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Influence of Frequency on Dynamic Mechanical Properties of Glass, Carbon and Bronze Filled Polytetrafluoroethylene Matrix Composites

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ABSTRACT

Under severe service conditions, the dynamic mechanical properties of polymer matrix composites play a significant function in regulating the reliability of composite structures. In this article, the dynamic mechanical properties of polytetrafluoroethylene (PTFE) filled with 25 wt. % glass fibre (GF25), 25 wt. % carbon fibres (CF25) and 40 wt. % bronze fibre (BF40) under varying frequencies of 2.5, 5.0 and 10.0 Hz were studied. The dynamic mechanical testing was performed according to ASTM D 5023 standard. Cole-Cole plot has been applied to ascertain the phase behaviour of the composites. The dynamic mechanical analysis results revealed that varying (increasing) frequency significantly influenced storage and loss moduli, glass transition temperature and damping factor of the PTFE and its composites. Cole-Cole analysis revealed heterogeneity of the composite materials. The filled-PTFE composites can be used in advanced applications including aerospace and automobile sectors.

Keywords: *Storage Modulus · Loss Modulus · Damping · Filled · PTFE Matrix Composites*

1. Introduction

Polymer matrix composites (PMCs) are potential structural materials owing to their high specific strength and specific modulus when compared to neat polymers. Polytetrafluoroethylene (PTFE) is a synthetic fluoropolymer matrix. It has numerous applications, particularly if the merits of heat-oxidation, chemical and good lubrication capability are needed for instance wear application in extreme conditions [1]. The increase of compressive strength and creep resistance of polymers can be achieved through reinforcing the polymers with fibres. The knowledge of dynamic mechanical properties of PMCs is significant while considering energy dissipation processes in cyclic loading applications and an abrupt change over a relatively small changes in temperature due to visco-elastic behaviour of polymers [2]. Viscoelastic characteristic is a typical property of polymers and it plays a key function in PMCs. This property can be studied by dynamic analysis, in which storage modulus (E'), loss modulus(E''), damping (tan δ) and glass-transition temperature (T_g) are four significant linear viscoelastic variables. These properties are affected by frequency, temperature and weight percentages of fibres [3].

Jin et al. studied the dynamic mechanical properties of multi-processed multi-walled carbon nanotube/polymethylmethacrylate composites. It was observed that storage and loss moduli and peak of tan δ increased with addition of carbon nanotube [4]. Hassan et al. investigated several properties of glass fibre reinforced polyamide 66 composites including dynamic mechanical properties. It was found that tan δ at ambient temperature and tan δ maxima increased with water absorption whereas temperatures at maximum tan δ in the high temperature and low-temperature regimes decreased [5]. Thongsong et al. investigated the effect of fly ash silica (FASI) and precipitated silica (PS) in the ratios of FASI: PS of 0:100, 75:25, 50:50, 25:75 and 0:100 on dynamic mechanical properties of natural rubber. It was found that with addition of FASI and PSI storage and loss moduli increased while damping decreased. Besides, composites with 75% PSI showed the best dynamic mechanical property [6]. Wang and Ying (2012) studied the dynamic mechanical properties of polypropylene reinforced with 5, 15 and 25 % carbon fibre. It was found that addition of carbon fibres increased the loss and storage moduli and damping of the propylene matrix with 25% carbon fibre reinforced propylene composite showing the highest damping, storage as well as loss moduli [7]. Ram, Khastgir and Rahaman reported an increase in storage and loss moduli but decrease in tan δ as multi-carbon nanotube was added to polyvinylidene fluoride (PVDF). Also, these properties decreased [8]. Suresha, Ravishankar and Sukankaya reported an increase and decrease in glass transition temperature, storage and loss moduli and tan δ, respectively of organomodified montmorillonite filled epoxy nanocomposites [9]. Mokhtari et al. studied creep and dynamic characteristic of filled with barium–titanium oxide (BT) and reduced graphene oxide (rGO) PVDF in the temperature range of -50-150 °C at varying frequency. It was observed that storage and damping increased with increasing frequency and that PVDF/rGO composites indicated higher storage modulus of 7500 MPa [10]. Rajashekaraiah et al. studied the influence of glass, carbon fibres and PTFE, silicon carbide (SiC) and alumina (Al_2O_3) on dynamic mechanical properties of thermoplastic copolyester elastomer matrix. It was observed that storage modulus was high at lower temperature with increasing fibre and filler and damping as well as loss modulus indicated higher values with inclusion of SiC and Al_2O_3 [11]. Zhang, Klein and Friedrich studied the dynamic mechanical properties of discontinuous carbon fibre reinforced PTFE composites in a temperature range of -150-150°C. The results indicated high values of storage, loss moduli and damping factor at lower temperature of -83 °C. However, damping reduced to about 16 times on addition of 23 wt.% carbon fibre [12]. Chen et al. investigated storage, loss moduli and damping of poly (butylene succinate) composites reinforced nanometre calcium carbonate. It was found that storage, loss moduli and tan δ decreased with increase in temperature and that addition calcium carbonate improved the dynamic mechanical properties of the matrix [13] . Tcherdynterv et al. studied thermal ad mechanical properties of polyimide (PI) powder reinforced fluorinated propylene (FEP) and polyethylene composites. It was observed that addition of the PI increased the storage, loss moduli and damping and these properties decreased with increase in temperature [14]. Mothé, Monteiro and Mothé added 1, 5, 10 and 15% of vegetal leaves to polypropylene matrix in order to study dynamic mechanical properties of the matrix. The results revealed the fibres significant influenced the viscoelastic behaviour but showed no influence on the glass transition temperature [15]. The dynamic mechanical properties of an exclusive type of smart material using shape memory polyurethane graphene reinforced nanocomposites was also reported [16].

