

ELECTRICAL AND OPTICAL CHARACTERIZATION OF PMMA DOPED WITH $\text{Y}_{0.0025}\text{Si}_{0.025}\text{Ba}_{0.9725}(\text{Ti}_{0.9}\text{Sn}_{0.1})\text{O}_3$ CERAMIC

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Abstract Poly(methylmetacrylate) (PMMA)/ $\text{Y}_{0.0025}\text{Si}_{0.025}\text{Ba}_{0.9725}(\text{Ti}_{0.9}\text{Sn}_{0.1})\text{O}_3$ (YBTS) composites were prepared at different weight ratios of YBTS (0 wt%, 5 wt%, 10 wt% and 20 wt% YBTS) in order to investigate effect of YBTS additions on the electrical and optical properties of PMMA host. The electrical properties (impedance, dielectric constant dielectric loss and AC conductivity) were studied in the frequency range 10 kHz–1 MHz and in temperature range 20–90°C. Upon increasing the contents of YBTS ceramic, we observed a reduction in the impedance and an increase in the dielectric constant, dielectric loss and AC conductivity of PMMA host. We also found that the relaxation process at high YBTS contents was due to relaxation in the ionic conductivity. The absorption coefficient (α) has been determined in the wavelength range 230–800 nm at room temperature for all YBTS-PMMA composites. Moreover, the addition of YBTS ceramic highly enhances the UV absorption of PMMA host especially below 300 nm. Addition of 20 wt% YBTS ceramic to PMMA host decreases the optical energy gap from 5 eV to 3.41 eV. Correlations between electrical, optical and SEM results are reported.

Keywords: Electrical; Optical; PMMA, Ceramic; Ferroelectric; Composites.

INTRODUCTION

Recently, polymer-ferroelectric ceramic composites gained much interest due to their potential use in various applications in opto-electronics. Fast growth of optoelectrical and electronic industry requires development of new materials and composites that ultimately find their way in new applications^[1–3].

PMMA (polymethylmethacrylate) is highly transparent to visible light, mechanically stable and excellent in insulating properties which made this polymer an excellent candidate for many optical and electrical applications^[4, 5]. Ferroelectrics such as titanates are used in many applications, such as capacitors, waveguides, ferroelectrics sensors and integrated circuit^[6–9]. The marriage between the two materials, polymer-titanate composite (especially in thin films), is expected to extend the application range for the new composites^[6–12].

It has been found that partial replacement of titanium by tin (Sn) improves the dielectric behavior of barium titanate $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$ (BTS). The increase of Sn content in $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$ (for $x \geq 0.10$) led to reduction of transition temperature of the phase transformation (from tetragonal to cubic at T_c). Doping BTS ceramic with Yttrium ion (Y^{+3}), resulted in n-type semiconducting properties. More over, the new material (YBTS) has ferroelectric and semiconducting properties at room temperature when the molar concentration of Sn is greater or equal to 0.1^[10, 11]. Extensive researches reported the effect of BT ceramic on the dielectric or optical properties of polymers^[6, 7, 13–21]. Recently, we found that the optical energy gap decreased with ceramic concentration while the absorption coefficient highly increased in the UV region by 18 wt% of the PC host^[22]. To the best of our knowledge, the effect of YBTS ceramic on the optical and dielectric properties of PMMA has

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not been studied. Generally, the optical and dielectric properties of polymer/ceramic composites depend on polymer type, ceramic type, morphology, nature and size of fillers and the degree of crystallinity^[10, 14].

In this paper, we present the effects of YBTS concentration and the frequency of the applied electric field on the electrical and optical properties of YBTS-PMMA composite films. The variations of electrical parameters with temperature are also presented. Morphology *via* SEM for YBTS-PMMA composites is also studied in this report. Various electrical and optical properties have been studied: impedance, dielectric constant, AC conductivity, absorption coefficient and the optical energy gap of the composite films.

