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Structural, Morphological and Dielectric Properties of Multiphase Nanocomposites Consisting of Polycarbonate, Barium titanate and Carbon Black Nanoparticles

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Abstract : Polycarbonate-Barium titanate-Carbon Black (PC/BT/CB) nanocomposites were used to find the structural, morphological, optical, and dielectric properties of BT and CB in PC. The PC/BT/CB nanocomposites films were prepared by solution casting method. The structural studies were carried out by FTIR and the X-ray diffraction (XRD). FTIR and XRD results indicate strong interaction between the PC and the nanoparticles. The optical properties of nanocomposites were investigated using UV-visible spectroscopy. From optical microscopic studies, it can be seen that the nanoparticles are evenly dispersed in the polymer matrix. The dielectric properties were investigated for (PC/BT/CB) nanocomposites films in the frequency range from 50 Hz - 20 MHz and temperature in the range 40-150 °C. Optical and electrical properties of these nanocomposites were modified by adjusting the CB and BT nanoparticles weight percentage in the PC matrix. The nanocomposite shows high dielectric constant with low dielectric loss. Such high-k nanocomposites can be used as a suitable candidate for high-k capacitor or embedded capacitor.

Keywords: Polymer nanocomposite, Carbon black nanoparticle, Barium titanate nanoparticle, Dielectric studies

1. Introduction

Polycarbonate has one of the important applications in the field of sensors and it was used to monitor the presence of harmful gases [1]. Conductive polycarbonate composites have also been fabricated for the detection of dichloromethane (DCM) and toluene [2]. The doping of nanoscopic organic or inorganic materials into polymeric matrices represents a strategic route to improve the performance of materials characteristic like structural, physical, chemical, optical, electrical and mechanical properties. These nanocomposites are of new class of materials made with nanosized fillers (clay, carbon black, nanotubes, etc.) to stabilize the blends and to improve the mechanical and dielectric properties has received a great attention. It was already reported that by adding CNT in polymer, which enhance the mechanical properties of polymer/CNT composites. However, the magnitude of reinforcement by CNT is found to be limited due to the challenges involved in the dispersion of CNT [3]. Transparent polymers like PC have excellent electrical applications, because it has high dielectric

strength and high volume resistivity. Due to this advantage it can be used in electrical insulators, connectors, and several applications [4, 5]. Furthermore, depending on addition of additives such as metal oxides, salts, and ceramic will modify the physical properties of PC matrix [6, 7].

Polymer nanocomposites based on Carbon Black (CB) have been shown to undergo substantial improvements in mechanical, electrical and dielectric properties. CB is having partially amorphous molecular structure. Because of this it as aggregated traditional particle with nanoscale dimension (1-100 nm) and high electrical conductivity but low aspect ratio. Depending on the method of production, average particle diameters of carbon blacks varies from 10-500 nm. Whereas for average primary aggregate diameters range from 100-800 nm. CB nanoparticles have been used to modify the mechanical, electrical and other physical properties of polymers [8-10]. Carbon materials, such as graphite, have low density and high conductivity so that they are widely used as fillers in conductive polymer composites. Recently carbon conductive filler in polymer matrices have emerged as another promising because of high aspect ratio, low cost, easy production and low resistance. Barium titanate (BT) is widely used as a dielectric material in ceramics capacitors [11-13]. Among the many crystallographic forms, the tetragonal phase has a high dielectric constant at about 130 °C [14-15]. The main objective of this work is to improve the dielectric properties of PC by adding the nano CB and BT at different loadings.

2. Experimental

2.1 Materials

PC of molecular weight 20,000 g/mole was purchased from Sigma-Aldrich, India. BT nanopowders (cubic crystalline phase) was purchased from Sigma-Aldrich, India. CB nanoparticles of particle size of about 21 nm were supplied by Plasma Chem. GmbH, Berlin, Germany. Dichloromethane (DCM) was purchased from Sisco Research Laboratory Chemicals, Pvt, Ltd.; Chennai, India.

2.2 Sample preparation

Multiphase PC nanocomposites were prepared using CB and BT nanoparticles as fillers by solution casting method. The different weight percentages of PC/BT/CB nanocomposites were shown in Table 1. First, PC was dissolved in dichloromethane (DCM) and stirred with a magnetic stirrer for 2h. The CB and BT were sonicated separately with DCM. Then the sonicated CB and BT dispersion were added to PC solution and re-stirred for 24 h until the CB and BT nanoparticles were homogeneously dispersed in the PC solution. The protocol for the synthesis is shown in Fig 1.

