# Cole-Cole Representation of MWCNTs and Graphene Nano fillers Reinforced Galss Fibre Reinforced Polymer Composites

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**Abstract:** Glass Fiber Reinforced Polymer (GFRP) composites were fabricated by incorporating Multi-Walled Carbon Nanotubes (MWCNTs) and graphene nanofillers separately into an epoxy matrix at varying weight fractions of 2%, 4%, and 6%, with glass fiber serving as the primary reinforcement. The nanofillers were uniformly dispersed within the epoxy resin using an ultrasonication technique to ensure effective distribution and interfacial interaction. Dynamic mechanical analysis revealed a significant enhancement in storage modulus, loss modulus, tan δ, and glass transition temperature (Tg) with increasing nanofiller content, exhibiting optimal improvement at 6 wt.% when compared to neat GFRP composites. Cole–Cole plots were constructed to evaluate the dispersion characteristics of the nanofillers within the epoxy matrix and to predict the extent of phase heterogeneity in the composite system. The results indicate that graphene nanofillers outperform MWCNTs in reinforcing GFRP composites, attributed to their superior dispersion uniformity and enhanced phase homogeneity within the epoxy matrix, thereby promoting improved interfacial integrity.

**Keywords:** Glass Fiber, Multi-Walled Carbon Nanotubes (MWCNTs), Graphene, Dynamic Mechanical Properties, Cole–Cole Plot.

## Introduction

Glass Fiber Reinforced Polymer (GFRP) composites are advanced structural materials in which glass fibers, arranged in a bidirectional woven configuration, serve as the primary reinforcement within a polymeric matrix. In the present study, epoxy resin incorporated with nanofillers—namely Multi-Walled Carbon Nanotubes (MWCNTs) and graphene nanoplatelets—was ultrasonically dispersed to enhance matrix bonding and ensure effective fiber orientation. Glass fibers are economically advantageous and exhibit superior flexibility compared to carbon fibers. Owing to their lightweight nature, high strength-to-weight ratio, non-conductive and non-magnetic characteristics, they are widely employed in diverse applications such as boat hulls, water storage tanks, complex molded components, and orthopedic casts. Additionally, glass fibers contribute to odor control in certain water treatment applications. In recent years, significant research attention has focused on reinforcing glass fiber composites with nanofillers to further enhance their mechanical and thermal performance. Nanofillers are available in various morphologies, including nanoplatelets, nanoparticles, and nanofibers. Common examples include nanoclay, single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), and, more recently, graphene, which has attracted considerable interest due to its exceptional mechanical strength, superior thermal conductivity, and improved flame-retardant properties. When incorporated into epoxy matrices, nanofibers and nanoplatelets modify the morphology, interfacial bonding, and miscibility of polymer composites. The extent of property enhancement largely depends on the quality of nanofiller dispersion within the polymer matrix.

Dynamic Mechanical Analysis (DMA) is a thermal characterization technique used to evaluate the viscoelastic response of polymer composites as a function of temperature, time, and applied frequency. Key viscoelastic parameters such as storage modulus (E′), loss modulus (E″), tan δ, and glass transition temperature (Tg) are determined through DMA. The dynamic mechanical property of a polymer refers to its response to a periodically applied force. Polymeric composites typically exhibit viscoelastic behavior, representing a combination of elastic (energy-storing) and viscous (energy-dissipating) responses.

An illustrative example of viscoelastic behavior is a ball dropped from a certain height. The height to which the ball rebounds corresponds to the stored elastic energy, analogous to the storage modulus (E′), representing material stiffness. The energy dissipated during impact corresponds to the loss modulus (E″), which characterizes viscous behavior or internal friction. The mechanical response of polymer composites is both temperature- and time-dependent, typically exhibiting four distinct regions: the glassy region, glass transition region, rubbery plateau region, and terminal (liquid flow) region, reflecting the amorphous nature of polymer matrices.

The Cole–Cole plot is a dielectric relaxation model used to analyze phase homogeneity and interfacial characteristics in polymer composites. It represents the relationship between storage modulus and loss modulus as a function of frequency and provides insight into phase heterogeneity and filler dispersion quality.

