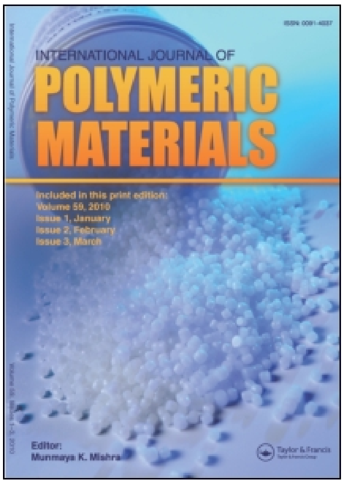

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Dielectric Relaxation and Electrical Conductivity Study in Thiourea-Doped Poly (Vinyl Alcohol)

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Dielectric Relaxation and Electrical Conductivity Study in Thiourea-Doped Poly (Vinyl Alcohol)

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FT-IR, UV-spectroscopy and X-ray diffraction of thiourea-Poly (vinyl alcohol) (PVA) complexes have been investigated. It was observed that thiourea affected the structure of PVA. X-ray study revealed that as the thiourea salt increases the crystallinity of PVA increases. The dielectric properties of thiourea-PVA complexes were investigated in the frequency range 0.2 to 100 kHz and the temperature range 293 to 433 K. All samples are characterized by high values of dielectric permittivity at low frequencies and high temperatures. The results are discussed in terms of interfacial Maxwell-Wagner-Sillars (MWS) polarization and space-charge polarization. Different relaxation modes, *i.e.*, β and α-relaxations have been observed in pure PVA. AC conductivity measurements of samples showed that the hopping conduction mechanism dominates at low temperature region, from room temperature to the glass transition temperature.

Keywords: Thiourea (PVA) dielectric; Electric conductivity

INTRODUCTION

Over the past several years the use of polymers in the electrical industry has increased remarkably. Polymer complexes represent a promising field of research and draw interest by consumers and producers of plastics. Attention has been given to polymer-salt complexes that are formed by polymers containing functional groups with dissolved salts, not only from a purely scientific reason but also

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because of their possible application in microelectronics, solid state batteries, fuel cells, memory devices, display panels and microwave technologies [1]. Within this class of materials, proton conducting polymer complexes have generally found to exhibit higher room temperature conductivity in comparison to alkali salt doped complexes [2].

A number of proton conducting polymeric complexes have been investigated. Among these materials, acid-PVA complexes have shown better room temperature conductivity [3]. On the other hand, Shukla and Agrowal have reported amonium thiouyanate doped-PVA complexes with high room temperature conductivity [4]. The dielectric properties of flexible polar polymers, such as PVA, depend on the position and direction of the dipolar group with respect to the chain backbone. Two main kinds of relaxation are generally observed in this tipe of polymer. A high temperature relaxation (α) associated with the chain backbone motion, and a low temperature relaxation (β) which originates from side group motions [5].

The dielectric investigations account for the dispersion behaviour associated with the molecular configuration and its ordering, which in turn affects the conductivity of the system. Moreover, careful study of the dielectric relaxation process is an important means of establishing knowledge about the frequency dependence of conductivity and dielectric response. Taking into consideration the above facts, it was considered interesting to examine the dielectric response of thiourea-PVA complexes. This paper presents results of an investigation of dielectric behaviour and conductivity of PVA complexed with thiourea over the frequency range from 0.2 Hz to 100 kHz and a temperature region from 293 to 433 K. It is hoped that this investigation will be helpful in providing a better understanding of the dependence of AC conductivity and dielectric relaxation behaviour on the composition and temperature of the complex.

MATERIALS AND EXPERIMENTAL WORK

The materials used in this work are poly(vinyl alcohol) (PVA), $M_w = 72000$, (Merck, Germany) and thiourea salt after recrystallization, $M_w = 76.12$, (El-Nasr Co., Egypt). Films of salt-containing PVA were prepared by dissolving them in distilled water at T = 343 K for about 10 hours. The solution was continuously stirred by means of a magnetic stirrer for about one hour to ensure homogeneous mixture. To prepare the samples for electrical measurements, the mixture was then cast onto a glass substrate in an oven at T = 418 K for several days. The thickness of the samples ranged from 40 to 60 µm, and was determined by using a digital micrometer (Mitutoyo No: 293-521-30, Japan). Carbon paste was used as a conducting electrode (Kontact-chemie, Germany). Measurements were carried out on pure PVA, thiourea, 0.7 wt% (low doped sample) and 40 wt% (high doped sample).