EXPERIMENTAL

Film Preparation

Mixture of ceramics powder was prepared by a conventional ceramic processing with BaCO₃ (99.999%, BDH Co.), TiO₂ (99.995%), Y₂O₃ (99%), SiO₂ (99%) and SnO₂ (99.9%) from Rare Earth Product Limited. Initial powders were weighted to form Y_{0.0025}Si_{0.025}Ba_{0.9725}(Ti_(0.9)Sn_{0.1})O₃ (YBTS) ceramic 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 then milled for 2 h. The milled powders were dried again at 500°C^[11]. Polymethylmethacrylate (PMMA)/YBTS composites were prepared by dissolving PMMA resin in chloroform solvent and stirred at 30°C by a magnetic stirrer for 24 h until highly viscous polymer solution was formed. The fine powder of YBTS (0 wt%, 5 wt%, 10 wt% and 20 wt%) was added and stirred until the solution composition became highly viscous and homogeneous. This viscous solution was cast in a glass petri dish (dia. of 5 cm). The solvent was evaporated at room temperature for 24 h and placed inside oven at 45°C for 2 h. Samples of different concentrations were kept inside vacuumed dissector. The thickness of the obtained films is about (*ca.* (0.450 ± 0.001) mm).

The morphology of the prepared films was examined using a JEOL scanning electron microscope (J.S.M. 6380) with low and high vacuum analysis including the energy dispersive X-ray analysis unit (EDS). Samples were coated with gold in an automatic sputter coater (Polaron SC 500), and then transferred to the electron microscope and was examined under applied voltage 20 kV. The electrical image shift was of ±50 μm.

Electrical Measurements

The electrical measurements (impedance (*Z*), dielectric constant (ϵ'), dielectric loss (ϵ'') and AC conductivity (σ_{ac})) on YBTS-PMMA composites of different YBTS contents were obtained at a frequency range from 10 kHz to 1 MHz and a temperature range from 20°C to 90°C. Measurements were carried out using LF Impedance Analyzer (HP 4192, with a sinusoidal source signal) connected to two copper electrodes placed in a shielded cell^[1]. The electrical parameters were calculated from impedance and phase angle values that obtained from the Impedance Analyzer. The real (*Z'*) and imaginary (*Z''*) components of the impedance can be calculated using the following relations^[1–3]:

$$Z' = Z \cos \varphi \quad (1)$$

$$Z'' = Z \sin \varphi \quad (2)$$

The dielectric constant (ϵ') and dielectric loss (ϵ'') were calculated from the following equations:

$$\epsilon' = \frac{Z'' d}{2\pi f \epsilon_0 A Z^2} \quad (3)$$

$$\epsilon'' = \frac{Z' d}{2\pi f \epsilon_0 A Z^2} \quad (4)$$

where *d* is the sample thickness, *A* is the cross sectional area of the sample, ϵ_0 is the permittivity of free space and *f* is the frequency (Hz). The AC conductivity (σ_{ac}) was calculated from:

$$\sigma_{ac} = \omega \varepsilon'' \varepsilon_0 = 2\pi f \varepsilon'' \varepsilon_0 \quad (5)$$

Optical Measurements

The absorption spectra of YBTS-PMMA composites in the UV-Visible region were measured using a Shimadzu UV-160 spectrophotometer with quartz reference in the wavelength range 230–800 nm. The scan step was 0.5 nm. The optical absorbance (A) spectra of YBTS-PMMA composites were collected at room temperature. The absorption coefficient $\alpha(\nu)$ was calculated from the absorbance (A). After correction for reflection, $\alpha(\nu)$ was calculated using the relation^[2, 22]:

$$I = I_0 \exp(-\alpha x) \quad (6)$$

$$\alpha(\nu) = \frac{2.303}{x} \lg\left(\frac{I_0}{I}\right) = \frac{2.303}{x} A(\nu) \quad (7)$$

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

RESULTS AND DISCUSSION

Morphology Results

Figure 1 illustrates the SEM micrograph for 5 wt% (a) and 10 wt% (b) YBTS samples. Both samples showed different morphology: the 5% sample showed point like ceramic material spread through matrix, while the 10% and 20% samples showed more rounded interconnected grains^[22]. This indicates that local electric field in the ferroelectric ceramic powder plays an important role in the way of ceramic aggregates formation. The uniform spread of the ceramic material further indicates the excellent compatibility between the PMMA and the YBTS particles with weak interfacial bonding between YBTS particles and PMMA host^[13, 15, 19, 22].