The primary objective of this study is to investigate the dynamic and thermal performance of GFRP composites reinforced with MWCNTs and graphene nanofillers at varying weight fractions. Cole–Cole plots were constructed specifically for graphene-reinforced GFRP composites at different weight percentages to evaluate dispersion behavior and phase integrity.

The raw materials employed in the fabrication process include MWCNTs, graphene nanoplatelets, epoxy resin (LY5561), hardener (HY951), and bidirectional woven E-glass fiber mats. The matrix system consisted of epoxy resin and hardener in a 10:8 ratio, with nanofillers incorporated at 2%, 4%, and 6% by weight.

For specimen preparation, MWCNTs at varying weight fractions (2%, 4%, and 6%) were ultrasonically dispersed in the epoxy resin for 40 minutes at room temperature to achieve uniform distribution. The hardener was subsequently added, and the mixture was further ultrasonicated for approximately 30 minutes to ensure homogeneous curing. The prepared matrix was then used to fabricate composite laminates in a rectangular mold conforming to ASTM standards. Two sets of specimens were produced for each nanofiller concentration. After curing, the laminates were cut according to ASTM specifications for Dynamic Mechanical Analysis testing.

## 2. Dynamic Mechanical Analysis

Dynamic Mechanical Testing was performed using a three-point bending Dynamic Mechanical Analyzer (DMA). A sinusoidal stress was applied to the specimens, and the resulting strain response was recorded as a function of temperature. The phase lag (δ) between the applied deformation and the material response was carefully analyzed to characterize the viscoelastic behavior of the composites.

epresentative responses corresponding to purely elastic, purely viscous, and viscoelastic materials were evaluated for comparison. DMA enables precise assessment of variations in mechanical performance arising from differences in composition and molecular architecture of polymer composites. The technique provides valuable insight into both the chemical constitution and the physical molecular structure of the material, while also identifying the temperature ranges over which significant transitions in mechanical properties occur.

Key viscoelastic parameters—including storage modulus (E′), loss modulus (E″), glass transition temperature (Tg), and damping coefficient (tan δ)—were determined as functions of temperature and time. The influence of Multi-Walled Carbon Nanotubes (MWCNTs) and graphene nanofillers, incorporated at varying weight percentages into GFRP composites, was systematically investigated using the three-point bending DMA configuration. This approach facilitated a detailed evaluation of nanofiller–matrix interactions and the corresponding enhancement in mechanical performance with increasing nanofiller content.

## 3.Cole-Cole Plot

The Cole–Cole plot is a widely adopted analytical tool for graphically representing frequency-dependent complex dielectric functions, specifically the storage modulus (E′) and loss modulus (E″). In this representation, the storage modulus (E′) is plotted along the horizontal axis, while the loss modulus (E″) is plotted on the vertical axis, enabling visualization of relaxation behavior within polymeric systems. Cole–Cole analysis is particularly applicable to polymer materials exhibiting one or more relaxation mechanisms occurring at comparable frequencies, consistent with Debye-type relaxation or the generalized Cole–Cole functional model. For an ideal Debye relaxation process, the Cole–Cole plot simplifies to a perfect semicircular arc, indicating a single, well-defined relaxation time. Deviations from this semicircular form reflect the presence of distributed relaxation times and phase heterogeneity within the material system.

