DYNAMIC MECHANICAL ANALYSIS OF GRAPHENE NANO PARTICLES REINFORCED EPOXY COMPOSITES FOR NANO HYBRID STRUCTURES

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Abstract: This paper presents Dynamic mechanical behavior of polymer Nano composites reinforced with various weight percentages of Nano particles with basalt/Glass fiber. The Graphene Nano Particles were used as fillers with epoxy resin. The resin mixture is the combination of epoxy resin, hardener and graphene. The mixture formed by the combination of resin and hardener in the good proportion. The graphene is mixed based on the different weight percentages required as mentioned above with respect to resin. The Nano composite plates were prepared using cold compression moulding technique. Finally, the prepared composite plates were sized in laser cutting according to ASTM standards and subjected to DMA test. A series of dynamic mechanical tests were performed for prepared composites over a range of testing temperatures. Test frequency was kept constant. The dynamic mechanical properties of prepared Nano composites were studied by recording storage modulus, loss modulus, tan δ and glass transition temperature (Tg). The graphs like storage modulus vs temperature, loss modulus vs temperature, stiffness vs temperature, tan delta vs temperature, stress vs temperature and cole-cole plot are plotted. It was found that the storage modulus (E') recorded was decreasing with increasing temperature. The loss modulus (E") and damping peaks (Tan δ) values were found to be increased with increasing in temperature up to certain value and beyond certain temperature it was found to be decreased. Also, the loss modulus (E") and damping peaks (Tan δ) values were found to be reduced with increasing reinforcements whereas Tg decreases as reinforcements increase.

Keywords: Dynamic mechanical analysis (DMA), Graphene, Dual Cantilever, Stress Modulus, Loss Modulus, tan delta

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1.INTRODUCTION

Graphene is attracting the attention of all composite inventors across the world. It is simple in structure, lightweight, potentially inexpensive and a renewable material [1]. What more could we want? However, the creation of graphene, its presence, and the characteristics it possesses are not without history. Since its discovery by Novoselov etal. in 2004, graphene, which is a single atom thick sheet of sp2 hybridized carbon atoms with exceptionally high elastic modulus, tensile strength, and very large specific surface area (about 3 times that of CNTs or even bigger), has sparked enormous interest among research and industry communities[2,3]. Being a nonmetal, carbon (C) is an element with atomic number 6 in the first row of group 4A of the periodic table. Its electron configuration is 1s2 2s2 2p2 [3]. Graphene is basically mono layers of carbon atoms arranged in a honeycomb structures. The layers of carbon atoms are held by weak attraction forces. However, the graphite allows the sheets to easily slide over each other. Graphene is an aromatic macro molecule that conducts both electricity and heat in 2 dimensions. Graphene is a single layer of pure carbon atoms bonded together with sp2 bonds in a hexagonal lattice pattern [2,3]. Stacked layers of graphene form graphite. Graphene, measuring one atom thick. Understanding how the carbon fiber interacts with the polymer matrix at the atomistic level is important for evaluating the role of matrix adhesion to the overall composite performance [4]. Before graphene was isolated, it was commonly believed that two dimensional compounds could not exist because they would be too unstable, but the carbon-to-carbon bonds in graphene are small and strong and completely stable [5]. While it's largely transparent, graphene, even at only one atom thick, can be seen with the naked eye. Here, the study we conducted is not only about graphene but the resin we incorporated with graphene [2–5]. Matrix modification with adding nanoparticles enables to enhance interface bond between polymer matrix and fibers [6]. Another important benefit of including nanoparticles in a polymer matrix is a large reduction in permeability as a result of the nanoparticles tortuous journey and high aspect ratio. The stiffness and thermal glass transition temperature (Tg) of the composites are increased, however, when the matrix is modified by the addition of hard nanoparticles6. This composite may be formed into durable products with excellent strength to weight ratios. Epoxies have strong chemical resistance when they are cured, which is necessary for building pipelines for chemicals or water. These epoxies can also be altered to increase their resistance to abrasion from chemicals or physical trauma. The epoxies are fragile and brittle at first. Rigid fillers are added to the resin to increase its toughness. .The composites are developed with multiple Nano particle reinforced epoxy and perform a comparative analysis of the mechanical properties [16-18].