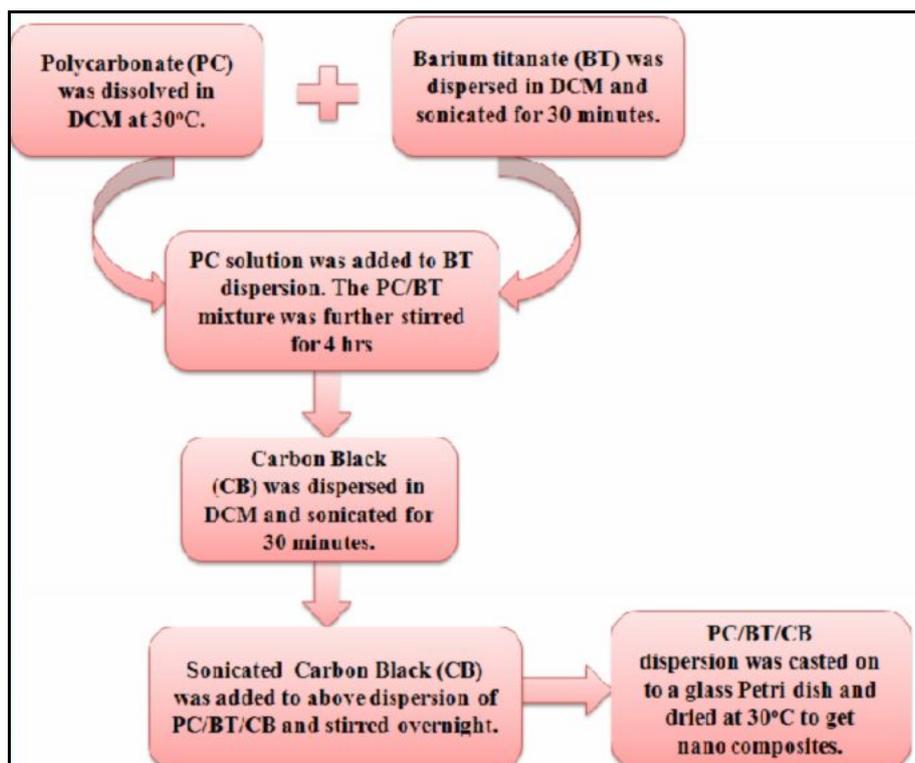


Fig. 1. Protocol for synthesis of PC/BT/CB nano composite

Table 1. Sample codes for CB and BT nanoparticles in PC matrix

Sample code	Weight percent (%)		
	CB	BT	PC
a	0	0	100
b	0	10	90
c	3	7	90
d	7	3	90
e	10	0	90

2.3 Characterization

X-ray diffraction of PC/BT/CB nanocomposite film was recorded using Cu K α radiation of wavelength $\lambda=1.54060 \text{ \AA}$ with a graphite monochromator produced by a Bruker AXS D8 focus advanced X-ray diffraction meter (Rigaku, Japan, Tokyo) with 'Ni-filtered'. The scans were taken in the 2θ range from $10\text{--}80^\circ$ with a scanning speed and step size of $1^\circ/\text{mm}$ and 0.01° , respectively.

FTIR spectroscopy of PC/BT/CB nanocomposite film was carried out with Fourier Transform Infrared Spectrophotometer (Shimadzu, IRAffinity-1, and Japan) in the wave number range $400\text{--}3500 \text{ cm}^{-1}$ in the transmittance mode.

UV-vis absorption spectroscopy of PC/BT/CB nanocomposites was obtained with a Shimadzu UV-2401PC, UV-vis spectrophotometer in the range of $190\text{--}600 \text{ nm}$.

The effect of filler on modified blend was characterized by Carl Zeiss AX10 vision LE optical microscope. Optical microscope images of the films were taken at 20x magnification.

The dielectric properties were measured using a Newton's 4th Impedance Analyzer (Newton's 4th UK). The composite films were silver coated on both sides for better electrode contact.