PTFE matrix composites are used in many applications including aircraft and automotive industries as they are subjected to varying frequencies. Therefore, this paper focuses on the dynamic mechanical properties of glass, carbon and bronze filled PTFE composites under the influence of varying frequency.

2. Materials and Methods

2.1 Materials

In this study, 25 wt. % of milled-E glass fibre, an amorphous petroleum coke 25 wt. % and 40 wt. % bronze particles and PTFE were used as fillers and resin, respectively. The fibres and the composites are coded as 25CF, 25GF and 40BF and GF25, CF25 and BF40, respectively. Due to limitation of manufacturing equipment, these materials were commercially acquired from Polymer Chemical Industry Ltd. (Polikim A.S., Gebze, and Turkiye) in the form of sheets of dimensions (500×500×7) mm. Table 1 displays some selected properties of the materials used in this study.

Table 1. Selected properties of materials used for the study

Materials	Tensile strength (MPa)	Compressive strength (MPa)	ε at break (%)
PTFE	37.27	4.90	400
GF25	23.54	6.86	270
CF25	20.59	10.79	110
BF40	27.46	10.30	280

2.2 Method

DMA was applied to characterise the temperature-dependent viscoelastic properties of the materials provided in Table 1. The experiment was carried out in a dynamic mechanical analyser DMA 242 E Artems from NETZSCH (Made in Germany). The experiment was performed based on ASTM D 5023-23 standard [17]. Here, the materials of rectangular cross section were tested in flexure as beams. The materials rested on two supports and were loaded by means of a loading nose midway between the supports. Using three-point bending, the materials were placed in mechanical linear displacement at fixed frequencies with linear temperature variation or variable frequencies at isothermal conditions. The elastic moduli or loss moduli, or both, of the polymeric material system are measured. As per this standard, the dimensions of the materials used in this study were 60 mm × 12 mm × 5 mm. The experiment was conducted at varying frequencies of 2.50, 5.0 and 10.0 Hz at a heating rate of 6 $Kmin^{-1}$. Curves of storage modulus (E'), loss modulus (E"), and damping/tan delta (tan δ) in the temperature range from 30 °C to 200 °C were recorded for all the materials. Figure 1 shows the schematic representation of the experimental setup. The DMTA instrument is computer operated meaning that it give results with certainty.

