

Thermal shock effect of nano-TiO₂ enhanced glass fiber reinforced polymeric composites: An assessment on tensile and thermal behavior

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Abstract

Fiber reinforced polymeric (FRP) composite materials are currently used in numerous structural and materials related applications. But, during their in-service period these composites were exposed to different changing environmental conditions. Present investigation is planned to explore the effect of thermal-shock exposure on the mechanical properties of nano-TiO₂ enhanced glass fiber reinforced polymeric (GFRP) composites. The samples were conditioned at +70°C temperature for 36 h followed by further conditioning at – 60°C temperature for the similar interval of time. In order to estimate the thermal-shock influence on the mechanical properties, tensile tests of the conditioned samples were carried out at 1 mm/min loading rate. The polymer phase i.e. epoxy was modified with different nano-TiO₂ content (i.e. 0.1, 0.3 and 0.5 wt. %). The tensile strength of 0.1 wt.% nano-TiO₂ GFRP filled composites exhibited higher ultimate tensile strength (UTS) among all other composites. The possible reason may be attributed to the good dispersion of nanoparticles in polymer matrix corresponds to proper stress transfer during thermal-shock conditioning. In order to access the variations in the viscoelastic behavior and glass transition temperature due to the addition of nano-TiO₂ in GFRP composite and also due to the thermal shock conditioning, dynamic mechanical thermal analysis (DMTA) measurements were carried out. Different modes of failures and strengthening morphology in the composites were analyzed under scanning electron microscope (SEM).

Keywords: Glass fiber reinforced polymer (GFRP); Nano-TiO₂; Thermal-shock; Ultimate tensile strength (UTS); Dynamic mechanical thermal analysis (DMTA)

1. Introduction

The tremendous usage of trending materials like fiber reinforced polymeric (FRP) composite materials makes it as a supreme choice of material throughout the globe. These materials can be used in different structural applications. But the applications are not limited to structural components, many more sectors use these materials such as aerospace, automotive, structural, sporting goods, low temperature applications and oil and gas pipelines. But, these polymeric composites during their in-service time are exhibited to different severely harsh environments along with different nature of loadings [1]. The structural parts of space vehicles and aircrafts were exposed to changing environmental conditions. Inclusion of different nanoparticles into the polymer matrix composites (PMC) is said to be an effective part of research investigation everywhere in the globe. Generation of specific behaviors of nano-particles in the PMC is a vital objective to accomplish improved mechanical, thermal, insulation and electrical behaviors. Several researchers have assessed the mechanical behavior of GE composites and the beneficial properties of addition of various nanofillers to these [2–4], as well as the property variation at different environments and loading conditions [5–8]. The addition of nano-TiO₂ particles improves bearing strength [9], storage modulus

[10] and glass transition temperature [11], flexural properties, thermal conductivity [11] etc. In the open literature there is scarcity of tensile performance of nano-TiO₂ enhanced PMC at thermal shock environment; however, the results associated to these tests are of excessive practical significance from application point of view. In this experimental investigation, polymer phase of the composite was tailored with different nano-TiO₂ content and the fabrication of laminated composite was carried out. Then the GFRP and nano-TiO₂ filled composites are conditioned to thermal shock environment and its tensile behavior was investigated. Furthermore, using DMTA the viscoelastic performance of the different composites was assessed.

Table 1: Mechanical behavior of epoxy and glass fibre

Property	Polymer(Epoxy)	Reinforcement Glass Fibre
Density (g/cm)	1.162	2.58
Tensile Strength (GPa)	0.11	3.4
Tensile modulus (GPa)	4.1	72.3
Failure Strain(%)	4.6	4.8
Areal weight of fabric (g/m ²)	-	360

2. Experimental technique

2.1 Materials

The preparation of control GFRP and nano-TiO₂ enhanced GFRP composites was carried out through the well-known hand layup technique. The polymer matrix used during fabrication process was well recognized with the vendor label with diglycidyl ether of bisphenol A type (DGEBA). The hardener is well known with triethylene tetra amine (TETA). The reinforcement used during fabrication process was woven fabric E-glass fiber having 0/90° as orientation in warp and weft direction respectively. The glass fibres was acquired from Owens Corning Industries. The resin (epoxy) and hardener are picked up from Atul Industries, Gujarat defining the manufacturer trade name as Lapox L-12 and K-6 respectively. During fabrication of glass/epoxy composites, the epoxy polymer to binder as hardener weight fraction was maintained at a ratio of 10:1.

