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PT/BORAX COMPOSITE AS A HIGH DIELECTRIC CONSTANT MATERIAL WITH LOWER DIELECTRIC LOSS

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ABSTRACT

In recent years, high dielectric constant composites have been considered as the key materials for many cutting-edge applications such as supercapacitors, memory devices, electrical, mechanical, and biochemical engineering. However, the high dielectric loss at low frequencies becomes a crucial problem which makes the material unsuitable for these technological applications. In this respect, this work has been devoted to prepare a new high dielectric constant composite material with low dielectric loss. From this point of view, Polythiophene /$Na_2B_4O_7$ (PT/Borax) composites with different borax contents varying from 10.0 wt.% to 50.0 wt.% have been prepared. The morphology and chemical structure of the composites as well as pure PT have been determined by Scanning Electron Microscopy (SEM) and Fourier Transformed Infrared (FTIR) Spectroscopy, respectively. The dielectric properties of the samples have been measured within 100Hz-16.5MHz frequency region at room temperature. The polymer composite with high dielectric constant and low dielectric loss at low frequency has been achieved for 50.0 wt.% Borax additive. The dielectric relaxation mechanism of the samples have also been identified as non-Debye type. The electrical conductivity properties of the samples have been discussed in terms of Jonscher's Universal power law.

Keywords: High dielectric constant, Low dielectric loss, Polymer composites, Polythiophene, Borax

1. INTRODUCTION

Polymer composites with a high dielectric constant, low dielectric loss (tan δ), and low process temperature are highly desirable for many applications ranging from microelectronics to pulse-power and energy-storage systems [1, 2]. Also, high dielectric constant (high-k) polymer-based composites utilized in gate dielectric and electrical energy storage applications due to their light-weight, good mechanical properties, simple fabrication process and facile processability. As a gate dielectric of advanced MOSFET's technology, silicon dioxide have been replaced with new high-k dielectrics [3, 4]. Generally, most polymers possess low dielectric constant (typically less than 10) due to the negligible contribution of the ionic component to total dielectric constant [5]. A promising way to increase the dielectric constant of a polymer is making a doping with high-k dopants, such as barium titanate, calcium copper titanate etc [6]. Among various dopants, borax can be considered as one of the most promising candidates because of its high dielectric constant and good dielectric loss properties [7].

Recently conducting polymers, like polythiophene, polypyrrole, and polyaniline, have been utilized for numerous technological applications such as electrochromic devices, corrosion protection, and electronic devices. Although the conducting polymers have some advantages such as low weight and cost, their processability is poor. Therefore, scientists generally choose modifications of the conducting polymers such as blends, copolymers, and composites in their research. The main focus of many of the studies were to combine conducting polymers with pure inorganic components to generate new polymer matrix composites in the past few decades. Moreover, the kind of polymerization method and doping materials considerably change the physical and structural attributes of the composites [8]. Although the synthesis of some polymeric blends and composites with borax content have been

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reported in the scientific literature, their dielectric properties have not been investigated up till now. Borax was utilized to form gel with glucomannan and poly(vinylalcohol) because of its highly crosslinking capability in some research. Kim et al. have reported the formation of H-bonding with that of hyaluronate aggregates, via PVA-borax crosslinking as a bridge, resulting in a network structure [7, 9].

In this study, disodium tetraborate ($Na_2B_4O_7$) i.e. Borax belonging to the category of boron compound has been used as doping material. As the conducting polymer, polythiophene has been chosen due to its broad variety of applications, such as transistors, solar cells, re-chargeable batteries, diodes, sensors, and electrochromic devices. The main goal of this study was to examine the effect of different borax doping concentration rate on morphological, micro-structural and dielectric properties of polythiophene.

2. EXPERIMENTAL

2.1. Materials

Disodium tetraborate i.e. Borax ($Na_2B_4O_7$) (Product Number: 221732) has been purchased from Sigma-Aldrich. Thiophene (C_4H_4S), anhydrous iron(III) chloride ($FeCl_3$) have been purchased from Merck (Germany). Chloroform ($CHCl_3$) and methanol (CH_3OH) have been supplied from Sigma-Aldrich.