The dynamic characteristics, such G', indicate the sample's elastic portion and hence reflect the sample's capacity to support a load. The dissipation energy is equivalent to the loss modulus (G"), which has a substantial impact on the samples' viscous behavior. And the loss factor tan delta designates the sample's damping capacity. Also shown by this dynamic research was that G' & G" rises when filler content does [7]. Four laminates of weight % 0.2, 0.4, 0.6, 0.8 which are reinforced by graphene nanoparticles are fabricated using hand layup technique and finally for better bonding of the materials hydraulic press is used. Basalt fabric, glass fabric, resin, hardener and graphene particles are used in the fabrication of the laminates. The resin mixture is the combination of epoxy, hardener, and graphene particles. Resin and hardener are mixed in the ratio of 10:1. The graphene particles are mixed on the requirement based on weight percentages 0.2, 0.4, 0.6, 0.8 of graphene in epoxy resin. The fabricated basalt glass fibers reinforced by graphene are taken for Dynamic mechanical analysis (DMA). The dynamic properties like storage modulus, loss modulus, tan delta, stiffness, stress, cole-cole point and glass transition temperature are determined by using DMA tests [7,8]. The graphs storage modulus vs temperature, stiffness vs temperature, loss modulus vs temperature, stress vs temperature, tan delta vs temperature and cole-cole plot are obtained. We used epoxy resins with graphene reinforcement for the dynamic mechanical analysis. By measuring the stress or strain a specific device applies to a sample over time, dynamic mechanical analysis, or DMA, can analyze the kinetic properties of the sample. In this study, the effects of temperature change on the samples' stress, stiffness, storage modulus, loss tan- gent, and tan delta values are examined. The temperature at which glass transitions occur is determined via dynamic mechanical analysis [9–12].

- A Dual Cantilever Clamp is used to measure the stiffness and material modulus of highly damped materials. It is the best mode for evaluating the cure of supported materials. Material modulus can be determined by multiplying the stiffness with geometry factor.
- Point Bend Clamp method is usually the best method for measuring medium to high material modulus materials. This method also conforms with ASTM standard test method for bending. In this method, the clamping effects are neglected; thereby, purest deformation mode is attained.

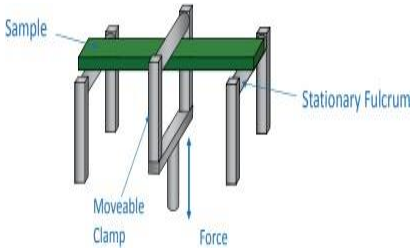

Fig 1: Bend clamp

- Film and Fiber Tension Clamp method is the best mode for measuring thin film and single fil- ament fibers. In this case, small samples of high modulus materials can be measured.

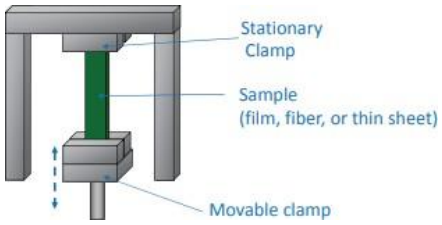

Fig 2: Tension clamp

- Compression Clamp method is the best mode for low to medium modulus materials (gels and elastomers). To support the static load of the ma- chine, the materials must provide some restoring force. There is also an option for customization by expansion and addition of penetrating measurements.

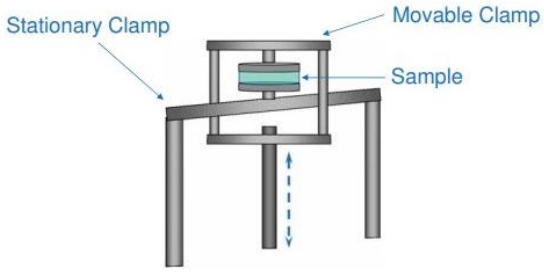

Fig 3: Compression clamp

- Shear Sandwich Clamp method provides pure shear deformation and shear moduli. This method is best suited for evaluating highly damped soft solids such as gels and adhesives & elastomers which have high glass temperature.

