Thermal and dielectric performance of melt processed polycarbonate /CaCu₃Ti₄O₁₂ composites

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Composites comprising Polycarbonate (PC) and CaCu₃Ti₄O₁₂ (CCTO) were fabricated via melt mixing followed by hot pressing by employing both micron (1-7µm) and Nano (75-100 nm) sized crystallites of CCTO. Both the micro and nano CCTO powders were self-synthesized using solid state and co-precipitation routes respectively. These were characterized using X-ray Diffraction (XRD), Thermo Gravimetric (TGA), Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM),Impedance analyzer for their structural, morphology and dielectric properties. Nanocomposites inducted with nCCTO-50 wt% exhibited better thermal stability than that of pure PC and composite embedded with micron sized CCTO. However, there was no significant difference in the glass transition (T_g) temperature between the polymer and the composites. The Nano composites (PC+nCCTO-50 wt%) exhibited 2.5 times higher permittivity values as compared to that of composites having 50 vol% micron sized CCTO crystallites.

Keywords: *Polycarbonate (PC); CaCu₃Ti₄O₁₂ (CCTO); Composite; Thermal, Dielectric Properties.*

1.0 INTRODUCTION

High permittivity polymer-ceramic composites have become increasingly promising materials for embedded capacitor applications.Ferroelectric ceramics such as $Pb(Mg_{1/3}Nb_{2/3})$ O_3-$PbTiO_3$, $Pb(Zr,Ti)O_3$ (PZT) and $BaTiO_3$ (BT) have been used as fillers in polymers to explore the possibility of obtaining high permittivity [1-10]. The permittivity values obtained in all these ceramic-polymer composites are invariably low as compared to that of the ceramics, because of the low permittivity associated with polymer matrices. Though the bulk ceramics possess high permittivity (>1000), the incorporation of highest possible volume fraction of these crystallites into the polymer matrix, the effective permittivity that could be achieved is lower than that of ceramics [1-8].For capacitor applications, the high permittivity accompanied by low loss is highly desirable. It is also necessary that the high permittivity to be maintained over a wide temperature range. Hence there is a continued interest in the search of the materials having high permittivity (ε'_r) over a wide temperature range.

Apart from these aspects, the lead (Pb) present in some of these ceramics is not environmental friendly and hence, lead-free material such as barium titanate (BT), $CaCu_3Ti_4O_{12}$(CCTO) were extensively used as filler in polymers for the development of high dielectric permittivity ceramic-polymer composites. It is well documented that the $CaCu_3Ti_4O_{12}$

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(CCTO) ceramic exhibiting large permittivity ($\varepsilon \sim 10^{4-5}$), which is nearly independent of frequency (upto 10mhz) and low thermal coefficient of permittivity (TCK) over 100-600 K temperature range [11,12]. It has been reported that, polymers such polyvinylidenefluoride (PVDF), poly(methyl methacrylate) (PMMA), polystyrene (PS), polyimide, polyethersulfone (PES), poly(vinylidene fluoride-trifluoroethylene) (P(VDF–TrFE), Nylon 6,9 and Epoxy were used for the fabrication of high permittivity composites by employing CCTO as filler [13-22]. It has been observed that the dielectric permittivity increases as function of a CCTO loading and decreases as the increase in frequency [14-22]. The reason for increased low frequency dielectric dispersion was attributed to high interfacial polarization triggered by high dielectric loss associated with CCTO [15].