2.2 Preparation of control GFRP and nano-TiO₂ enhanced GFRP composites

The laminated layered GFRP composites are produced with nine sheets of glass fiber consuming 50:50 weight percentage of glass fibers and epoxy respectively. The values of different mechanical assessment of, glass fibers and epoxy are shown in table 1. To accomplish better mechanical properties of the GFRP composites, proper scattering of nano-particles in polymer region was becomes vital. Thus, altering the different weight fractions of nano-particles in polymer phase by the help of in ultra-sonicator and magnetic stirrer. For curing of composites laminate hot compression hydraulic press was used at 60°C temperature at around 500 kPa pressure for a duration of 20 minutes. The composite was made according to ASTM D3039 standard. A diamond wheel cutter was used to the cut the composites. Furthermore, to ensure proper curing of composites, post curing of different sort of composite specimens was conducted with the help of hot oven at 140°C temperature for a duration of 6 hrs [12].

2.3 Different test parameters of control GFRP and nano-TiO₂ enhanced composite

The tensile tests were done using universal testing machine i.e. Instron 8862 to accomplished the tensile

tests at ambient temperature for the different thermal shock composite specimens such as control GFRP and nano-TiO₂ enhanced composites. All the tests were carried out at 1 mm/min loading rates. DMTA measurements were carried out to assess the viscoelastic properties and glass transition (T_g) performance of numerous composites. Scanning electron micrography (SEM) was carried out for the fractured specimens to define the strengthening mechanisms and accumulation of nano-TiO₂ particles.

3. Results and discussion

3.1 Effect of tensile behavior of nano-TiO₂ enhanced GFRP composite at thermal shock environment

Fig 1. depicts the stress vs strain plot of control GFRP, 0.1, 0.3 and 0.5 wt. % nano-TiO₂ enhanced GFRP composites tested at a loading rate of 1 mm/min. It was evident from fig. 1 that the tensile strength of 0.1 wt. % GFRP/nano-TiO₂ composites exhibited higher strength among all other composites. Further, with enhancement in nano-particles into the polymer phase shows decrease in the value of overall composite strength. The cause possibly governed by the accumulation of nano-particles in the PMC. These clusters of nano-TiO₂ particles experiences inadequate transfer of load along the direction of fiber/matrix interfacial section.

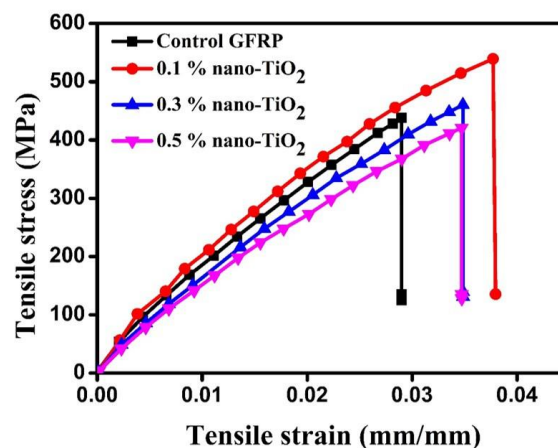


Figure 1. Stress Vs strain curve for control GFRP and nano-TiO₂ enhanced GFRP composites at several nano-TiO₂ particles contents at thermal shock environment

