Dynamic mechanical behavior of unfilled and graphite filled carbon epoxy composites

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Abstract. In the present study, the viscoelastic behavior of graphite filled and unfilled carbon epoxy composite is investigated through dynamic mechanical analysis. The investigation has been conducted using a three-point bend test (flexure mode) in the range of temperature from 30 to 200° C at one Hz frequency at a rate of heating of 2° C/min. The viscoelastic characteristics including loss modulus, storage modulus, damping factor, and composite glass transition temperature have been determined. It was found that the dynamic mechanical characteristics of the carbon fabric reinforced epoxy are highly dependent on the presence of graphite particulate composites. The storage modulus, glass-transition temperature, and loss modulus of filled graphite composites were higher than the unfilled ones. However, combining a graphite filler with carbon epoxy composite limits polymer molecules movement that leads to a decrease in tan δ.

Keywords: carbon, graphite, viscoelastic, tan delta, loss modulus, storage modulus.

1. Introduction

Because of its high basic strength and special rigidity, composites have not grown only in the aerospace weight-sensitive field into attractive building materials, as well as in the railway, structural engineering sectors, marine, and automobile. A careful matrix selection and reinforcement process will produce a composite with overall strength and modulus equivalent or much stronger than those of traditional metallic materials. The mechanical, thermal, and physical properties could be further changed by applying a solid filler process to the matrix body during the fabrication of the composite, which would offer a synergism in terms of enhanced properties and efficiency and reduce material cost.

The in-plane tensile characteristics of the composites are generally described by fiber reinforced polymer, although the compression characteristics along the thickness direction are determined through the properties of the matrix resin. The most frequently utilized polymer matrix for advanced composite components is epoxy resin. Over the years, several experiments were formed to change epoxy by inserting either nano or micro fillers to enhance the matrix-dominated characteristics of the composites. Fiber is believed to be the most powerful strengthening stage in polymer materials and high mechanical performance of the fiber-reinforced composites. Particularly carbon fibers have excellent characteristics like greater strength and modulus, better electrical and thermal properties than other fibers. Thus, the most commonly used reinforced composites today are carbon fibers.

Dynamic mechanical measurements generally offer a better understanding of the behavior of the material under load than other tests, although other mechanical tests theoretically may convey the same information. These research methods were commonly used to analyze the structures and viscoelastic properties of polymeric materials to assess irrelevant hardness and damping properties for different applications. The rigidity depends on the mechanical characteristics of the material and is transformed into a modulus. Tan delta is represented in damping and is related to the quantity of energy that a material can store. The DMA is the most sensitive technique for regulating events like glass transitions because when relaxation behavior is detected, its mechanical properties change.
drastically (Nielsen [1]). When calculated on a variety of temperatures and frequents, the dynamic properties of polymer materials have significant functional importance.

The three essential parameters that must be achieved during DMA are: (1) storage modulus—that calculates the peak energy contained in a material during one oscillation period; (2) loss modulus—proportional to the quantity of energy which has been dissipated through the sample as heat; and (3) Mechanical tan delta damping term, which is the ratio of loss to the storage modulus, which relates to the degree of molecular mobility of the polymer material. Dynamic tests are adaptive to all types of resin matrix relaxation and transitions mechanisms as well as the composite morphology. Data and information produced can then be used to locate polymer systems of the glass transition temperature (Tg). Tg is the optimum transition in either the loss modulus or loss tangent curve (Nielsen [1]).

Daniel and Yasmin [2] investigated the mechanical and thermal characteristics of graphite-epoxy platelet composites, suggesting that composite storage modulus and the glass transfer temperature were increased by increasing the concentration of graphite platelet. They have also found that higher graphite concentrations improve composite heat stability than pure epoxy. Huimin et al. [3] investigated the impact of nano SiO2 on polyamide 66 composite morphology, dynamic mechanical characteristics, and crystallization. In comparison with the cleanly polyamide 66, dynamic mechanical properties showed substantial improvements in the storage and loss modulus. The tan δ peak showing the temperature of glass-transition to the maximum temperature of nanocomposites. Frederico et al. have studied the complex mechanical parameters of ramie fiber-enhanced epoxy composites [4]. In a flexural mode, studies have been considered in the temperature ranges from 20 to 200°C at 1Hz below the nitrogen level. Based on the experimental findings, they noted that the inclusion of ramie fiber appears to enhance the viscoelastic rigidity and epoxy matrix damping ability. Zhou et al. [5] conducted unfilled and multi-walled CNT (Carbon Nano Tube) filled epoxy and carbon composites mechanical and thermal characterization. The findings illustrate that the temperature of glass transition, the flexural strengths, and the temperature of decomposition have been increased by infusing CNT. Nirmal and Amar [6] have observed the viscoelastic activity of polyethylene fiber (PEF) and unidirectional fiber-glass reinforced polymethyl methacrylate composites for different relative PEF volume fractions with a mechanical dynamic analyzer. It had been reported that the relative volume of PEF increased and Tg enhanced to a higher region with a damping efficiency in the hybrid composite.