## 4.Results and Discussion

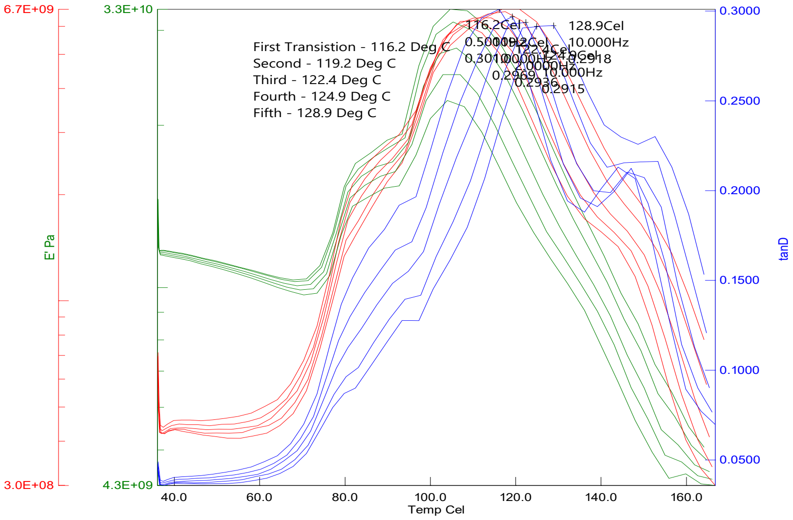
### Effects of Viscoelastic Properties: Multi-Walled Carbon Nanotube Reinforced GFRP at Varying Weight Percentages

The storage modulus (E′) represents the stiffness of a polymer composite as a function of temperature and is directly proportional to the elastic energy stored during Dynamic Mechanical Analysis (DMA). It reflects the load-bearing capability of the material under oscillatory deformation.

The loss modulus (E″) characterizes the internal friction within the material and corresponds to the energy dissipated as heat during cyclic loading. It is therefore proportional to the viscous component of the viscoelastic response.

The phase angle (δ), commonly expressed as the loss factor (tan δ), is defined as the ratio of the loss modulus (E″) to the storage modulus (E′). It represents the damping behavior of the viscoelastic system and quantifies the extent of energy dissipation relative to energy storage under dynamic loading conditions. As temperature increases, variations in tan δ reflect changes in molecular mobility and energy recovery characteristics.

Moreover, tan δ serves as a critical parameter for determining the glass transition temperature (Tg), typically identified at the peak of the tan δ versus temperature curve, indicating the transition from the glassy to the rubbery state of the polymer composite.

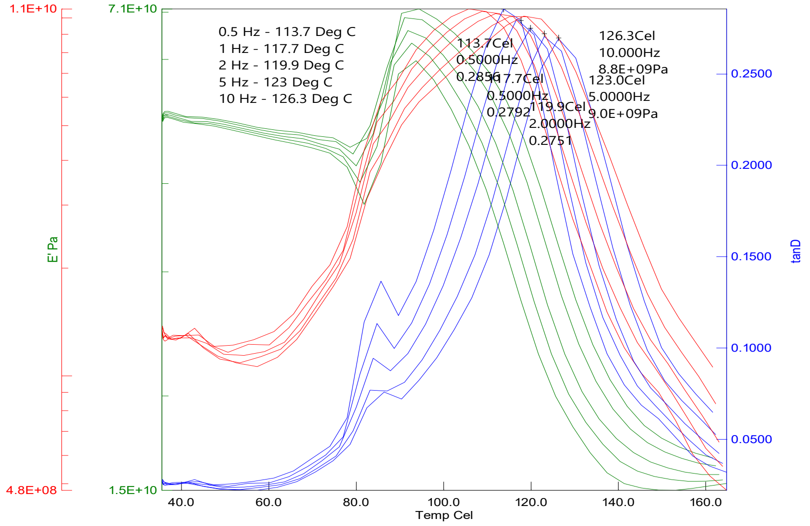


Visco-elastic Properties with 2% Weight MWCNTs reinforcement in GFRP

The MWCNT-reinforced GFRP composite specimens containing varying weight fractions (2%, 4%, and 6%) were evaluated using a three-point bending Dynamic Mechanical Analyzer across multiple frequencies (0.5, 1, 1.5, 2, and 2.5 Hz). Figures 3 to 5 present the comparative viscoelastic behavior corresponding to each filler concentration.

The viscoelastic response demonstrates a progressive enhancement in storage modulus (E′) with increasing MWCNT content, indicating improved stiffness of the composite system. The stiffness exhibited a marginal rise in the lower temperature regime, followed by a decline within the temperature range of approximately 116°C to 128°C across different frequencies, corresponding to the transition region. At 6 wt.% MWCNT loading, the storage modulus displayed a more pronounced and systematic reduction beyond the glass transition region, reflecting the onset of increased molecular mobility. Variations in the glass transition temperature (Tg) were observed within the range of 80°C to 110°C, depending on filler content and testing frequency.