3. Result and Discussion

3.1 FTIR spectroscopy

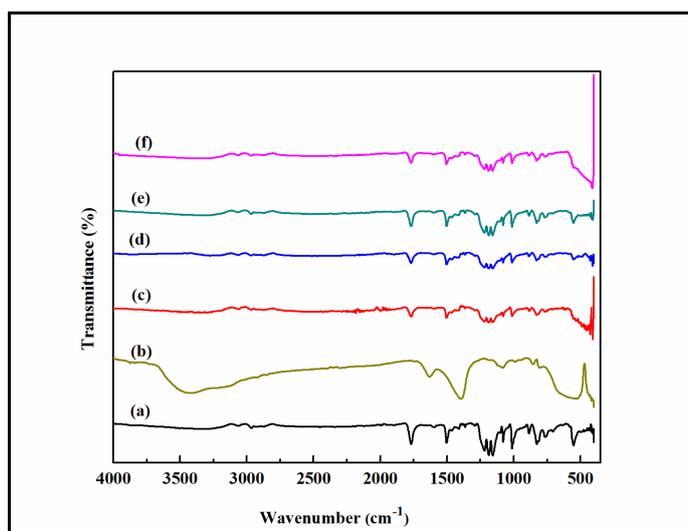


Fig. 2 FTIR spectra of PC/BT/CB composite film (a) P pure PC (b) pure BT (c) PC/BT10% (d) PC/BT7%/CB3% (e) PC/BT3%/CB7% (f) PC/CB10%

The FTIR spectra of BT nanoparticles and PC/BT/CB nanocomposites are shown in Fig 2. The FTIR spectrum of pure PC (Fig 2(a)) shows peaks at 1773 cm^{-1} which is due to C=O stretching. The peak observed around 1500 cm^{-1} is due to the C=C stretching. Asymmetric stretching of carbonate group (O-C-O) is observed at $1228\text{--}1157 \text{ cm}^{-1}$. The peak at 1075 cm^{-1} is due to CH_3 vibration. The peak observed near 1015 cm^{-1} is due to

symmetric stretching of carbonate group (O-C-O) deformation. The FTIR spectrum of BT nanoparticles is shown in Fig 2(c). The peak observed at $520-589\text{ cm}^{-1}$ is due to the Ti-O stretching of BT and the peak around 858 cm^{-1} is due to the C-C stretching. The peaks observed at 1397 and 1633 cm^{-1} is due to C=O and C=C stretching respectively. The wide peak near $3690-3294\text{ cm}^{-1}$ is due to O-H stretching. The FTIR spectra of PC/BT/CB nanocomposite film show various FTIR peaks which are common between the FTIR of individual materials, indicating that the significant interaction has occurred between them. Thus, from the FTIR spectra, the successful formation of PC/BT/CB polymer composites can be confirmed.

3.2 XRD analysis

The XRD pattern of BT nanoparticles and PC/BT/CB nanocomposite films are shown in Fig 3. The single peak is observed around $2\theta=15^\circ$ for pure PC (Fig 3(a)) which indicates the amorphous nature of the polymer. The XRD pattern of the BT nanoparticles with the hkl parameters as shown in Fig 3(c). By adding the BT into the PC it shows all the peaks corresponding to the BT, which indicates the homogeneous dispersion of BT. The results are shown in Fig 3(b, d, e). The intensity of the peaks goes on decreasing due to the decreasing wt% of BT. Fig 3(f) shows the PC with 10 wt% of CB loading. Because of partial amorphous nature of CB it is not showing any sharp peaks in the PC matrix. From the spectrum of all nanocomposites, it can be seen that the BT and CB nanoparticles were homogeneously dispersed in the PC matrix.

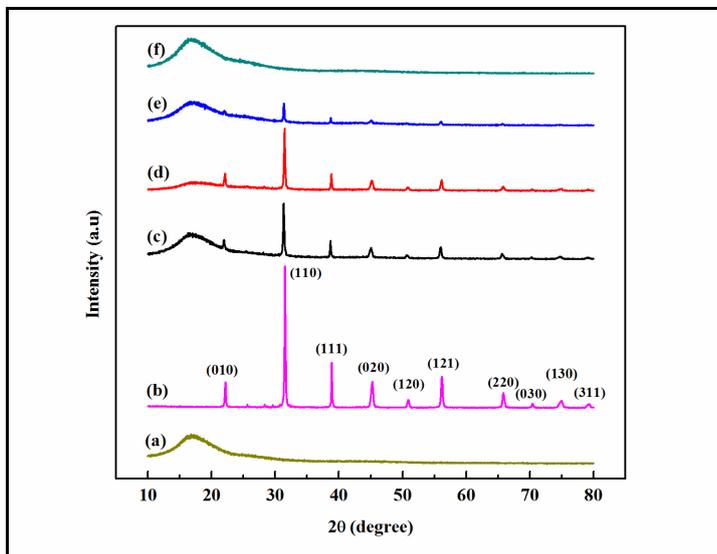


Fig. 3 XRD spectrum of PC/BT/CB composite film (a) pure PC (b) pure BT (c) PC/BT10% (d) PC/BT7%/CB3% (e) PC/BT3%/CB7% (f) PC/CB10%