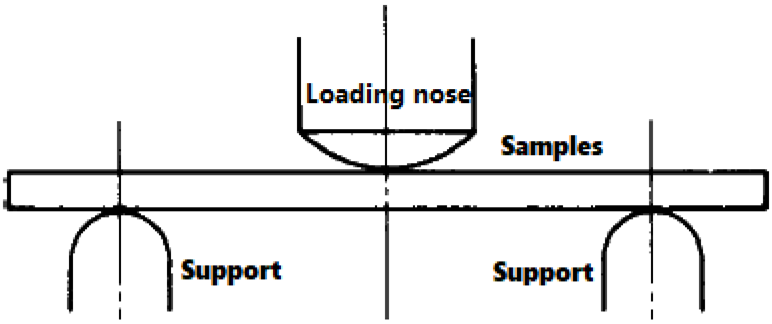

Figure 1. Schematic representation of the experimental setup of the DMTA

3. Results and Discussion

3.1 Dynamic Mechanical Analysis (DMA)

DMA data gives an insight into the stiffness of composites as well as matrices, representing the elastic behaviour of materials [18].

3.1.2 Storage modulus (E')

E' is the real component of the complex modulus and is proportion to energy stored by materials per cycle. It indicates the load-carrying capacity and stiffness of viscoelastic materials. The E'against temperature of filled PTFE composites at different frequencies of 2.50, 5.0 and 10.0 Hz is shown in Figure 2 (a), (b), (c) and (d) for PTFE, GF25, CF25 and BF40 composites, respectively. It is observed that in the glassy region (<50 °C) of the materials, E' shows the maximum magnitudes. This is because at glassy region majority of the polymer chains are frozen due to tight packing of atoms of the materials thus storing more energy [19]. It was also seen that E' increased with varying frequencies from 2.50-10.0 Hz. However. E' decreases due to increasing temperature in all regions. This agrees with the results reported in [20].

In the transition region, a sudden drop in E' for the composites above T_g could be noticed. This is related to increasing molecular mobility of polymer chains due to softening of the composites thereby decreasing its stiffness at higher temperatures. It also should be noted that the frequency played a key function at higher temperatures. In the rubbery region (>150 °C), which is the region with motions of long polymer chains, a minor impact of frequency (curves are completely merged) could be observed at higher temperatures [21]. This means that E′ is virtually unchanged at its minimum magnitudes. In other words, no significant change in E′ was noticed because the macromolecules of polymer were in a highly entangled state [22]. At higher temperature the influence of frequency might not be effective as it cannot control the motion of polymer chains. In all cases, E′ was found to increase with varying frequency in the following order: E′10.0 Hz>E′5.0 Hz>E′2.5 Hz. The increase in E′ with frequency is due to the segment of the polymer composites possessing smaller relaxation time for varying the frequency. Additionally, it is attributed to less mobility of polymer chains at higher frequencies leading to increase in stiffness of the investigated materials.

Influence of fillers on E′of PTFE showed enhancement in E′ of the PTFE. Due to addition of 40 wt. % BF, 25 wt. % GF and 25 wt.% CF into PTFE, E′ of PTFE substantially increased from 429.94 to 820.16, 829.67 and 1033.64 MPa at 2.50 Hz, from 44.64 to 844.89 and 1058.26 MPa at 5.0 Hz and from 458.54 to 870.35, 881.17 and 1084.00 MPa at 10.0 Hz, respectively. This is attributed to the fillers militating against the motion of PTFE molecular chains and a possible good interfacial adhesion between the fillers and polymers [23]. Furthermore, CF25 composite found to have the highest E′ in comparison to GF25 and BF40 composites. This is because CF has higher stiffness than GF and BF.

