Effect of Ba(Ti_(0.9)Sn_{0.1})O₃ ceramic doping on optical, thermal and dielectric properties of polycarbonate host

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Abstract. Ba(Ti_(0.9)Sn_{0.1})O₃ (BTS) ceramic was prepared by a conventional ceramic processing. BTS–polycarbonate (PC) composites were prepared at different BTS concentrations by weight in order to study their optical and dielectric properties. The absorption coefficient (α) was determined in the wavelength range from 250–600 nm at room temperature for all BTS–PC composites. The optical gap (E_{opt}) was also determined for BTS–PC composites. The variation of the absorption coefficient (α) and optical gap (E_{opt}) with BTS content are reported. It was found that BTS ceramic highly enhances the UV absorption of PC host at 300 nm. The optical gap decreases up to the value of 3.93 eV as BTS content increases up to 35 wt% and this was attributed to the formation of localized states in the forbidden gap. The relative dielectric permittivity, dielectric loss and loss tangent were measured at temperature range from room temperature up to 150°C and at frequency values 1 kHz, 10 kHz and 50 kHz. Addition of BTS to PC host, however, will increase relative dielectric permittivity, dielectric loss and loss tangent. Besides, increasing of temperature will also increase relative dielectric permittivity, dielectric loss and loss tangent especially above the glass transition temperature of PC host and this behaviour was attributed to the segmental motion of polymer chains. On the other hand, this study shows that there is a good agreement between SEM, DSC and dielectric results and also between optical gap and a.c. conductivity results. Moreover, SEM and DSC results reveal that addition of BTS ceramic particles to PC host will reduce the physical bond between polymer chains or may be will increase the free volume in the polymer host and consequently will enhance the segmental motion of polymer chains and this behaviour is independent of ceramic phase.

Keywords. Ceramic–matrix composites (CMCs); electrical properties; thermal properties; scanning electron microscope (SEM); casting.

1. Introduction

Recently, polymer composites consisting of ferroelectric ceramic gained much interest because of their attractive properties which are useful for many applications such as optoelectrical applications. Furthermore, fast growth of optoelectrical and electronic industry requires development of new materials. The required developments run parallel with intense series of studies aiming to enlighten the structure–property relationship of the modified materials (Saq'an *et al* 2004; Ayesh 2008; Ayesh and Abdel-Rahem 2008). However, polycarbonate is mechanically stable, highly transparent to visible light and excellent for electrical applications (Ayesh 2008; Ayesh *et al* 2008). Besides, ferroelectric ceramic such as barium titanate (BT) is promising for the integrated circuit, because of its unique properties of large dielectric constant, low direct current leakage, low loss tangent and stable operation at

high temperatures. Additionally, BaTiO₃ is found to be useful in many applications such as waveguides, ferroelectrics sensors, and luminescent materials. Besides, pure polymers are easy to process into mechanically robust components but generally suffer from a low dielectric constant. At the same time, typical high-dielectric constant materials, such as ferroelectric ceramics, are brittle and require high-temperature processing which is often not compatible with current circuits integration technologies. The ideal solution would be a high-dielectric constant material that is mechanically robust and processable at ambient temperatures. This has raised a great interest in hybrid materials, such as ferroelectric ceramic–polymer composites that may combine desired properties of the components. Therefore, polymer–titanate composite films are expected to combine the processibility of polymers and high dielectric constant or high capacitance of titanates (Popielarz *et al* 2001; Olszowy 2003; Singh and Chandra 2003; Kobayashi *et al* 2005).

Many studies show that partial replacement of titanium by tin (Sn) improves the dielectric behaviour of barium

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titanate (BT). Also they reported that the increase of Sn content in $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$ (for $x \geq 0.025$) powders decreases the temperature of phase transformation from tetragonal to cubic at T_c . However, $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$ (BTS) have attracted attention because of their high dielectric constant, lead-free relaxor behaviour and sensor applications (Marković *et al* 2007). Generally, the optical and dielectric properties of ferroelectric ceramic-polymer composites depend on polymer type, ceramic type, morphology content, nature and size of fillers, degree of crystallinity, etc (Golego *et al* 1998; Singh and Chandra 2003).

