Mechanical performance of CNT-filled glass fiber/epoxy composite in in-situ elevated temperature environments emphasizing the role of CNT content

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Abstract

Carbon nanotubes (CNTs) are one of the prime choice nano-filler reinforcement for fibrous polymeric composites. But the stability of the CNT/polymer interface is yet to be ensured for elevated temperature engineering applications. Present study deals with the assessment of elevated temperature durability of glass fibre/epoxy (GE) composite with various level of multi walled carbon nanotube (MWCNT) loading. Flexural testing at room temperature revealed that addition of 0.1% MWCNT yielded maximum strength (+32.8% over control GE) and modulus (+11.5% over control GE) amongst all the CNT modified composite systems. Further, MWCNT-GE composites resulted in accelerated degradation of mechanical performance with increasing temperature as compared to GE composite. Dynamic mechanical thermal analysis (DMTA) was carried out to study the viscoelastic behaviour of all composites over a range of temperature. The design parameters were evaluated by Weibull probability function. Fractographic analysis figured out various failure modes in all composites at various temperatures.

Keywords: A. Polymer-matrix composites (PMCs); A. Carbon nanotubes and nanofibers; D. Mechanical testing; D. Fractography.

1   Introduction

In recent years, the addition of nano fillers to the conventional fiber reinforced polymer (FRP) composites has drawn significant attention from both academia and industry [1–3]. Laminated composites exhibit poor matrix dominated and interlaminar properties [4–6] and often susceptible to various harsh and hostile environments [7–9]. Few studies have suggested that the mechanical response of these potential materials is significantly altered when they are exposed to elevated temperature environment [10]. Incorporation of nanofiller such as carbon nanofiber, carbon nanotube (CNT) has been successfully used to improve the

matrix dominated and interlaminar properties [6,11,12]. CNTs exhibit unique structural properties such as exceptionally high specific stiffness and specific strength. Further addition of CNTs to the FRP composites has its own challenges [13,14]. The main challenge is to uniformly disperse them in the polymer matrix [15] in order to obtain high interfacial area through which stress can be transferred from the weak matrix to the strong nanotubes. Effective stress transfer through the CNT/polymer interface is the key to obtain superior mechanical properties in the CNT modified laminated composites [16]. The high surface area due to its nano dimension and very high aspect ratio is desirable for an efficient load transfer but undesirably provides high attraction forces between the CNTs themselves which leads to the formation of agglomerates when these CNTs come close to each other in the polymer matrix. Various methods have been demonstrated in the literature to disperse the CNTs in polymer resins such as stirring, sonication and calandering. Recently, an interesting result shows that a negative correlation exists between modulus and density of CNT reinforced polymer nano composites due to the inherent nano porosity of CNTs, which is quite beneficial for mobile structural applications [17]. Jiang et al. [18] have reported a dramatic enhancement in both modulus and strength by about 1200% and 300% respectively by incorporation of aligned CNTs into polyimide matrix. Investigation focused on the cryogenic durability of CNT modified epoxy composite by Lau et al. [19] suggested nearly 42% increment in young's modulus at 77K by addition of 1 wt.% coiled carbon nanotubes in the epoxy matrix. The volume content of the CNTs in the polymer composite has also an influential role on its mechanical performance [20]. Ashrafi et al. [21] have reported several benefits of adding 0.1% single walled carbon nanotube (SWCNT) into carbon fiber/epoxy composite such as 3.5% superior compression after impact strength in addition to improvement in mode I and mode II fracture toughness by 13% and 28% respectively. Further various studies have suggested that chemical functionalization is another way to improve the dispersion in the polymer matrix [13,22–24]. The type of CNT and type of functionalization strongly influence the CNT/polymer character and hence the mechanical performance of the FRP composite [25]. But the functionalization is again very much time consuming and increases the economic load in the final composite product. Keeping these issues in mind, present investigation is focused on the development of very economic and efficient fabrication method for structural GE composite modified with MWCNT. Low and cryogenic property enhancement due to CNT addition into FRP composites has been reported [26–28]. Still to the best of authors' knowledge there is a dearth of open literature on the mechanical response of these potential materials at elevated temperature environment. The

originality of the present study is the assessment of structural performance of these GE composite with a range of CNT loading at various elevated temperature environments.

2   Experimental Details

2.1   Materials

For fabricating the GE composites, Diglycidyl ether of Bisphenol A type epoxy resin with Triethylene tetra amine as hardener was used which were supplied by Atul Industries, India. The E-glass fiber used in this study was a 3K plain weave with filament diameter 15 μm purchased from Owens Corning, India. The MWCNT used for modifying the epoxy resin was of 6-9 nm outer diameter with 5 μm length purchased from Sigma-Aldrich.

2.2   Fabrication of the laminates

2.2.1   Fabrication of control GE laminate

The laminates in this study were prepared with 14 layers of glass fiber by hand lay-up technique followed by compression moulding at 60 °C temperature with 10 kg/cm^2 pressure for 20 minutes. During fabrication the fraction of epoxy and glass fiber in the laminates was maintained at 40:60 by weight. 10% (as per the weight of epoxy resin) hardener was mixed in the epoxy resin as per the supplier's instruction. The control GE composite was fabricated without any MWCNT. At the same time some amount of epoxy/hardener mixture was also poured into a disc shaped mould for differential scanning calorimetry (DSC) studies. For making MWCNT embedded GE composites, MWCNTs were dispersed in the resin prior to going for fabricating the laminates. To study the effect of MWCNT content in the final composite, three different compositions were chosen, i.e. 0.1%, 0.3% and 0.5% MWCNT with respect to the weight of epoxy. The final volume fractions of epoxy and glass fibres in the laminate were determined by the resin burn-off test.