The loss modulus (E″), which represents internal friction and the energy dissipated through vibrational motion, exhibited an increase beyond the glassy region. A distinct peak was observed in the glass transition region, followed by a gradual decline with further temperature rise. This behavior indicates enhanced interfacial interactions and restricted polymer chain mobility due to the presence of MWCNTs within the matrix. Notably, higher filler loadings resulted in elevated peak loss modulus values, suggesting improved energy dissipation capacity. Effective dispersion of MWCNTs within the epoxy matrix appears to constrain polymer chain movement up to the glass transition region, thereby contributing to the observed enhancement in viscoelastic performance.

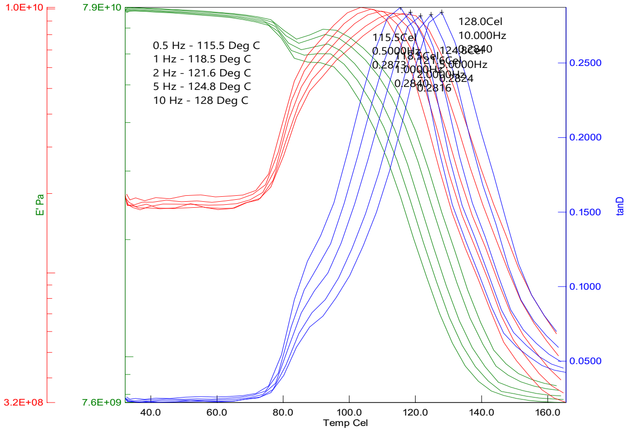


Visco-elastic Properties with 4% Weight MWCNTs reinforcement in GFRP

The damping factor, tan δ, represents the ratio of energy dissipated to energy stored during cyclic deformation and serves as an indicator of the material's viscoelastic balance. A higher tan δ peak corresponds to greater inelastic (viscous) deformation, whereas a lower peak signifies a more elastic response with improved energy recovery.

The breadth of the tan δ peak provides insight into the homogeneity of the polymeric network. A broader peak, as observed in Figures 3 and 4, suggests a wider distribution of relaxation times, indicating structural heterogeneity and the presence of varied polymer chain configurations. With increasing temperature, such broadening reflects enhanced molecular mobility and pronounced viscous behavior.

In contrast, the incorporation of 6 wt.% MWCNTs (Figure 5) results in a comparatively narrower tan δ peak. This narrowing signifies a more uniform molecular architecture and a restricted distribution of relaxation processes within the polymer composite. Hence, a sharp and well-defined tan δ peak is indicative of improved structural homogeneity and more consistent interfacial interactions in the composite system.



Visco-elastic Properties with 6% Weight MWCNTs reinforcement in GFRP

The damping factor (tan δ) is a dimensionless parameter that quantifies the ratio of energy dissipated to energy stored during cyclic loading. In the present study, the maximum peak value of approximately 0.3 was observed for the composite containing 2 wt.% MWCNTs, indicating relatively higher viscous dissipation at this filler concentration.

As the MWCNT content increased, a noticeable reduction in peak height and sharpness was observed in the tan δ curves. This behavior suggests restricted mobility of the polymer molecular chains due to enhanced interfacial interaction between the MWCNTs and the epoxy matrix. The incorporation of higher nanofiller content limits segmental motion within the polymer network, thereby altering the relaxation dynamics.

Furthermore, the increase in damping with temperature corresponds to progressive molecular chain mobility and structural softening within the composite. Elevated temperatures contribute to a reduction in elastic response, as the polymer transitions toward a more viscous-dominant behavior, ultimately affecting the integrity of the molecular chain structure.