Fig. 2 depicts the deviation in tensile strength and modulus picked up from fig.1. Fig. 2 was plotted against different nano-TiO₂ content for unmodified GFRP and nano-TiO₂ enhanced GFRP composites. The tensile behaviors are highly relying on the content of nano-particles in the GFRP composites. By accretion of 0.1 wt % nano-TiO₂ in the GFRP composite, the thermal shocked composites caused in enhancement in UTS as well as in modulus value than control GFRP composites as shown from fig. 2(a) and fig. 2(b). By the fusion of 0.1 wt.% nano-TiO₂ particles improved the tensile strength by 18.82% than control GFRP composite. This enhancement in strength could be governed by the high specific surface area of nano-TiO₂ particles that possesses high interfacial zone across the composite. However, for appropriate stress transfer this high specific surface area induces easily the stress across the interfacial zone. Finally, the 0.1 wt.% nano-TiO₂ filled composite possesses higher strength than control GFRP composite at thermal shocking environment. But, with further accumulation of nano-TiO₂ particles (0.3 and 0.5 wt. %) in the GFRP composites owed to reduction in modulus and strength values. This reduction in strength and modulus corresponds to the accumulation of nano-particles in the polymer phase of the composite at a particular zone.

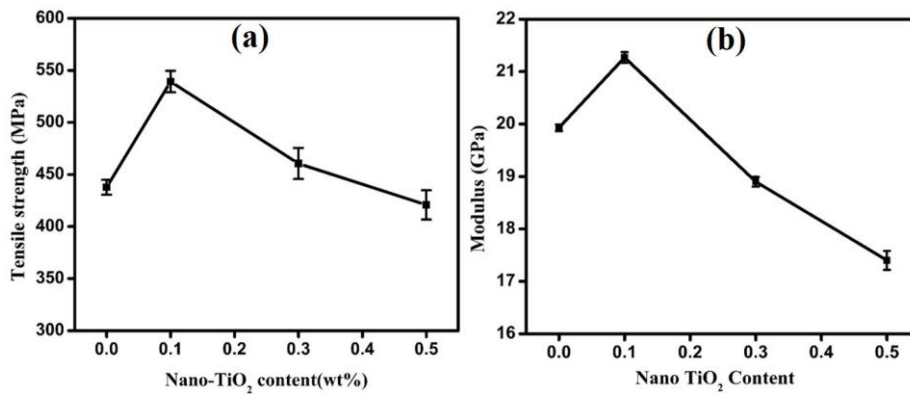


Figure 2. Difference in (a) Tensile strength and (b) modulus with GFRP and nano-TiO₂ filled GFRP composites

Mostly, at the interfacial zone poor wettability led to weaker adhesion between the nano-TiO₂ particles, fiber and matrix and this arises owing to accumulation of nano-TiO₂ particles. The tensile strength of nano-TiO₂ filled GFRP composite containing 0.1 wt. % nano-TiO₂ was found to remain more as related to rest other composites. The modulus vs nano-TiO₂ content of GFRP composites are revealed in fig.2(b). The modulus was found to be 6.27 % higher in 0.1 wt. % nano-filler enhanced GFRP composite as related to unmodified GFRP. This increase of modulus value corresponds to proper bonding behavior of matrix/fiber/ nano-TiO₂ particles in composite. Fig. 3 demonstrates the failed pictures of GFRP and nano-TiO₂ enhanced GFRP composite with numerous failure patterns tested after the tensile tests at a 1 mm/min loading rate of. The sample A reveals fracture at the middle part of the composite, while sample B, C and D indicates cracks mostly near the tab area of the composite samples.

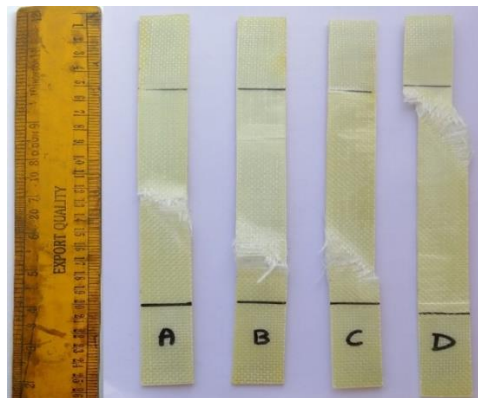


Figure 3. Failed configurations of (a) Unmodified GFRP (b) 0.1 % nano-TiO₂ (c) 0.3% nano-TiO₂ and (d) 0.5 % nano-TiO₂