2.2.2   Fabrication of MWCNT incorporated GE laminates

Usually in the as received condition from the manufacturer, the MWCNTs are present in agglomerated form to reduce their net surface energy. Thus to deagglomerate the existing MWCNT agglomerates, required amount of MWCNT was first dispersed in 150 mL acetone which was then stirred at 1000 rpm for 1 hour followed by 1 hour of bath sonication. Due to the high rotation speed in stirring and high frequency waves in sonication, shearing forces are developed between the MWCNTs and between the MWCNT and acetone, facilitating the

process of deagglomeration. This MWCNT/acetone mixture was then added to the preweighed epoxy. The epoxy/MWCNT/acetone suspension was then stirred at 70 °C with 1000 rpm till evaporation of all acetone was ensured. This also facilitates dispersion of MWCNT in epoxy. The left over epoxy/MWCNT suspension was then sonicated at 70 °C for 1 hour to further make a better dispersion of MWCNT in epoxy resin. During the whole process of stirring and sonication there is a significant probability of entrapment of air bubbles in the suspension. These bubbles should be removed to the maximum possible extent from the suspension else they will remain as voids in the final composite which is detrimental for the mechanical properties of the composite. Hence the epoxy/MWCNT suspension was kept under vacuum for 18 hrs. Then required amount of hardener was added to the epoxy/CNT suspension followed by hand lay-up technique with 14 layers of glass fiber and compression moulding with the same parameters as that of the control GE composite as described in section 2.2.1 to fabricate GE composites with 0.1%, 0.3% and 0.5% MWCNT. The schematic of this whole procedure is shown in figure 1. From the remaining epoxy/MWCNT/hardener suspension, a disc shaped sample was prepared for DSC studies. Then all the laminates were kept at room temperature for 24 hrs. After this all the laminates exhibit a thickness of 4.0±0.1 mm. For characterizing the materials, standard samples were cut from the laminates using diamond wheel cutter for resin burn off test, short beam shear (SBS) test, flexural test and dynamic mechanical thermal analysis (DMTA). The samples were then post-cured at 140 °C for 6 hr [29].
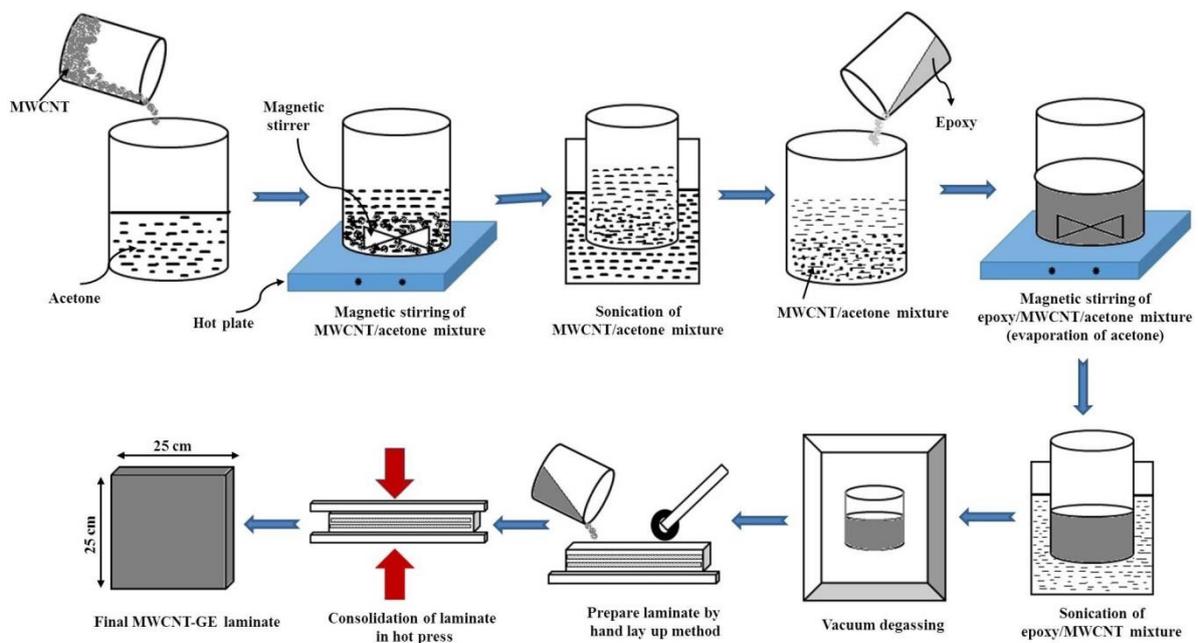
Figure 1: Schematic of fabrication of MWCNT-GE composite laminate.

2.3 Material Characterization

For determining the void content in each laminate resin burn off test was carried out. A piece of 25 mm × 25 mm sample from each of the laminate was taken in different silica crucibles. These crucibles were then kept at 575 °C for 5 hours in a muffle furnace and then allowed to cool inside the furnace. Then the fiber volume fraction and void content were determined as per ASTM D 3171 – 99.

For getting information on the bending properties of the materials flexural test (as per ASTM D7264) was performed. To evaluate the apparent inter-laminar shear strength (ILSS), short beam shear (SBS) test (as per ASTM D2344) was conducted. The flexural and ILSS properties of the GE composites with various MWCNT content were evaluated using the 3-point bending fixture in Instron 5967 attached with environmental chamber. These properties were measured at room temperature (20 °C) and various in-situ elevated temperatures (70 °C, 90 °C and 110 °C) with a holding time of 10 minutes at a loading rate of 1 mm/min.

The dynamic properties of the GE composites with various MWCNT loading were also evaluated using the 3-point bending fixture in a dynamic mechanical thermal analyser (DMTA) (Netzsch DMA 242E). The temperature was increased from 40 °C to 200 °C at a heating rate of 5 °C/min using a frequency of 1 Hz.

In order to determine the effect of MWCNT in epoxy, DSC analysis was carried out on neat epoxy and epoxy/MWCNT (0.1, 0.3 and 0.5 wt.%) nanocomposites using Mettler Toledo DSC. The experiments were carried out in a temperature range of 40-150 °C at a heating rate of 5 °C/min.

3 Results and Discussion

3.1 Void content in the as fabricated composites

Figure 2 represents the fiber volume fraction and void content in the composite laminates as a function of MWCNT content. The fiber volume fraction remains approximately 48% for all composite laminates (figure 2(a)). The void fraction was increased from 0.9% to 1.6% due to addition of 0.1% MWCNT and remains almost unaltered thereafter with further MWCNT addition as shown in figure 2(b). Perhaps, during vacuum degassing all the entrapped air bubbles (formed because of stirring and sonication during MWCNT dispersion in epoxy resin) could not be removed from the viscous epoxy/CNT suspension and hence the void

content is higher in case of MWCNT embedded GE composites. But clearly there is no change in void content when the MWCNT content was increased from 0.1% to 0.5%.
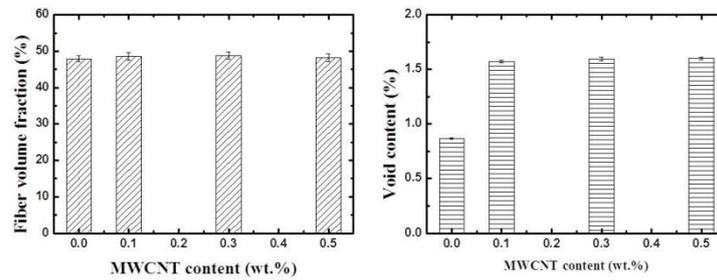
Figure 2: (a) Fiber volume fraction and (b) void content in the laminate as a function of MWCNT content.