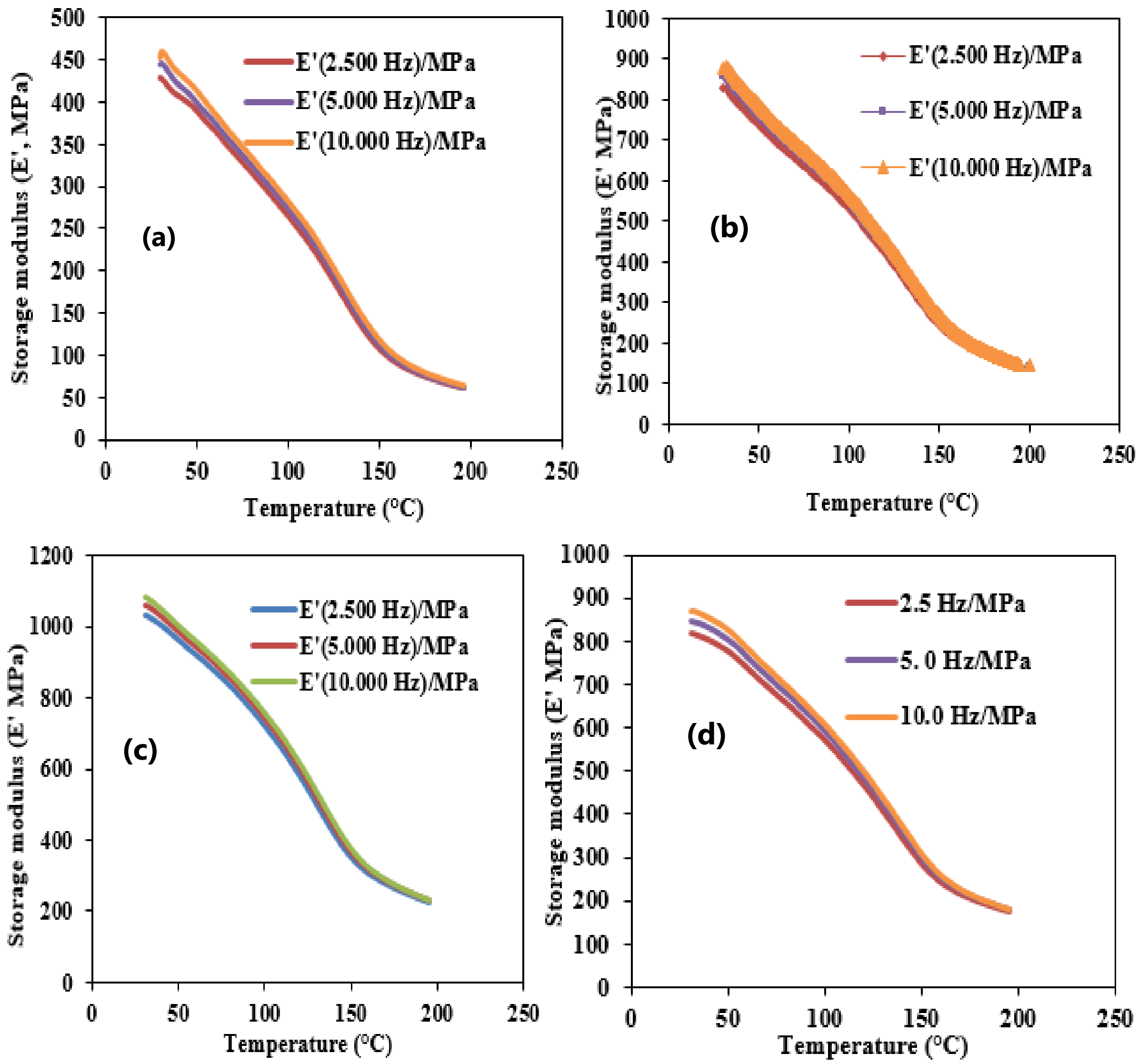

Figure 2. E′ curves under varying frequencies for (a) PTFE, (b) GF25, (c) CF25 and (d) BF40

3.1.2 Loss modulus (E′′)

E′′ (Loss modulus or viscous modulus) signifies the imaginary part of the complex modulus. It is the viscous response of polymer matrix composites. A very significant parameter of viscous materials is glass transition temperature (T_g, °C). E'' versus temperature of PTFE matrix composites under varying frequencies of 2.50, 5.0 and 10.0 Hz is shown Figure 3 (a), (b), (c) and (d) for PTFE, GF25, CF25 and BF40 composites, respectively. The highest values of T_g is computed from the highest peaks of E'' as a function of temperature curves at varying frequencies are presented in Table 2. As noticed, E'' appreciated up to its T_g and then depreciated. A rise in frequency appreciated E''.