UV-absorption spectra were obtained in the range from 200 to 450 nm using UV/VIS Unicam, Mattson, UK. FT-IR was performed for the samples in the range from 200 to 4000 cm^{-1} by using FT-IR spectroscopy, Mattson, UK. X-ray diffraction spectra (WAXD) have been taken by using a Philips PW 1729 x-ray diffraction instrument (Cu K_{α}, 40 kV, 20 mA).

Dielectric measurements were carried out in a frequency range from 0.2 Hz to 100 kHz, by using Stanford Research Systems, SR830 Lock-in amplifier. The measured temperature range was from 293 to 433 K. The temperature was controlled by using a temperature controller model 89000-15, Digi Sence, Cole-Parmer, USA. All the measurements were done in an evacuated system ($\sim 10^{-3}$ Torr) to eliminate the effect of moisture. A suitable standard resistance was used to avoid stray capacitance effect. The applied voltage (V_{rms}) was 0.05 V.

RESULTS AND DISCUSSION

Sample Characterization

Figure 1 displays FT-IR spectra of the samples under investigation. The main characteristic bands of pure PVA (Fig. 1a) are observed at 1540 cm^{-1} (NHCO), 1720 cm^{-1} (C=O) and strong and broad band at 3500–3100 cm^{-1} (OH) intermolecular hydrogen bonded. The bands at 1330, 1250 and 1180 are due to the interaction between O-H bending and C-O stretching. On the other hand, thiourea salt (Fig. 1b) has been characterized by many bands, such as 700–600 cm^{-1} (N-H out of plane bending), 1150–1050 and 1570–1420 cm^{-1} (C=S

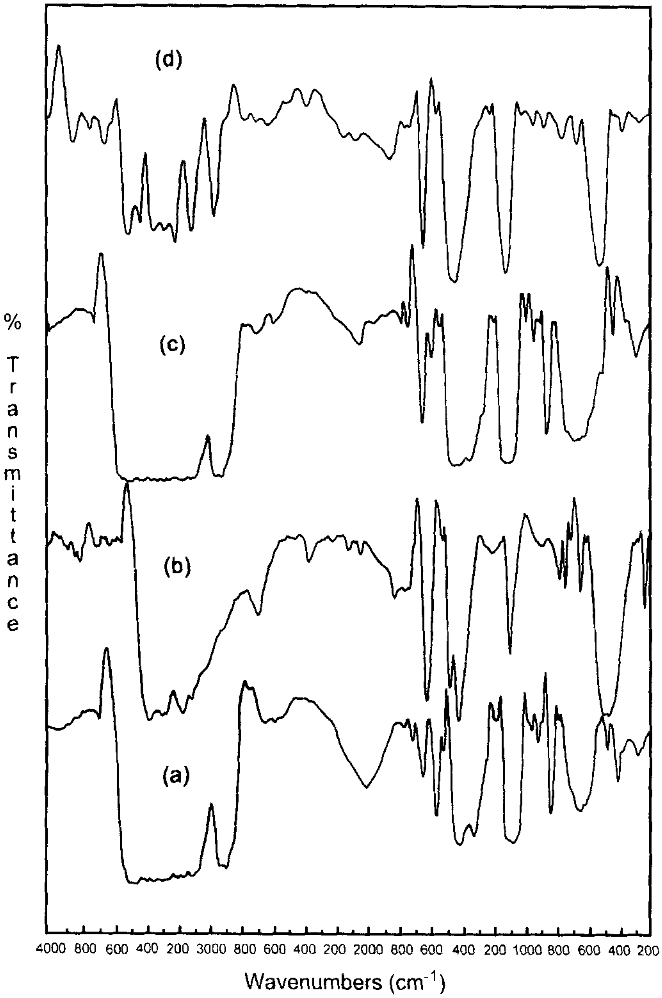

FIGURE 1 FT-IR spectra of (a) pure PVA, (b) pure thiourea, (c) low doped sample and (d) high doped sample.

linked to nitrogen), 1425 cm^{-1} (C-N stretching), 1600 cm^{-1} (N-H amide) and 3300 – 3247 cm^{-1} (N-H stretching). Several other bands in the 1563 to 700 cm^{-1} range can be attributed to vibrations involving interaction between C=S stretching and C-N stretching [6]. On doping, some bands of pure PVA has been affected such as, 1725, 1660, 1340 and 980 cm^{-1} (Fig. 1 c, d).