3.2   Flexural test
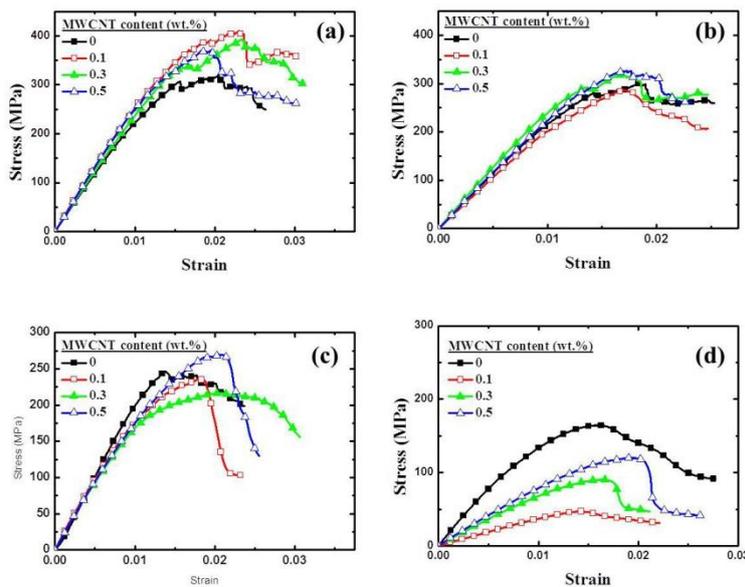
Figure 3: Flexural stress-strain curves for GE composites at various MWCNT contents at (a) RT (20 °C), (b) 70 °C, (c) 90 °C and (d) 110 °C.

The flexural stress ~ strain plots for samples with various MWCNT loading at various in-situ temperatures are shown in figure 3. The service temperature of these materials is limited in accordance with their glass transition temperature (T_g). Hence the maximum in-situ testing temperature was so chosen that it is close to the T_g of the composites (nearly 110 °C). The impact of temperature on GE composite with 0% (control) and 0.1% MWCNT can be noticed

from figure 4. The properties obtained from these stress ~ strain plots are then reported in table 1 and plotted in figure 5.
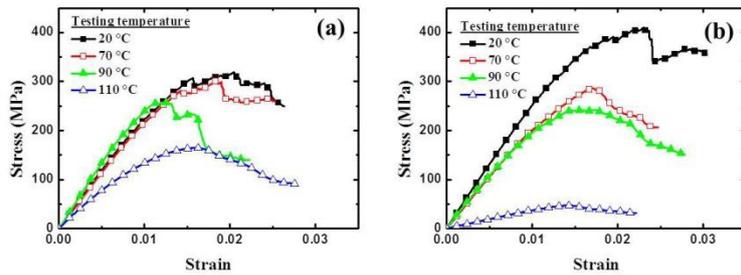
Figure 4: Flexural stress-strain curves for GE composites with (a) 0% and (b) 0.1% MWCNT contents at various in-situ temperatures.
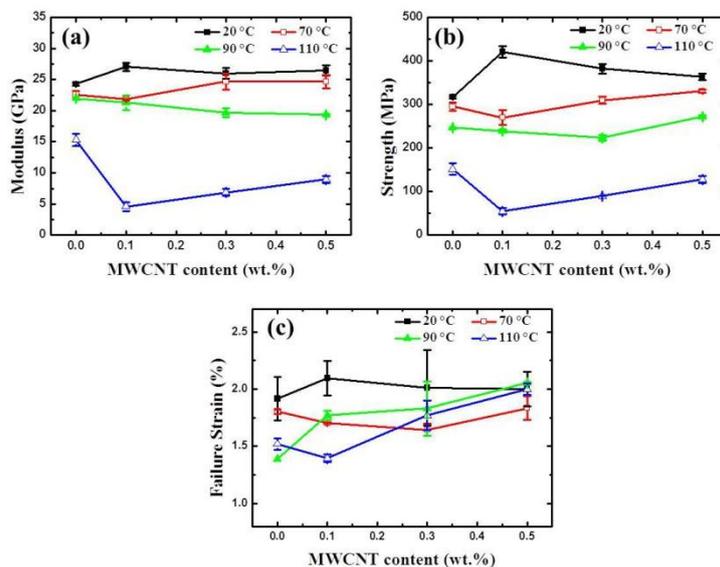
Figure 5: Variation in (a) flexural modulus, (b) flexural strength and (c) failure strain with MWCNT content in GE composite at various in-situ temperatures.

The through thickness properties of laminated composites is mostly governed by the matrix and/or interface/interphase. Thus suitable modification of the matrix and/or interface/interphase by nano-fillers is one of the possible ways to improve its flexural performance. For structural applications, load transfer from matrix to CNTs is the foremost requirement which enables CNTs to actively participate in the load carrying action.

Addition of 0.1% MWCNT into the GE composite resulted in enhancement of both modulus and strength by 11.5% and 32.8% respectively when tested at room temperature as shown in figure 5 (a) and figure 5 (b). This huge increment in strength might be attributed to the

efficient stress transfer from the soft polymer matrix to the stiff MWCNT through the subtle CNT/polymer interface. The potential exploitation of CNTs in a composite can only be achieved if majority of the load could be transferred from the matrix to the nanotube. In case of CNT reinforced epoxy, the strength enhancement is a function of, (i) CNT/epoxy interfacial bond strength and (ii) total available CNT/epoxy interfacial area. The CNT/epoxy interfacial bond strength is again influenced by the various types of physical, chemical and mechanical interaction between CNT and epoxy and these factors appear to be dependent on molecular nature of both components and independent of the CNT content in the composite. The later factor, i.e. CNT/epoxy interfacial area is the controlling factor for mechanical performance alteration for GE composites with varying content of MWCNTs. Due to its nano dimension, MWCNT exhibits enormous high specific surface area (surface area per unit mass or volume) which ultimately converts to a very large CNT/epoxy interfacial area in the final composite. Availability of such a large interfacial area reduces the interfacial stress concentration and hence facilitates stress transfer from the matrix to the MWCNT. This enables the composite material to sustain a higher stress, hence increases its strength. In addition to the interfacial stress transfer, the other factors which may directly or indirectly influence the flexural modulus and strength are; (i) decrease in free volume due to mating accommodation of CNTs into the polymer network, (ii) rigidity may be enhanced due to restriction of inter-chain slippage resulting from inter-chain bridging by CNTs, (iii) higher strength may be expected due to micro crack deflection and/or dissolution which is highly anticipated in the interfacial area and (iv) it may further be reasonably assumed that CNTs may migrate to the fiber/polymer interface and may enhance the strengthening effect by small interactions.