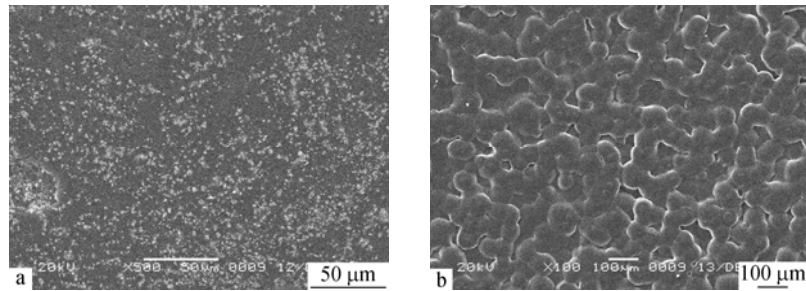


Fig. 1 SEM micrograph for (a) 5 wt% and (b) 10 wt% YBTS-PMMA composites

The X-ray energy dispersion spectra for YBTS-PMMA composites performed on the prepared samples indicated that the concentration of Y^{+3} , Ba^{+2} , Ti^{+4} Sn^{+2} ions qualitatively agrees with the nominal composition of the starting materials used in preparing the samples.

Electrical Results

Impedance (Z), dielectric constant (ε'), dielectric loss (ε'') and AC conductivity (σ_{ac}) were determined in the frequency range 10 kHz–1 MHz and in the temperature range 20–90°C. The obtained results are presented in Figs. 2–7. A common feature can be seen from all the figures is that the addition of YBTS decreases the impedance (Z) and increases the dielectric constant, dielectric loss and AC conductivity of PMMA host. Since YBTS ceramic is an n-type semiconductor, its addition in the matrix is expected to reduce the impedance of PMMA host. Moreover, the interfacial polarization inside the composites may also cause these changes^[19]. Generally, YBTS ceramic clearly enhances the electrical conductivity and the polar character of PMMA host. The variations of dielectric parameters such as dielectric constant with frequency can also be explained in terms of the relaxation time: at low frequencies, the electric dipoles have sufficient time to align with the field before

the field changes its direction; consequently the dielectric constant is high. At high frequencies, the dielectric constant value decreases due to the insufficient time available for the dipoles to align^[1].

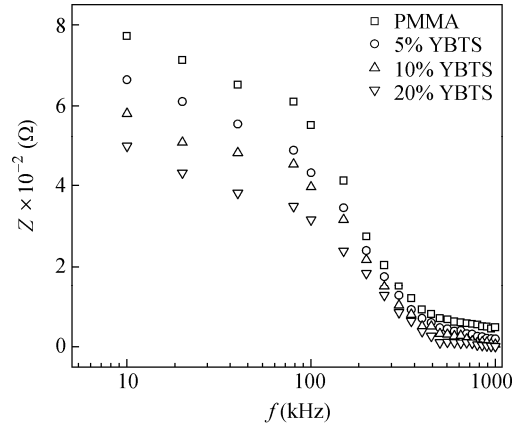


Fig. 2 Variation of impedance (Z) with frequency for YBTS-PMMA composites

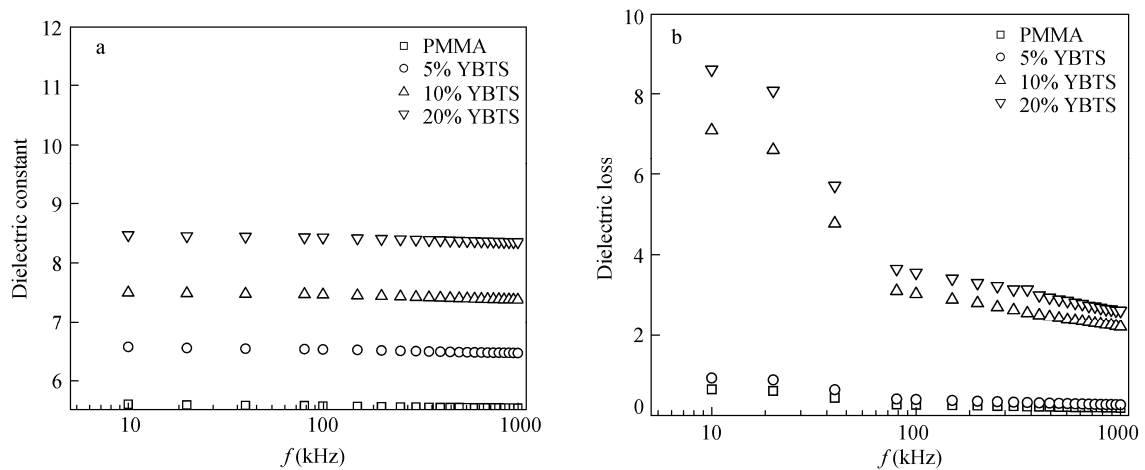


Fig. 3 Variation of (a) dielectric constant (ϵ') and (b) dielectric loss (ϵ'') with frequency for YBTS-PMMA composites