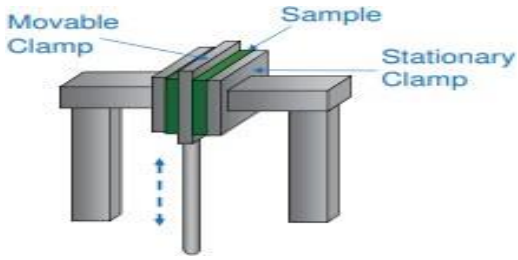

Fig 4: Compression clamp

In this experimentation, four laminates of graphene are fabricated with 0.2, 0.4, 0.6, 0.8 weight percentages. The laminates are fabricated using hand layup technique and a hydraulic press. Resin mixture is prepared using magnetic stirrer. The dynamic properties like storage modulus, loss modulus, stiffness, tan delta,[13–15] cole-cole point and glass transition temperature are deter- mined and the graphs are obtained with respect to temperature[7,8].The above properties are determined using Dynamic mechanical analyzer.

2. EXPERIMENTAL INVESTIGATIONS

2.1 MATERIALS

Basalt fabric (380gsm), glass fabric, resin (ARALDITE LY 556), hardener (ARUDRA HY951) and graphene nanoparticles are the materials that are used in the fabrication of basalt glass fiber reinforced by graphene. The specifications of the basalt fabric are 100 mm width, mm thickness and areal density is 380 gm/m^2. Glass fabric is of 0.24mm thickness 40" width, the weave type is plain and the areal density is 303.9 gms/m^2.The resin is of clear liquid resin without impurities, color index is 0.1, epoxide index is 5.411 and the dynamic viscosity at 25 ^{0}c is10920mpa-s and specific gravity is of 1.16 and volatile is 0.5%. The hardener of color index of 26, dynamic viscosity at 25^{0}c is 15 mpa-s and moisture content is of 0.09%. graphene of thickness 0.8-1.6 nm, number of layers is 5 and bulk density is 0.018 g/cm3.The fundamental monomer unit of epoxy resin, known as BADGE or DGEBA, is produced by reacting BPA with epichlorohydrin (ECH), the two chemicals that are used to make epoxy resins. A chemical process known as curing or hardening determines the properties of the cured epoxy resins. Epoxy composites are polymers in which the polymer matrix is epoxy resin. Other kinds of fibres or fillers are added to this polymer matrix to strengthen it.

2.2 Fabrication Process

Basalt fabric, glass fabric, resin, graphene and hardener are the materials used in the fabrication process of the basalt glass fibre reinforced by graphene. The first step of the fabrication process is preparing the resin mixture. In preparing resin mixture resin and hardener are mixed in the ratio of 10:1 and the graphene are mixed as per the required weight percentage. Initially, apply the grease on the lower part of the mold and place the transparent sheet on it. Apply gentle pressure on the transparent sheet to remove air bubbles. Epoxy resin is mixed with hardener in the ratio of 10:1 in a glass jar. Pour the matrix material on the plastic sheet and spread evenly. Place the basalt fabric on the resin and pour some more, so that fiber gets soaked in resin and add the Nano graphene particles accordingly. Follow the same for the upper mold also, leave the mold for 24 hours for curing.

Fig 5: Fabrication process Step1

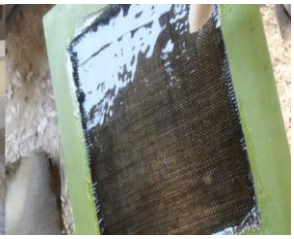

Fig 6: Fabrication process Step 2

Fig 7: Fabrication process Step 3

Fig 8: Fabrication process Step 4

Fig 9: fabrication process step 5

2.3 Experimental Procedure

Dynamic Mechanical Analysis was done on a NETZSCH DMA 242E Artemis setup with dual cantilever mode. It is manufactured by NETZSCH- Gerätebau GmbH (95100 Selb, Germany). It has a controlled force range upto 24 N for measurements of stiff samples. The force resolution can be increased upto 8N. It has a static travel range of 20mm which allows for precise testing of specimens which experience change in their dimensions during DMA. The analyzer also has 30 different sample holders for optimal adjustment of measurement. The sample mass was in the range from 5-10mg. The heating rate was 10^{0}C/min over the temperature range from 30 to 600^{0}C.