Mostly, the literature reports on the impact of nanofillers and nanofibers on the dynamic characteristics of polymers as well as polymer composites; the dynamic behavior of reinforced particulate fiber composites is being assessed with little effort. Therefore, in the current investigation, an attempt is made to research the effect of graphite filler on the viscoelastic behavior of carbon epoxy composite.

2. Experimental

2.1 Material

Unfilled and graphite filled carbon epoxy composites were fabricated by hand layup technique, followed by compression molding, were manufactured for the present study. The composite consists of a two-way plain-woven carbon (200g/m² density) fabric comprising poly acryl nitrile (PAN) carbon fiber, strengthened with the matrix content of the resin epoxy (LAPOX -12), at room temperature cure polyamine hardener (K5). The filler material was used with graphite particulates 40-60 μm. The weight fraction of a graphite filler is used to produce four composite laminates. Table 1 shows the details of the samples composite manufactured with reinforcement, fillers, and a weight fraction of the matrix.
Table 1. Details of composite samples prepared.

| Sample       | Matrix (% Epoxy) | Reinforcement (% Carbon Fabric) | Filler (% Graphite) |
|--------------|------------------|---------------------------------|---------------------|
| Unfilled     | 40               | 60                              | 0                   |
| 2% filled    | 38               | 60                              | 2                   |
| 4% filled    | 36               | 60                              | 4                   |
| 6% filled    | 34               | 60                              | 6                   |

2.2 Dynamic Mechanical Analysis

The mechanical characteristics of materials are measured according to temperature, frequency, and time by DMA (Dynamic Mechanical Analysis). The mechanical reaction of a sample subject to a particular temperature program is a thermal analytical process. In general, this technique is used to qualitatively characterize the viscoelastic properties of composites and polymers.

DMA measures stiffness & damping and are recorded as tan delta and modulus. The modulus represented as a phase component, a phase-out component, and storage modulus are the loss modulus since sinusoidal force is added. The viscoelastic polymers storage and loss modulus test the energy stored and lost during oscillation respectively. The first demonstrates the elastic section, and the second demonstrates the viscous section. The loss-to-storage modulus ratio is tan delta and is also referred to as damping. It is an indicator of the material's energy dissipation. For researchers, manufacturers, and consumers of polymers and composites, modulus knowledge extracted from dynamic mechanical testing is really useful for structural purposes.

The moduli for storage ($E'$) and loss ($E''$) are represented as:

$$E' = \frac{\sigma_o}{\varepsilon_o} \cos \delta \quad \text{N/mm}^2$$  \hspace{1cm} (1)

$$E'' = \frac{\sigma_o}{\varepsilon_o} \sin \delta \quad \text{N/mm}^2$$ \hspace{1cm} (2)

here strain $\varepsilon_o$ and dynamic stress $\sigma_o$

$$\tan \delta = \frac{E''}{E'}$$ \hspace{1cm} (3)

A three-point bending test according to ASTM D5023[7] has been carried out in Tri-Tec 2000B (Triton Technology, UK). The parameters like storage modulus, damping factor ($\tan \delta$), glass transition temperature, and loss modulus are measured from the DMA tests. Samples have been measured with a rate of heating of 2° C per minute at 1 Hz frequency in the range of temperature from 30-200° C.

3. Results and discussion

The design and the distribution of the matrix material, characteristics of fiber, the presence of additives like filler, the nature of the interface fiber matrix, and the mode of testing effects the dynamic mechanical behavior of polymer composites. The chemical and physical structure of the fiber in a particular matrix and the relative composition variations of each fiber and matrix can also lead to major changes in the overall dynamic mechanical characteristics of the composite (Kevin [8]).

