanced and affects the properties of developed composite laminates [46]. But at higher weight fraction of nanoparticles loading created agglomeration/clustering effects which result in a sudden decrement in the mechanical properties [8, 47].

**Micro-hardness**

The ability to resist localized plastic deformation of any material is known as the hardness of the material [48].
Figure 7 showed the microhardness of developed composite laminates and recorded the highest micro hardness of 36.42 Hv for GFRP-T1.0 composites which was 48.53% higher than GFRP-T0.0 composite laminates. From the result, it was notified that the addition of TiO₂ nanoparticles from 0.5 to 1% increased the microhardness of developed composites. This increment at a lower weight fraction may be attributed to a greater interfacial bond of matrix-fiber with the dispersion of TiO₂ nanoparticles. But further increment of nanoparticles weight fraction (1.5–2%), the continuously decrements in microhardness values were recorded. This may be due to the agglomeration/clustering of nanoparticles at higher weight fractions [49].

**Impact strength**

To identify the shock and energy absorption ability of developed composite laminates, Charpy impact testing has been performed. Figure 7 represented the impact strength of different developed composite laminates. From the test result, it was observed that the addition of TiO₂ nanoparticles (up to 1%) along with glass fiber reinforcements showed an increment in impact strength while further increment of TiO₂ nanoparticles weight fraction (more than 1 wt%) observed decrement in impact strength. The better dispersion of nanoparticles in GFRP composite laminates helps to make better interfacial bonding between reinforcing material and matrix materials that showed an increment in impact strength at a
lower weight fraction of nanoparticles. But excessive addition of nanoparticles (more than 1 wt%) in developed composite laminates make it more brittle and that evidence of brittleness revealed a reduction in impact strength values as well as a reduction in elongation before break value for tensile and flexural specimen composite laminates [50]. The maximum impact strength was recorded for the GFRP-T1.0 (27.43 KJ/m²) which was 327.10 % more than GFRP-T0.0 composite laminates.

**Inter-laminar shear strength (ILSS)**

One of the major failure criteria of composite laminates are investigated when the load is subjected to transverse direction and these failures are analyzed due to inter-laminar shear stress. So, for the design and development process of laminated composites, it is very important to investigate the ILSS. To examine the ILSS properties of developed composites, short beam shear testing has been performed. Figure 7 represented the result of the inter-laminar shear test and maximum inter-laminar strength was observed for GFRP-T1.0 (39.44 MPa) which was 25.22 % greater than GFRP-T0.0 composite laminates. The addition of TiO₂ nanoparticles with glass fiber reinforcement results in better interfacial bond with better dispersion of nanoparticles that improved the ILSS of developed composites. This might be happened due to strong shear strength between laminates up to 1 % loading of TiO₂ nanoparticles while, further increments of nanoparticles loading, the decrements were recorded in inter-laminar bonding strength due to high brittleness and agglomeration of the nanoparticles [51].

**Fracture properties**

The fracture toughness and fracture energy of developed composite laminates have been investigated and represented in Fig. 8. Due to the presence of a high cross-link structure in epoxy polymer, the polymer showed brittle in nature and low fracture toughness value (0.58 MPa-m¹/²). The addition of glass fiber with epoxy matrix increased the toughness value up to 3.35 MPa-m¹/². This increment suggests that the addition of fiber made the material ductile. Now the addition of TiO₂ nanoparticles with glass fiber composite showed a further increment in toughness value. The maximum toughness and fracture energy values of 3.92 MPa-m¹/² and 5.86 KJ/m² respectively were recorded for the GFRP-T1.0 composite which was 17.01 % and 40.19 % higher than GFRP-T-0.0 composite laminates respectively. But further addition of nanoparticles (more than 1 %) showed a decrement in toughness and fracture energy values. The increments in fracture properties are analyzed due to crack path deflection, crack pining and plastic void growth where the dispersion of nanoparticles creates Vander wall bond between molecular chains of epoxy and TiO₂ nanoparticles that leads to enhance constrained between nanoparticles/polymer chain and polymer chain itself [52].

At a low weight fraction, the nanoparticles interrupted the crack front propagation inside the composite laminates. These
nanoparticles create obstacles at the crack front and result in crack front bowing in the middle of nanoparticles. This may lead to creating secondary crack which results in increments of fracture toughness and fracture energy [44]. But for the higher weight fraction of $TiO_2$ nanoparticles, the bonding strength decreased rapidly due to the agglomeration of nanoparticles that reduce the homogeneity and effective weight fraction of nanoparticles. Therefore, debonding of the nanoparticles with epoxy polymer chain reduces that creates the cavity and hence, lower fracture toughness and fracture energy are recorded at a higher weight fraction of $TiO_2$ nanoparticles [53].