3.3 UV-Visible Spectroscopy

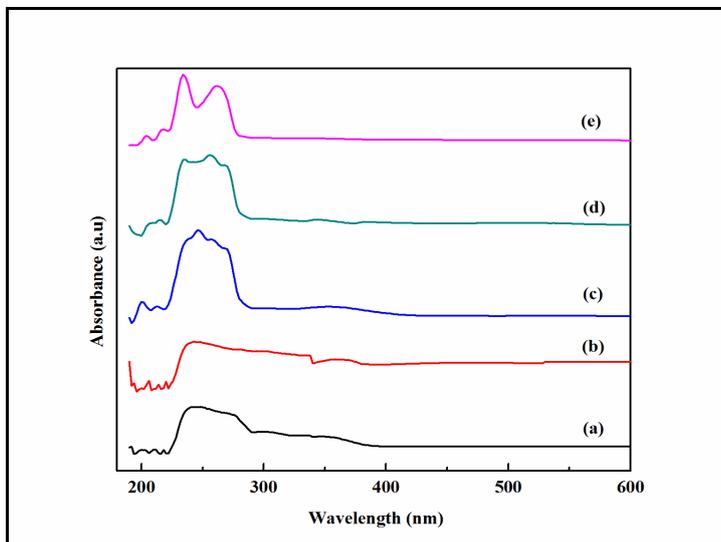


Fig.4 UV Visible absorbance spectrum of PC/BT/CB composite film (a) pure PC (b) PC/BT10% (c) PC/BT7%/CB3% (d) PC/BT3%/CB7% (e) PC/CB10%

The UV absorption spectroscopy is used for the investigation of optical properties of polymeric materials. Fig. 4 shows the absorption spectrum of PC/BT/CB nanocomposites in DCM at the wavelength ranges from 190 to 800 nm. The UV absorption of DCM limited the wavelength detection range from 233 to 400 nm. From the Figure, the variation of absorption spectrum observed between 280 nm to 220 nm. In the nanocomposites the strong absorption peak observed around 261nm due to CB while BT has a strong absorption peak below 246nm. The UV shielding region of PC/BT/CB nanocomposites either above 200 nm or below 300 nm could be controlled by the weight ratio of BT/CB nanoparticle mixture in the PC matrix.

3.4 Optical Microscopy

Optical microscopy images are used to determine the size, distribution and orientation of nanoparticles. The optical microscopic images of PC/BT/CB nanocomposites are shown in Fig. 5(a)-(e) for different filler concentrations. From the figure it was very clear that the BT and CB nanoparticles are homogeneously dispersed in PC with low degrees of agglomeration.

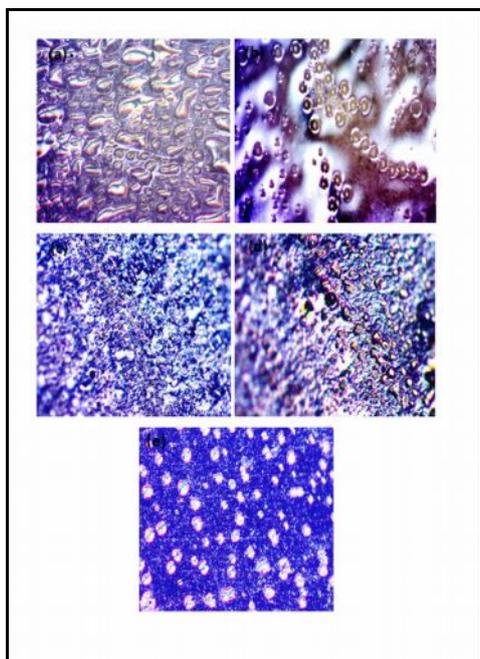


Fig.5 Optical microscopic images of PC/BT/CB composite film (a) pure PC (b) PC/BT 10% (c) PC/BT7%/CB3% (d) PC/BT3%/CB7% (e) PC/CB10%

3.5 Dielectric studies

The study of dielectric constant and dielectric loss as a function of frequency and temperature are shown in the Fig. 6(a)-6(e). The dielectric constant of PC film shows maximum value up to 1 MHz and decreases suddenly up to 20 MHz. The maximum value of dielectric constant for PC film was 0.793, observed at 50 Hz and at 50°C, as shown in the Fig 6a. For PC/BT10% composite films, the dielectric constant decreases with increasing frequency up to 10 MHz at all the temperatures investigated. The maximum value of dielectric constant was 10.326, observed at 50 Hz and at 150 °C, as shown in the Fig 6(b). The dielectric constant value of PC/BT7%/CB3% nanocomposites which showing maximum value at 50 Hz and goes on decreasing with increasing frequency up to 20 MHz for all the temperatures. The results are shown in Fig 6(c). The similar change was observed for the nanocomposite films with (PC/BT3%/CB7%), which is shown in Fig 6(d). By comparing all the nanocomposite films with PC/CB10%, shows maximum dielectric constant 17066 at 50 Hz and at 120 °C, which is shown in Fig 6(e). This could be due to the fact that carbon black has large surface area and also a wide range of electrical properties. The dielectric properties of CB/polymer composites are strongly dependent on the particle size, aggregate structure, and conductivity of the carbon blacks.