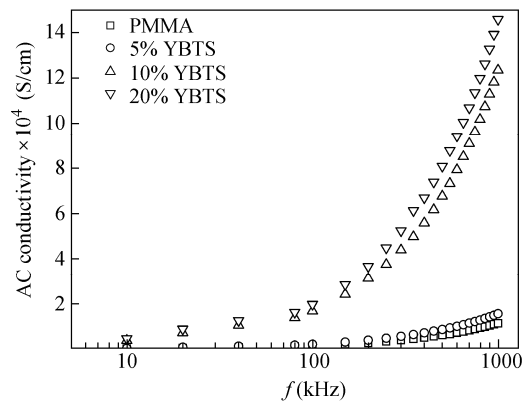


Fig. 4 Variation of AC conductivity (σ_{ac}) with frequency for YBTS-PMMA composites

In Figs. 5, 6 and 7, we present our measurements of the impedance, dielectric constant, dielectric loss and AC conductivity of YBTS-PMMA composites with varying YBTS content and temperature at 90 kHz. The figures clearly indicate a reduction in impedance and increase in the dielectric constant, dielectric loss and AC conductivity of PMMA host upon increasing the temperature. This can be attributed to the increase in the segmental mobility of PMMA chains^[18]. Generally, the variation of impedance, dielectric constant, dielectric loss and AC conductivity of the PMMA host with YBTS content and temperature can be also attributed to the existence of three competitive mechanisms which are responsible for these changes^[18]: (a) segmental mobility of polymer chains; (b) thermal expansion of PMMA 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 YBTS from ferroelectric phase to paraelectric phase.

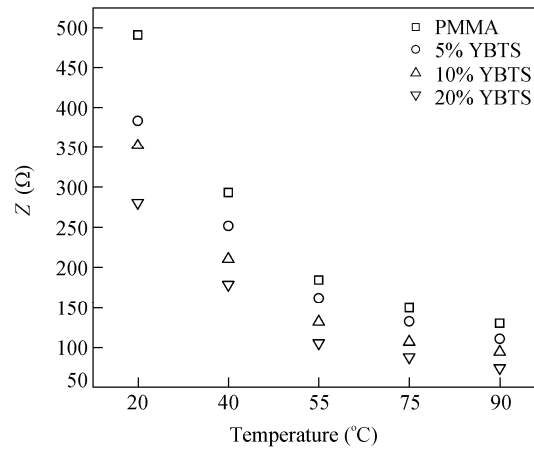


Fig. 5 Variation of impedance with temperature for YBTS-PMMA composites at 90 kHz

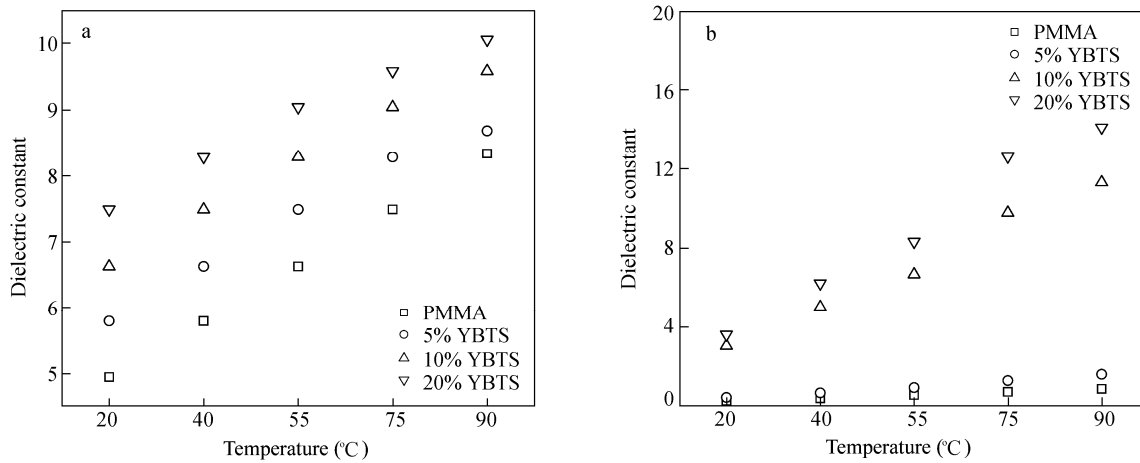


Fig. 6 Variation of (a) dielectric constant (ϵ') and (b) dielectric loss (ϵ'') with temperature for YBTS-PMMA composites at 90 kHz