Table 2. T_g (°C) of PTFE and its composites

Materials	2.50 Hz	2.50 Hz	5.0 Hz	5.0 Hz	10.0 Hz	10.0Hz
	E''	Tan δ	E''	Tan δ	E''	Tan δ
PTFE	30.32	138.32	32.82	141.82	33.27	144.32
GF25	32.77	141.27	31.77	143.27	33.7	145.27
CF25	32.77	140.27	31.27	143.27	31.77	146.27
BF40	32.77	143.77	32.77	146.27	32.77	147.77

Besides, at appreciating frequency, the peaks of E'' as a function temperature curves were shifted to higher temperatures with higher values of T_g. The increasing values of T_g at increasing frequency is perhaps due to lower mobility of polymer chains at higher frequency [24]. Additionally, at high frequencies, the flow time of the materials was short thereby raising the values of E''.

$E''$was enhanced at varying frequencies following the introduction of fillers into PTFE. The maximum peak of PTFE E'' increased from 44.58, 46.19 and 46.74 MPa to 82.32, 85.84, 89.24 MPa for BF40 composites, 83.15, 87.62, 93. 48 MPa for CF25 composite, and to 90.59, 93.69 and 96.92 MPa for GF25 composite at 2.5, 5 and 10 Hz, respectively. This enhancement at varying frequency is credited to fillers inhibiting relaxation process brought about by higher number of PTFE chain. These results are consistent with reported in [25]. However, here CF25 filled PTFE composites exhibited the high value of loss modulus.