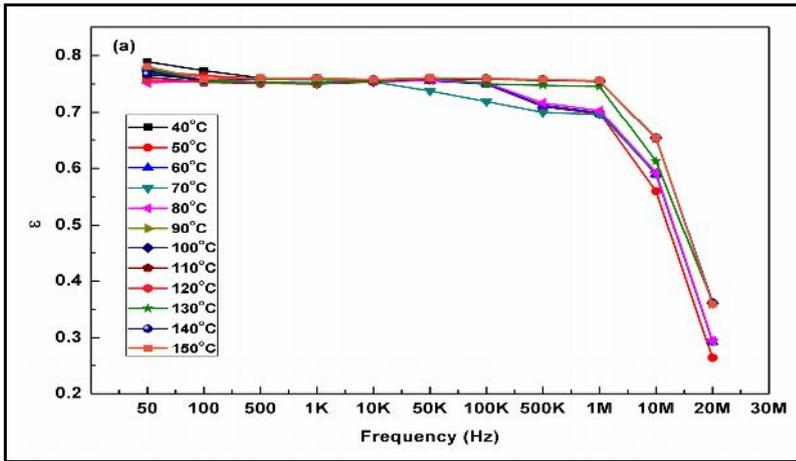


Fig.6 (a): Variation in dielectric constant of pure PC as a function of frequency at various temperatures

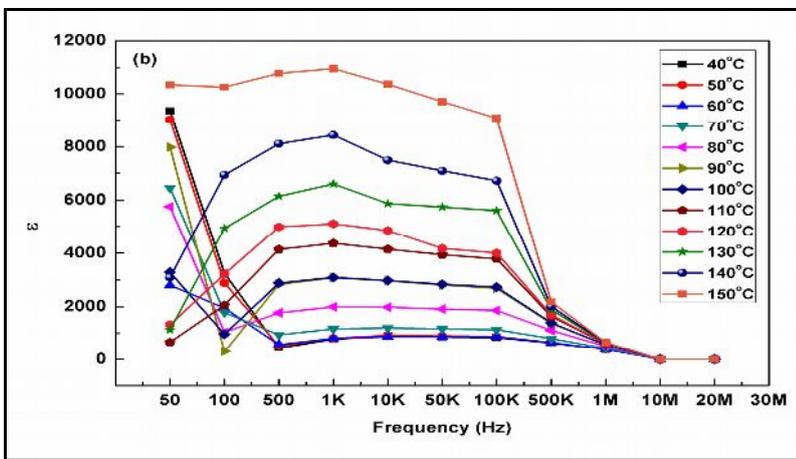


Fig. 6 (b): Variation in dielectric constant of PC/BT nanocomposite with 10 wt% BT loading as a function of frequency at various temperatures.

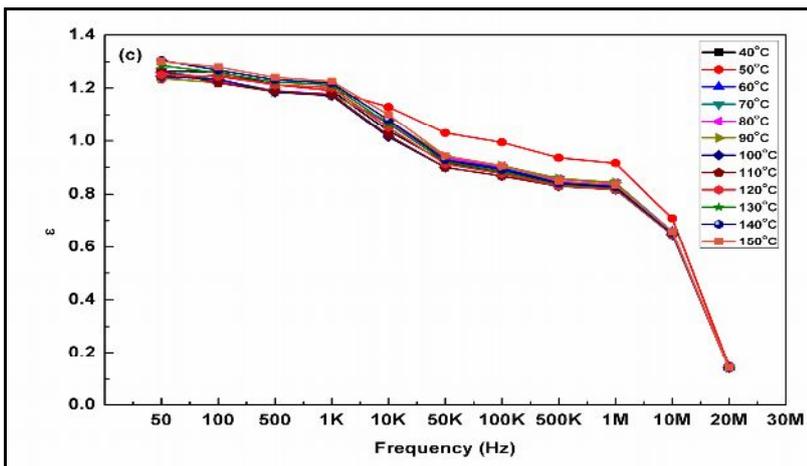


Fig.6 (c): Variation in dielectric constant of PC/BT/CB nanocomposite with 7wt% BT and 3 wt% carbon black loading as a function of frequency at various temperatures.

