

Tuning the Coefficient of Thermal Expansion of Epoxy Resin with Graphene - A Study via Modulated TMA

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Abstract

In this study, modulated thermomechanical analysis (MT-TMA) was used to study how graphene affected the coefficient of thermal expansion (CTE) of epoxy resin. Epoxy resin nanocomposites with different graphene concentrations (0-1 wt%) were prepared by dispersing graphene in epoxy resin using an ultrasonication and probe-sonication technique. The MT-TMA results showed that graphene reduced both the dimension change and the CTE of epoxy resin. The CTE of epoxy resin dropped from 182.9 to 127.8 $\mu\text{m}/\text{m}\cdot^{\circ}\text{C}$ as the graphene concentration increased from 0 to 1 wt%. The MT-TMA results could also be represented by reversible and irreversible components of dimensional changes which corresponded to the elastic thermal expansion and influence of graphene on epoxy behaviour. The reversible component showed a reduction in CTE by graphene, indicating that graphene restricted the thermal expansion of epoxy resin. The irreversible component showed a negative slope of dimension change by graphene incorporation which indicated that the negative CTE of graphene had a direct influence on the epoxy property by delaying the crosslinking reaction of epoxy resin. These results showed that graphene could effectively reduce the CTE of epoxy resin and enhance its dimensional stability.

Key words:

Graphene; Epoxy resin; Coefficient of Thermal Expansion (CTE); Modulated Thermomechanical analysis (MT-TMA)

Citation

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1.0 Introduction:

Epoxy resin, a thermosetting polymer widely employed in industries such as aerospace, defence, automotive, electronics, and coatings [1], undergoes a reaction between epoxy base resin and curing agents or hardeners to form a crosslinked network structure. With desirable properties like high mechanical strength, good adhesion, chemical resistance, and thermal stability, epoxy resin fulfils the requirements of various industries. However, certain drawbacks, such as low fracture toughness, high coefficient of thermal expansion (CTE), and poor electrical conductivity, limiting its potential applications across many industries. These limitations negatively impact the performance and durability of epoxy-based composites, especially in harsh conditions like fluctuating high temperatures during processing or service [2]. Graphene, a two-dimensional carbon nanomaterial having excellent properties, like high specific surface area, aspect ratio, Young's modulus, thermal conductivity, and electrical

conductivity makes it the most suitable filler for property improvement. By incorporating graphene as a nanofiller, epoxy resin can be strengthened, leading to improved mechanical, thermal, and electrical properties [3].

CTE is an important parameter affecting the properties of epoxy resins and their fibre-reinforced composites. CTE is a measure of how much a material expands or contracts when its temperature changes. CTE of epoxy resins is generally higher than that of their reinforcing fibres, which can cause thermal mismatch and residual stress during processing or service [4]. Thermal mismatch and residual stress can lead to microcracking, delamination, and reduced mechanical performance of epoxy-based composites. The CTE of epoxy resins can be influenced by several factors such as curing conditions, molecular structure, crosslink density, filler type and content. Among these factors, fillers such as graphene and graphene-based materials can significantly affect the CTE of epoxy resins by forming the network structure and changing their thermal properties [5]. CTE of these materials can be measured by sophisticated dimension change measuring instruments. Several studies have reported the

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effect of graphene-based materials on the CTE of epoxy resins using Thermomechanical analysis (TMA) and other techniques. For example, Ackermann et al. investigated the effect of amine-functionalized reduced graphene oxide (frGO) on the mechanical, thermal, and electrical properties of epoxy/carbon fibre-reinforced polymers (CFRP) [6]. They found that frGO increased CFRP's apparent interlaminar shear strength and transverse electrical conductivity, but did not affect Young's modulus, T_g, storage modulus, specific heat capacity, thermal conductivity at room temperature, and in-plane electrical conductivity. They also observed that frGO slightly increased the CTE of CFRP compared to unfunctionalized reduced graphene oxide (rGO) and neat CFRP. Domun et al. studied the effect of plasma-functionalized graphene nanoplatelets (f-GNP) on epoxy resin's fracture toughness and thermal properties [7]. They found that f-GNP improved the fracture toughness and T_g of epoxy resin at low filler content (0.25 wt%). They also reported that f-GNP increased the CTE of epoxy resin by 22% at 0.25 wt% compared to neat epoxy resin. Wang et al. synthesized triethanolamine-modified graphene oxide (TEA-GO) and used it as a nanofiller for epoxy resin-based coatings. They found that TEA-GO improved the dispersion and interfacial interaction of graphene oxide (GO) in epoxy resin. They also found that TEA-GO decreased the CTE of epoxy resin-based coatings compared to GO and neat epoxy resin [8].