### Effects of Viscoelastic Properties: Graphene Reinforced GFRP at Varying Weight Percentages

Multi-Walled Carbon Nanotubes (MWCNTs) and graphene are prominent allotropes of carbon, with graphene emerging as a highly promising nanofiller in recent years owing to its exceptional mechanical strength, superior thermal conductivity, and remarkable surface area.

In this study, graphene nanofillers were incorporated into the epoxy matrix at varying weight fractions of 2%, 4%, and 6% for the fabrication of Glass Fiber Reinforced Polymer (GFRP) composites. The prepared specimens were subsequently evaluated using a three-point bending Dynamic Mechanical Analyzer to investigate their viscoelastic behavior and to assess the influence of graphene reinforcement on the mechanical performance of the composite system.

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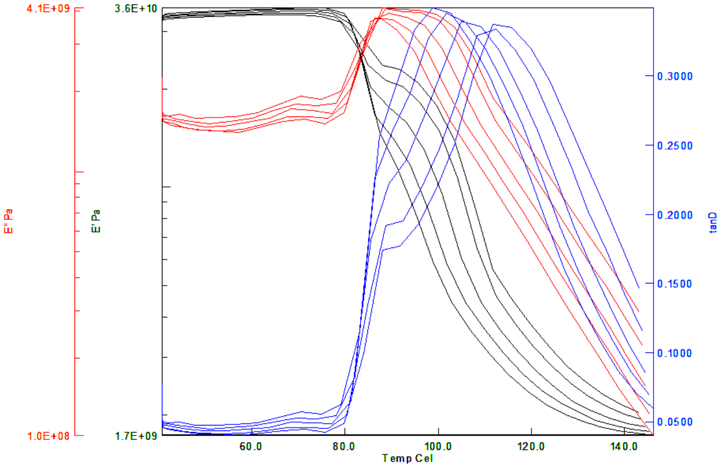
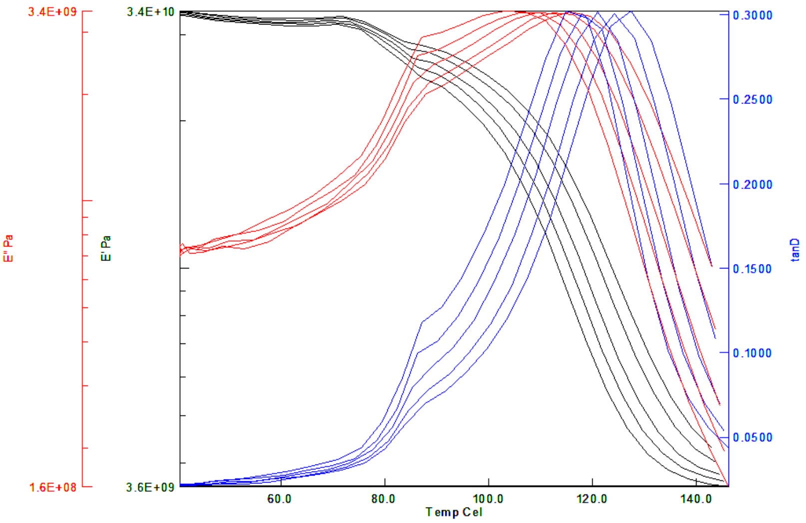


Visco-elastic Properties with 2% Weight Graphene reinforcement in GFRP

Figures illustrate the comparative viscoelastic behavior of graphene-reinforced GFRP composites at 2%, 4%, and 6% weight fractions. The storage modulus (E′), representing the stiffness of the composite, exhibited a decline beyond approximately 80°C, followed by a progressive reduction with further increase in temperature, corresponding to the transition toward the rubbery region.

An overall enhancement in storage modulus was observed with increasing graphene content, indicating improved stiffness due to effective nanofiller reinforcement. At 4 wt.% graphene, the storage modulus demonstrated a relatively uniform and systematic decline beyond the transition region, reflecting stable filler–matrix interaction. In the case of 6 wt.% graphene, the storage modulus increased up to approximately 100°C before undergoing a pronounced drop at higher temperatures.