The failure strain (strain at peak stress) also increased by 9.5% due to this amount of MWCNT addition to GE composites (figure 5 (c)). Any event which restricts the formation or growth of crack enhances its toughness. In this context, presence of significant number of ultra-strong MWCNTs ahead of the crack-tip in GE composite hinders the crack propagation rate and thus restricts or deflects the crack. At the same time toughness of the material may also be enhanced by nanotube pull out [30] and crack bridging [31] by CNTs. This probably is the prime factor for improving the toughness of the 0.1% CNT-GE composite as confirmed from strain to failure plot shown in figure 5(c). Hence addition of only 0.1% MWCNT into GE composite not only makes it stronger, stiffer but also toughens the material, broadening its area of application with a higher reliability and durability.

Addition of further higher amount (0.3% and 0.5%) of MWCNT results in no significant change in modulus, whereas a significant drop in strength was noticed. The strength of the composite gradually decreases with increasing MWCNT content when the MWCNT content exceeds the critical concentration (i.e. 0.1%). This suggests that addition of MWCNT beyond 0.1% essentially reduces the MWCNT/epoxy interfacial area, which is in principle contradictory to what is expected (i.e. interfacial area should increase with high CNT content). As the void content in all MWCNT-GE composite are mostly same as confirmed from figure 2(b), the reason to this contradiction may be attributed towards the agglomeration of MWCNTs when present in a bulk amount in the matrix. The surface energy of MWCNTs is very high which makes it quite unstable and when a bunch of MWCNTs are placed close to each other, they tend to agglomerate to reduce the net surface energy of the system which enhances their stability. From the above discussion, we conclude that addition of MWCNTs beyond a certain limit (0.1% here) reduces the MWCNT/epoxy interfacial area due to agglomeration of MWCNTs. In addition, aggregated CNTs act as stress concentrators [32].

As temperature increases, both glass fiber and epoxy try to expand and the rate of expansion depends upon their respective co-efficient of thermal expansion (CTE). The CTE for epoxy is 6.2×10^{-5} K^{-1} [33], which is one order of magnitude higher than that of glass fiber ($5\text{-}12 \times 10^{-6}$ K^{-1}) [34]. Hence radial expansion of glass fibres take place at a much slower rate than the epoxy surrounding it which develops residual internal stress at the glass fiber/epoxy interface. This stressed interface acts as potential nucleation site for debonding and hence generation of micro-cracks. Hence, the strength of the GE composite is significantly lowered. In addition to this, softening of the polymer at elevated temperature also contributes towards this strength degradation. Another thing which can be observed from figure 5(b) is that the rate of strength degradation increases with increasing temperature and at 110 °C, the degradation rate is quite high as this temperature is quite close to its corresponding T_g (112.6 °C).

In addition to these glass/epoxy interface some more interfaces do exist in case of MWCNT modified GE composites, i.e. the MWCNT/epoxy interface. As MWCNT exhibits a CTE ($\sim 1 \times 10^{-5}$ K^{-1} [35]) which is around $1/6^{th}$ that of epoxy, the MWCNT/epoxy interface experience a stress. The magnitude of this stress is again a function of temperature, i.e. higher the temperature, higher is the stress and hence the stress concentration. As epoxy expands at a higher rate than MWCNT at elevated temperature, debonding is expected at the MWCNT/epoxy interface. This in-turn proposes that the rate of strength degradation with

increasing temperature is higher for MWCNT embedded GE composites than control GE composite. Again if we consider all the three MWCNT reinforced GE composites, we can clearly observe that the rate of strength degradation is highest in case of the 0.1% MWCNT-GE followed by 0.3% MWCNT-GE and 0.5% MWCNT-GE. The number of potential nucleation sites for debonding at MWCNT/epoxy interface is certainly a direct function of the total available MWCNT/epoxy interfacial area, which supports the experimental results. As it is already confirmed that the MWCNT/epoxy interfacial area is highest in case of 0.1% MWCNT-GE composite (due to best dispersion among all MWCNT-GE composites), the rate of strength gradation in this composite is higher than 0.3% MWCNT-GE and 0.5% MWCNT-GE due to highest available debonding sites at 70 °C, 90 °C and 110 °C. At 110 °C, a linear trend between flexural strength and MWCNT content is noticed as per the following equation.

At 110 °C; for $0.1 \leq x \leq 0.5$;

$$\sigma_C = 35.37 + 182.31x \qquad \qquad \text{...(1)}$$

where σ_C and x represent the flexural strength (in MPa) of the composite and MWCNT content (in wt.%) in the composite respectively.

3.2.1 Constitutive deformation model

For a reliable structural application, the mechanical performance of the given material must be predictable with a high degree of accuracy. In case of FRP composites several strengthening, toughening and failure modes get activated independently or combinedly depending upon the flow behaviour of the matrix, reinforcement and the interface/interphase. Fiber fragmentation, fiber pull-out, matrix cracking, interfacial debonding, matrix crack bridging by fiber, crack pinning and many more such micro-mechanical events control the overall flow behaviour of the bulk composite. The statistical variation of the mechanical performance of this class of materials is well addressed by Weibull probability distribution function. The simulated stress (σ) ~ strain (ε) relationship can be expressed by the below mentioned equation [36,37].

$$\sigma = E\varepsilon \exp\left[-\left(\frac{E\varepsilon}{\sigma_o}\right)^{\beta}\right] \qquad \qquad \text{...(2)}$$

E represents the elastic modulus of the composite in the direction of applied load. σ_o and β are the weibull design parameter. σ_o is known as scale parameter which is an indicative of the

nominal strength (higher σ_o represents higher strength) of the composite whereas β is the shape parameter indicating the extent of scatter in the performance (higher β means lower scatter).

