Effect of thermally reduced graphene oxide on dynamic mechanical properties of carbon fiber/epoxy composite

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Abstract: The Carbon fiber (CF)/epoxy composites are being used in the automotive and aerospace industries owing to their high specific mechanical strength to weight ratio compared to the other conventional metal and alloys. However, the low interfacial adhesion between fiber and polymer matrix results the inter-laminar fracture of the composites. Effects of different carbonaceous nanomaterials i.e., carbon nanotubes (CNT), graphene nanosheets (GNPs), graphene oxide (GO) etc. on the static mechanical properties of the composites were investigated in detail. Only a few works focused on the improvement of the dynamic mechanical of the CF/epoxy composites. Herein, the effect of thermally reduced grapheme oxide (TRGO) on the dynamic mechanical properties of the CF/epoxy composites was investigated. At first, GO was synthesized using modified Hummers method and then reduced the synthesized GO inside a vacuum oven at 800 ºC for 5 min. The prepared TRGO was dispersed in the epoxy resin to modify the epoxy matrix. Then, a number of TRGO/CF/epoxy laminates were manufactured incorporating different wt% of TRGO by vacuum assisted resin transfer molding (VARTM) technique. The developed laminates were cured at room temperature for 24 h and then post cured at 120 ºC for 2 h. The dynamic mechanical analyzer (DMA 8000 Perkin Elmer) was used to examine the dynamic mechanical properties of the TRGO/CF/epoxy composites according to ASTM D7028. The dimension of the specimen was 44×10×2.4 mm^3 for the DMA test. This test was carried out under flexural loading mode (duel cantilever) at a frequency of 1 Hz and amplitude of 50 µm. The temperature was ramped from 30 to 200 ºC with a heating rate of 5 ºC min^{-1}. The dynamic mechanical analysis of the 0.2 wt% TRGO incorporated CF/epoxy composites showed ~ 96% enhancement in storage modulus and ~ 12 ºC increments in glass transition temperature (T_g) compared to the base CF/epoxy composites. The fiber-matrix interaction was studied by Cole-Cole plot analysis. It proved the homogeneous dispersion of the epoxy resin and TRGO. The homogeneous dispersion of the TRGO in the epoxy matrix increased the overall enhancement of the dynamic mechanical properties of the hybrid composites.
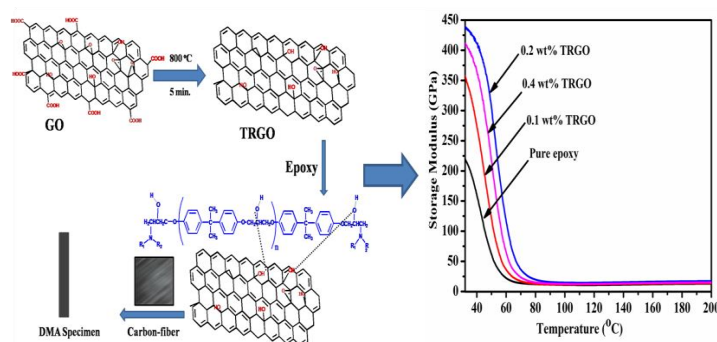
1. Introduction