In the chemical synthesis of polythiophene, $FeCl_3$ has been used as an oxidant, molar ratio of $n_{oxidant}/n_{monomer}$ was 2.5. For this purpose, 0.022 mole thiophene has been mixed 70 ml chloroform. 0.055 mol $FeCl_3$ has been dissolved 180 ml chloroform and this solution has been added into the above solution by dropwise fashion. The final solution has been stirred for 24 h at room temperature. The precipitate obtained after polymerization has been filtered and washed three times chloroform and methanol to remove residual monomer and oxidant. The polythiophene precipitate has finally been dried at 60 °C for 24h.

2.2. Methods

To investigate the effects of borax on the dielectric properties of PT, PT/Borax composites have been prepared by mixing of pure PT with different weight percentages (10.0 wt.%, 25.0 wt.%, and 50.0 wt.%) of Borax. The composite materials prepared have been compressed with a cold press at room temperature to obtain a pellet form. The pellets were having 13±0.02 mm diameter, 0.500±0.050 g weight and 1.8-2.3 mm thickness.

Fourier-Transform Infrared spectroscopy analysis (FT-IR) has been performed by Perkin Elmer Spectrum 100 one FT-IR spectrometer. All spectra of pure PT and PT/Borax composites have been taken between 4000-650 cm^{-1} wave number, with a resolution of 2 cm^{-1} after 4 scans. The FTIR measurements have also been performed in the transmittance mode. Furthermore, the surface morphologies of composite samples have been visualized by using a Scanning Electron Microscope (SEM) model Zeiss-EVO® LS 10.

The dielectric measurements have been carried out with a two-point probe arrangement. Dielectric measurements have been performed by using HP 4194A Impedance Analyzer in the frequency range from 100 Hz–16.5 MHz at room temperature with a high accuracy (0.17% typ.). GPIB (General Purpose Interface Bus) cable has been utilized for the data transfer from impedance analyzer to the computer and hence the data have been simultaneously recorded by computer. The experimental set-up for the measurements has also been shown in Figure 1. In this work, the overall errors of the dielectric measurements were 2.5% and the RMS amplitude of the instrument was approximately 500mV.

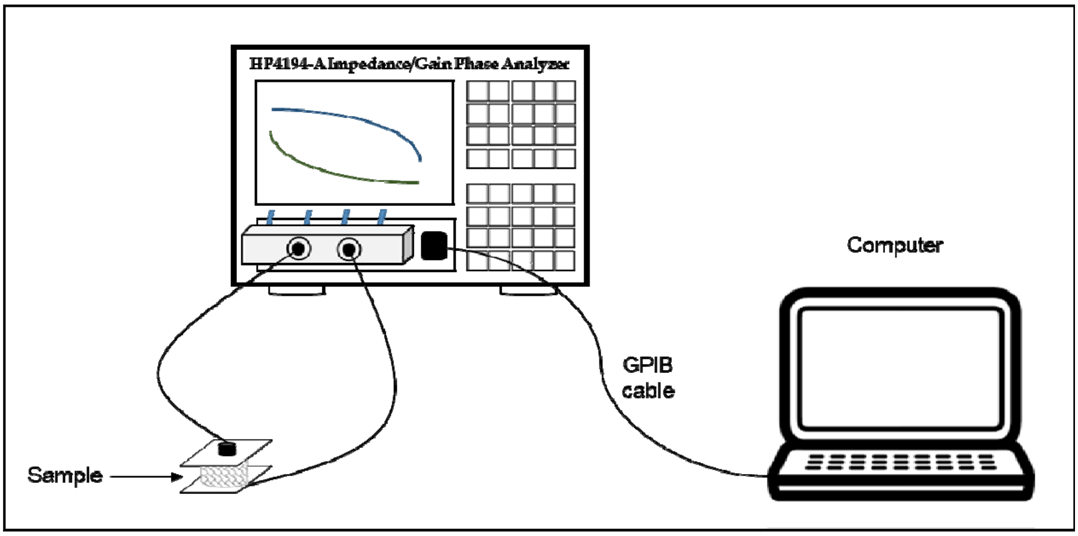

Figure 1. The experimental set-up for the dielectric measurements

3. RESULTS AND DISCUSSIONS

3.1. Fourier-Transformation Infrared (FTIR) Spectroscopy Analysis

The FTIR spectra of pure borax and pure PT have been shown in Figure 2(a). The bands between 3600-3200 cm^{-1} observed for borax represent the OH groups' coordination in borax structure and hydrogen bonding between OH groups [10]. The bands at 1695 and 1650 cm^{-1} correspond to the H-O-H bending mode. The peaks determined at 1425, 1360 cm^{-1} and 1000-950 cm^{-1} belong to the asymmetric and symmetric stretching vibrations of BO_3, respectively [11]. The band at 1161 cm^{-1} is also the in-plane bending of B–O–H. The bands at 1145-1045 cm^{-1} and 837-829 cm^{-1} are the fingerprint of asymmetric and symmetric stretching of BO_4, respectively [11].