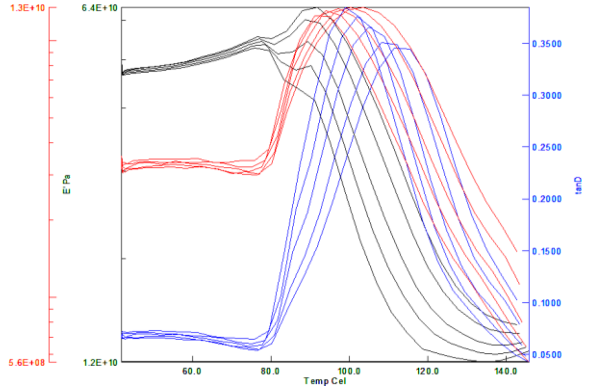
This behavior suggests that while graphene incorporation enhances stiffness up to an optimal loading level, excessive filler addition may lead to agglomeration or reduced interfacial efficiency, ultimately contributing to deterioration in the mechanical integrity of the polymer composite beyond a certain threshold.



Visco-elastic Properties with 4% Weight Graphene reinforcement in GFRP

An increase in the loss modulus (E″) of graphene-reinforced GFRP composites was observed beyond the glassy region, indicating enhanced internal friction and energy dissipation as the material approached the transition phase. In particular, Figure 7 demonstrates intensified molecular motion and interfacial friction between the graphene nanofillers and the epoxy matrix at 4 wt.% loading, suggesting effective stress transfer and improved filler–matrix interaction.

The glass transition temperature (Tg) was identified within the range of approximately 85°C to 125°C, depending on filler concentration and testing conditions. However, at 6 wt.% graphene loading, the loss modulus peak shifted and exhibited a decline around 100°C. This reduction may be attributed to filler agglomeration or restricted polymer chain mobility at higher filler content, leading to altered relaxation dynamics and diminished energy dissipation efficiency within the composite system.



Visco-elastic Properties with 6% Weight Graphene reinforcement in GFRP

Figure 8 illustrates the effect of incorporating 6 wt.% graphene into the glass fiber reinforced polymer composite, where a noticeable reduction in the damping coefficient (tan δ) is observed compared to the 2 wt.% and 4 wt.% graphene-reinforced specimens.

Up to 4 wt.% graphene addition, the tan δ peak appears relatively narrow, indicating uniform dispersion of graphene within the epoxy matrix and a homogeneous distribution of molecular motion throughout the composite structure. This suggests effective interfacial bonding and controlled segmental mobility of the polymer chains.

However, with further increase to 6 wt.% graphene, the tan δ curve becomes broader, reflecting a wider distribution of relaxation times. This broadening is indicative of possible nanofiller agglomeration and non-uniform dispersion within the matrix, which adversely affects the dynamic mechanical behavior. The observed trend suggests that beyond an optimal filler loading, the reinforcement efficiency diminishes due to aggregation effects, leading to reduced damping performance and structural heterogeneity in the composite system.

## Cole–Cole Representation of Dielectric Relaxation in Graphene-Modified GFRP Composites

The dynamic and thermal performance of MWCNT- and graphene-reinforced GFRP composites was systematically evaluated, with particular emphasis on their viscoelastic behavior. Comparative analysis of the two carbon allotropes revealed that graphene exhibited superior reinforcing efficiency when integrated with glass fiber composites.

Significant enhancement in dynamic mechanical properties was observed at an optimal graphene loading of 4 wt.%, indicating improved interfacial interaction and effective stress transfer within the composite system.

Furthermore, the Cole–Cole plot was constructed for the graphene-reinforced glass fiber composite to assess phase homogeneity and relaxation characteristics, and the corresponding graphical representation is presented in Figure .