The stress applied on the sample by the dual cantilever of the DMA as a function of time:

$$\sigma(t) = \sigma\sin(\omega t + \delta) \quad \text{---------- (1)}$$

Where, σ is the maximum stress applied on the sample and δ is the phase angle. Phase angle can be defined as the angle between the changes in the phase of the characteristic waveform.

Similarly, if strain is involved:

$$\varepsilon(t) = \varepsilon\sin(\omega t) \quad \text{---------- (2)}$$

Where, ε is the maximum strain amplitude experienced by the sample and ω is the frequency of the DMA.

$$\sigma(t) = E(\omega t)\varepsilon(t) \quad \text{---------- (3)}$$

Where E is the dynamic modulus of the sample which can be defined as the ratio of stress to strain under vibratory conditions. The dynamic modulus can be calculated by the measurement of the pulse velocity of the DMA probe.

Fig 10: Standerd DMA specimen

Table 1: DMA specifications

Temperature range	-170^{0}c to 600^{0}c
Heating range	0.01 k/minto 20 k/min
Frequency range	0.01 Hz to 100 Hz
Force range with high force Force range with high resolution	24 N(max) 8 N
Maximum controlled strain amplitude	240μm
Static deformation	Up to 20mm
Modulus range	10^{-3} to 10^6Mpa
Damping range(tan δ)	0.005 to 100
Deformation modes	• 3-point bending • Single/dual cantilever bending • Tension • Compression/penetration
Sample geometries thickness: 5mm	Dependent on the deformation mode, sample dimensions: length:60mm Width : 12mm,

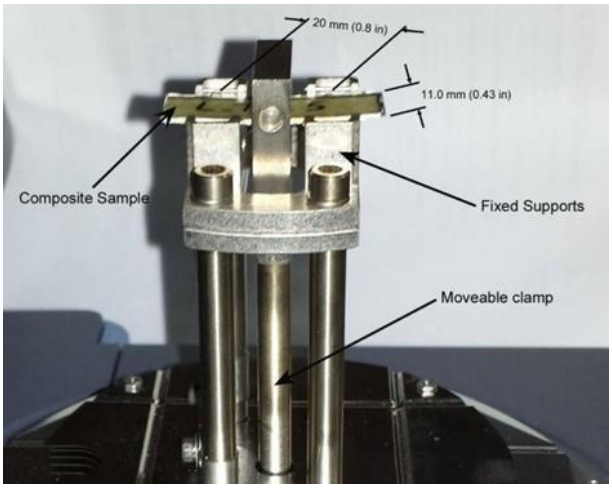

Fig 11: Dynamic Mechanical Analyzer

In view of ASTM D3039 the malleable test is finished on the basalt glass fiber built up by Graphene. The standard components of the example in light of ASTM D3039 are 250 mm (length) × 15 mm (width) × 3 mm (thickness). The state of the example is rectangular. INSTRON 3382 General Testing Machine of 100 kN load cell (Instron, Norwood, Mama, USA) is utilized in this tractable trial of the examples. The testing strategy for FRP composites, where a clasp on extensometer with a 25mm check length was connected to the example to gauge its prolongation during testing. The crosshead speed was set at 2mm/min, and the information was recorded and dissected utilizing PC programming. Five examples were tried for each FRP composite framework.
Dynamic mechanical investigation (DMA) hardware is utilized to decide the Young's modulus, storage modulus, loss modulus, Stress and damping coefficient tan δ as a component of temperature, recurrence or time.