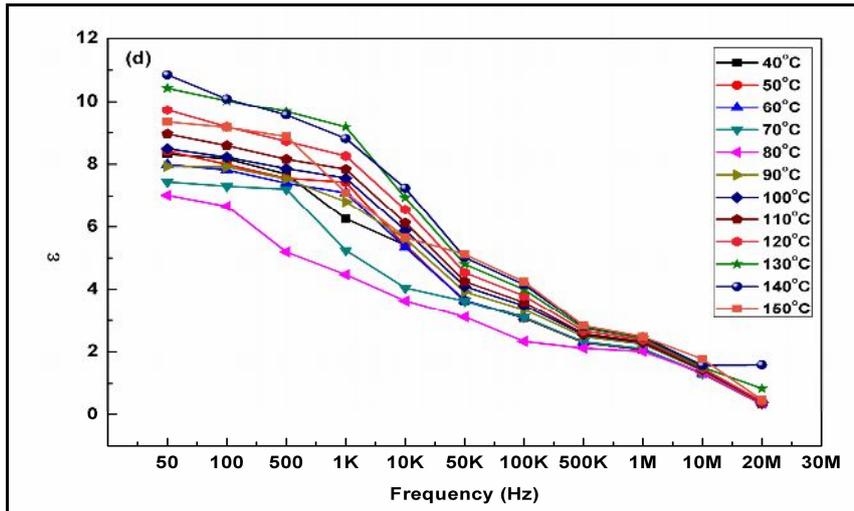


Fig.6 (d): Variation in dielectric constant of PC/BT/CB nanocomposite with 3wt% BT and 7 wt% carbon black loading as a function of frequency at various temperatures

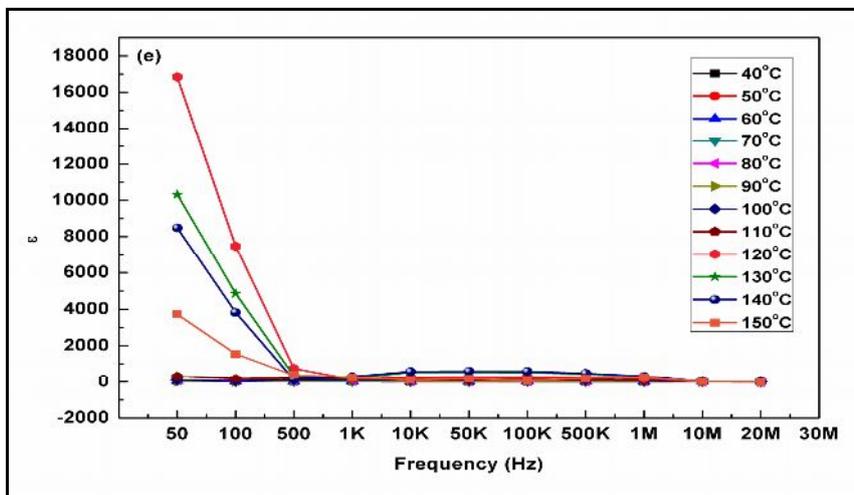


Fig.6 (e): Variation in dielectric constant of PC/CB nanocomposite film with 10 wt% CB loading as a function of frequency at various temperatures

The dielectric loss has been defined as the inability of the polarization process in a molecule according to the change in applied electric field. Fig (7(a) - 7(e)) shows plots of dielectric loss ($\tan \delta$) of nanocomposite films in the frequency range of 50 Hz to 20 MHz and temperature in the range of 40-150 °C. For PC films (Fig. 7(a)), $\tan \delta$ has a minimum value up to the frequency 10 MHz and with further increase in frequency the loss value increases. For nanocomposites of PC/BT10% (Fig 7(b)) $\tan \delta$ value decreases with an increase in frequency up to 500 Hz. From 500 Hz to 20 MHz the $\tan \delta$ values were almost constant at all temperatures investigated. The PC films with 7%BT and 3% CB loading (Fig 7(c)) have minimum dielectric loss up to 1 KHz and further increase in frequency $\tan \delta$ value increases from 1 KHz to 100 KHz. Further increase in frequency up to 100 MHz the dielectric loss remains the same and suddenly increases at 20 MHz. The PC films with 3% BT and 7% CB loading (Fig 7(d)) shows minimum dielectric loss value up to 50 KHz. With further increase in the frequency up to 20 MHz, dielectric loss values increases for 500 KHz and 10 MHz. For the sample with 10 Wt% of CB loading (Fig7 (e)), dielectric loss plots shows very low value up to 50 KHz. Further increase in frequency up to 100 KHz, the dielectric loss values increased and then decreased when the frequency increased to 20 MHz.