Polycarbonate (PC), which is an amorphous and polar thermoplastic polymer, highly used as engineering plastic. In order to obtain hybrid materials, with high permittivity and low loss including better thermal stability and dimensional stability, PC has been chosen as matrix materials. PC is also possesses high dielectric strength and high volume resistivity, which is ideal for electrical applications [23-27].Extensive research work has been carried out on the thermal, mechanical, electrical and dielectric behavior of PC based composite systems and well documented in the literature [28-40].The permittivity for PC reaches a constant value at higher frequency, but the rise in permittivity as the temperature increased is due to the increase in the degree of crystallinity [40-42]. The frequency and temperature dependence of the permittivity has been attributed to interfacial and orientation polarization respectively. Whereas, the temperature dependence of the permittivity is associated with the conduction loss [24]. Improved thermal properties were achieved for the PC–ZrO$_2$ nano composites system that was prepared by melt mixing method [44]. However, the interface region playing a very important role to achieve the end properties of modified composites [45]. In order to improve the electrical, rheological, and mechanical properties, carbon nanotubes were incorporated into the PC matrix and studied

in detail [29-31,46]. But, to our knowledge no studies have been disclosed the effect of CCTO particles onthe dielectric properties of PC.

In this present investigation, synthesis of both microns sized ($\mu CCTO$) and nano sized ($nCCTO$) ceramics and fabrication of PC/CCTO composites by melt mixing followed by hot pressing has been carried out. These composites were characterized using X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Thermo gravimetric (TGA), Differential scanning calorimetry (DSC), and Impedance analyzer to study their structural, thermal and dielectric properties.

2.0   EXPERIMENTAL

2.1   Synthesis of CaCu$_3$Ti$_4$O$_{12}$ powders

The solid-state reaction route was adopted for synthesizing CCTO ceramic powders [12]. The stoichiometric amounts of AR grade caco$_3$, cuo and tio$_2$ was weighed, mixed using acetone and ball milled (300 rpm) for 5h. The homogeneous mixture thus obtained was dried in an electric oven for about 1h . This stoichiometric mixture was taken in a re-crystallized alumina crucible and heated at 1000°C for 10h to obtain phase pure CCTO [12].In order to get submicron particles, the CCTO powders were ball milled for about 12h using a planetary mill and sieved thro 400 mesh. It is observed that the CCTO crystallites are in the 1-7μm range, was consistent with the results reported in our previous work [19]. This has been designated as "$\mu CCTO$" and this notation has been used throughout the text.

CCTO nanoparticles were also synthesized using complex oxalate precursor method [13]. In a typical preparation, titania gel was prepared from the aqueous TiOCl$_2$ (0.05M) by adding NH$_4$OH (aq) (at 25°C) till the pH reached ~ 8.0 and NH$_4$Cl was washed off on the filter funnel. This gel was added to 0.4 or 0.8 moles of oxalic acid (2 M solution) (1:1 or 1:2 ratio of Ti: $C_2O_4^{2-}$) which was kept warm (~40°C). To the clear solution obtained, calcium carbonate was added in aliquots and stirred. An aqueous solution containing

titanyl oxalic acid together with calcium titanyl oxalate remained clear without any precipitate formation. This solution was cooled to 10°C to which cupric chloride dissolved in acetone along with water (80/20) was added and stirred continuously. The thick precipitate was separated out by further addition of acetone. Subsequently, the precipitate was filtered, washed several times with acetone to make it chloride-free and dried in air. The precursor was isothermally heated around 700°C to get nanocrystals (20-75nm) of phase-pure $CaCu_3Ti_4O_{12}$ ceramics [20]. This has been designated as *"n CCTO"* and this notation has been used throughout the text.

2.2 Particle Size Analyzer

The particle size analyses were carried out on both the μCCTO and *n*CCTO ceramics synthesized in this work and the same is given in the Figure 1 (a&b). The ceramic powders were dispersed in acetone and sonicated before placing in the instrument for analysis. The particlesize distribution databobtained shows that the mean particle size distribution for μCCTO powder is around 7μand for the *n*CCTO powder (Figure 1b), it is around1076 *nm*.