In the FTIR spectrum of pure PT shown in Figure 2(a), the bands at the range from 600 cm^{-1} to 1500 cm^{-1} are the characteristic region of PT. The peak located 656 cm^{-1} indicates C–S stretching of the thiophene ring [12-15]. In addition, the peak observed at the vicinity of 711 cm^{-1} is attributed to C–S bending mode [14, 15]. The spectrum of pure PT also displayed the C–H out-of-plane deformation at 772 cm^{-1} and in plane C–H aromatic bending vibrations at 1084 cm^{-1} and 1191 cm^{-1} [12-14]. The peaks at 1385 cm^{-1} and 1634 cm^{-1} correspond to C–C [32] and C=C stretching vibrations, respectively. The peak showed at 3353 cm^{-1} is also attributed to O–H stretching vibrations [13].

The large descending base line observed in the spectral region of 2000-4000 cm^{-1} for the composites has been attributed to the free–electron conduction (See Figure 2(b)). As shown in Figure 2(a), this type of behavior has not been observed in pure PT [16]. The spectrum also showed the (C–S) bending band at 749 cm^{-1}; (C–H) in plane bending band at 1113 cm^{-1} and (C=C) stretching band at 1458-1596 cm^{-1}. The doping induced band at 1021 cm^{-1} was originating from the modifications in the conjugated backbone because of the electron donating and electron withdrawing dopants on the polymer chain and the counter ion balancing appeared at 1458, 1309 and 1113 cm^{-1} [17, 18].

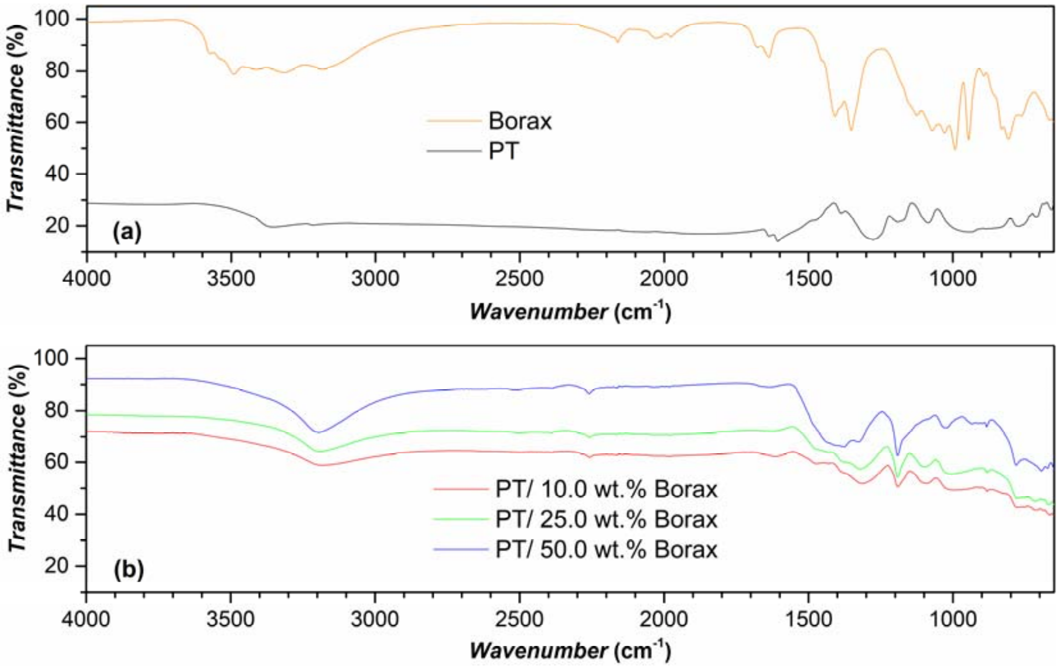

Figure 2. FT-IR spectra of **(a)** pure Borax and pure PT, **(b)** PT/Borax composites.