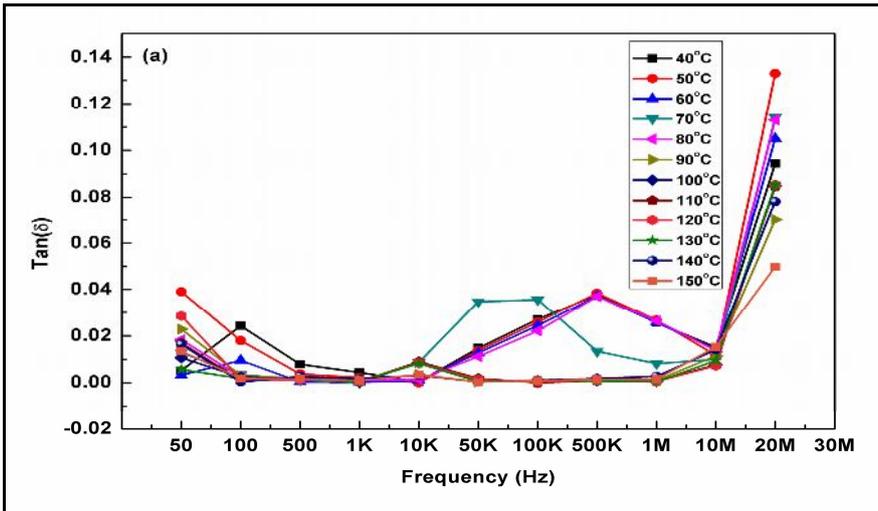


Fig.7 (a): Variation in dielectric loss of pure PC as a function of frequency at various temperatures.

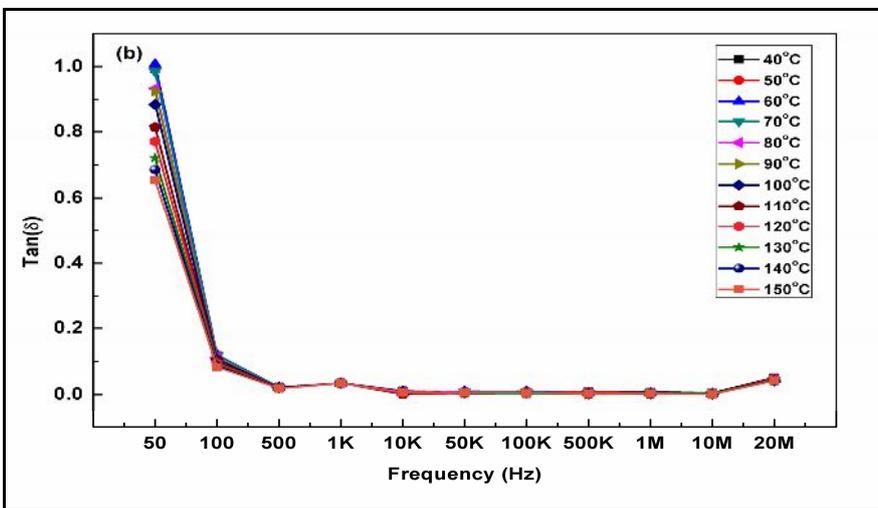


Fig.7 (b): Variation in dielectric loss of PC/BT nanocomposite with 10 wt% BT loading as a function of frequency at various temperatures

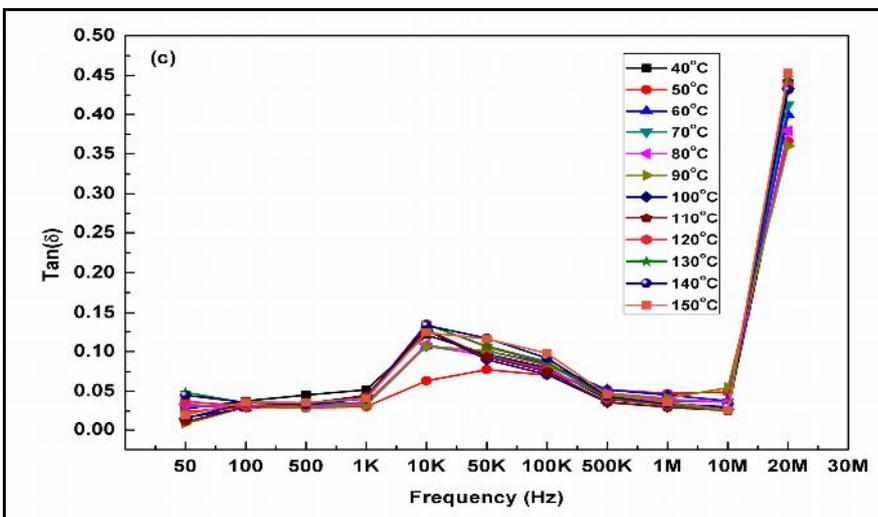


Fig.7 (c): Variation in dielectric loss of PC/BT/CB nanocomposite with 7wt% BT and 3 wt% carbon black loading as a function of frequency at various temperatures