2.3 Fabrication of Polycarbonate / $CaCu_3Ti_4O_{12}$ composite sheets

Polycarbonate, having Molecular weight of 1,10,000 (Make: LG Corporation) was used as matrix material. For the fabrication of composites, initially, the as received PC granules were heated around 230°c in Brabender Plasticorder (Model: PLE331) till the PC granules were thoroughly melted. To this melt, μccto powders (0 to 50 % by weight) was slowly added and mixed for 30 min at this temperature. The mixture was taken out from the Plastic order and hot-pressed at this temperature to obtain a sheet of 100 mm² with 0.5 mm in thickness. Similarly, a nano composite PC+*n*CCTO-50 wt%) was also fabricated by employing *n*CCTO. The flowchart depicting various steps involved in the fabrication of ceramic and polymer-ceramic composites are given in the Figure 2.
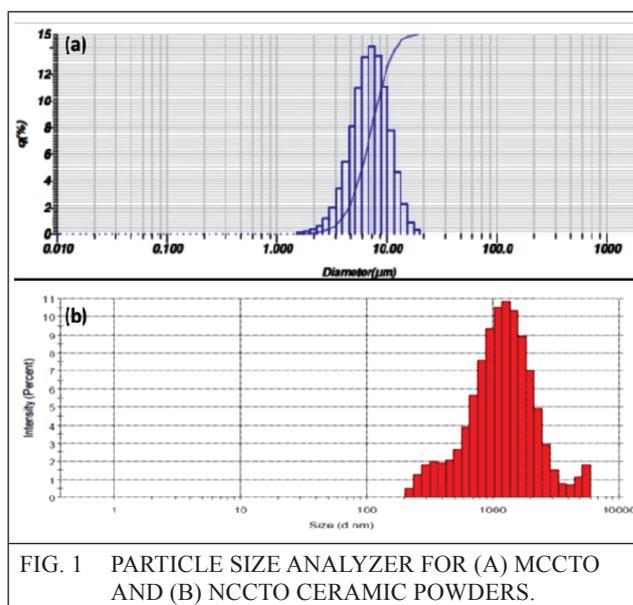

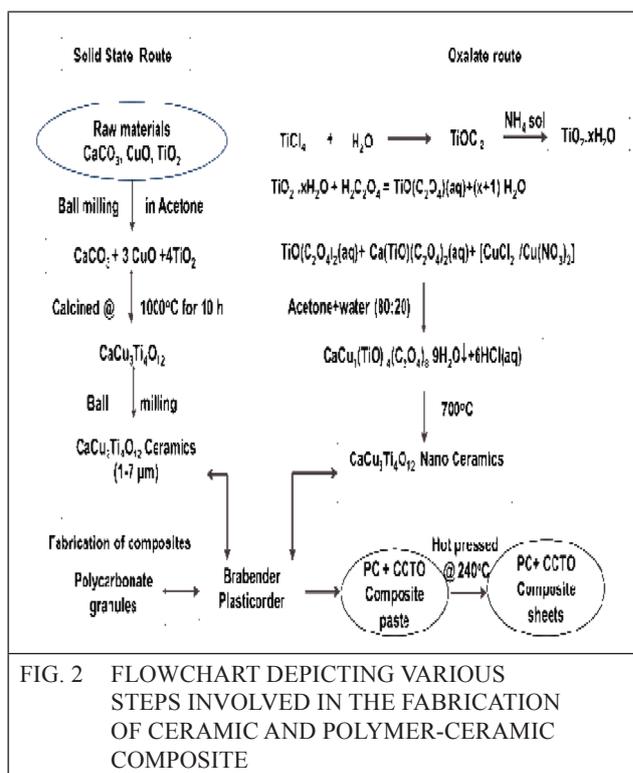FIG. 1   PARTICLE SIZE ANALYZER FOR (A) MCCTO AND (B) NCCTO CERAMIC POWDERS.