Carbon fiber (CF) reinforced epoxy composites have enormous applications in light-weight composite part constructions [1]. However, the low interfacial adhesion between CF and epoxy resin creates inter-laminar fracture of the composites. Therefore, lots of works were carried out to find out the improvement in static mechanical properties of the composites by using different carbonaceous nano-structured materials i.e., carbon nanotubes (CNT), graphene nanosheets (GNPs), graphene oxide (GO) etc [2-4]. However, the incorporation of these carbonaceous nanofillers complicated the curing process of the CF/epoxy composites in presence of the dispersing solvents. In addition, the processing temperature, vacuum pressure and particle size of the nanofillers affects the cross-linking density of the composite materials. Trappe et al. cured epoxy resin at 50 and 60 $^{\circ}$C over 15 h and noticed that the crack propagation speed of the epoxy resin cured at 60 $^{\circ}$C is 10 times lower than that of the epoxy cured at 50 $^{\circ}$C [5]. However, the fracture toughness of both the samples remained same. The degree of curing is usually determined by using dynamic mechanical analysis (DMA) [6]. The DMA study not only expresses the cure kinetics of the composite materials but also the damping capacity of the composites. Most of the research works are based on DMA study of the fiber reinforced epoxy composites [7, 8]. There are also a few reports on the in depth investigation of the symmetric laminated composites. Therefore, an attempt has been paid on the detail DMA study of TRGO incorporated symmetric CF/epoxy laminated composites. The GO was synthesized by modified Hummers method and then reduced through heat treatment at high temperature. The prepared TRGO was dispersed in epoxy resin for manufacturing the TRGO/CF/epoxy laminate. The VARTM process was used to manufacture the TRGO reinforced CF/epoxy laminate. The main objective of using TRGO was to restore the graphene like properties of GO. The partially reduced GO was expected to increase the interfacial interaction with the epoxy resin as well as increase the glass transition temperature (T_g) of the composites.

2. Materials and methods

Graphite flakes purchased from Sigma Aldrich, India was used to prepare the GO. Merck India supplied the chemicals i.e. H_2SO_4 (98% vv), HCl (35% v/v) and H_2O_2 (30% v/v) etc. Plain weave carbon cloth with an areal density of 200g/m^2 was purchased from Flips India Engineering (Mumbai) for reinforcement. A low viscous Bisphenol-A epoxy resin (LAPOX*C-51) and modified cycloaliphatic amine hardener (Lapox AH-428) was purchased from Atul Limited (Gujarat, India) to prepare the matrix system in this work. A heavy-duty silicon spray mold release agent and an adhesive spray were purchased from Aerol Formulation Pvt. Ltd. (New Delhi, India).

At first GO was prepared by using modified Hummers method as stated earlier work [9]. Then, about 1 g of GO was taken in a crucible and then the crucible was placed inside a muffle furnace at 800 $^{\circ}$C for 5 min. The amount of TRGO was ~ 500 mg. In order to modify the epoxy resin, the required amount of TRGO was first dispersed in THF solvent. Similar experimental procedure was described in our previously reported work [10]. The dispersion was then poured into epoxy resin to get the 0.05, 0.1, 0.2 and 0.4 wt% TRGO incorporated epoxy matrix as compared to the total weight of resin and hardener. Then the THF was removed under reduced pressure from the TRGO/epoxy dispersion by evaporation at 85 $^{\circ}$C for an hour. The TRGO/epoxy mixture was allowed to cool down to room temperature and stirring was continued for 4 h with a magnetic stirrer. The desired amount of curing agent was added with TRGO/epoxy mixture and stirred at 500 rpm for 2 min to obtain homogeneous dispersion. Finally, the modified TRGO/epoxy matrix was used for the manufacturing of CF/TRGO/epoxy laminate after degassing the TRGO/epoxy suspension in a vacuum chamber. The CF were cut with a dimension of 150 × 150 mm and the CF/TRGO/epoxy laminates were prepared by VARTM process. The lamina's thickness was 0.3 mm. The stacking sequence of the lamina was [(0/90)$_5$]$_s$. The CF/TRGO/epoxy laminates were cured at room temperature for 24 h and then post cured at 120 $^{\circ}$C for 2 h. Finally, the rectangle shape samples were cut from the laminates for DMA study. DMA of the TRGO/CF/epoxy composite materials were carried out by using a dynamic mechanical analyzer (DMA 8000 Perkin Elmer) according to ASTM D7028. The specimen dimension was 45×10×2.5 mm^3 for the DMA test. This test was carried out under flexural loading mode (duel

cantilever) at a frequency of 1 Hz and amplitude of 50 μm. The temperature was ramped from 30 to 200ºC with a heating rate of 5ºC min^{-1}. Field emission scanning electron microscopy (FE-SEM) images were recorded with Σigma HD, Carl Zeiss, Germany to find out the dispersion of TRGO in the epoxy resin.