3.2. Scanning Electron Microscope (SEM) Analysis

Figure 3 showed the morphology of pure PT, pure Borax and PT/50.0 wt.% Borax composite samples. According to Figure 3(a) and (b), while pure PT showed fibrous structure with a small globular structure, pure borax has rock like irregular rectangular shaped particles with various dimensions. Comparing the SEM images of pure PT and borax added PT sample, borax heaps can be easily distinguished. In other words, borax wasn't diffused into the PT and also not dissoluted but borax doping was resulted in the formation of a composite structure. Dielectric results which are given in below are changing by borax concentration. Therefore, it has been deduced that borax doping is effective on the properties of composite material.

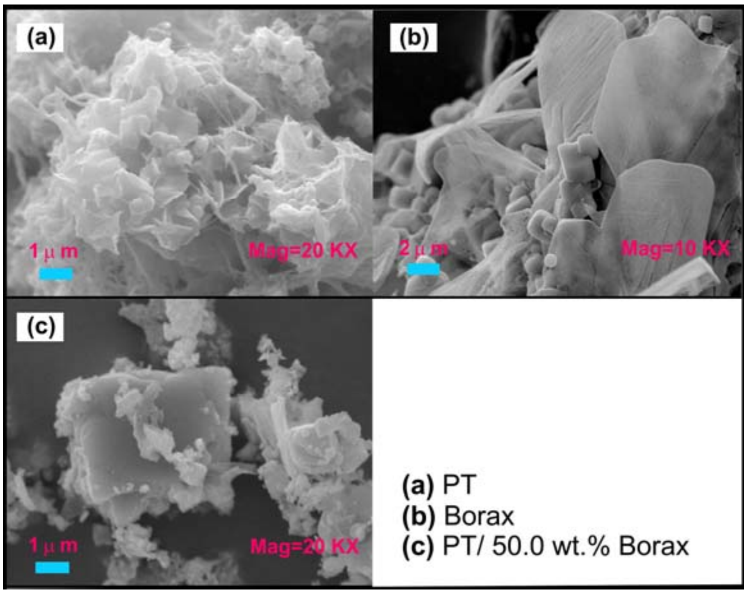

Figure 3. The SEM micrographs of the samples.

3.3. Dielectric Analysis

The angular frequency dependence of the real and imaginary components of complex dielectric function (ε' and ε'') of pure PT and PT/Borax composites samples have been shown in Figure 4(a) and (b), respectively.

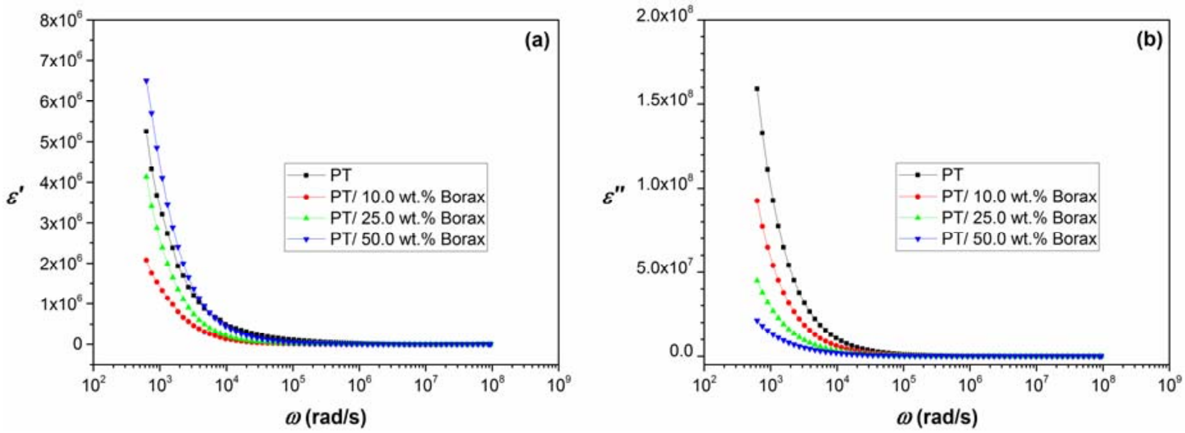

Figure 4. (a) The real and (b) imaginary components of complex dielectric function for pure PT and PT/Borax composites.