Figure 2 represents the UV spectra of pure PVA, pure thiourea and doped PVA. Three bands characterize the spectrum of pure PVA at 226, 283 and 330 nm, as shown in Figure 2a. The band at 283 nm is attributed to the absorption of the carbonyl groups. Yamaguchi and Moroso *et al.*, reported absorption bands at 230 and 283 nm and assigned them to the existence of carbonyl groups associated with the ethylenic unsaturation of the type $\text{-CO-(C}=\text{C)-}$ and $\text{CO-(C}=\text{C)}_2\text{-}$, respectively [7, 8]. The band at 330 nm was assigned to the appearance of the $\text{-CO-(C}=\text{C)}_3$-groups. On the other hand, three bands at 268, 327 and 354 nm have characterized thiourea salt. The band at 286 nm could be attributed to $n \rightarrow \pi^*$ transition. This band has been observed as a shoulder shown in the inset of Figure 2. The other bands are due to $n \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ transitions of the thiocarbonyl group [9]. Moreover, a new band located at about 270 nm is to be seen in the spectrum of PVA-thiourea complex, as shown in Figure 2c.

X-ray diffraction patterns of pure and doped PVA are illustrated in Figure 3. As seen from the Figure, pure PVA is characterized by broad

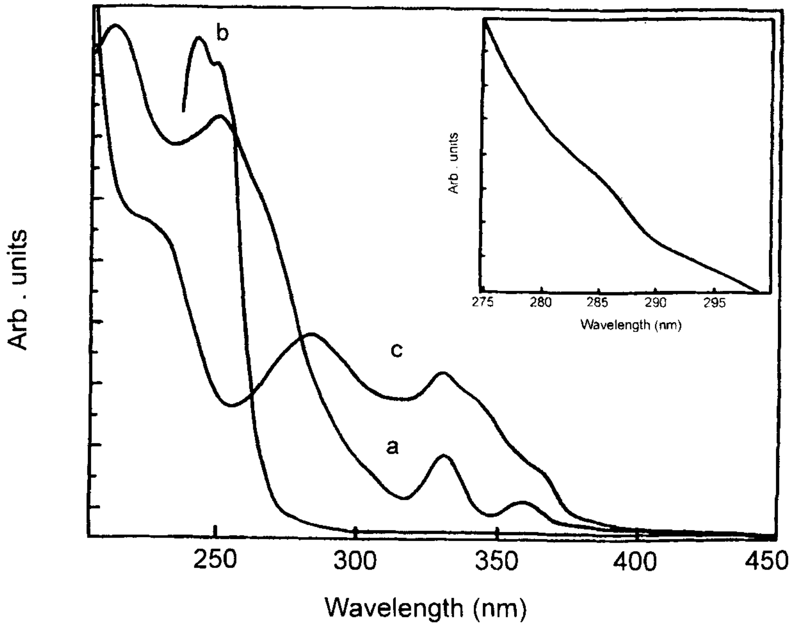

FIGURE 2 UV spectra of (a) pure PVA, (b) pure thiourea, (c) highly doped sample.

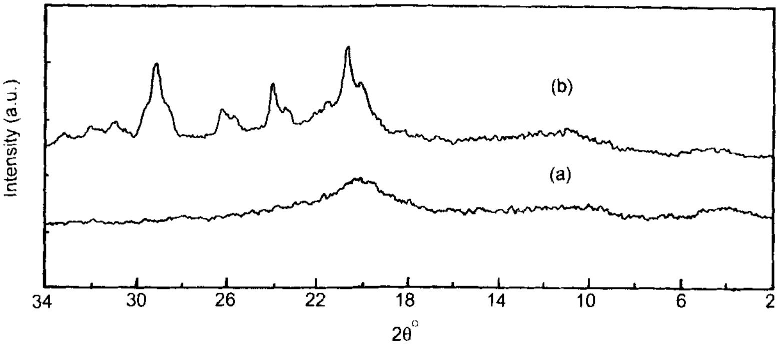

FIGURE 3 X-ray diffraction patterns of (a) pure PVA and (b) high doped sample.

reflection at 2θ ~ 20°, This pattern is associated with the amorphous nature of the sample. On the other hand, the PVA-thiourea complex spectrum showed many reflections at 2θ ~ 20.5, 24 and 29°. The sharp and broad reflection indicates semicrystallinity of the doped sample [10].