FIG. 2   FLOWCHART DEPICTING VARIOUS STEPS INVOLVED IN THE FABRICATION OF CERAMIC AND POLYMER-CERAMIC COMPOSITE

2.4 Characterization

To examine the structure, an XPERT-PRO Diffractometer (Philips, Netherlands) was used. Electron transmission microscopy was carried out using FEI-Technai TEM (G-F30, Hillsboro, USA). The mean particle size of the as prepared μCCTO is analyzed using Horiba Laser Scattering Particlesize Distribution Analyzer LA-950 and for *n*CCTO Particle Size analyzer Malvern
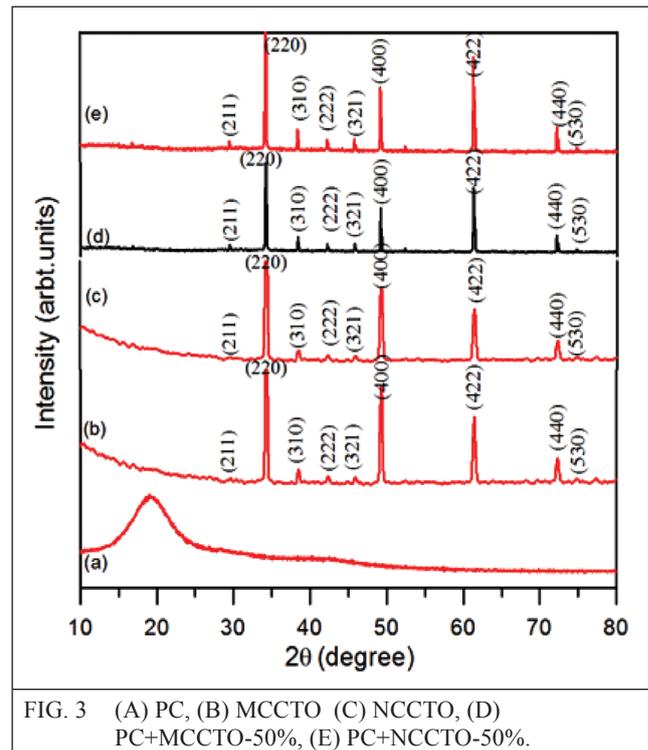
Instruments Ltd is used. Scanning electron microscope (FEI-Technai TEM–Sirion) was used for the microstructure analysis of the composite samples. Thermo gravimetric (TGA) analyses were done using the TA Instruments (UK, Model: TGA Q500) in Nitrogen atmosphere at a flow rate of 60ml/min, and at a heating rate of 10 deg/min. Differential Scanning Calorimeter, (Make: Mettler Toledo, Model : DSC 821e) was employed at a heating rate of 10°C/min under nitrogen atmosphere at a flow rate of 60ml/min, using Aluminium pan). For carrying out the dielectric measurements, the composite sheets were polished using fine emery paper to achieve smooth and parallel surfaces. Further, these samples were cleaned under ultra-sonication and subsequently the surfaces were electrode with silver paste and cured at 50°C. An LCR meter (Model: HP4194A) was used for the capacitance measurements as a function of frequency (100 Hz–1MHz) at room temperature. The measurement accuracy of the instrument is less than 5%. The permittivity was calculated using the relation, $\varepsilon_r = C \times d / \varepsilon_o A$ where C =capacitance, d is the thickness of the sample, ε_o = 8.854X10^{-12} F/m and A is the electrode area of the sample.

3.0 RESULTS AND DISCUSSION

3.1 X-Ray Diffraction (XRD)

Figure 3(a-f) shows the XRD pattern recorded for the PC, CCTO ceramics, and for the PC+CCTO composites. Figure 3 (b-c) shows the XRD pattern recorded for the *μCCTO and nCCTO* ceramics prepared by both solid state chemistry route as well as by oxalate precursor route. These XRD patterns indicate the single phase nature, which is in agreement with the results reported [12,13].

The Figure 3 (d-e) shows the XRD pattern recorded for both the composites samples with 50 wt %. As the CCTO ceramics content is dominant in the composites, the peak corresponds to only CCTO is visible (Figure 3 (d&e)). These results confirm the presence of CCTO crystallites in the polymer matrix.

FIG. 3   (A) PC, (B) MCCTO (C) NCCTO, (D) PC+MCCTO-50%, (E) PC+NCCTO-50%.