Equation (2) can be rewritten as;

$$\frac{\sigma}{E\varepsilon} = \exp\left[-\left(\frac{E\varepsilon}{\sigma_o}\right)^{\beta}\right] \qquad \text{…(3)}$$

Taking logarithms of both sides of equation (3), we get

$$\ln\left(\frac{\sigma}{E\varepsilon}\right) = -\left(\frac{E\varepsilon}{\sigma_o}\right)^{\beta}$$

$$\text{Or, } \ln\left(\frac{E\varepsilon}{\sigma}\right) = \left(\frac{E\varepsilon}{\sigma_o}\right)^{\beta} \qquad \text{…(4)}$$

Taking again logarithms of both sides of equation (4),

$$\ln\left[\ln\left(\frac{E\varepsilon}{\sigma}\right)\right] = \beta \ln(E\varepsilon) - \beta \ln(\sigma_o) \qquad \text{…(5)}$$

Hence, from the experimental stress (σ) ~ strain (ε) data and the obtained elastic modulus (E) of the respective specimen, if a graph between $\ln(E\varepsilon)$ and $\ln\left[\ln\left(\frac{E\varepsilon}{\sigma}\right)\right]$ is plotted, a straight line is expected with slope of β. From the value of β and intercept ($-\beta \ln(\sigma_o)$), the value of σ_o can be determined. The scale and shape parameters of all the composites at various in-situ service temperatures are shown in figure 6. At all the temperatures, the scale parameters show similar trend as that of the flexural strength which can be seen from figure 5(b). The shape parameter shows a linear trend with MWCNT content at room temperature as can be seen from figure 6(a) as expressed in the below equation.

$$\beta = 2.52 - 0.39x \qquad \text{…(6)}$$

where x represents the MWCNT content in wt.%. This shows that addition of MWCNT decreases the β value and hence increases the extent of scattering. But again it seems that addition of MWCNT decreases the scatterness at 70 °C and 110 °C as confirmed from figure 6(b) and figure 6 (d), whereas at 90 °C a higher degree of scatter is noticed for MWCNT-GE composites (figure 6 (c)).
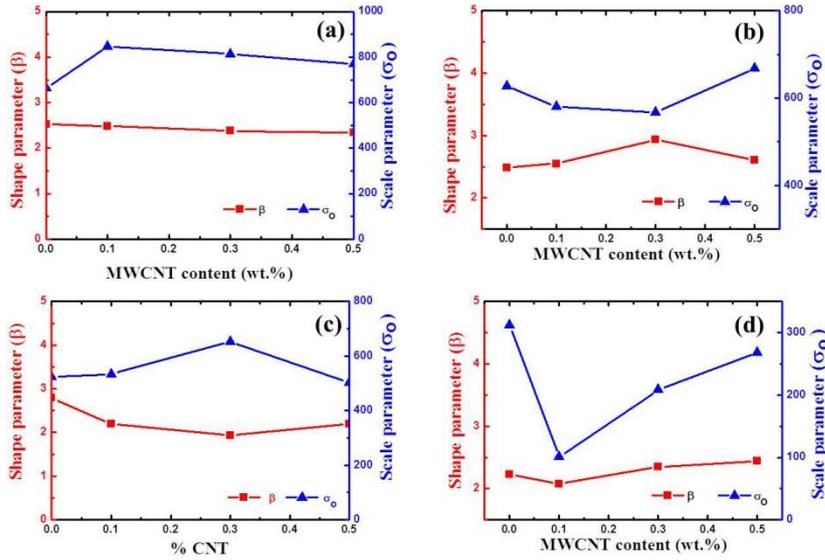
Figure 6: Weibull scale (σ_o) and shape (β) parameters of GE composites with various MWCNT content at (a) RT (20 °C), (b) 70 °C, (c) 90 °C and (d) 110 °C.

3.2.2 *Fractography*

Post failure analysis of all the fractured samples were carried out in order to understand various micro and nano scale failure mechanisms. Addition of MWCNT to the epoxy can significantly contribute towards various strengthening and toughening mechanisms at nanoscale which can modify the failure behaviour of conventional FRP composites. Further the in-service environment has a strong impact on the damage micro-mechanisms in the composite materials.

Figure 7 represents the delamination surfaces of the samples tested at room temperature. For GE composite very smooth fibre imprints were observed on the delamination front (figure 7 (a)) whereas addition of MWCNT contents alters the imprint morphology. All MWCNT-GE composites contain fibre imprints accompanied with matrix deformation on the delaminated surface as can be seen from figure 7 (b), figure 7 (c) and figure 7 (d). In case of 0.5% MWCNT-GE composite in-plane matrix crack were observed as shown in figure 7 (d) which may be contributing towards the loss of mechanical properties of 0.5% MWCNT-GE composites.
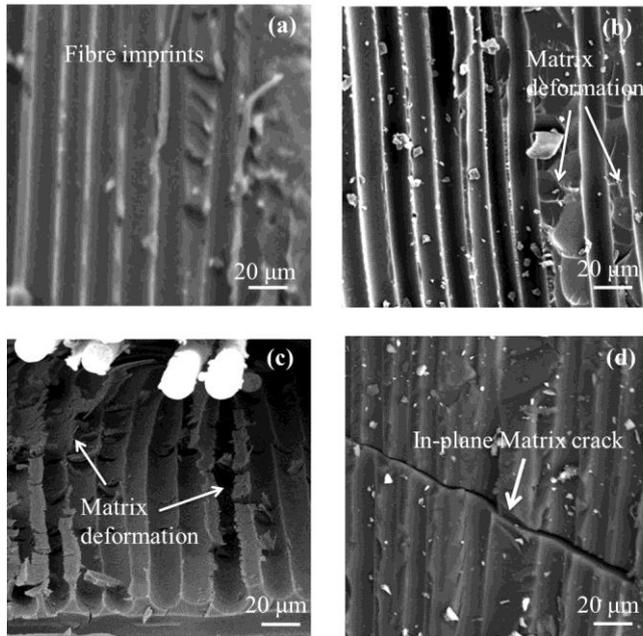
Figure 7: SEM images of the imprints on GE composite with (a) 0%, (b) 0.1%, (c) 0.3% and (d) 0.5% MWCNT content at RT.