The above studies show that graphene-based materials can affect the CTE of epoxy resins in different ways depending on their surface modification, dispersion state, interfacial interaction, filler content, and matrix composition. In addition to that, the difference in reported results may be occurred due to the influence of the mode of testing used for Epoxy samples. Therefore, it is important to understand how these factors influence the CTE of epoxy resins and their composites with graphene nanofillers. This study aims to investigate the effect of graphene on the thermomechanical behaviour of epoxy resin using modulated TMA (MT-TMA).

2.0 Experimental

Material: Epoxy resin of commercial grade was procured from Venus trading corporation and Graphene of ~99% purity (mentioned by the vendor) was procured from Ad-Nano Technologies Pvt Ltd.

Procedure: Suitable amount of graphene and Epoxy was weighed to obtain 4 different compositions of 0.1 wt%, 0.25wt%, 0.5 wt% and 1wt%. Graphene was mixed in epoxy and ultrasonicated in a bath sonicator for 1 hr followed by probe sonication for 15 min in pulse mode (2 sec pulse and 0.5 sec gap). After graphene dispersion, a hardener was added to the Epoxy/Graphene composite solution ((Epoxy: Hardener):: (2:1)) and samples were prepared.

Characterization: All epoxy and composite samples were tested in a Thermo-mechanical analyser instrument, TMA 450-E (TA Instruments, USA). The samples were tested for

the modulated temperature of 5°C for 300 sec, with a temperature ramp of 3°C/min from 50°C to 150°C.

3.0 Results and Discussion

3.1 Difference between standard TMA and MT-TMA

As mentioned above, standard TMA is a technique that measures the dimensional changes of a material as a function of temperature under a constant load. Standard TMA can provide information such as T_g, CTE, and thermal stress for various materials but its effect on monitoring minor changes and transition has major false reports for epoxy and epoxy composites. On the other hand, Modulated temperature TMA (MT-TMA) is a variant of TMA that applies a sinusoidal temperature modulation on top of a linear heating or cooling ramp. MT-TMA can also enhance sensitivity by reducing the effects of thermal lag and drift [9]. Figure 1 represents the difference between standard TMA Vs MT-TMA of epoxy resin, where MT-TMA is better suited for conducting epoxy resin studies.

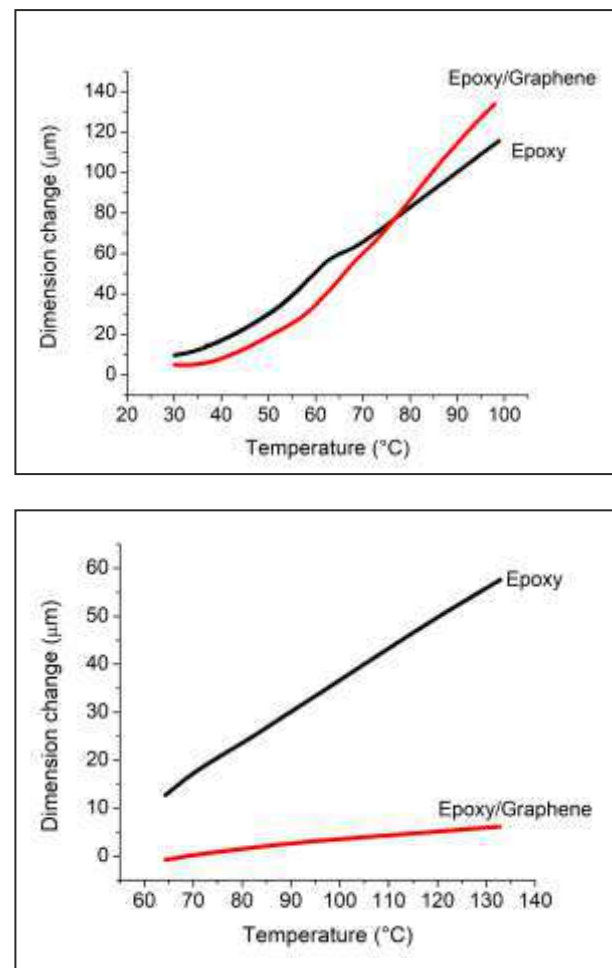


Figure 1: Standard TMA Vs Modulated TMA of Epoxy resin

As shown in the graphs, MT-TMA gave more consistent and expected values of dimension change than standard TMA, since Graphene has negative CTE and incorporation of

Graphene in epoxy should restrict dimension change than increase it. These show that MT-TMA has some advantages over TMA for testing epoxy resins and their composites, such as higher sensitivity, resolution, accuracy, and reliability.