Dynamic Mechanical Analysis (DMA) is widely used materials properties such as glass transition temperature (Tg), the coefficient of thermal expansion (CTE) and visco-elastic properties with the help of various fixtures such as single/dual cantilever, three point bending, tension and compression, and shear in composite materials. DMA is a technique where a small deformation is applied to a sample in a cyclic mode. This allows the materials response to stress, temperature, frequency and other values to be studied. Dynamic mechanical analysis has become more popular because of their significant properties and to provide information about materials such as viscoelastic properties in particular polymers. In this study, Dynamic Mechanical Analysis was done on a NETZSCH DMA 242E Artemis setup with dual cantilever mode. It is manufactured by NETZSCH-Gerätebau GmbH (95100 Selb, Germany). It has a controlled force range upto 24 N for measurements of stiff samples. The force resolution can be increased upto 8N. It has a static travel range of 20mm which allows for precise testing of specimens which experience change in their dimensions during DMA. The analyzer also has 30 different sample holders for optimal adjustment of measurement. The sample mass was in the range from 5-10mg. The rate of heating is 10^0C/min over 30 to 600^0C temperature range.

3. RESULTS AND DISCUSSIONS

3.1 DYNAMIC MECHANICAL PROPERTIES OF GRAPHENE/NANOCOMPOSITES

- **Storage Modulus**

Storage modulus or elastic storage modulus is defined as the ratio of the elastic stress to strain. It indicates the ability of a material to store energy elastically. Storage modulus basically determines the strength or character of the polymer or sample. If the storage modulus is high, the polymer is difficult to break. The elastic behavior of the sample is assessed by calculating the storage modulus of the sample. It is different from Young's modulus. Young's modulus refers to the tensile modulus, whereas storage modulus refers to the energy stored by the material when oscillating loads are applied on the sample or material. In the below figure, the storage modulus remains constant upto certain rise in temperature and decreases significantly, as indicated by a steep curve and becomes zero at a certain temperature.

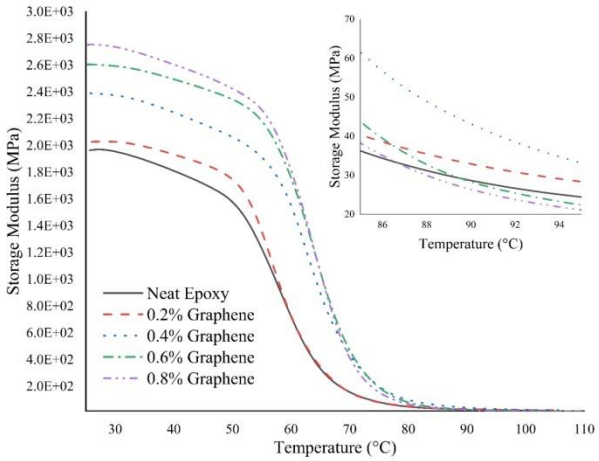

Fig 12: Storage Modulus Curve

•Loss Modulus

Loss Modulus is a measure of the energy dissipated or lost per cycle of sinusoidal deformation. This factor represents the elastic nature of the sample. As the chains begin to move freely, loss modulus increases. When the loss modulus increases, the sample becomes less stiff and more rubbery. The material or sample is said to be elastic if the phase shift is below 450. The loss modulus represents the amount of energy dissipated by the sample. In this case, the loss modulus increases sinusoidally upto a point and at peak glass temperature (Tg). After that peak, the loss modulus values gradually decrease as the temperature increases above glass temperature as shown in the below figure.