Figure 8 indicates the dispersion state of MWCNTs in the matrix of 0.1% and 0.5% MWCNT-GE laminated composites. The MWCNTs are mostly isolated from each other and uniformly distributed throughout the matrix of 0.1% MWCNT-GE composite (figure 8 (a)) whereas in 0.5% MWCNT-GE composites, local bunches of MWCNTs are found which form agglomerates as shown in figure 8 (b). The reduction of strength at higher MWCNT content can be attributed towards formation of these agglomerates, reducing the total CNT/epoxy interfacial area. The toughness increment in GE composite due to addition of 0.1% MWCNT may be attributed to the nanotube pullout and crack bridging by nanotubes as can be seen from figure 8(c).
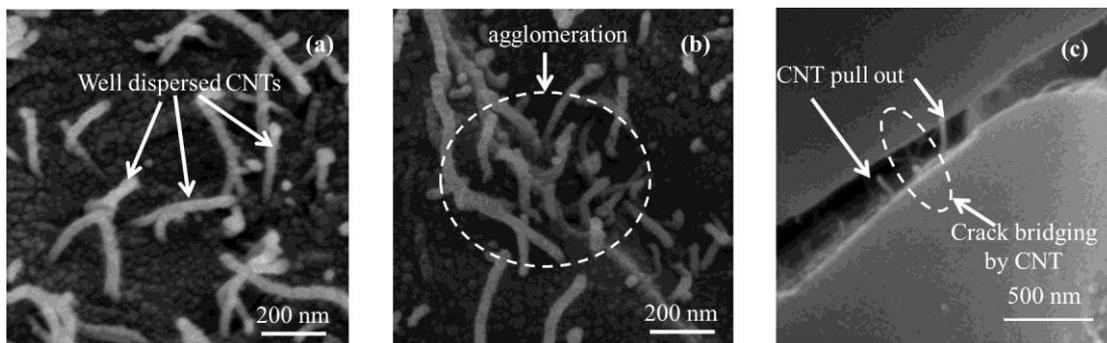
Figure 8: Dispersion of (a) 0.1%, (b) 0.5% MWCNT in GE composite, and (c) CNT pull out and crack bridging by CNT in 0.1% MWCNT-GE composite after room temperature testing.

Figure 9 indicates various deformation features observed in samples tested at 70 °C temperature. Figure 9 (b) contains severe matrix deformation and can be correlated for the loss in strength and modulus in 0.1% MWCNT-GE composite as compared to control GE composite shown in figure 9 (a). Fractured micrograph of GE tested at 70°C shows highly oriented shear cusps in the interfiber spacing which is an indicative of effective load transfer from fiber to fiber through matrix. Figure 9 (c) and figure 9 (d) show the riverlines on the surface of 0.3% MWCNT-GE and 0.5% MWCNT-GE composite. Increasing number of river line markings roughly represents the number of isolated well dispersed MWCNTs [32]. These CNTs forced the cracks to propagate bypassing the CNTs and taking longer path which in-turn resulted in dissipation of more energy through pinning and crack tip bifurcation mechanisms [32].
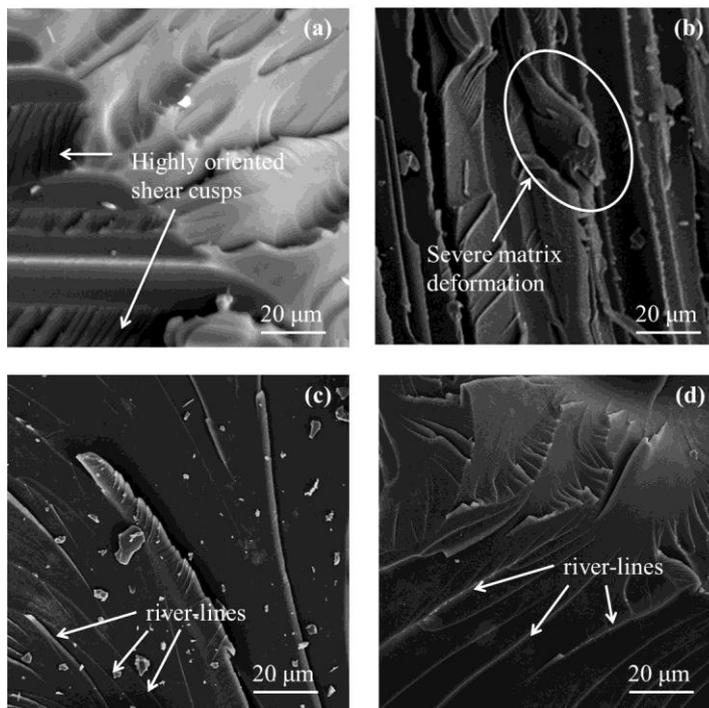
Figure 9: SEM images of the fractured GE composites with (a) 0%, (b) 0.1%, (c) 0.3% and (d) 0.5% MWCNT content at 70 °C.

Figure 10 is an attempt to have an insight to fiber/matrix interfacial zone in GE and MWCNT modified GE composites tested at 90°C temperature. GE composite (figure 10 (a)) shows some debonded interfaces along with drainage of the matrix at some places, whereas figure

10 (c) shows heavy matrix drainage in case of 0.3% MWCNT-GE composite. In 0.1% MWCNT-GE composite (figure 10 (b)) matrix cracking close to the debonded interfacial zone is observed. Figure 10 (d) shows a good fiber/matrix interfacial bonding (though interfacial debonding at very few locations) through which efficient load transfer occurs, making the GE composite with 0.5% CNT to exhibit the highest strength at this testing temperature.
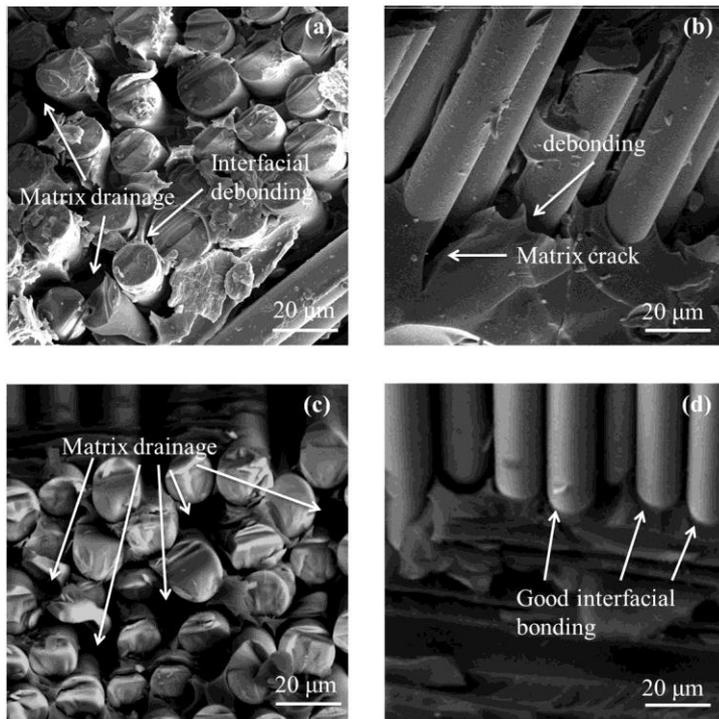
Figure 10: The glass fiber/epoxy interfacial zone of GE composite with (a) 0%, (b) 0.1%, (c) 0.3% and (d) 0.5% MWCNT content at 90 °C.