3. Results and Discussion

The dispersion state of TRGO in the epoxy matrix was analyzed with FE-SEM image analysis as shown in Figure 1 (a-d). Figure 1(a) represents the surface micrograph of pure epoxy resin, which was very smooth indicating the absence of guest materials in the epoxy resin. In contrast, the surface of the TRGO/epoxy composite appeared with rough morphology due to presence of TRGO. The presence of TRGO in the epoxy resin has been shown by indicating an arrow in the Figure 1(c). The composites with 0.4 wt% of TRGO loading in the epoxy resin is shown in Figure 1 (d) and it is clearly shown that the TRGO particles were agglomerated in the epoxy resin.
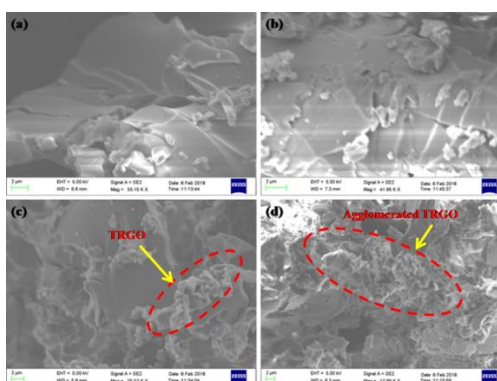
Figure 1. Surface micrographs of (a) Pure epoxy (b) 0.1 wt% (c) 0.2 wt% and (d) 0.4 wt% TRGO/epoxy dispersions

DMA investigates the curing kinetics and damping capacity of the prepared CF/epoxy and TRGO incorporated CF/epoxy composite. It measures the changes in stiffness of materials in terms of storage modulus (E'), loss modulus (E") and damping property by damping factor (tan δ). The E' signifies the stiffness or rigidity of a material and E" signifies the damping capacity of the material. The changes of E' of pure CF/epoxy and TRGO reinforced CF/epoxy composites by varying the temperature as shown in Figure 2(a). The E' increased with the addition of TRGO in the prepared composites. It indicated that the TRGO increased the stiffness of the CF/epoxy composites. The molecular mobility of the epoxy resin increased with the increase of temperature and decreased the value of E' corresponding to the temperature. The molecular mobility of the TRGO/CF/epoxy composites was lower compared to the pure CF/epoxy composite. The 0.1 wt% of TRGO incorporation in the epoxy resin did not influenced the modulus of the matrix material due to the less interactions of small number of functional groups of TRGO. The increment of TRGO loading in the CF/epoxy composites showed a significant enhancement of the composite modulus. The functional groups present at the TRGO surfaces are capable to interact with the epoxy resin and curing agent and enhanced the filler-matrix interaction. Thus, the E' increased by ~ 96% with 0.2 wt% of TRGO loading in the CF/epoxy composites as compared to pure CF/epoxy composite. The TRGO/CF/epoxy composite showed high E' at higher temperature.
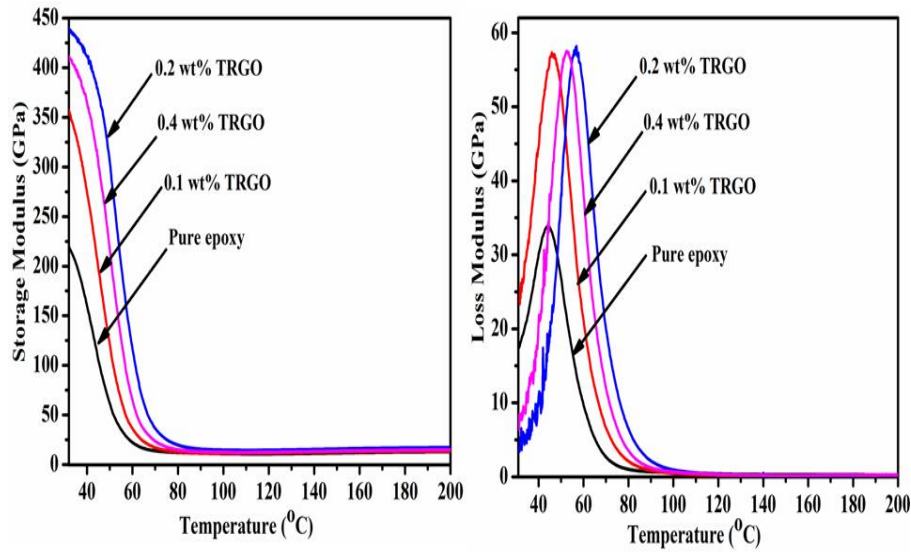
Figure 2. Variation of (a) Storage Modulus and (b) Loss Modulus of the TRGO/CF/epoxy composites
as a function of temperature