3.2 Microstructure analysis

Figure 4(a) shows the SEM micrograph recorded for the powders derived from the solid statesynthesis route, exhibiting that the crystallites are in the range of 1-7 μm.
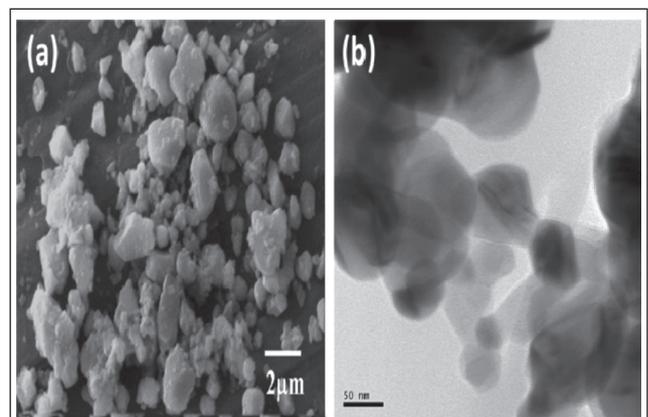

FIG. 4   (A) SEM MICROGRAPH FOR MCCTO, (B) TEM IMAGE FOR NCCTO.

The Figure 4(b) presents the bright field TEM images of the phase-pure CCTO powders obtained from the thermal decomposition of the oxalate precursor at 700-900°C.The particles are weakly agglomerated and the size of the particles, as measured by the intercept method from the micrographs, is in the range of 30-200 nm.

3.3 Thermogravimetric Analysis.

TGA thermographs obtained for the pure PC and for the composites (10 to 50 wt%) are shown in the Figure 5. The onset of decomposition temperature (temperature at 10% weight loss) [8].
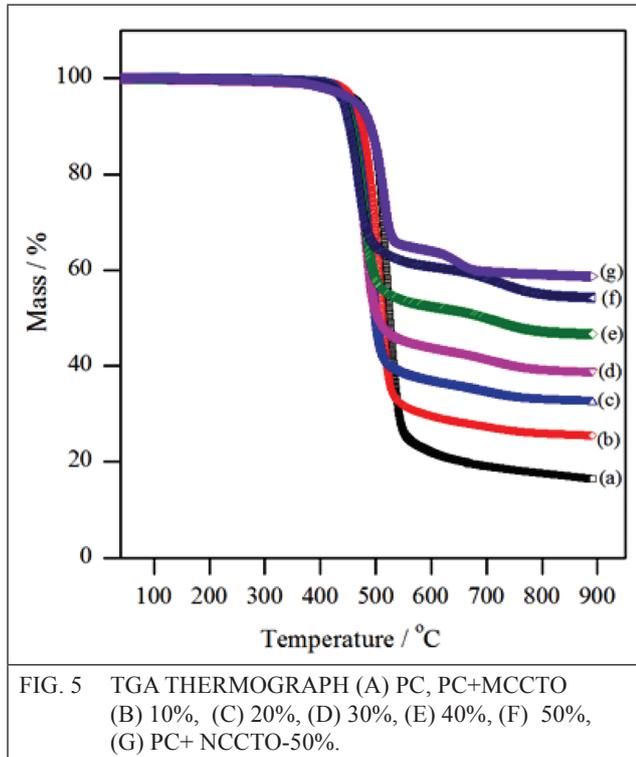

FIG. 5   TGA THERMOGRAPH (A) PC, PC+MCCTO (B) 10%, (C) 20%, (D) 30%, (E) 40%, (F) 50%, (G) PC+ NCCTO-50%.

Incorporation of $n$ccto into PC matrix increases the thermal stability of the composites. The composite undergoes two stages, the first weight loss was observed in the temperature range of 300-500^{0}C due to swelling of host polymer systems and dissociation of inorganic filler. The second wight loss of observed in the range of 500-900^{0}C which may be due to the degradation of alternate single and double carbon bonds, resulting in the formation of a carbonaceous/hybrid residue. This indicates that there is strong interaction between PC and hybrid which results in enhanced thermal stability of the composites.