3.2 Dynamic Mechanical Thermal Analysis (DMTA) of thermal shocked conditioned composites

The thermo-mechanical analysis of thermal shocked conditioned control GFRP and nano-filler enhanced GFRP composites was done in accordance with ASTM D7028 standard in the DMTA (Model; Netzsch DMA 242E) in between 30 °C to 200 °C temperature. The rate of heating used during experiment was 5 °C/min. During DMTA, the sample was placed in the 3-point bending fixture. The frequency was maintained at 5 Hz. The equipment supplies dynamic stress to the specimen and the corresponding result was monitored in terms of dynamic displacement. In case of a perfectly solid elastic material, the supplied load and produced strain keep on in a phase. However, there was a phase

alteration observed in polymeric (i.e. viscoelastic) material. The elastic modulus of the measured material was represented as storage modulus (E'), whereas the viscous modulus represents the loss modulus (E'') replicates the viscoelastic composites. The coefficient of damping ($\tan \delta$) was determined between the fraction of E'' to E' . Fig. 4(a)-(d) represent the deviation in E' , E'' , $\tan \delta$ and glass transition behavior (T_g), with temperature variation for control GFRP and nano- TiO_2 filled GFRP composites. Fig. 4(a) depicts that the E' for 0.1 wt.% nano-filler enhanced GFRP composites was more as that of control GFRP composite at temperature below T_g . The inception of sharp alteration in slope of E' with temperature was measured as the T_g of the corresponding composite. Fig. 4(b) indicates the alteration in E'' owing to fusion nano particles with the GFRP composites. The value of E'' was recorded maximum at 0.1 wt.% nano-filler enhanced GFRP composite. The $\tan \delta$ value reduces as the nano- TiO_2 particles starts to accumulates presenting higher brittle behavior in the composite as observed from fig. 4(c). Fig. 4(d) illustrates that incorporation with 0.5 wt. % nano- TiO_2 particles in the GFRP composites reduces the T_g from 125.3 °C to 108.6 °C. As the content of nanofillers increases in the GFRP composites the T_g values goes on decreasing. The lowering of T_g value could be recognized by the interference of developments of crosslinks owing to entrapment of nano- TiO_2 particles in between the polymeric chains.

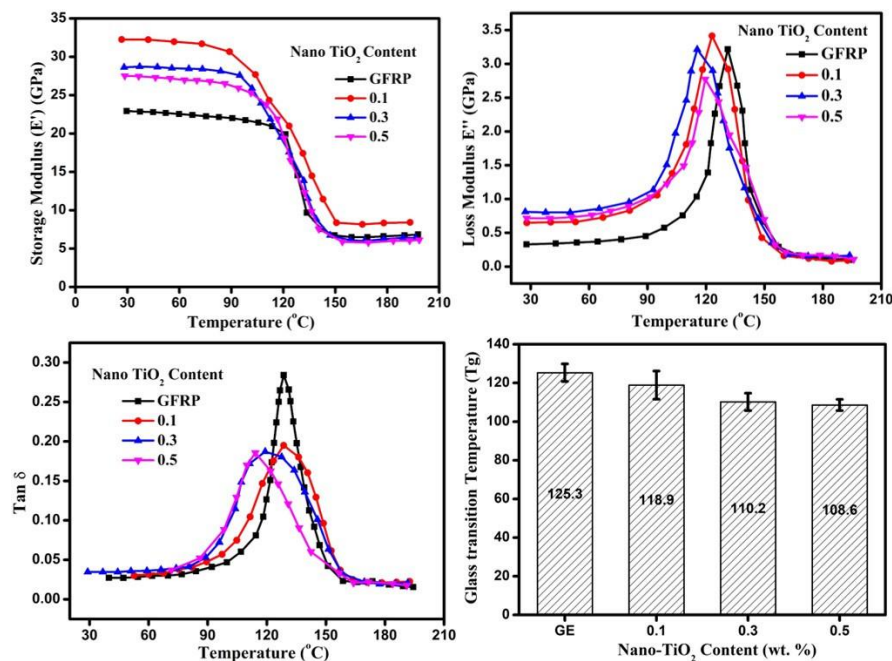


Figure 4. Representation of (a) Storage modulus, (b) Loss modulus and (c) Damping coefficient ($\tan \delta$) with variation in temperature and (d) T_g with different nano- TiO_2 content for GFRP composite