Figure 11 represents the micrographs of the specimens tested at 110°C temperature. Figure 11 (a) and figure 11 (b) shows the riverlines at the GE and 0.1% MWCNT-GE composite surface. The riverlines are closely spaced in GE composites as compared to 0.1% MWCNT-GE composite indicating more ductile behaviour. The strength, modulus and strain to failure in 0.1% MWCNT-GE composite are lower as compared to all other composites tested at 110°C temperature. The micrographs of 0.3% MWCNT-GE and 0.5% MWCNT-GE composites are in close agreement of the strain to failure of these materials as it can be seen from the figure 11 (c) and figure 11 (d) which shows extensive plastic deformation of the matrix. This shows that 0.5% MWCNT-GE composite exhibits highest strain to failure followed by 0.3% MWCNT-GE, GE and 0.1% MWCNT-GE which is in good agreement with the results shown in figure 5 (c).
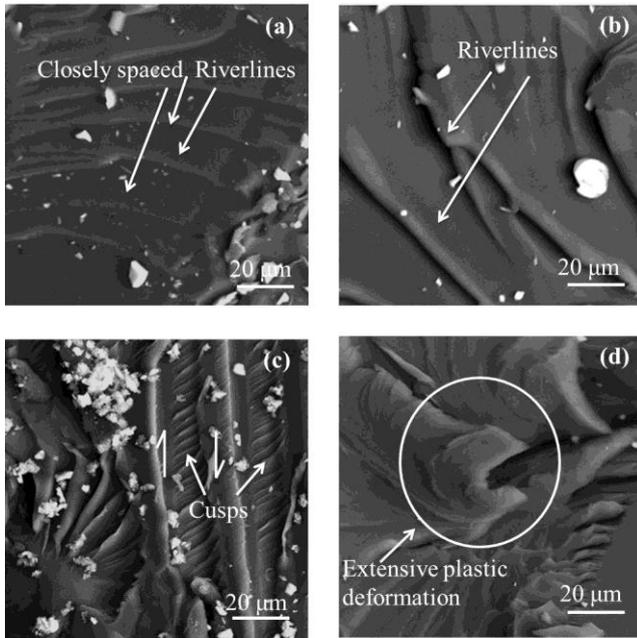
Figure 11: The deformation behaviour in the matrix phase of GE composite with (a) 0%, (b) 0.1%, (c) 0.3% and (d) 0.5% MWCNT content at 110 °C.

3.3   *Short beam shear (SBS) test*
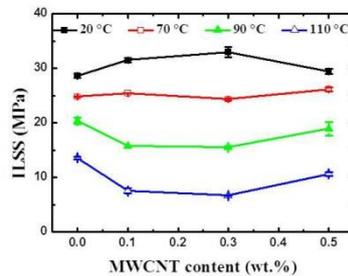
Figure 12: Variation in ILSS with different MWCNT content at various in-situ temperature environments.

The variation of apparent interlaminar shear strength (ILSS) for control GE and various MWCNT-GE composites at different elevated temperature is shown in figure 12. At 20 °C (room temperature) the ILSS increases with the addition of MWCNT upto 0.3wt% and then further addition of MWCNT resulted in decrease in ILSS. The maximum increase in ILSS obtained was about 15% for 0.3% MWCNT-GE composites over control GE composites at 20°C. Although, the better dispersion of MWCNTs were observed in 0.1% MWCNT-GE composite but the ILSS of 0.1% MWCNT-GE and 0.3% MWCNT-GE composite are nearly similar which can be attributed to good intralaminar and interlaminar strengthening due to

CNTs. At 70°C temperature, no significant change in ILSS was observed with the addition of MWCNTs to GE composites.

The variation trend of ILSS with MWCNT content at 90°C and 110°C temperature are similar and the lowest shear strength is observed for 0.3% MWCNT-GE composites. Again at both 90°C and 110°C temperatures, GE composite exhibited higher ILSS as compared to all other MWCNT modified composites. It is very interesting to note that the maximum drop in ILSS with increasing in-situ testing temperature were observed for 0.3% MWCNT-GE composite although at room temperature it exhibits the highest ILSS amongst all composites. The probable reason for this high rate of reduction can be attributed to the failure of MWCNT/epoxy interface with increasing temperature.

3.4 *Dynamic Mechanical Thermal Analysis (DMTA)*

The variation in dynamic mechanical properties i.e. storage modulus (E′), loss modulus (E″) and loss tangent (tan δ) with temperature (T) for the GE composites with various MWCNT content (0%, 0.1%, 0.3%, 0.5%) are shown in figure 13 in the temperature range of 40 °C to 200 °C. It can be observed from figure 13(a) and 13(a′) that at the earlier glassy state (e.g. at 70 °C and 90 °C) of the composites, the storage modulus shows a linear increase with MWCNT content which is not so nicely followed in case of flexural modulus as shown in figure 5(a) for 70 °C and 90 °C. The difference might be due to the different thermal history of the samples (in DMTA analysis temperature was increased from 40 °C to 110 °C at 5°C/min, whereas in flexural testing there was a holding time of 10 minutes at the testing temperature and the heating rate is set by the instrument, which is can't be controlled). But, coincidentally the trends of storage modulus and flexural modulus are quite similar at 110 °C. Again in the rubbery state (e.g. at 160 °C) a slight higher E′ is noticed for MWCNT-GE composites over GE composite. The reason might be attributed towards the increased viscosity of the epoxy matrix due to the presence of MWCNTs which restricts the deformation rate.
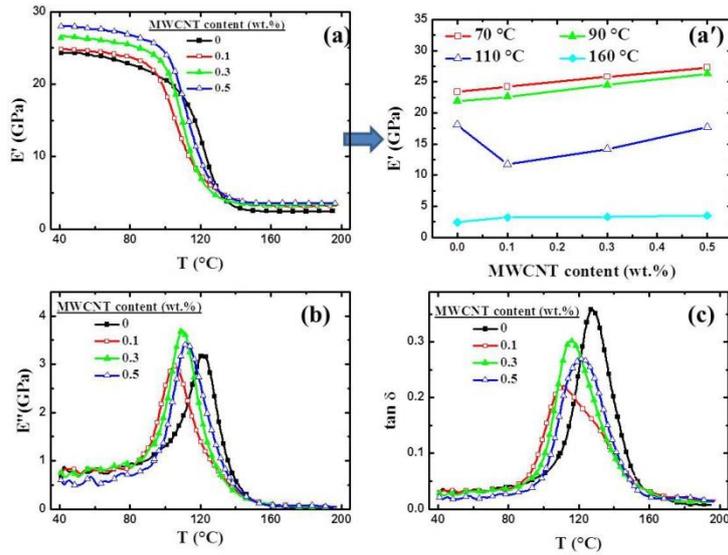
Figure 13: Variation in (a) storage modulus (E′), (b) loss modulus (E″) and (c) tan δ with temperature (T) for GE composites with varying MWCNT contents, (a′) the storage modulus of GE composite with various MWCNT content at different temperatures.