The activation energy E_a has been evaluated from the variations of the conductivity with temperature (Fig. 8), using Arrhenius equation. The data are presented in Table 1; we have:

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{k_B T}\right) \quad (8)$$

where σ , is the conductivity, σ_0 is the pre-exponential factor of conductivity which has the units of conductivity, k_B is the Boltzmann constant, T is the temperature in Kelvin, and E_a is the activation energy. It is clear from Table 1 that activation energy value decreases with increasing the YBTS content. The addition of YBTS ceramic to PMMA host enhances the electrical conduction of PMMA host due to the electronic and impurity contributions arising from the YBTS ceramic^[1-3].

Table 1. The values of activation energy (E_a) and optical energy gap (E_{opt}) for YBTS-PMMA composites

YBTS-PMMA (wt%)	E_a (eV)	E_{opt} (eV)
0	0.159	5
5	0.145	4.9
10	0.143	4.79
20	0.142	3.41

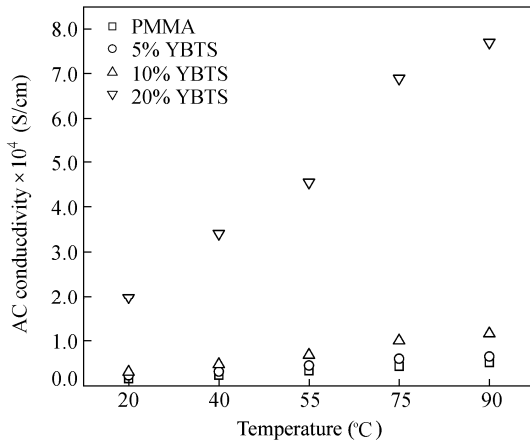


Fig. 7 Variation of AC conductivity with temperature for YBTS-PMMA composites at 90 kHz

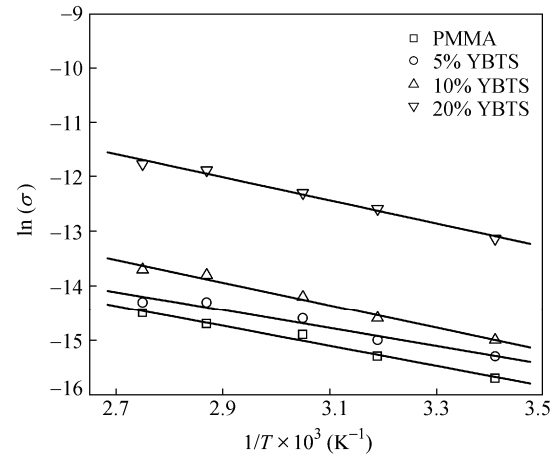


Fig. 8 $\ln(\sigma)$ versus $1000/T$ for YBTS-PMMA composites at 90 kHz

Relaxation Process

Recently, we have shown that if Argand plot between imaginary part (M'') versus real part (M') of electric modulus has semicircular behavior then the relaxation is due to conductivity relaxation process, otherwise, it is due to viscoelastic relaxation (or polymer molecular relaxation)^[1]. In the present work, the values of M' and M'' were determined from:

$$\begin{aligned} M^* &= \frac{1}{\varepsilon^*} = \frac{1}{\varepsilon' - i\varepsilon''} = \frac{\varepsilon' + i\varepsilon''}{(\varepsilon' - i\varepsilon'')(\varepsilon' + i\varepsilon'')} \\ M^* &= \frac{\varepsilon'}{(\varepsilon' - i\varepsilon'')(\varepsilon' + i\varepsilon'')} + i \frac{\varepsilon''}{(\varepsilon' - i\varepsilon'')(\varepsilon' + i\varepsilon'')} \\ M^* &= \frac{\varepsilon'}{(\varepsilon'^2 + \varepsilon''^2)} + i \frac{\varepsilon''}{(\varepsilon'^2 + \varepsilon''^2)} = M' + iM'' \end{aligned} \quad (9)$$