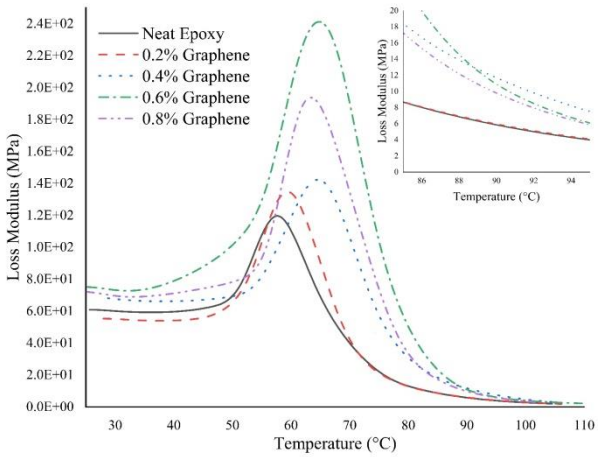

Fig 13: Loss Modulus Curve

•Tan delta

Tan delta or Loss Factor can be defined as the ratio of loss modulus to the storage modulus. In other words, it represents the ratio of viscous to elastic response of a viscoelastic material. When a load is applied to a polymer, some part of the load is dissipated by the energy dissipation mechanisms due to the change in the position of the chains when moved. Tan delta provides the information about the overall flexibility of the material or sample. The area of the tan delta curve indicates the overall amount of energy absorbed by the sample. The molecular mobility can also be assessed by considering the values of tan delta. In the below figure, the tan delta values rise exponentially as the temperature of the sample increases and at a given point of temperature, the values drop down in a very quick manner which is indicated by the steep fall in the curve.

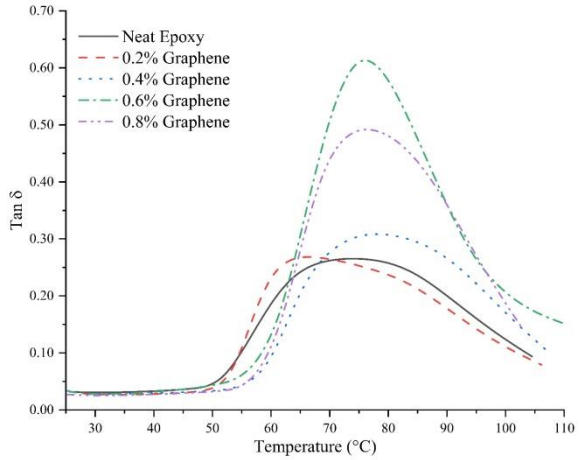

Fig 14: Tan Delta Curve

•Stiffness

Stiffness can be defined as the resistance to a force causing a material or sample to bend. The rigidity of a structural member can also be expressed as stiffness. Stiffness is essential for every material since it assesses the amount of load required in order for the material to withstand loads. Stiffness is the product of the force of load applied over a distance. In the below figure, as the temperature of the sample increases, the stiffness gradually decreases which is indicated by the steady fall of the curve.

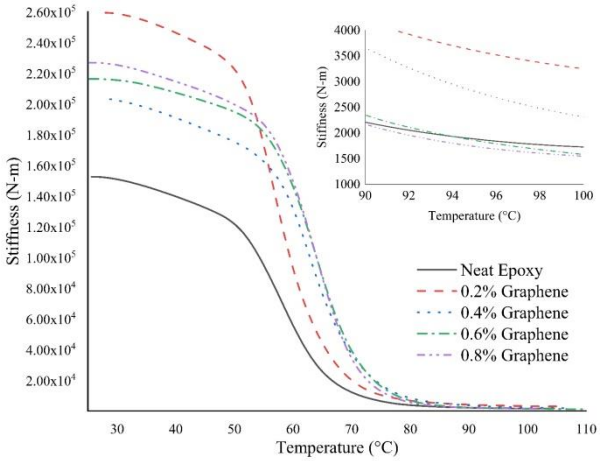

Fig 15: Stiffness Curve

•Stress

Stress can be defined as the applied force divided by the un-deformed area over which the force is applied. There are 3 types of stresses; tensile, compressive and shear stresses. When a certain load is applied over a certain area, the stress assesses the ability of the sample or material to withstand the load before fracturing or bending. In this study, the dual cantilever applies the force exactly on the center of the material. The below figure represents the change in stress, when the temperature of the material or sample is varied with respect to time. Initially, there is a decrease in the stress values experienced by the sample. After a certain temperature, the stress values increase and remain constant throughout the testing.