3.2 Effect of graphene concentration on epoxy and composite properties via MT-TMA mode of testing:

As mentioned earlier, MT-TMA is a technique that measures the dimensional changes of a sample as a function of temperature, time and force in a more sensitive way by applying a sinusoidal temperature modulation on top of a linear temperature ramp and measures the linear expansion of the sample under a constant force. Figure 2 represents the MT-TMA of all composite samples.

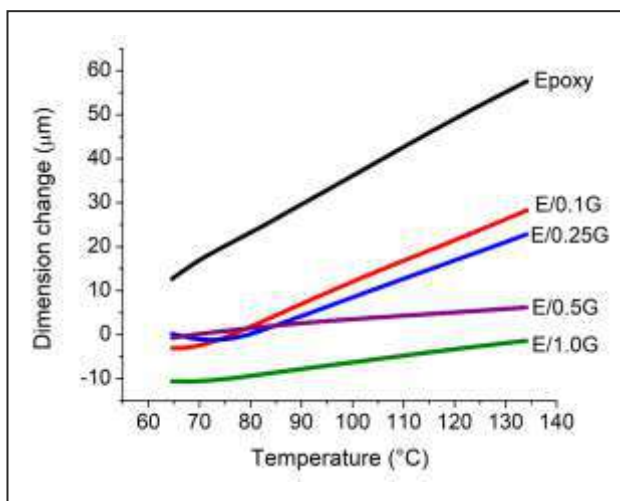


Figure 2: MT-TMA overlay of Epoxy/Graphene composite samples

Incorporating graphene into epoxy resin had a significant effect on the epoxy's dimensional stability, as represented by experimental results. The dimensional change of the epoxy resin reduced as the graphene concentration increased. This effect was more noticeable at high temperatures, where graphene improved the epoxy's viscoelastic properties. These findings can be explained by the properties of graphene, which improved the both thermal and mechanical properties of epoxy resin. To further explore the causes of this effect in more detail, we performed MT-TMA to examine both reversible and irreversible factors that contributed to this dimensional change.

MT-TMA can separate the reversible and irreversible components of the dimensional changes, which can be affected by different factors such as curing, relaxation, crystallization, and decomposition. The reversible component of the dimensional change is associated with the thermal expansion or contraction of the material, which depends on the temperature rate of change. The reversible component can be used to measure the CTE of the material, which is a measure of how much a material expands or contracts when its surrounding temperature changes. The

irreversible component of the dimensional change is associated with the deformation or recovery of the material, which depends on both time and temperature. While, the irreversible component can be used to measure the stress relaxation, softening or shrinkage of the material, which are related to the molecular structure, crosslink density, filler type and content, and interfacial interaction of the material. Epoxy and the composite with various concentrations of graphene have exhibited both reversible and irreversible dimensional changes during MT-TMA. The reversible component can reflect the CTE of the epoxy matrix and filler, while the irreversible component can reflect the curing, and stress relaxation of the epoxy matrix and graphene. By separating these components, MT-TMA can provide more information on the thermomechanical behaviour of epoxy resins and their composites than standard TMA.

- Reversible dimensional change

In MT-TMA, the reversible dimensional change is calculated by analysing the amplitude of the modulated signal [9]. The modulated signal is a small sinusoidal deformation that is superimposed on a larger deformation. By analysing the amplitude of the modulated signal, it is possible to determine the reversible component of the dimensional change, which is in phase with the temperature changes. This reversible component is related to the viscoelastic properties of the material, which are affected by the addition of graphene. Figure 3 represents the comparative overlay of reversible dimensional changes observed via MT-TMA.