where ε' : permittivity, ε'' : dielectric loss, M' : electric modulus, and M'' : electric loss modulus. Large differences between the properties of viscoelastic relaxations and the properties of conductivity relaxations can be seen in polymers and composites. The obtained results are presented in Fig. 9. For pure PMMA (Fig. 9a) and 5 wt% YBTS composite (Fig. 9b), the plots do not follow semicircular behavior, while in case of 10 wt% and 20 wt%

YBTS (Figs. 9c and 9d), the plot can be fitted to semicircular behavior. This indicates that, at the domain frequency range, the relaxation process in case of pure PMMA and 5 wt% YBTS-PMMA composites is due to viscoelastic relaxation process, while the relaxation in case of 10 wt% and 20 wt% YBTS-PMMA composites is due to ionic conductivity relaxation process with single value of relaxation time^[1].

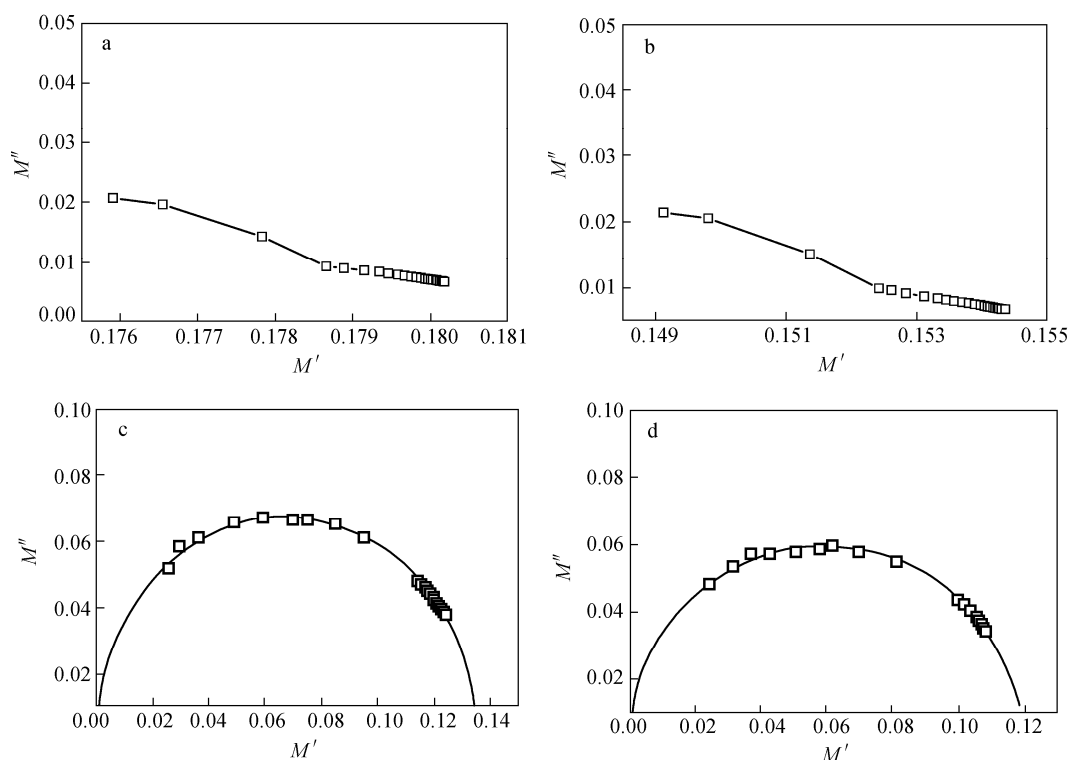


Fig. 9 Argand plots of (a) pure PMMA, (b) 5 wt%, (c) 10 wt% and (d) 20 wt% YBTS-PMMA composites

Optical Results

The absorption coefficient spectra for YBTS-PMMA composites are shown in Fig. 10. The figure indicates that YBTS ceramic enhances the UV absorption of the PMMA host especially below 300 nm and at high YBTS content. In our previous research^[22], we measured the absorption spectrum for the YBTS ceramic and we found