It has been observed that $\varepsilon'(\omega)$ curves showed a decreasing behavior with increasing frequency at the low frequency region and tends to approach a constant value at high frequency region. The strong dispersion observed for $\varepsilon'(\omega)$ at low frequency region for all samples can be explained by the fact that the electric dipoles in the materials orient themselves along the electric field applied and this behavior totally contribute to the polarization process. As shown in Figure 4(a), while 10.0 wt.% and 25.0 wt.% borax additives lower the $\varepsilon'(\omega)$ values, 50.0 wt.% borax doping increases the $\varepsilon'(\omega)$ values for the same frequency domain. In other words, when borax fraction approaches a critical or optimum concentration, the $\varepsilon'(\omega)$ values increases. This behavior can be explained by an increase of grain boundary resistance for higher borax concentration which causes high dielectric constant. Because, the frequency dependence of the real part of complex dielectric function implies that the materials investigated have layered structure consists of semiconducting grains followed by insulating grain boundaries. The conductivity for this layered dielectric materials can also be explained by Koop's model [19]. From this point of view, the highest dielectric constant i.e. the highest charge storage capacity has been obtained for 50.0 wt.% Borax doped PT composite.

$\varepsilon'(\omega) = f(\omega)$ curves have also been fitted by Origin Lab 2015 graphic program in accordance with Cole-Cole equation given by Eq. (1)

$$\varepsilon'(\omega) = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)\frac{1 + (\omega\tau_0)^{1-\alpha}\sin\frac{1}{2}\alpha\pi}{1 + 2(\omega\tau_0)^{1-\alpha}\sin\frac{1}{2}\alpha\pi + (\omega\tau_0)^{2(1-\alpha)}} \qquad (1)$$

where ε_∞ and ε_s represent the high and low limiting angular frequency dielectric constants, respectively. τ_0 and α also define the relaxation time and absorption coefficient, respectively [20, 21]. The difference between ε_s and ε_∞ identifies the relaxation strength parameter, $\Delta\varepsilon$ (See Eq. (2)). Relaxation strength is considered as a measure of overall polarizability of the dielectric material

$$\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty \tag{2}$$

Absorption coefficient varies between zero and one $(0 < \alpha \leq 1)$. When α equals zero, it corresponds to standard Debye type relaxation. If $\alpha \neq 0$, non-Debye type relaxation is valid [22]. According to Cole-Cole equation given in Eq. (1), the fitting results of $\varepsilon'(\omega) = f(\omega)$ have been listed in Table 1.

Table 1. Absorption coefficient (α), relaxation times (τ_0), the high and low limiting angular frequency dielectric constants (ε_∞ and ε_s), and relaxation strength ($\Delta\varepsilon$) values for pure PT and PT/Borax composites.

Sample	α	τ_0 (s)	ε_s	ε_∞	$\Delta\varepsilon$
PT	0.22286	0.01397	$5.241\text{x}10^6$	21692.829	$5.219\text{x}10^6$
PT / 10.0 wt.% Borax	0.17947	0.00171	$2.093\text{x}10^6$	-4201.448	$2.097\text{x}10^6$
PT / 25.0 wt.% Borax	0.15651	0.00265	$4.137\text{x}10^6$	-1591.336	$4.139\text{x}10^6$
PT / 50.0 wt.% Borax	0.17615	0.00204	$6.511\text{x}10^6$	-3377.254	$6.514\text{x}10^6$

The absorption coefficient values given in Table 1 showed that $0 < \alpha \leq 1$ condition is valid for all samples. Due to this reason, relaxation type of all samples have been considered as non-Debye type. Since all samples exhibit non-Debye type of relaxation; it has been deduced that all electric dipoles in the material do not relax with the same relation time. The high relaxation strength value observed for PT/ 50.0 wt.% Borax composite may be related to the occurrence of very mobile electric dipoles in the sample [23].

The $\varepsilon'' = f(\omega)$ curves given in Figure 4(b) have a characteristic decreasing behavior at low frequency and frequency independent behavior at the high frequency region. This tendency of the curves can be attributed to having high resistivity at low frequency and low resistivity for high frequency regimes [24]. In addition, the lowest dielectric loss at low frequency region has been achieved for 50.0 wt.% borax doped PT composite. From this point of view, it has been revealed that 50.0 wt.% Borax additive has a remarkable effect on the improvement of dielectric properties of PT. In this respect, it has been understood that PT/ 50.0 wt.% Borax composite is a promising material for supercapacitor and memory device applications.