This decrease in T_g temperature can be defined in relations to the rearrangement of the polymeric chains in the interfacial zone. It can be expected that the interfacial region comprises of two classes of polymeric films [13]. The primary layer is strongly bound to the nanofiller owing to multi-layer adsorption. The secondary layer is lightly stacked to the polymer, i.e. not harshly exaggerated but has important influence in the interphase area and hold a little altered arrangement in structure than that of polymer at the higher content of polymer region and has comparatively lower role in the T_g of the composite material.

3.2 Fractography analysis by SEM

SEM was carried out for control GFRP and nano-TiO₂ filled GFRP composites and different strengthening morphology and reduction in strength value of composites were examined and are presented in fig. 5.

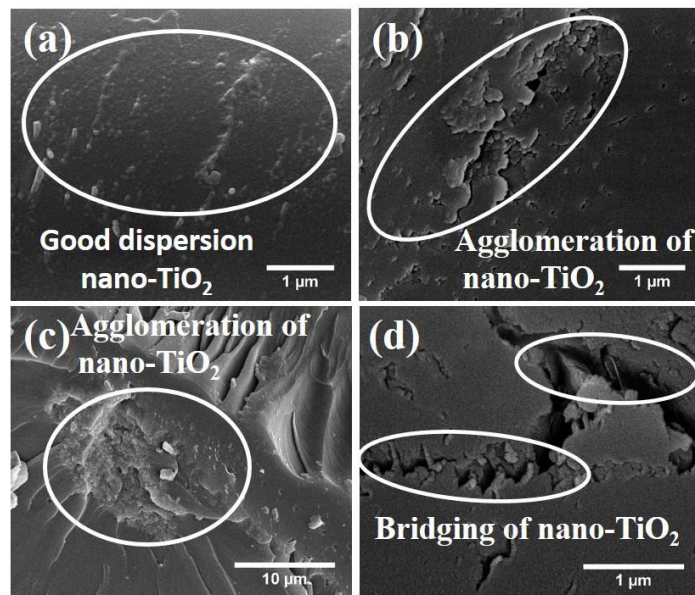


Figure 5. SEM micrographs of (a) 0.1 wt. % nano-TiO₂/GFRP (b) 0.3 wt. % nano-TiO₂/GFRP (c) 0.5 wt. % nano-TiO₂/GFRP (d) 0.1 wt. % nano-TiO₂/GFRP

Fig. 5(a) shows 0.1 wt. % nano-filler enhanced GFRP composite illustrating good scattering of nano-TiO₂ particles all over the composites. Proper scattering of nano-filler in the PMC carries appropriate stress transfer across the polymer matrix to the fiber. Accumulation of nano-TiO₂ particles are seen in case of 0.3 and 0.5 wt.% nano-filler enhanced GFRP composites as shown in fig. 5(b) and 5(c). These accumulations of nano-TiO₂ particles at a particular zone of epoxy polymer zone corresponds to inappropriate stress transfer through the matrix phase following with decrease in modulus and strength values. In case of 0.1 wt. % nano-TiO₂ bridging phenomenon was observed between the nanoparticles at the epoxy polymer region as shown in fig. 5(d).

4. Conclusions

The current exploration of control GFRP and nano-TiO₂ filled GFRP composites in thermal shock environmental conditions have the following pertinent outcomes as follows;

- The tensile strength of 0.1 wt.% nano-TiO₂ GFRP filled composites exhibited higher UTS among all other composites.
- With the incorporation of 0.1 wt.% nano-TiO₂ in the GFRP composite improved the tensile strength and modulus by 18.82% and 6.27% respectively than control GFRP composite.
- DMTA analysis reveal that the storage modulus was found to be maximum for 0.1 wt.% nano-TiO₂ GFRP filled composites and T_g decreases with increase in nano-TiO₂ content.
- SEM micrographs shows strengthening mechanisms by crack bridging phenomenon between nanoparticles in 0.1 wt.% nano-TiO₂ filled GFRP composites, whereas in higher percentage enhanced GFRP composites indicates agglomerations of nanoparticles.