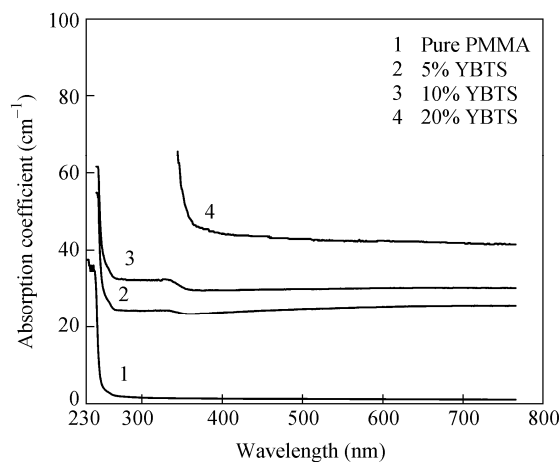


Fig. 10 The optical absorption coefficient spectrum of YBTS-PMMA composites

that it has a strong absorption peak below 300 nm. Also we found that addition of YBTS to PC will enhance the UV absorption of the PC host especially below 300 nm and at high YBTS content. Furthermore, Sharma *et al.*^[23], reported that barium-strontium titanate films showed excellent UV absorption and transparency in the visible region. Golego *et al.*^[16], showed that BaTiO₃ has a strong absorption at UV region and with a peak below 300 nm. Similar result obtained in the present work in case of YBTS-PMMA. This indicates that YBTS ceramic can acts as an excellent ultraviolet shield for PMMA host especially at high YBTS content.

At high absorption coefficient levels the absorption coefficient $\alpha(\nu)$ for amorphous materials can be related to the energy of the incident photon ($h\nu$) according to Mott, Davis, and Tauc formula:^[2, 3, 23–26].

$$\alpha(\nu)h\nu = \begin{cases} \beta(h\nu - E_{\text{opt}})^r & \text{for } h\nu > E_{\text{opt}} \\ 0 & \text{for } h\nu < E_{\text{opt}} \end{cases} \quad (10)$$

where β is a constant equals to $(4\pi\sigma_0/nc\Delta E)$, σ_0 is the extrapolated DC conductivity, ΔE is energy gap tail (or energy which is interpreted as the width of the tail of localized states in the forbidden band gap), n is the refractive index, E_{opt} is the optical energy gap and r is an index. The value of r determines the type of electronic transition causing the optical absorption; it can take values 1/2, 3/2, 2, and 3 for direct-allowed, direct-forbidden, indirect-allowed, and indirect-forbidden transitions, respectively. Figure 11 shows $(\alpha h\nu)^{1/r}$ versus photon energy $h\nu$ plot according to Eq. (10). The best straight line obtained for all composites was with $r = 1/2$, indicates that the electron transition is direct transition in the k -space. The values of E_{opt} were obtained from extrapolating the straight line in the higher energy portion of Fig. 11 to $(\alpha h\nu)^2 = 0$. The results obtained are listed in Table 1