Influence of graphite filler on dynamic properties of carbon epoxy composite
In the current research, graphite filler affects on Loss modulus (E''), glass transition temperature (Tg), storage modulus (E'), and tan δ of composites of carbon epoxy are assessed. Table 2 provides unfilled and graphite filled composites with the determined performance of the dynamic properties (Storage Modulus (E'), Loss Modulus (E''), tan δ, along with Tg).

**Table 2. Dynamic properties of filled and unfilled graphite composites.**

| Composite Sample | Storage Modulus (E')(GPa) | Loss Modulus (E'')(GPa) | Tan δ By E''peak | Tg (°C) By tan δ peak |
|------------------|--------------------------|------------------------|------------------|----------------------|
| Unfilled         | 16.11                    | 3.962                  | 0.3766           | 118.1                | 25.0                 |
| 2 % filled       | 23.86                    | 5.518                  | 0.3424           | 118.3                | 25.1                 |
| 4 % filled       | 24.72                    | 4.210                  | 0.2468           | 129.1                | 33.0                 |
| 6 % filled       | 28.18                    | 5.732                  | 0.3703           | 124.2                | 30.6                 |

3.1 Storage modulus (E')

The analysis of the storage modulus for a range of temperatures considered to be extremely in the evaluation of the polymer structure changes in performance characteristics. In dynamic load conditions, the storage modulus (E') indicates the inherent rigidity of the material. The storage modulus vs. temperature curve is used for determining the mechanical characteristics of the material on the molecular basis, because the molecular weight, the level of cross-connection, and the interfacial fiber-matrix bonding are very sensitive to structural changes (Pothan et al. [9]). The variance of carbon epoxy composites storage modulus with a frequency temperature of 1 Hz is shown in figure 1 for different weight percent of graphite filler. The effect of the inclusion of graphite particles in the carbon epoxy composite causes a variation of storage modulus.

![Figure 1](image-url) **Figure 1** Variation of E' with temperature for composite samples

The integration of the carbon epoxy composite graphite filler had a good impact on the storage modulus both at glass transition temperature (Tg) and beyond that, which confirms improved elastic characteristics of the composite by incorporating the graphite filler. This indicates that graphite incorporation increased the rigidity of the composite. The storage modulus rises to the limit in the
glassy region (temperature $<T_g$), then falls inside the rubbery region ($T_g<$temperature). The decrease in modulus relates to the shift of materials from a glassy to a rubbery state.

In the glassy area $E'$ relies on the loading of graphited that the gap between composite sample storage modulus and a different filler weight percentage in the glassy area more, but not important in the rubbery region and characteristic curves overlap. Composite filled with six percent graphite filler initially illustrated a maximum $E'$ at room temperature and the temperature of glass transition ($T_g$), while for all composite samples $E'$ declined in the rubbery region with a maximum $E'$ of a graphite filler with 4 percent. But the graphite filled composite was higher $E'$ than the non-filled in both the glassy and rubbery regions. The $E'$ value was increased with the graphite particle percentage increase as shown in Table 2. The findings from Asma and Isaac [10] are close. They found that the storing modulus of pure epoxy was increased through the integration of graphite particles into epoxy nanocomposites; they also stated that the storage modulus increased consistently with the rise in the concentration of graphite particles.

3.2 Loss modulus ($E''$)

The loss modulus is described as the energy that is dissipated or lost during material deformation as heat. It is the material's viscous response. The loss modulus is most susceptible to molecular movements. The loss factor for polymer composites varies by temperature and exceeds optimum levels at $T_g$ since their inner damping arises from the polymer matrix's viscoelasticity. The increased damping capacity without compromising the storage module is achieved.

The difference in carbon epoxy composite temperature loss modulus shows in Figure 2.

![Figure 2](image)

Figure 2 Variation of $E''$ with temperature for composite samples.