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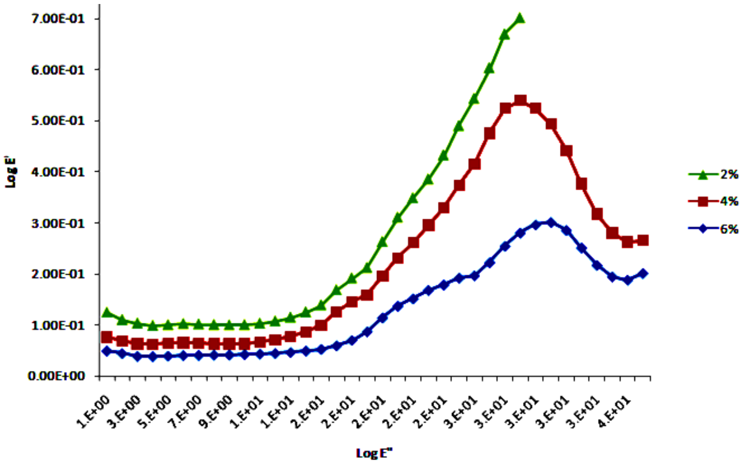

Cole-Cole Plot of Graphene reinforced GFRP in varying weight percentage

The Cole–Cole plot was constructed using the experimentally obtained storage modulus (E′) and loss modulus (E″) data to characterize the dispersion behavior of nanofillers within the polymer matrix. This analysis facilitates evaluation of the linear viscoelastic response of the glass fiber reinforced polymer (GFRP) composite, particularly within the glass transition region. The Cole–Cole representation provides insight into molecular structural changes induced by graphene nanofiller reinforcement and serves as an effective tool for assessing phase homogeneity in polymer composites.

The Cole–Cole curve corresponding to 4 wt.% graphene exhibited an approximately semicircular profile, indicating uniform dispersion and homogeneous phase distribution within the composite. In contrast, the curve for 2 wt.% graphene deviated from the semicircular form, suggesting incomplete dispersion and structural heterogeneity.

With further increase to 6 wt.% graphene, the Cole–Cole plot showed a pronounced deviation from the ideal semicircular shape, reflecting increased phase heterogeneity, likely due to nanofiller agglomeration and non-uniform distribution.

Figure 9 presents the comparative Cole–Cole plots for GFRP composites reinforced with 2%, 4%, and 6% graphene. The semicircular nature of the 4 wt.% curve confirms optimal dispersion and improved interfacial integrity, whereas the distorted profiles at lower and higher filler loadings indicate heterogeneous composite structures.

## 5. Conclusions

Dynamic Mechanical Analysis (DMA) was conducted to evaluate the influence of nanofillers—Multi-Walled Carbon Nanotubes (MWCNTs) and graphene—on the viscoelastic performance of GFRP composites. The interfacial adhesion between the nanofillers and the epoxy matrix was assessed through variations in viscoelastic parameters obtained from the DMA response.

An overall enhancement in storage modulus (E′) was observed with increasing temperature and frequency, reflecting improved stiffness and load-bearing capability due to nanofiller incorporation. However, at elevated frequencies, a reduction in storage modulus was noted, attributed to molecular rearrangement and relaxation phenomena within the composite system, which tend to minimize localized stress concentrations under rapid oscillatory loading.

The results confirm a significant improvement in composite stiffness across all temperature ranges upon nanofiller addition. Notably, graphene-reinforced GFRP exhibited superior storage modulus values compared to MWCNT-reinforced GFRP, highlighting the enhanced reinforcing efficiency of graphene. A measurable shift in the glass transition temperature (Tg), from approximately 80°C to 100°C, was recorded following nanofiller incorporation, indicating restricted polymer chain mobility and strengthened filler–matrix interaction.

The damping coefficient (tan δ) analysis further demonstrated that the composite containing 4 wt.% graphene exhibited a narrower peak, signifying limited molecular mobility and improved structural homogeneity with increasing temperature.

Cole–Cole plots were subsequently constructed using the DMA-derived storage and loss modulus data for graphene-reinforced GFRP composites. The plot corresponding to 4 wt.% graphene displayed an approximately semicircular profile, confirming homogeneous dispersion and uniform phase distribution within the composite. In contrast, the 6 wt.% graphene composite exhibited a marked deviation from the semicircular form, indicating increased phase heterogeneity, likely resulting from nanofiller agglomeration at higher loading levels.

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