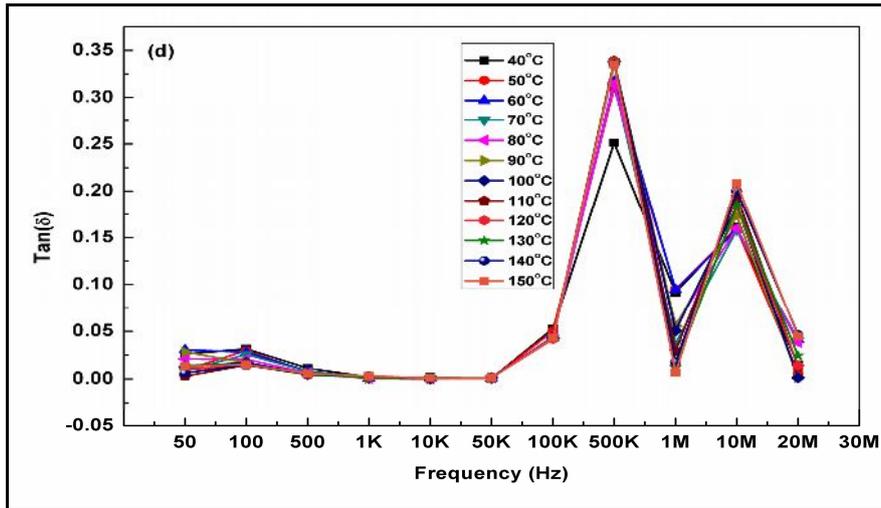


Fig.7 (d): Variation in dielectric loss of PC/BT/CB nanocomposite with 3wt% BT and 7 wt% carbon black loading as a function of frequency at various temperatures

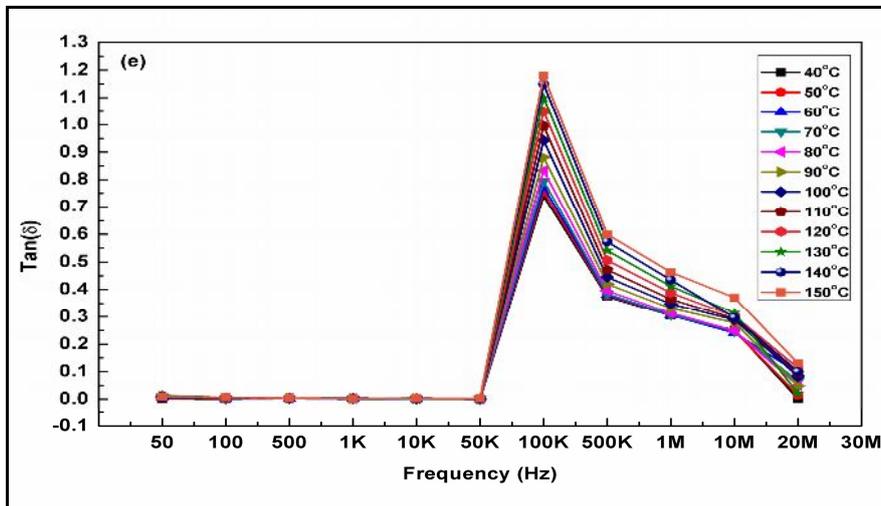


Fig.7 (e): Variation in dielectric loss of PC/CB nanocomposite film with 10 wt% CB loading as a function of frequency at various temperatures

4. Conclusion

The PC/BT/CB composites for various wt% of BT and CB were prepared using solution casting technique and characterized by XRD, FTIR, and UV-Visible spectroscopy. XRD data confirms that BT nanoparticles were having crystalline phases which can be observed in the XRD spectra of nanocomposite. FTIR spectrum reveals the strong interaction between BT, CB and polymer matrix. The UV-Vis spectrum of polymer nano composites shows good optical property. The optical microscopic image shows the evenly dispersed both nano fillers (BT/CB). Dielectric properties demonstrated very high dielectric constant and relatively low dielectric loss for nanocomposites indicating that these nanocomposite films can be used as a high-k material for embedded capacitor applications.

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