Many investigators reported the effect of BT on the dielectric properties of polymer and all concluded that BT enhances the polar character of polymer host and increases the relative dielectric permittivity (Golego *et al* 1998; Popielarz *et al* 2001, 2007; Olszowy 2003; Singh and Chandra 2003; Choa *et al* 2004; Kobayashi *et al* 2005; Ramajo *et al* 2005; Xie *et al* 2005; Xiaojun *et al* 2006; Ayeshe *et al* 2008). But to our knowledge, no studies have been reported on the effect of BTS content on the optical and dielectric properties of PC. However, very interesting results are reported by us on the optical and dielectric properties of PC-YSiBTS composites (Ibrahim *et al* 2009).

This paper reports the effect of BTS concentration (by weight) on the optical and dielectric properties of BTS-PC composite films through spectrophotometer technique (in the UV-visible region) and the lock-in amplifier (at frequency values 1 kHz, 10 kHz and 50 kHz). The variations of dielectric parameters with temperature are also presented. Variations of the glass transition temperature with BTS concentration in addition to the morphology observation via SEM for BTS-PC composite are also presented. Interesting effects of the BTS ceramic content were observed on the structure, thermal, optical and dielectric properties as morphology, glass transition temperature, absorption coefficient, optical energy gap, a.c. conductivity, relative dielectric permittivity, dielectric loss and loss tangent of the composites films showed frequency, content and temperature dependence.

2. Experimental

2.1 Films preparation

$\text{Ba}(\text{Ti}_{(0.9)}\text{Sn}_{0.1})\text{O}_3$ ceramic powder was prepared by a conventional ceramic processing with BaCO_3 (99.999%, BDH Co.), TiO_2 (99.995%) and SnO_2 (99.9%, Rare Earth Product Limited). Initial powders were weighed according to the composition $\text{BaCO}_3 + 0.9 \text{ TiO}_2 + 0.1 \text{ SnO}_2$ to form $\text{Ba}(\text{Ti}_{(0.9)}\text{Sn}_{0.1})\text{O}_3$ powder. Initial powders were mixed in a planetary mill with zirconia balls in pure alcohol for 2 h and then dried. The dried powders were calcined at 1150°C for 6 h and milled for 2 h. The milled powders were dried again at 500°C . The average grain

size of BTS ceramic powder was $4\text{--}10 \mu\text{m}$ and the average density was $5.62 \text{ g}\cdot\text{cm}^{-3}$. BTS-PC composites were prepared by dissolving PC resin (product by ACROS ORGANICS Company, New Jersey (USA), MW 64,000 and density of $1.2 \text{ g}\cdot\text{cm}^{-3}$) in methylene chloride solvent and was stirred at 30°C by a magnetic stirrer for 2 h until transparent polymer solution formed. Then, the fine powder of BTS was added at weight ratios 0, 5, 10, 20 and 35 wt%. The mixed solution was again stirred for 24 h until the solution composition became highly viscous and homogeneous with minimum ceramic aggregations. This viscous solution was carefully casted in a glass petri dish (dia. of 10 cm). The solvent was evaporated at room temperature for 24 h and placed inside an oven at 40°C for 2 h. Samples of different concentrations kept inside vacuumed dissector. The film thickness ($\sim 0.1 \text{ mm}$) was measured using electronic digital micrometer (MOTOTOYO – China) with 0.001 mm resolution.

The morphology of the prepared films was examined using a Jeol scanning electron microscope (JSM 6380) with low and high vacuum analyses. The operation system was controlled by IBM computer. Samples were coated with gold in automatic sputter coater (Polaron SC 500), and then transferred to the electron microscope to be examined under an applied voltage of 20 kV. The magnification of the sample image was 200X and the electrical image shift of $\pm 50 \mu\text{m}$.

Measurements of the glass transition temperature (T_g) were carried out using a Mettler DSC FP85, calibrated with the melting transition of indium, at a heating rate of $5^\circ\text{C}/\text{min}$. The midpoint on the DSC thermogram was taken as the glass transition temperature. Each sample was carefully prepared and measured to have approximately the same weight ($5 \pm 2 \text{ mg}$).