For the graphite filled composites, the loss module ($E''$), that represents the power for energy dissipation, was substantially higher than the unfilled one across the entire temperature range, with the highest increase at approximately $T_g$. This shows that energy dissipation also increases with the incorporation of graphite into the carbon epoxy composite. The graph represents that $E''$ is minimum at room temperature and almost equal in all composite samples, so it increases as the temperature rises to $T_g$ and then continues to decrease and it eventually reaches zero. The highest $E''$ peak exhibited 6 percent graphite filled composite (Table 2). Huimin et al. [3] found a major improvement in storage and loss modulus by the incorporation of nano-SiO$_2$ when experimenting with the nano-SiO$_2$ filled polyamide 66 composites.
3.3 Loss tangent (Tan δ)
Damping characteristics are related to the molecular movements and phase transitions of the dynamic loss modulus (or viscous) to the dynamic storage modulus (or elastic). The damping peak happens in the region of the glass transition from a stiff state to a more elastic condition where the material is related to the movement of small molecular groups and chains within the polymer structure. Thus, Tan δ is susceptible to all molecular motions occurring in polymers. The integration of fibers into a composite system will impact damping. This is primarily due to the accumulation of shear stress at the ends of the fiber along with the further viscoelastic energy dissipation of the matrix material. The temperature function of Tan δ is illustrated in Figure 3 for all composite samples.

![Figure 3 Variation of tanδ with temperature for composite samples](image)

The thermogram indicates that tanδ stays at the beginning nearly constant up to a certain temperature, then rises and reaches a maximum value and then reduces. This polymer behavior is typical throughout the transitional area. The integration of graphite filler in the carbon epoxy composite reduces the motion of polymer molecules which results in a lower tan δ value (Table 2). It is noted that the value of tan δ with an increased % filler content does not differ linearly. The maximum value of unfilled composite was recorded and the Tan δ decrease was recorded at 2 and 4% and the value was further increased by the weight of graphite filling into composites by 6%. More dampness at the interface, less adhesion at the interface. Therefore, a strong interface for graphite-filled composites adhesive is reported. Basavaraj et al. [11] have stated, although substantiating the above findings, that tan δ decreases with an increase in polyamide 66/ carbon black composite molybdenum disulphide material.

3.4 Glass transition temperature (Tg)
Tg is usually known as the temperature at which the loss tangent (tan δ) peaks occur; the temperature at loss modulus peaks (E") versus the temperature curve is also often defined. Tg as a result of E" peak and not tan δ peak results in a way that is in line with the standard of stress safety of the matrix with fibers in composites. The temperature of Tg via E" peak shows even more specifically that stiffness has deteriorated significantly. Thus the, Tg by E" is more reliable and more acceptable than the one dependent on the tan δ peak for advanced composite materials (Akay [12]). Table 2 indicates the value of Tg defined by the peak E" and the peak tan δ. From the table, it can be noted that the tan δ peak temperature is above than peak of E". Tg difference calculated for these 2 maximum values is
between 4 and 8°C. Such as tan δ, for Tg there is no linear trend with an increase in the proportion of graphite filler is observed, the maximum value of 4% is reported as a graphite filled composite. These findings comply with those of Akay [12] which recorded similar results for the single-direction carbon epoxy or carbon fiber laminates. Furthermore, he observed that glass transition temperatures filled with graphite composites are more than unfilled. Kumaresan et al. analyzed the dynamic mechanical behavior of the silane-treated SiC particulate filled carbon epoxy composites [13]. From the outcomes, it was identified that the SiC-filled composite glass transition (Tg) temperature was higher than the unfilled composite. Basavaraj et al. [14] stated that polycarbonate and carbon black composite glass transition temperature increased as molybdenum disulfide content increased [14].

4. Conclusions
The following conclusions are made from the dynamic mechanical tests of the carbon epoxy composite:

- The dynamic mechanical characteristics of the composites heavily dependent on the presence of graphite particles.
- The incorporation of the graphite filler has had a positive impact on the storage modulus above and below Tg, suggesting that composite elastic characteristics have been enhanced due to the inclusion of the graphite filler. The value of E’ increased by an increase in graphite particulate percentage.
- The loss modulus that represents the potential of energy discharge for graphite filled composites, has been significantly higher than the unfilled over the entire temperature range examined and the rise was maximal around Tg. This shows that energy dissipation is also increased with the introduction of graphite into carbon epoxy composites.
- Addition of graphite filler to the carbon epoxy composite limits the motion of polymer molecules to reduce tan δ. Higher the damping at the interface, the poorer the adhesion interface. Therefore, the graphite filled composites have a strong interface connection.
- The glass transition temperature (Tg) is represented as the temperature of the tan δ peak reached E”.. The gap in Tg value determined by these two peak values is between 4 and 8°C. Further, graphite filled composites have more Tg than unfilled ones.

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