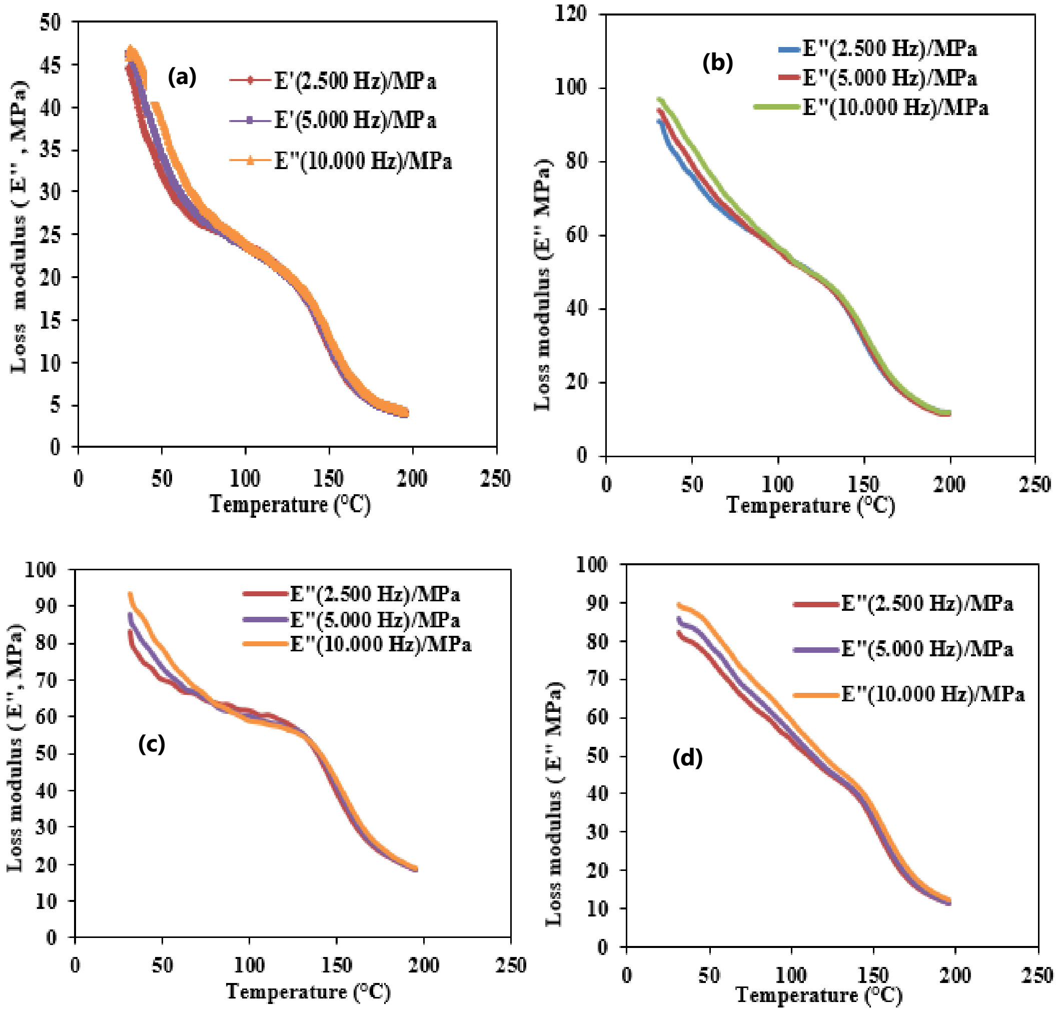

Figure 3. E′′ curves under varying frequencies for PTFE, GF25, CF25 BF40

3.3.3 Damping

The damping (tan δ or loss factor) is the ratio of E′′ to E′. Tan δ versus temperature at frequencies of 2.5, 5 and 10 Hz for PTFE, GF25, CF25 and BF40 composites is displayed in Figure 4 (a), (b), (c),d), respectively. It was observed that varying the frequency decreased the damping factor of both PTFE and its composites with exception GF25 composites. The peak value of damping mostly occurs in the glass transition region and is related to motion of side groups or low molecular weight unit and molecular chains in the rubbers. Consequently, the higher the damping peak, the greater the degree of molecular mobility [26]. The magnitudes of T_g obtained from the highest peaks of tan δ curve at various frequencies are provided in Table 2. With increasing frequency, the magnitudes of T_g grew from 138 °C to 144 °C for PTFE and from 141 °C to 145 °C, from 140 ^{0}C to 146 °C and 143 °C to 147 °C for GF25, CF25 and BF40 composites, respectively. The magnitudes of T_g determined from E′′ versus temperature curve were lower than those obtained tan δ against temperature plot. In addition, the peaks of tan δ curves decreased with increasing frequencies.

It is observed that addition of 40 wt. % BF and 25 wt. % CF reduced the damping of PTFE but that of 25 wt. % GF increased the PTFE's damping. The reason being that the BF and CF acted as elastic materials capable of storing energy within their structure that the fibres. It can be mentioned that quantifying damping is an efficient way to appraise the interfacial bonding in composites. A bad fibre-matrix bonding leads to a higher damping and vice versa. This is because a strong interface reduces the motion of polymer chains thereby lowing the damping. A lower magnitude of damping exemplifies good load-carrying capacity. Hence, it can be concluded that GF25 composite exhibited poor stiffness while BF40 and CF25 composites better heat stability and load-carrying capacity as the frequency increased. The reason being that as frequency increased internal heat generation increased due to friction and molecular movement. GF25 softens under this condition thus its stiffness is degraded. However, BF40 and CF25 maintain their structural integrities and mechanical properties at elevated frequencies owing to their superior thermal resistance. Additionally, there was no better bonding between glass fibre and the PTFE while as a good bonding exist between the bronze and carbon fi*b*res with the PTFE [25].