Dielectric Measurements

Figure 4 displays the dielectric permittivity (ε′) spectra for pure PVA, thiourea and blended PVA, at different temperatures in the frequency range from 0.2 Hz to 100 kHz, respectively. Generally, a decrease in dielectric permittivity with increase of frequency was observed. This decrease is rapid at lower frequencies and slower at higher frequencies. Figure 4 is characterized by high values of (ε′) at low frequencies and high temperatures. The high values of (ε′) at low frequency and high temperatures may be attributed to free charge building up at the interfaces within the bulk of the sample (interfacial or Maxwell-Wagner-Sillars (MWS) polarization) and at the interface between the sample and the electrodes (space-charge polarization) [5, 11]. Naturally a semicrystalline polymer contains two phases. The amorphous phase will give rise to higher mobilities than the crystalline phase. If the amorphous phase contains sufficiently large number of conducting species, interfacial polarization results. It is generally manifest by the presence of a large loss peak. The phenomenon is due to the presence of two phases, one of much higher conductivity than the other.

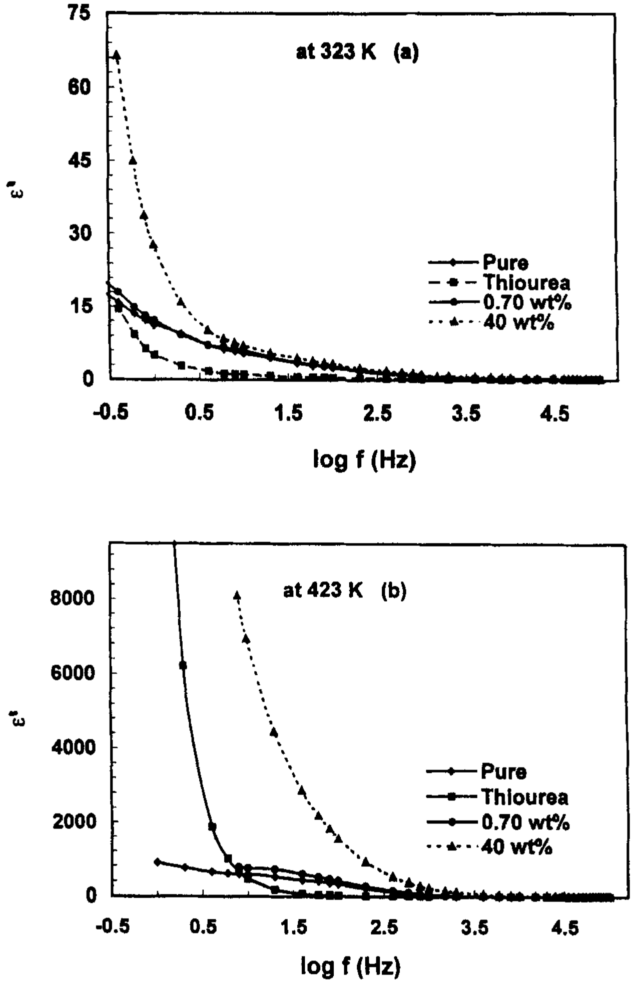

FIGURE 4 Dielectric permittivity (ε') as function of frequency measured for all samples (a) at T = 323 K and (b) at T = 423 K.

Therefore, contribution of interfacial MWS polarization may be due to the inhomogeneous nature of the samples (thiourea and PVA) [12].