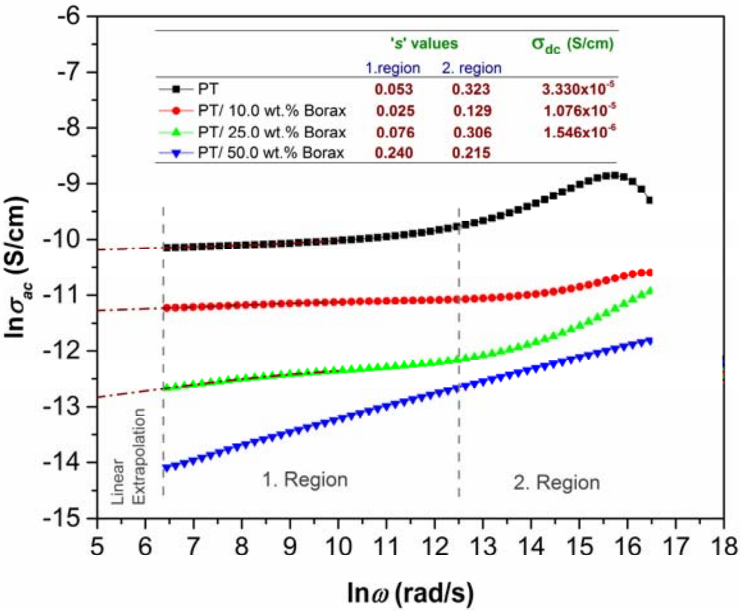

Figure 5. The angular frequency dependence of ac conductivity at natural logarithmic scale

The alternative current (ac) electrical conductivity, σ, has been calculated by

$$\sigma = G\frac{d}{A} \tag{3}$$

where G is the conductance, d is the thickness of the sample and A represents the active electrode area. In general, electrical conductivity of the sample is investigated in terms of dc and ac parts which correspond to frequency independent and dependent regimes:

$$\sigma = \sigma_{dc} + \sigma_{ac} = \sigma_{dc} + B\omega^{s} \tag{4}$$

where B is a constant which describes the strength of polarization and s is called as frequency exponent which defines the pre-dominant conduction mechanism. According to Jonscher's Universal power law [25], s takes values between zero and one.

The angular frequency dependences of electrical conductivity of all samples in natural logarithmic scale have been shown in Figure 5. By taking the slopes of each curve for two different angular frequency regions, frequency exponent values have been determined. (See Table in Figure 5) Except for 50.0 wt.% Borax doped PT composite, other samples exhibit nearly frequency independent i.e. dc conductivity for the first region by referring observation of "s" values which are very close to zero. In this respect, the conductivity values at $\omega = 0$ (i.e. σ_{dc}) have been calculated by making a linear extrapolation. On the other hand, except for 10.0 wt.% Borax doped PT composite, the other samples exhibit frequency dependent conductivity for the high frequency region. Moreover, since all "s" values satisfy the $0 < s < 1$ condition, all samples obey Jonscher's Universal power law. In addition, it can be concluded that the contribution of borax at 50.0 wt.% makes the PT to have a frequency dependent conductivity at the entire measurement frequency range.

4. CONCLUSIONS

In the present work, it has been planned to prepare a new high dielectric constant composite material with low dielectric loss. From this point of view, Polythiophene (PT) and $Na_2B_4O_7$ (Borax) have been chosen as the host polymer and additive, respectively. Including pure PT, three PT/Borax composites with different borax content have been prepared and characterized their surface morphology and chemical structures by Scanning Electron Microscopy (SEM) and Fourier Transformed Infrared (FTIR) Spectroscopy, respectively. The dielectric properties of the samples have been measured within 100Hz-16.5MHz frequency region at room temperature. It has been determined that, when borax content in PT composites approaches a critical concentration (50.0 wt.%) the dielectric constant value increases and dielectric loss decreases at low frequency. In this context, it has been concluded that borax doping with high concentrations can be considered as an effective and cheap tool for improvement the dielectric properties of PT for various microelectronic applications such as capacitor, memory devices, MOS devices etc. In addition, it has been revealed that borax additive does not change the dielectric relaxation type of PT even at very high borax content but also lowers the ac conductivity values at low frequency for 50.0 wt.% borax doping.

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