2.2 Optical measurements

Shimadzu UV-1601 PC spectrophotometer with quartz reference was used in order to measure the absorption spectra of the composites in the wavelength range 250–600 nm. The scan step was 0.5 nm. The optical absorbance (A) spectra of ceramic-PC composite was collected at room temperature. The absorption coefficient α was calculated from the absorbance (A).

After correction for reflection, α was calculated using the relation (Ayeshe *et al* 2008; Ibrahim *et al* 2009)

$$I = I_0 \exp(-\alpha x), \quad (1)$$

$$\alpha = \frac{2.303}{x} \log \left(\frac{I}{I_0} \right) = \frac{2.303}{x} A(\nu), \quad (2)$$

where I_0 and I are the incident and transmitted intensity, respectively, and x is sample thickness.

Figure 1. SEM micrographs for (a) 10 wt% and (b) 35 wt% BTS-PC composite.

Figure 2. DSC thermogram for BTS-PC composite (35 wt%).

2.3 Dielectric measurements

The dielectric parameters (relative dielectric permittivity (ϵ_r), dielectric loss (ϵ'') and loss tangent ($\tan \delta$)) were carried out at frequency values 1 kHz, 10 kHz and 50 kHz and temperature range from room temperature up to 150°C using SR830 DSP lock-in amplifier. The samples under test were inserted between two copper sheets with a small pressure using weak spring. The two leads from both sheets were connected to the lock-in amplifier. The sample area and the average thickness were 2.5 cm² and 0.1 mm, respectively. The relative dielectric permittivity values (ϵ_r) were calculated from the measured capacitance data (C) using the equation (Ibrahim *et al* 2009)

$$C = \epsilon_0 \epsilon_r \frac{A}{l} \quad (3)$$

Dielectric loss was calculated from

$$\epsilon'' = \epsilon_r \tan \delta \quad (4)$$

where ϵ_0 is the permittivity of free space ($8.85 \times 10^{-12} \text{ Fm}^{-1}$), A the area of the sample and l the sample thickness.

A personal computer was used to collect the data using IEEE card and also to control the temperature by using a temperature controller with Digi-Sense R/s using the RS232 connection.

3. Results and discussion

3.1 SEM and DSC results

Figure 1 illustrates the SEM micrographs for 10 wt% and 35 wt% BTS samples. Similar morphology was obtained by us in a previous work with PC/YSiBTS ceramic composites (Ibrahim *et al* 2009). However, nearly sphere shape is clearly observed. The obtained SEM results indicated excellent compatibility between the PC and the BTS particles with weak interfacial bonding between BTS particles and PC host, additionally, local electric field in the ferroelectric ceramic powder playing an important role in the way of ceramic aggregates which may effect on the optical and dielectric properties of BTS-PC composites (Xie *et al* 2005; Hossain and Ali 2006; Patil *et al* 2007; Ibrahim *et al* 2009; Sirirat *et al* 2009).

The glass transition temperature (T_g) is an important physical parameter to characterize the structural property of an amorphous polymer in terms of chain rigidity and intermolecular forces. Figure 2 shows a DSC thermogram of BTS-PC composite (35 wt%). The values of T_g determined from the measured thermographs are shown in table 1. However, T_g values slightly decrease with increasing BTS content and the change in the value of T_g , within 5°C, with increasing BTS content up to 35 wt%. Both results (SEM and DSC) indicate weak interfacial bonding between BTS ceramic particles and polymer

Table 1. Values of optical energy gap (E_{opt}), a.c. conductivity at room temperature and glass transition temperature (T_g) for BTS–PC composites.

BTS–PC (wt%)	BTS–PC volume fraction (%)	E_{opt} (eV)	A.c. conductivity (Ωm) ⁻¹ at 10 kHz	T_g (°C)
0	0	4.44	0.526×10^{-6}	143
5	1.19	4.43	2.070×10^{-6}	143
10	2.47	4.30	2.980×10^{-6}	142.8
20	5.40	4.05	5.144×10^{-6}	141.2
35	10.94	3.93	8.718×10^{-6}	138.2

Figure 3. Optical absorption coefficient spectrum of BTS–PC composites. **Figure 4.** Variation of optical absorption coefficient with BTS concentration at 300 nm for BTS–PC composites.

host. At the same time, SEM and DSC results reveal that addition of BTS ceramic particles to PC host will reduce the physical bond between polymer chains or may increase the free volume in the polymer host (Saq'an *et al* 2004; Ayesh 2008; Ibrahim *et al* 2009).