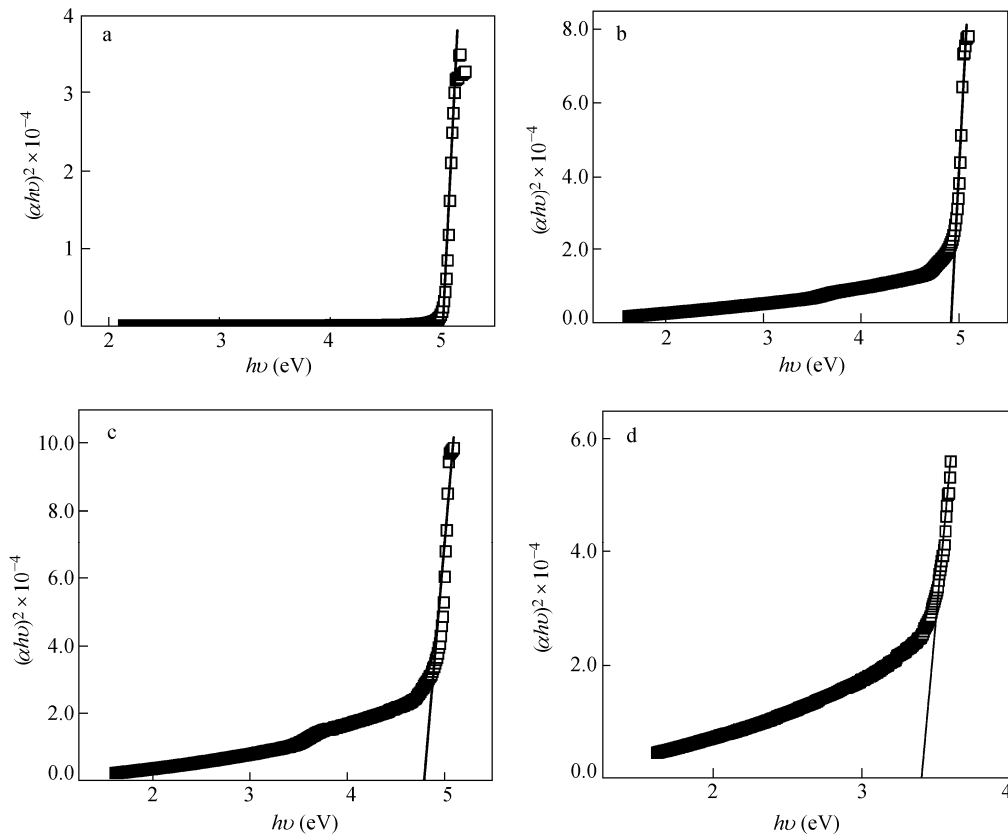


Fig. 11 $(\alpha h\nu)^2$ versus photon energy for: (a) pure PMMA, (b) 5% YBTS, (c) 10% YBTS and (d) 20% YBTS-PMMA composites

and presented in Fig. 12. The optical energy gap decreases from 5.00 eV (for pure PMMA) to 3.41 eV as YBTS concentration increases up to 20 wt%. Golego *et al.*^[16] reported that the optical energy gap of BaTiO₃ thin films varies from 3.1 eV to 3.8 eV depending on preparation conditions and annealing temperature. Also, Sharma *et al.*^[23] reported that the optical band gap for BT thin films varied considerably from 3.0 eV to 3.95 eV and concluded that the higher E_{opt} value could be attributed to a smaller crystallite size. Also they reported that in the high-energy region, the factor $(\alpha h\nu)^2$ varies linearly with $h\nu$, but at low-energy, the absorption spectrum deviates from linear behavior, in agreement with results presented in Fig. 11. The above results can be explained in the light of the fact that the increase in YBTS ceramic concentration increases the localized states within the forbidden gap. This directly affects the decrease in the optical energy gap of the PMMA host^[25]. However, there is a good agreement between AC conductivity and optical energy gap results.

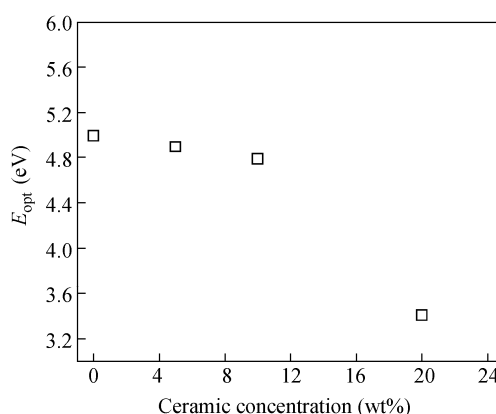


Fig. 12 Variation of the optical energy gap (E_{opt}) with YBTS concentration

CONCLUSIONS

YBTS-PMMA composites were prepared in order to study the effect of YBTS ceramic on the electrical and optical properties of PMMA host. The electrical and optical results of YBTS-PMMA composites exhibit frequency and ceramic concentration dependence. As YBTS content and temperature increases, the impedance decreases and the dielectric constant, dielectric loss and AC conductivity of PMMA host increase. This study shows that the relaxation process at high YBTS contents is due to ionic conductivity relaxation. SEM results reveal that the uniform spread of the ceramic material further indicates the excellent compatibility between the PMMA and the YBTS particles with weak interfacial bonding between YBTS particles and PMMA host. The addition of YBTS ceramic highly enhances the UV absorption of PMMA host especially below 300 nm. Addition of 20 wt% YBTS ceramic to PMMA host decreases the optical energy gap from 5 eV to 3.41 eV due to the increase of the localized states within forbidden gap.

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