**Thermal stability of composite laminates**

To identify the thermal stability of the developed composites, thermogravimetric analysis has been performed. Figure 9 showed the thermograms of the composite laminates. From obtained results, it was observed that the mass loss of the composites has occurred in three stages. The first stage was recorded at 450 °C, the second was at 550 °C and the third stage was up to 650 °C. The degradation of mass at each stage has been tabulated in Table 1. From the results, it was analyzed that, the addition of $TiO_2$ nanoparticles increased the thermal stability of the developed composite laminates. This may be happened due to the catalytic effect of $TiO_2$ nanoparticles with cross-link nature epoxy polymer where the cross-link density results to improve the decomposition temperature of the developed composites [54].

At low $TiO_2$ nanoparticles loading the thermal degradation were high and low residual mass at 900 °C was analyzed for developed composite laminates. The residual of 44.64 % for GFRP-T0.0 composite was recorded that followed by

![](image_url)

**Table 1** Thermal decomposition of developed composite laminates

| Composite Code | First stage weight loss up to 450 °C (%) | Second stage weight loss up to 550 °C (%) | Third stage weight loss up to 650 °C (%) | % residual mass at 900 °C |
|----------------|--------------------------------------|--------------------------------------|--------------------------------------|------------------------|
| GFRP-T0.0      | 45.72                                | 50.25                                | 55.82                                | 44.64                  |
| GFRP-T0.5      | 42.83                                | 47.60                                | 51.69                                | 48.31                  |
| GFRP-T1.0      | 38.77                                | 43.14                                | 46.52                                | 53.48                  |
| GFRP-T1.5      | 37.91                                | 41.27                                | 44.64                                | 55.56                  |
| GFRP-T2.0      | 31.27                                | 38.53                                | 42.77                                | 57.23                  |
GFRP-T0.5 < GFRP-T1.0 < GFRP-T1.5 < GFRP-T2.0 composite laminates where the residual mass of 48.31%, 53.41%, 55.36% and 57.23% are observed. Therefore, it revealed that, as the weight fraction of TiO2 nanoparticles increases, the percentage of residual mass also increases due to the ceramic nature of TiO2 nanoparticles. These nanoparticles created a barrier to oxygen and heat inside the epoxy matrix that results in better thermal stability for developed composite laminates [55].

Glass transition temperature ($T_g$)

To investigate the glass transition temperature of developed composite, differential thermal analysis (DTA) has been performed. The DTA measured the temperature difference between the specimens and the reference materials. When the heating began, the temperature change ($\Delta T$) was measured with differential thermocouples until the static state was reached [56]. The measured $\Delta T$ is also known as the glass transition temperature ($T_g$) of the materials. Figure 10a showed the DTA curve with $T_g$ value and observed that, as the weight fraction of TiO2 nanoparticles increased, the $T_g$ of the developed composite was also increased (up to 1.5% of TiO2 loading), moreover, there is a sudden drop was observed for 2% nanoparticles loading. The comparative $T_g$ value at a different weight fraction of TiO2 nanoparticles are represented in Fig. 10b. The maximum $T_g$ was observed for GFRP-T1.5 (116 °C) which was 20.83% greater than GFRP-T0.0 composite laminates. For thermosetting polymer (epoxy resin) based composites, factors like- molecular weight, cross-link density, fiber/ filler- matrix interfacial bonding and polymer tactility played a vital role to identify the $T_g$ value of the composites [57]. In the present study, the addition of nanoparticles (up to lower weight fraction, 1.5%) along with glass fiber increased the interfacial interaction between matrix and reinforcing material where the dispersion of TiO2 nanoparticles played a vital role for increments in thermal stability and glass transition temperature. However, at a higher weight fraction of nanoparticles, clusterization and agglomeration effect has been observed, which reduced the cross-link density of epoxy matrix and interfacial interaction between matrix and reinforcing material [58]. Therefore, the glass transition temperature for GFRP-T2.0 decreased rapidly.