3.4 Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) measurements were carried out to determine the glass transition temperature (T_g) of pure PC and the composites, as this is an important physical parameter to characterise the structural property of an amorphous polymer in terms of chain rigidity and intermolecular forces [38]. Figure 6 shows the DSC thermogram recorded for the PC and PC+CCTO composites. The pure PC has $T_g$value of 140 ^{0}C, which had decreased as the $\mu ccto$ content increased in PC. The change in the value of T_g is within 5°c, as the $\mu ccto$ content is increased to 50% by wt. The change in glass transition temperature (T_g) is observed for the $nccto$ also
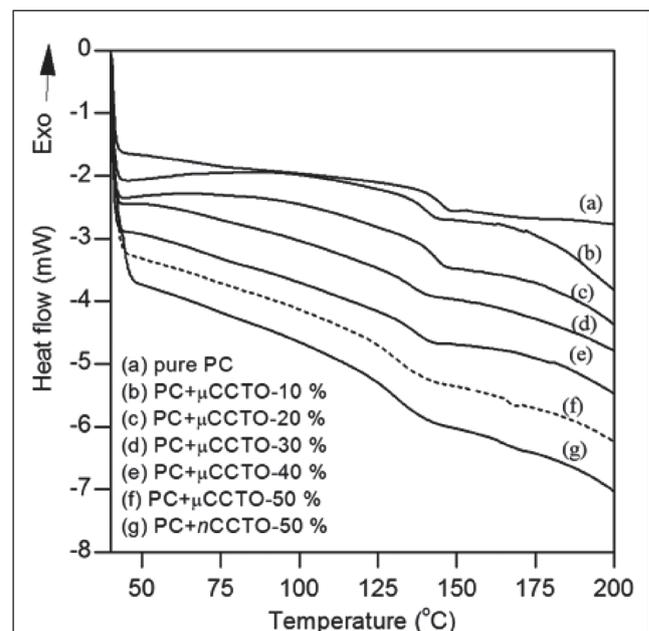

FIG. 6   DSC TRACES   (A) PC, PC+MCCTO (B) 10%, (C) 20%, (D) 30%, (E) 40%, (F) 50%, (G) PC+ N CCTO-50%.

3.5 Frequency dependence of room temperature permittivity

The room temperature effective permittivity data (ε_{eff}) for PC/CCTO composites for different weight percents of µCCTO are given in Figure 7. The permittivity of the pure PC is around 3.8 @100Hz, which is nearly constant over the entire frequency range covered in the present investigation (Figure 7). As expected, the room temperature permittivity has increased as the   µCCTO content increased in the PC. However, the increase is not appreciably high upto 40 wt %. The permittivity value obtained is around 5.0 @100Hz for the PC+µccto-40% composite. When the µccto content increased to 50 % by wt, the permittivity value had increased

to 8.3 at 100Hz. Interestingly, the nanocomposite (PC+nCCTO-50%) had exhibited high permittivity values of 20 at 100Hz as compared to that of PC+μCCTO-50% composite.
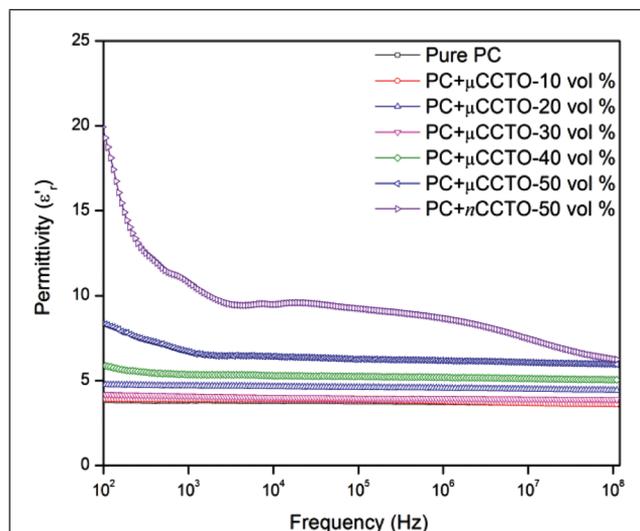

FIG. 7   FREQUENCY-DEPENDENT DIELECTRIC PERMITTIVITY, (A) PC, PC+MCCTO (B) 10%, (C) 20%, (D) 30%, (E) 40%, (F) 50%, AND (G) PC+ N CCTO-50%.