The viscous response of the TRGO/CF/epoxy composite is expressed by E″ and it is the ratio of stress
to the strain. E″ evaluates the energy dissipation of the CF/epoxy composites as heat per unit cycle
under deformation. The conversion of mechanical energy into thermal energy per unit cycle can be
expressed according to the equation [11],

$$\Delta E\,(\omega) = \int_0^{2\pi/\omega} \sigma(\omega)\varepsilon(\omega)dt \qquad\qquad\qquad (1)$$

$$= \omega\sigma_0\varepsilon_0 \int_0^{2\pi/\omega} (\cos\omega t\cos\delta\sin\omega t\,+\,\sin\omega t\sin\omega t\sin\delta)\,dt \qquad\qquad (2)$$

$$= \pi\,\varepsilon_0^2\,(\omega)\,E'' \qquad\qquad\qquad (3)$$

Where, $\sigma(\omega)$ = the stress function at frequency ω with amplitude σ_0, $\varepsilon(\omega)$ = the strain function at
frequency ω with amplitude ε_0, δ = the phase angle between stress and strain. Equation 3 signifies that
the E″ is directly proportional to energy dissipation of the material under cyclic excitation. The
changes of E″ with the increase of temperature of the TRGO/CF/epoxy composites is shown in Figure
2(b) and it showed narrow peak of E″ for the TRGO incorporated CF/epoxy composites. The narrow
peak of E″ suggested less inhibition in relaxation process of the TRGO/CF/epoxy composites. The
increment of E″ also improved the damping capacity of the composites. The tan δ (ratio of E″/E')
curve of the prepared composites is shown in Figure 3(a). The tan δ is associated with the T_g of the
composites. The T_g was the maximum of the tangent of the delta peak. It was found that below T_g the
damping was low as the polymer chains were in frozen state. It is renowned that the Tg increased
with the increment of the cross-link density or chain stiffness in polymer films. The large amount of
energy is required for the segmental movement of the closely dense polymer network i.e. the Tg value
of the closely dense polymer films is greater than the loosely dense polymer. Therefore, the
segmental movement and cross-linking density of the matrix material is dependent on T_g. The TRGO
based CF/epoxy composites displayed higher T_g values than the pure CF/epoxy composites. The
overall dynamic mechanical properties of the prepared composites were summarized in Table 1. From
Table 1 and Figure 3(a), it was observed that the prepared CF/epoxy composites containing 0.1 % of
TRGO were higher T_g value. Increasing the content of TRGO resulted in increase on T_g of the
CF/epoxy composites up to 0.2 wt%.
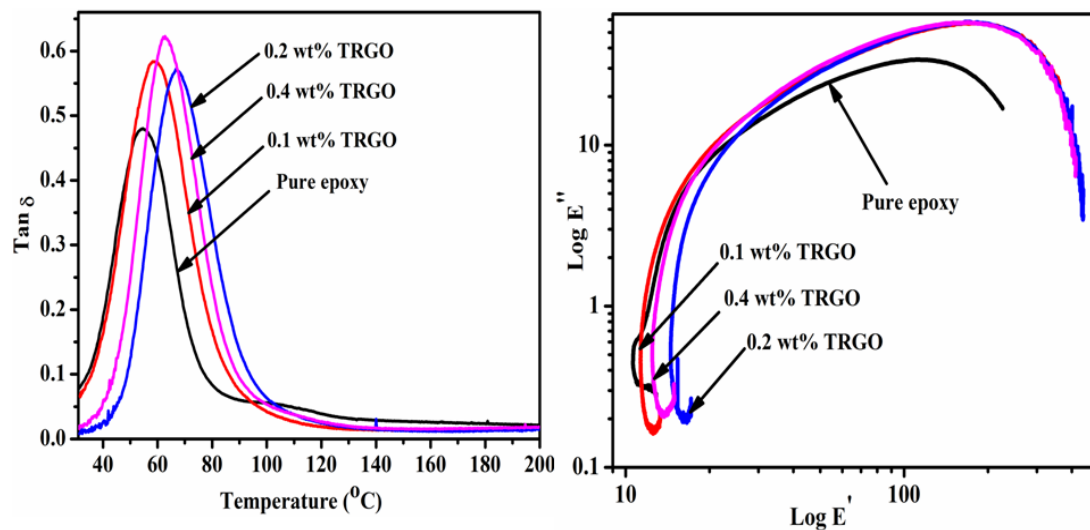
Figure 3. (a) tan δ vs. temperature and (b) Cole - Cole plot of the prepared CF/epoxy composites