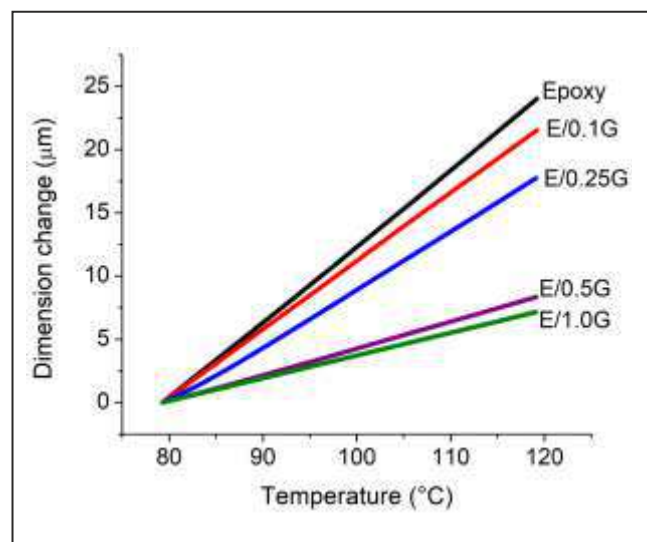


Figure 3: Reversible dimension overlay of Epoxy/Graphene samples

In the case of graphene-epoxy composites, the addition of graphene showed improvement in the mechanical and thermal properties of the material, which leads to a reduction in the reversible dimensional change. This reduction in reversible dimensional change indicates that the material is more resistant to deformation and can recover its original shape more effectively (as represented in Table 1). This can

happen when the interfacial interaction between graphene and epoxy is strong or stable, which means that there is a low internal thermal resistance (ITR) between them. A low ITR means that heat can easily flow from epoxy to graphene during heating or cooling, which can reduce the thermal stress and deformation in the composite. This can also increase the molecular mobility and free volume of epoxy, which can reduce its CTE.

Table 1: Dimensional changes and CTE of epoxy and epoxy composite samples

Sample name	Graphene conc.	Dimension change (μm)	CTE ($\text{mm/m}^\circ\text{C}$)
Epoxy	0%	44.8	182.9
E/0.1%G	0.1%	31.35	172.8
E/0.25%G	0.25%	22.66	167.0
E/0.5%G	0.5%	9.22	138.6
E/1.0%G	1.0%	6.85	127.8

- Irreversible dimensional change

Thermal expansion and contraction are not the only phenomena that affect the dimension change of composites. There are also non-reversible phenomena such as stress relaxation and filler influence that depend on the applied stress and processing time of the composite. Stress relaxation is the decrease in stress over time under constant strain, while filler influence is the effect of filler on polymer composite due to interfacial bonding and inherent properties. When a composite is subjected to thermal stress or strain, it can deform both elastically and viscously. The elastic deformation is reversible and returns to its original shape when the stress or strain is removed, while the viscous deformation is irreversible and causes a permanent change in shape. Graphene has a negative coefficient of thermal expansion, which means that it contracts when heated [11]. The irreversible deformation caused by Graphene may have caused the negative non-reversible dimension changes in composites, which means that they contract due to the release of internal stresses or the rearrangement of molecular chains (as shown in Figure 4). Also, the negative slope of irreversible dimension change represents that the crosslinking reaction is slower and smooth in graphene-incorporated composite films than in their thermal expansion

References :

- [1] Memon, Hafeezullah, Yi Wei, and Chengyan Zhu. "Recyclable and reformable epoxy resins based on dynamic covalent bonds—Present, past, and future." *Polymer Testing* 105 (2022): 107420.

[12]. This also indicates that the material releases more internal stress by thermal expansion than it generates by cross-linking. This internal stress causes the material to contract irreversibly in order to balance these stresses.