Surface morphology and failure mechanism

The surface microstructure and fracture behavior of developed composite laminates are characterized with help of scanning electron microscopy (SEM). The morphology analysis was examined with a high magnification of 100x to 5000x and voltage of 5 kV at atmospheric temperature. The dispersion of TiO2 nanoparticles with epoxy matrix and stacking sequence of glass fiber were analyzed and showed in Fig. 11. The different types of failure such as brittle fracture of the epoxy matrix, fiber breakage, debonding, pullout, crushing and delamination of developed composites under tensile and flexural testing were also analyzed on the fracture surfaces [59]. The results examined that, dispersion of TiO2 nanoparticles in the epoxy matrix is properly mixed with less than 1% of voids, results in a superior interfacial bond with glass fiber reinforcements. A similar observation
is also reported with previous studies \([60, 61]\). The thermo-
mechanical performances of developed composites indi-
cated that incorporation of TiO\(_2\) nanoparticles up to 1.5 %
TiO\(_2\) nanoparticles are well dispersed with epoxy matrix
and create a strong interfacial bond with glass fibers. The
glass fiber can be transferred its high reinforcing potential to
TiO\(_2\) nanoparticles and matrix materials that revealed high
mechanical and thermal properties with less fiber breakage
and pullout \([25]\). Whereas, the presence of an excess amount
of nanoparticles showed visible clusterization and agglomer-
ate with epoxy matrix. The effects of clustering/agglomera-
tion act as the stress concentration sites on the developed
composite due to generation of cavitations, void, debonding,
and cracks with epoxy matrix and finally, affect the per-
formances of composite materials \([25, 38]\). Thus, further
increments of TiO\(_2\) nanoparticles loading (more than 1.5 %)
showed improper bonding with epoxy matrix and reduction
in their mechanical and thermal performances were recorded
for developed composite laminates. The current developed
composite laminates are mostly failed due to brittle fracture
of epoxy resin with linear behavior of stress-strain curve up
to failure and there is no plastic deformation occurred.

**Conclusions**

Nanoparticles are gaining too much attention to embedded with
glass fiber reinforced epoxy composites due to their advanced
physical and structural properties. In this study, the effective role
of TiO\(_2\) nanoparticles has been demonstrated towards the fabri-
cation of superior physical, mechanical and thermal properties
based on epoxy glass fiber composites. The TiO\(_2\) nanoparticles
are prepared with sol-gel methods and mix in epoxy matrix with
help of mechanical starring and sonication to ensure better disper-
sion. Then, vacuum-assisted resin infusion molding techniques
(VARIM) are used to fabricate the composite laminates with
reinforcements of glass fibers. The effects of different weight fractions (0.5%, 1.0%, 1.5%, and 2.0%) of TiO₂ nanoparticles on glass fiber reinforced epoxy composites are studied and compare the thermo-mechanical properties of glass fiber reinforced composites (GFRP-T0.0). Based on the characterization, the following conclusions are drawn.

- The physical and chemical characterization of derived TiO₂ nanoparticles with XRD and FTIR confirmed the better structure and functional properties to enhance the dispersion qualities with matrix and proved that the dispersion of nanoparticles to be very efficient to make the better interfacial bond with an epoxy matrix that reduces the voids and defaults in developed composites.

- The physical and chemical absorption of water contents were analyzed with TGA/DTG and percentage weight loss and weight loss rate was recorded. The physically absorbed water evaporated at 120°C with 13.8% of water contents that made a weak bond with TiO₂ while, chemical absorption of water made a strong bond with TiO₂ at 300°C with 9.88% of water contents.

- The surface morphology and microstructure of TiO₂ nanoparticles were characterized by TEM and FESEM and showed better crystallographic structure with spherical shape to improve the thermo-mechanical properties of developed composite laminates.

- The developed composite laminates were used to perform tensile, flexural, impact, inter-laminar shear, micro-hardness, and fracture tests and observed that the inclusion of TiO₂ nanoparticles up to 1.0% with glass fiber epoxy composites (GFRP-T1.0) enhanced their tensile, flexural, ILSS and impact strength while tensile and flexural modulus were recorded maximum for GFRP-T1.5 due to high stiffness and rigidity provided by TiO₂ nanoparticles.

- The highest micro-hardness (36.42Hv), fracture toughness (3.92 MPa-m⁰.⁵) and fracture energy (5.86kJ/m²) were exhibited for GFRP-T1.0 composite laminates while further increments of nanoparticles loading agglomerate with an epoxy matrix that increased the brittleness of materials and reduction in thermo-mechanical properties were recorded.

- The maximum thermal stability and decomposition of developed composites are characterized where the degradation temperature starts at 450°C and is degraded at 650°C. The maximum glass transition temperature (T_g) of 116°C for GFRP-T1.5 composites were recorded due to mobility loss of cross-link density of epoxy with the interaction of TiO₂ nanoparticles.

- The morphology analysis at fracture surfaces was characterized by SEM and failure of developed composites were analyzed with fiber breakage, fiber pullout, fiber/nanoparticles debonding, cracking of epoxy matrix with brittle fracture. The excess presence of nanoparticles showed agglomeration and clustering due to cavitations and debris formed with epoxy matrix.

The effective results and investigations conclude that the improvement of thermo-mechanical properties due to the principle of toughening mechanism may have interesting for various industrial applications.

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Declarations

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