The permittivity value obtained for PC+nCCTO-50% is 2.5 times higher than that of PC+μCCTO-50%. Nanocrystallites are more attractive due to their intriguing properties arising from their size associated with large surface area. The insertion of nanoscale fillers may improve the electrical and dielectric properties of the host polymers and the properties can be tailored to a particular performance requirement [42-45]. This is clearly indicated the role played by the particle size of the $nCCTO$ crystallites, which has been proven to influence the effective permittivity in the composite. However, compared to the large dielectric permittivity of ceramic, the enhancement in the permittivity of the nanocomposites is not remarkable as the volume fraction of $nCCTO$ increased. This phenomenon can be attributed to the large difference in the dielectric permittivity between ceramic particles and the polymer matrix. But the significance difference between the permittivity values obtained for the $nCCTO$ and $μCCTO$ composites is clearly indicates the role played by the nanoceramics, which brings some structural changes in the polymer matrix. The introduction of $nCCTO$into the polymer

matrix increases the interfacial polarization due to the decreased particle size having large surface area [46]. This increase in dielectric permittivity that is observed for PC+nCCTO-50% composite at 100Hz, may be assigned to the interfacial polarization effects.
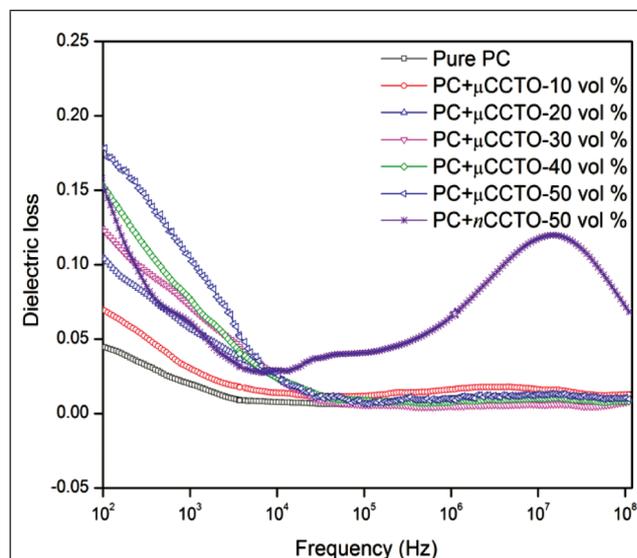

FIG. 8   FREQUENCY-DEPENDENT DIELECTRIC LOSS, (A) PC, PC+MCCTO (B) 10%, (C) 20%, (D) 30%, (E) 40%, (F) 50%, AND (G) PC+ N CCTO-50%.

The dielectric loss (Figure 8) is considerably higher especially at low frequencies which is mainly attributed to inhomogeneous conduction vis-à-vis interfacial polarization [19,20]. The nanocomposite exhibited low dielectric loss and the loss value (at1kHZ) obtained for the nanocomposite (PC+nCCTO-50%) is 0.060 as compared to the to the PC+μCCTO-50% composite, which is 0.10.

4.0   CONCLUSIONS

Melt mixing technique is found to be easy method for the fabrication of ceramic-polymer composites and ceramics loading upto 50 wt % in polymer could be fabricated. There was no significant difference in the glass transition (Tg) temperature between the polymer and the composites. Nanocomposites inducted with nCCTO-50 wt% exhibited better thermal stability than that of pure PC and composite embedded with micron sized CCTO. The Nano composites (PC+nCCTO-50

wt%) exhibited 2.5 times higher permittivity values as compared to that of composites having 50 vol% micron sized CCTO crystallites.

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