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References

- [1] K.K. Mahato, K. Dutta, B.C. Ray, Static and Dynamic Behavior of Fibrous Polymeric Composite Materials at Different Environmental Conditions, *J. Polym. Environ.* (2017) 1–27. doi:10.1007/s10924-017-1001-x.
- [2] R.K. Nayak, K.K. Mahato, B.C. Ray, Water absorption behavior, mechanical and thermal properties of nano TiO₂ enhanced glass fiber reinforced polymer composites, *Compos. Part Appl. Sci. Manuf.* 90 (2016) 736–747. doi:10.1016/j.compositesa.2016.09.003.
- [3] J. Kathi, K.-Y. Rhee, J.H. Lee, Effect of chemical functionalization of multi-walled carbon nanotubes with 3-aminopropyltriethoxysilane on mechanical and morphological properties of epoxy nanocomposites, *Compos. Part Appl. Sci. Manuf.* 40 (2009) 800–809. doi:10.1016/j.compositesa.2009.04.001.
- [4] R.K. Nayak, K.K. Mahato, B.C. Routara, B.C. Ray, Evaluation of mechanical properties of Al₂O₃ and TiO₂ nano filled enhanced glass fiber reinforced polymer composites, *J. Appl. Polym. Sci.* 133 (2016). doi:10.1002/app.44274.
- [5] K.K. Mahato, D.K. Rathore, K. Dutta, B.C. Ray, Effect of loading rates of severely thermal-shocked glass fiber/epoxy composites, *Compos. Commun.* 3 (2017) 7–10. doi:10.1016/j.coco.2016.11.001.
- [6] B.C. Ray, Loading Rate Sensitivity of Glass Fiber–Epoxy Composite at Ambient and Sub-ambient Temperatures, *J. Reinf. Plast. Compos.* 25 (2006) 329–333. doi:10.1177/0731684406060246.
- [7] B.C. Ray, Effects of crosshead velocity and sub-zero temperature on mechanical behaviour of hygrothermally conditioned glass fibre reinforced epoxy composites, *Mater. Sci. Eng. A.* 379 (2004) 39–44. doi:10.1016/j.msea.2003.11.031.
- [8] K.K. Mahato, A.O. Fulmali, R. Kattaguri, K. Dutta, R.K. Prusty, B.C. Ray, Effect of severely thermal shocked MWCNT enhanced glass fiber reinforced polymer composite: An emphasis on tensile and thermal responses, *IOP Conf. Ser. Mater. Sci. Eng.* 338 (2018) 012057. doi:10.1088/1757-899X/338/1/012057.
- [9] O. Asi, An experimental study on the bearing strength behavior of Al₂O₃ particle filled glass fiber reinforced epoxy composites pinned joints, *Compos. Struct.* 92 (2010) 354–363. doi:10.1016/j.compstruct.2009.08.014.
- [10] A. Omrani, A.A. Rostami, Understanding the effect of nano-Al₂O₃ addition upon the properties of epoxy-based hybrid composites, *Mater. Sci. Eng. A.* 517 (2009) 185–190. doi:10.1016/j.msea.2009.03.076.
- [11] Y. Hu, G. Du, N. Chen, A novel approach for Al₂O₃/epoxy composites with high strength and thermal conductivity, *Compos. Sci. Technol.* 124 (2016) 36–43. doi:10.1016/j.compscitech.2016.01.010.
- [12] D.S. Kumar, M.J. Shukla, K.K. Mahato, D.K. Rathore, R.K. Prusty, B.C. Ray, Effect of post-curing on thermal and mechanical behavior of GFRP composites, *IOP Conf. Ser. Mater. Sci. Eng.* 75 (2015) 012012. doi:10.1088/1757-899X/75/1/012012.
- [13] G. Tsagaropoulos, A. Eisenberg, Dynamic Mechanical Study of the Factors Affecting the Two Glass Transition Behavior of Filled Polymers. Similarities and Differences with Random Ionomers, *Macromolecules.* 28 (1995) 6067–6077. doi:10.1021/ma00122a011.