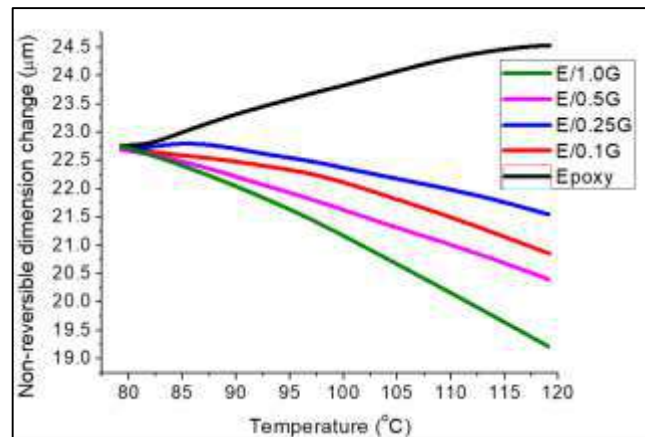


Figure 4: Irreversible dimension overlay of Epoxy/Graphene samples

4.0 Conclusion

TMA has some limitations in detecting minor changes and transitions in epoxy and epoxy composites. Modulated temperature TMA (MT-TMA) is a variant of TMA that applies a sinusoidal temperature modulation on top of a linear heating or cooling ramp which enhances the sensitivity and resolution by reducing the effects of thermal lag and drift. Graphene incorporation has affected the CTE and dimension change of epoxy composites by influencing the thermal conductivity and interfacial interaction between graphene and epoxy molecules. Graphene incorporation can reduce the CTE of epoxy composites by reducing the reversible dimension change due to thermal expansion. This can happen when the interfacial interaction between graphene and epoxy is strong or stable, which means that there is a low ITR between them. Graphene incorporation made the negative slope of irreversible dimension change in epoxy composites by influencing the crosslinking reaction and internal stress in the epoxy matrix. The strength and type of interfacial interaction can affect the heat transfer and stress transfer between graphene and epoxy, which in turn affects the crosslinking reaction and internal stress in the epoxy matrix.

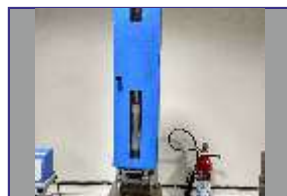
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- [2] Sun, Qiangsheng, et al. "High performance epoxy resin with an ultralow coefficient of thermal expansion cured by conformation-switchable multi-functional agent." *Chemical Engineering Journal* 450 (2022): 138295.
- [3] Gantayat, Subhra, et al. "Expanded graphite as a filler for epoxy matrix composites to improve their thermal, mechanical and electrical properties." *New Carbon Materials* 30.5 (2015): 432-437.
- [4] Ahmed, Ashraf, et al. "Study of thermal expansion in carbon fiber-reinforced polymer composites." *SAMPE international symposium proceedings*. Charleston (SC), USA: SAMPE, 2012.
- [5] Osman, Amr, et al. "A comprehensive review on the thermal, electrical, and mechanical properties of graphene-based multi-functional epoxy composites." *Advanced Composites and Hybrid Materials* 5.2 (2022): 547-605.
- [6] Ackermann, Annika C., et al. "Mechanical, thermal, and electrical properties of amine-and non-functionalized reduced graphene oxide/epoxy carbon fiber-reinforced polymers." *Polymer Composites* (2023).
- [7] Domun, Nadiim, et al. "Improving the fracture toughness properties of epoxy using graphene nanoplatelets at low filler content." *Nanocomposites* 3.3 (2017): 85-96.
- [8] Ban, Chun-guang, et al. "Triethanolamine modified graphene oxide for epoxy resin-based coatings: Corrosion inhibition on metal substrates." *Surface and Interface Analysis* 54.11 (2022): 1151-1162.
- [9] Blaine, Roger L., and T. A. Instruments. "Modulated Thermomechanical Analysis—Measuring Expansion and Contraction Simultaneously." *TA Instruments* (2003).
- [10] Wan, Yan-Jun, et al. "Improved dispersion and interface in the graphene/epoxy composites via a facile surfactant-assisted process." *Composites Science and Technology* 82 (2013): 60-68.
- [11] Yoon, Duhee, Young-Woo Son, and Hyeonsik Cheong. "Negative thermal expansion coefficient of graphene measured by Raman spectroscopy." *Nano letters* 11.8 (2011): 3227-3231.
- [12] Vryonis, Orestis, et al. "Understanding the cross-linking reactions in highly oxidized graphene/epoxy nanocomposite systems." *Journal of Materials Science* 54.4 (2019): 3035-3051.

Installation Damage of Geosynthetics

The geosynthetics are prone to some amount of damage during their installation. To assess the quantity of the installation damage, a standard method was initially developed by Watts and Brady of the Transport Research Laboratory in the United Kingdom. The procedure has also discussed in the ASTM D 5818 with similar requirements. We are at BTRA doing the test following same ASTM D 5818 method followed by respective tensile strength. For the time being we are using the construction site for the sample preparation. If customer will agree, BTRA will collect the sample from site after standard procedure and provide the report.



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