The CF/epoxy composites containing 0.4 % of TRGO presented lower T_g value than 0.2 % of TRGO loaded composite. The decrease in T_g value referred the presence of voids close to the agglomerates in the composites. However, the incorporation of TRGO in the epoxy resin made a higher interfacial adhesion between CF and the epoxy resin and decreased the chain mobility of the epoxy resin and consequently increased the T_g. Thus, the T_g of the CF/epoxy composites varied with the TRGO content. The dispersion of TRGO in epoxy resin was analyzed by Cole-Cole plot analysis. The mechanical properties of the composites obtained by DMA study were expressed on Cole-Cole complex plane E = f(E') [12], when the properties were evaluated as a function of temperature and frequency. The appearance of a semi-circle in the Cole-Cole plot suggested homogeneous dispersion of TRGO in the epoxy matrix and a heterogeneous system exhibits an imperfect semi-circular curve [13] and it has been shown in Figure 3(b). From the Figure 3(b), it was observed that with increase of TRGO content, the curve shows more semi-circular compared to others i.e. more homogeneous.

Table 1 The Dynamic mechanical properties of the TRGO/CF/epoxy laminate

wt% of TRGO	T_g	E' (GPa)	E''(GPa)	tan δ
0	54	221	34	0.48
0.1	58	360	57	0.58
0.2	62	435	58	0.57
0.4	66	410	57.5	0.62

4. Conclusions

The DMA study of the TRGO/CF/epoxy was utilized to investigate the effect of TRGO nanofiller on the dynamic mechanical properties of the CF/epoxy composites. It was observed that the TRGO acted as a good filler material for increasing the adhesion between the CF and epoxy resin via better cross-linking with epoxy resin. The dynamic mechanical analysis of the TRGO/CF/epoxy composites showed ~ 96% enhancement in storage modulus and ~ 12 ºC increments in glass transition temperature (T_g) with 0.2 wt% of TRGO incorporation compared to the base CF/epoxy composites. The fiber-matrix interaction was studied by Cole-Cole plot analysis. It confirmed the homogeneous dispersion of TRGO in the epoxy resin. The homogeneous dispersion of the TRGO in the epoxy matrix increased the overall enhancement of dynamic mechanical properties of the composites.

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