From figure 13(b), it is very evident that due to addition of MWCNT into GE composite the peak position of the loss modulus (E″) shifts towards left and for GE composite with 0.3% and 0.5% MWCNT the peak height is higher than that of control GE composite. This suggests that the presence of MWCNTs dissipate some energy because of the visco-elastic deformation of the polymer at the MWCNT/epoxy interface [38,39]. The ratio of the full width at half maximum of the tan δ peak to the peak height represents the peak factor. This peak factor is a qualitative representative of the homogeneity of the polymer structure. Among the four composite systems, the GE composite exhibits the lowest peak factor as can be seen from figure 13 (c) which concludes that the crosslinking density is highest in the GE composite [40]. This can also be figured out from the glass transition temperature (T_g) of the composites determined from the onset of the E′ vs. T plot which is shown in figure 14.
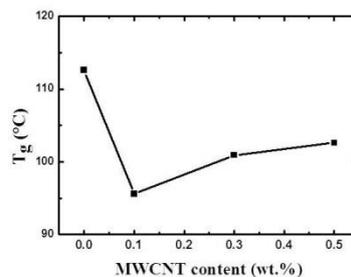
Figure 14: Effect of MWCNT content in GE composite on its glass transition temperature (T_g).

For neat epoxy and CNT/epoxy nanocomposites, T_g was determined from the onset of their heat flow vs. T curves as shown in figure 15 (a). The T_g of the control GE composite was 112.6 °C which was dropped by 17 °C by addition of 0.1% MWCNT. In the 0.1% MWCNT-GE, the single and well dispersed MWCNTs penetrate into the inter-chain spacing of the polymer and hence restricts the formation of crosslinks which in-turn responsible for a lower T_g. Similar effect was also noticed in case of nanocomposites. The T_g of neat epoxy was found to be 104.7 °C, which was reduced by 13.5 °C in case of epoxy/0.1%MWCNT nanocomposite. Further as the MWCNT content increases, agglomerates are formed. Hence, the probability of these agglomerates to penetrate into the inter-chain spacing of the polymer is reduced and hence the restriction to the crosslink formation is lowered. This is probably the responsible factor for a higher T_g at higher MWCNT content as evident from figure 14 and figure 15 (b).
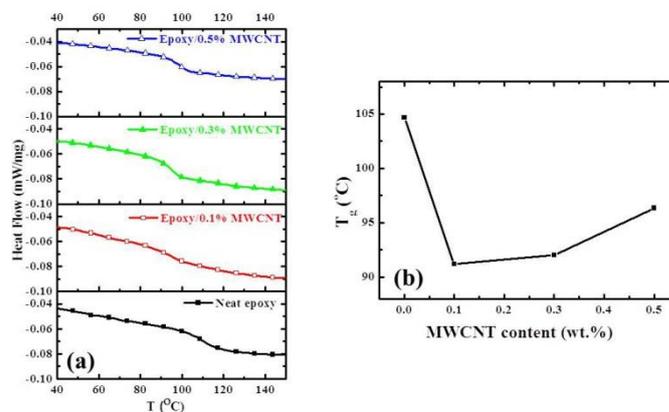
Figure 15: DSC analysis of neat epoxy and nanocomposites; (a) heat flow vs. temperature (T) and (b) T_g vs. MWCNT content.

4   Conclusion

1. Present investigation demonstrates an economical and promising processing technique for pristine MWCNT reinforced glass fiber/epoxy composites. With present processing parameters, 0.1 wt % of MWCNT exhibited best dispersion in the polymer matrix.

2. Incorporation of 0.1% MWCNT to the conventional structural glass fibre/epoxy composite resulted in 32.8 % and 11.5% increment in flexural strength and modulus respectively.

3. The results of in-situ elevated temperature testing suggested that the in-service temperature has higher impact on the mechanical performance of the MWCNT reinforced glass/epoxy composites as compared to conventional glass fiber/epoxy composites. Further, the rate of degradation of mechanical properties was higher for 0.1% MWCNT-GE composites as compared to all other compositions. The reason may be attributed to the high interfacial area present in 0.1% MWCNT-GE composite which is susceptible to form micro-cracks at MWCNT/epoxy interface under elevated temperature due to differential thermal expansion at this interface.

4. The DMTA results suggested that there was continuous increase in storage modulus in the earlier glassy state with increasing MWCNT content from 0 % to 0.5%. Further in the glass-transition region the higher reduction in storage modulus is observed for all MWCNT-GE composites as compared to GE composite. In addition to that, incorporation of 0.1% MWCNT to the matrix leads to the highest decrement in glass transition temperature (by about 12°C) as compared to 0.3% and 0.5% MWCNT content.

5. SEM analysis confirmed good dispersion of 0.1% MWCNT in the matrix as well as presence of agglomeration when the MWCNT content was increased to 0.5%. Fractographic analysis showed various modes of failure in GE and different MWCNT-GE composites.

It is very interesting to note that at 110 °C temperature the heavy matrix deformation is observed which is indicative of relatively ductile failure of 0.5% MWCNT-GE composite.

So the addition of nanofiller may not always judicious to obtain higher mechanical properties rather it depends on the in-service environmental temperature.

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