3.2 Optical results

Figure 3 shows the absorption coefficient spectrum of BTS–PC composites (0, 5, 10, 20 and 35 wt% BTS ceramic) samples at wavelength range from 250–600 nm. It is clear that the absorption of PC host increases with BTS content at 300 nm. Figure 4 illustrates the variation of absorption coefficient with BTS concentration at 300 nm. From this figure we can see that BTS ceramic enhances the UV absorption of PC host especially at 300 nm. Golego *et al* (1998) showed that BaTiO₃ has a strong absorption at UV region and a peak value near 300 nm. Also, Sharma *et al* (2005) reported that barium–strontium titanate films showed excellent UV absorption and transparency in the visible region. The values of the optical energy gap were determined for all BTS–PC composites and are listed in table 1 and graphically shown in figure 5. The method of calculation was reported elsewhere by Golego *et al* (1998) and also by us (Ayesh *et al* 2008; Ibrahim *et al* 2009). It is clear that the values of the optical energy gap decreases from 4.44 eV up to 3.93 as BTS increases from 0 wt% up to 35 wt%, respectively. The transition process was forbidden-direct transition for all BTS–PC composites. This result can be explained in the light of the fact that the increase in BTS ceramic concentration could lead to an increase in the structural imperfections of the composites and hence there is localized states formed within the forbidden gap (Hirankumar *et al* 2005; Ayesh *et al* 2008; Mohammad *et al* 2009).

3.3 Dielectric results

The relative dielectric permittivity (ϵ_r), dielectric loss (ϵ'') and loss tangent ($\tan \delta$) were determined at frequency values 1 kHz, 10 kHz and 50 kHz in the temperature range from room temperature up to 150°C for 0, 5, 10, 20 and 35 wt% BTS–PC composites. The obtained results

Figure 5. Variation of optical energy gap and a.c. conductivity with BTS concentration at room temperature for BTS-PC composites.

Figure 6. Relative dielectric permittivity (ϵ') vs temperature at 10 kHz for BTS-PC composites.

Figure 7. Dielectric loss (ϵ'') vs temperature at 10 kHz for BTS-PC composites.

Figure 8. Loss tangent ($\tan \delta$) vs temperature at 10 kHz for BTS-PC composites.

are plotted in figures 6–8. A.C. conductivity was also determined for all composites at room temperature and frequency value of 10 kHz using the equation (Ayesh 2008; Ibrahim *et al* 2009)

$$\sigma_{a.c.} = \omega \epsilon'' \epsilon_0 = 2\pi f \epsilon'' \epsilon_0, \quad (5)$$

where f is the frequency (Hz), ϵ_0 the permittivity of free space ($8.85 \times 10^{-12} \text{ Fm}^{-1}$), A the area of the sample and l the sample thickness.

The obtained results are listed in table 1 and presented graphically in figure 5. It is clear that there is a good agreement between the increase of a.c. conductivity and the decrease in the optical gap with BTS content. Such conclusion was also obtained in case of PC/ MnCl_2 composites (Ayesh *et al* 2008).

Figures 6–8 illustrate the variation of relative dielectric permittivity, dielectric loss and loss tangent with temperature and BTS concentration by weight at 10 kHz frequency. It is very clear that addition of BTS ceramic to

PC host will increase the relative dielectric permittivity, dielectric loss and loss tangent of PC host. This could be interpreted by interfacial polarization inside the composites in applied alternating field (Xie *et al* 2005). On the other hand, it is very important to mention that BTS ceramic is a ferroelectric material below its phase transition temperature ($T_C = 50^\circ\text{C}$) and paraelectric above this temperature.

Figure 9 illustrates the variation of relative dielectric permittivity of BTS ceramic powder with temperature at 1 kHz. It is clear from this figure that at $T_C = 50^\circ\text{C}$, phase transformation from tetragonal to cubic can be clearly observed (Marković *et al* 2007). This transition, however, will disappear in case of BTS–PC composites. This could be attributed to the fact that the amount of energy required for this transition will be absorbed by PC chains. In case of BTS–PC composites, increase in temperature

Figure 9. Relative dielectric permittivity vs temperature for BTS ceramic powder.