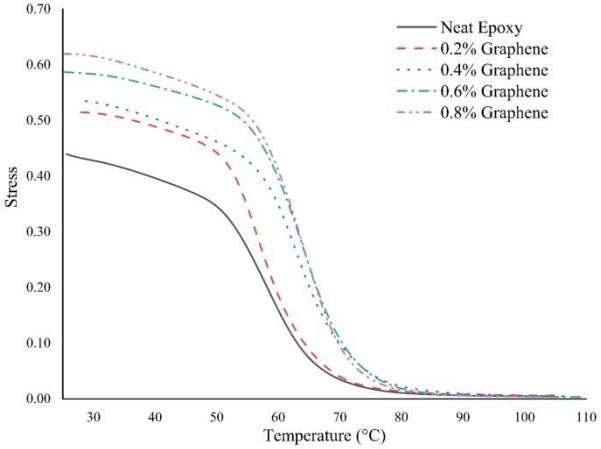

Fig 16: Stress Curve

•Cole-Cole plot

Cole-Cole plot is plotted between the loss modulus and the storage modulus of the sample. Cole- Cole plot is used to assess the dielectric relaxation produced in the sample. This phenomenon can be defined as the adjustment of the dielectric displacement to the time dependent electric field. The dielectric relaxation can be measured as the momentary delay

in the dielectric constant of the sample. Due to the movement of the dipoles (dipole relaxation) and the movement of electric charges (electric relaxation) which are produced due to an applied alternating field, dielectric relaxation is obtained. Dielectric spectroscopy deals with these dielectric properties of samples. Generally, the dielectric relaxation varies between the frequencies ranges of 102-1010Hz. In the below figure, a sluggish or imperceptive rise in the loss modulus is observed when the storage modulus values increase. At a certain temperature, the curve experiences a steep increase in the loss modulus when the storage modulus is decreased. Not only that, the curve exhibits variations during controlled temperatures at maximum storage modulus values.

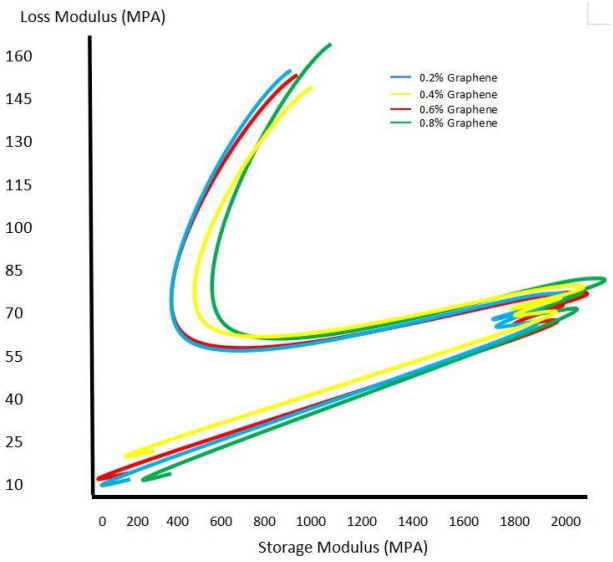

Fig 17: Cole-Cole plot

4. CONCLUSION

Dynamic mechanical properties of prepared composites were successfully investigated at different temperatures with the following conclusions. The influence of Graphene Nano particles with Bassalt /Glass fibers, epoxy was studied using DMA. From the above results, as the temperature increases, there is a decrease in the stress values experienced by the sample. After a certain temperature, the stress values increase and remain constant throughout the testing. When it comes to the stiffness, it gradually decreases which is indicated by the steady fall of the curve. The tan delta values rise exponentially as the temperature of the sample increases and at a given point of temperature, the values drop down in a very quick manner which is indicated by the steep fall in the curve. The loss modulus increases sinusoidally upto a point and at peak glass temperature (Tg). After that peak, the loss modulus values gradually decrease as the temperature increases above glass temperature (Tg). All the results and values indicate that the graphene reinforcement plays a vital role in increasing the strength and stiffness of the epoxy resin. The cost of graphene is very cheap and can be made from trash. But, the process of synthesis is relatively costly. There is a lot of scope for research in graphene and the applications are vast.

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