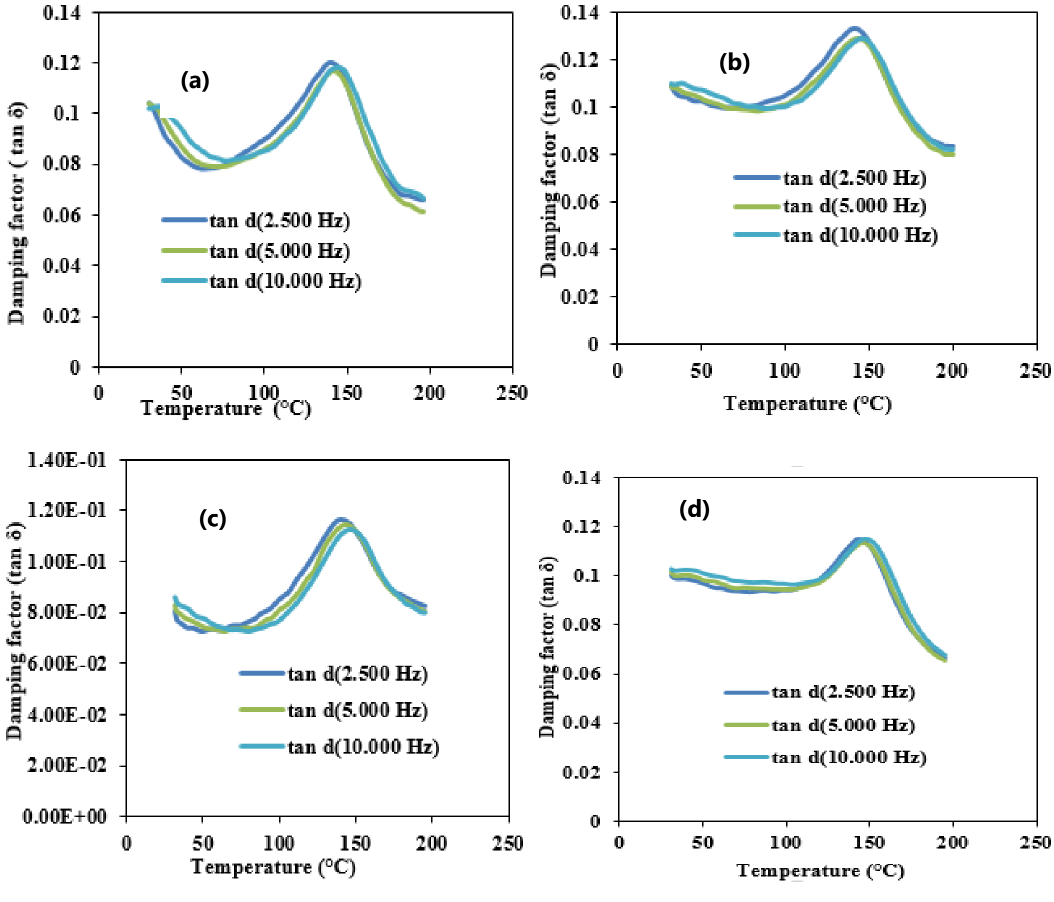

Figure 4. Tan δ curves under varying frequencies for (a) PTFE, (b) GF25, (c) CF25, and (d) BF40

3.4 Cole-Cole Plot Analysis

Cole-Cole is used to illustrate the connection between E” and E′ moduli. In general, homogeneous systems show a semicircle whereas dual-phase systems indicate modified circles. Figure 5 depicts the Cole-Cole plots of the composites in this study. From Figure 5 it is obvious that the composites exhibited behaviour different from homogeneous system. This might be related to the presence of macrospically heterogeneous distributed fibres and of the different interphase effect. The heterogeneity of the materials signifies increase in (storage modulus and loss modulus).

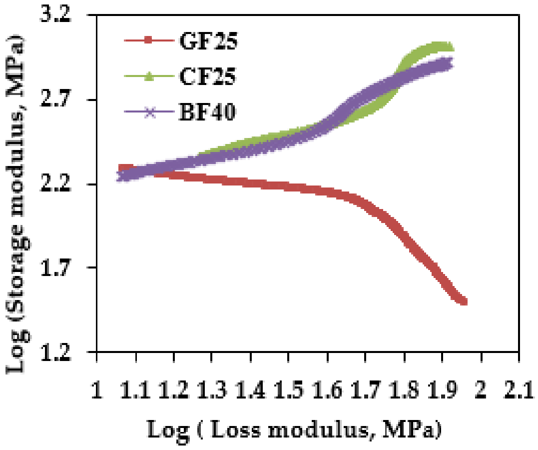

Figure 5. Cole-Cole plot of the PTFE matrix composites

4. Conclusions

In this study, the influence of varying frequency on storage, loss moduli and damping of polytetrafluoroethylene (PTFE) matrix composites has been assessed from temperature of 30-200 °C. It was found that storage, loss moduli, glass-transition temperature of PTFE and its composites increased with varying (increasing) frequency but damping decreased. Increase in temperature caused a decrease in storage, loss moduli, glass transition temperature as well as damping capacity. The maximum values for storage, loss moduli and glass transition temperature and minimum value of damping were obtained at the highest frequency of 10.0 Hz. It was found that addition of glass, carbon and bronze fibres into PTFE increased storage and loss moduli of the PTFE. It was also found that addition of bronze and carbon fibres into PTFE improved PTFE’s damping capacity but damping deteriorated when glass fibre was added to PTFE. Cole-Cole plots revealed that all the composites in this study are heterogeneous in nature.

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