Figure 10. Variation of relative dielectric permittivity difference ($\Delta\epsilon' = \epsilon'_2 - \epsilon'_1$) vs BTS concentration.

will enhance relative dielectric permittivity, dielectric loss and loss tangent of BTS–PC composites and this could be attributed to the existence of three competitive mechanisms which are responsible for these changes (Ramajo *et al* 2005): (a) segmental mobility of polymer is increased above T_g of PC; (b) thermal expansion of PC host and ceramic disrupting the chains of contacting particles and (c) changes in the ceramic structure at T_C (Curie temperature), at this temperature, phase transition will occur in BTS from ferroelectric phase to paraelectric phase. However, in order to realize the effect of BTS addition on the behaviour of dielectric parameters with temperature, the value ($\epsilon_{r2} - \epsilon_{r1}$) was calculated for each composite before and after the phase transition temperature of BTS ($T_C = 50^\circ\text{C}$) at frequency 10 kHz, where ϵ_{r1} is the relative dielectric permittivity value at room temperature and ϵ_{r2} is the value of relative dielectric permittivity at 41°C (before T_C) and at 145°C (after T_C).

The obtained results are presented graphically in figure 10. It is clear that BTS content increases in the PC host as the value ($\epsilon_{r2} - \epsilon_{r1} = \Delta\epsilon_r$) increases in both phases (ferroelectric and paraelectric) of BTS ceramic. This means that BTS ceramic enhances the segmental motion of polymer chains and not restrict this motion. Good agreement between results obtained from dielectric and those obtained from DSC and SEM are seen. As a general conclusion we can say that BTS ceramic particles reduce the physical bond between polymer chains and consequently enhance the segmental motion of polymer chains and this behaviour is independent of ceramic phase (Ayesh 2008; Ibrahim *et al* 2009).

Figure 11 illustrates the effect of frequency on the variation of the relative dielectric permittivity with temperature for BTS–PC composites. The relative dielectric permittivity of composites, however, decreases with increasing applied frequency. This behaviour usually exists in polymer composites, resulting from dielectric relaxation processes occurring within the polymer matrix (Popielarz *et al* 2001). Same behaviour was observed for BT–TMPTA composites (Popielarz *et al* 2001) and BT–epoxy composites (Ramajo *et al* 2005). Moreover, this behaviour can also be explained in the light of the fact that at low frequencies the dipoles have sufficient time to align with the field before it changes direction and consequently the relative dielectric permittivity is high. When applied frequency increased toward higher values, the relative dielectric permittivity value decreases due to insufficient time for dipoles to align before the field changes direction (Schwartz *et al* 2005; Ayesh *et al* 2008; Prashant and Gaur 2008).

4. Conclusions

BTS–PC composites were prepared in order to study effect of BTS ceramic on the optical and dielectric

Figure 11. Variation of relative dielectric permittivity with temperature at different frequency values: (A) pure PC, (B) 25 wt% BTS and (C) 35 wt% BTS.

properties of PC host. The optical and dielectric results of the prepared BTS–PC composites exhibit frequency and ceramic concentration dependence. Addition of BTS ceramic to PC host will enhance UV absorption of PC host especially at 300 nm. The optical energy gap decreases up to a value of 3.93 eV when 35 wt% of BTS was added to PC host and this is attributed to the increase of localized states within forbidden gap. Both SEM and DSC results indicate weak interfacial bonding between BTS ceramic particles and polymer host and also BTS particles. BTS particles may reduce the physical bonding between polymer chains or increase the free volume in the polymer. There is good agreement between increase of a.c. conductivity and the decrease in the optical gap with BTS content. However, as BTS content and temperature increases, relative dielectric permittivity, dielectric loss and loss tangent of PC host increases. Besides, SEM and DSC results reveal that addition of BTS ceramic particles to PC host will reduce the physical bond between polymer chains or will increase the free volume in the polymer host and consequently enhance the segmental motion of polymer chains and this behaviour is independent of ceramic phase.

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