For very low frequencies there is sufficient time for the charges to move over macroscopic distances and to build up at the interfaces between the sample and the electrodes within half cycle at the applied

AC field. This effect results in very high values of the effective dielectric permittivity (ε') (space charge polarization, macropolarization of ions in a finite dielectric layer) [5, 13]. At higher frequencies there is practically no time for buildup of the charges at the sample-electrode interfaces, but only for the transport of the charges over microscopic dimensions and their buildup at the boundaries of conducting species in the material (MWS) polarization. At even higher frequencies the charges cannot follow the changes in the electric field and only bulk polarization mechanisms characteristic of the molecular structure (α and β process) contribute to the electric polarization and thus to (ε') [14]. In addition, the highly doped sample is characterized by very high dielectric constant value. This value could be attributed to the presence of semiconducting grains (thiourea) dispersed in insulating grain boundaries (polymer matrix). This gives rise to barriers at grain – grain

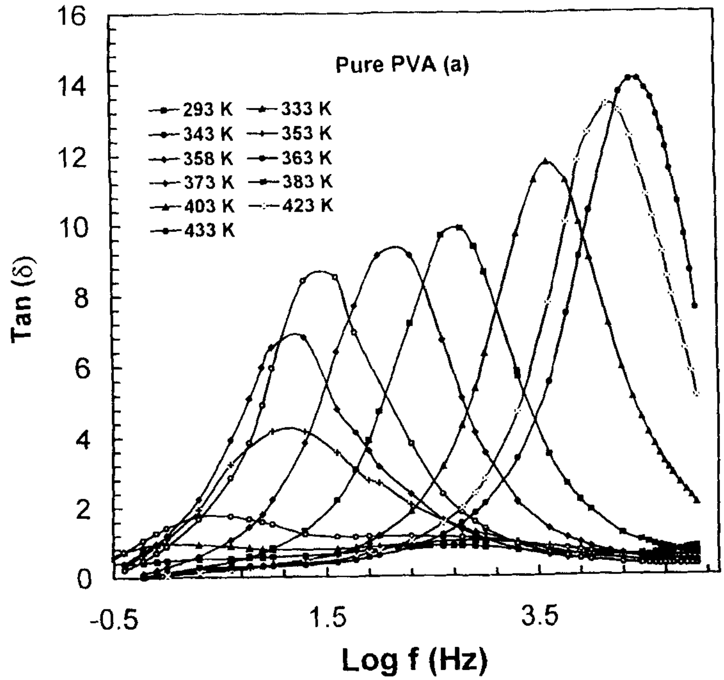

FIGURE 5 Tangent dielectric loss (tan δ) as function of frequency measured (a) Pure PVA, (b) at T = 423 K for all samples and (c) high doped sample.

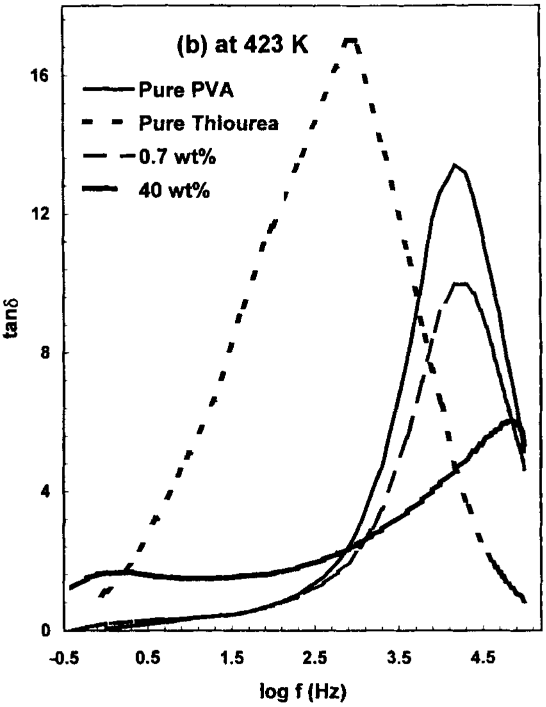

FIGURE 5 (Continued).

boundary interfaces, which impart a very high value of dielectric constant to the resulting polymer complex. This forms the basis of manufacturing barrier layer capacitors [15, 16].

Figure 5 shows the dielectric loss tangent of pure PVA, thiourea and doped PVA samples at different temperatures. Firstly, for pure PVA, we can clearly distinguish two different temperature regions: at lower temperatures (293–363 K) the peaks are broad and have low amplitude, whereas, at higher temperatures (373–433 K) they are narrow with higher amplitude, as shown in Figure 5a. The relatively low doped sample has similar spectra (figure not shown). In this sample, the narrower region started at T = 363 K. Whereas, the highly doped sample showed broad spectra, *i.e.*, every spectrum is characterized by many peaks. The marked broadening of loss curves at low temperatures suggests that the motions are more complex and possibly correspond to two components. The first is a high frequency

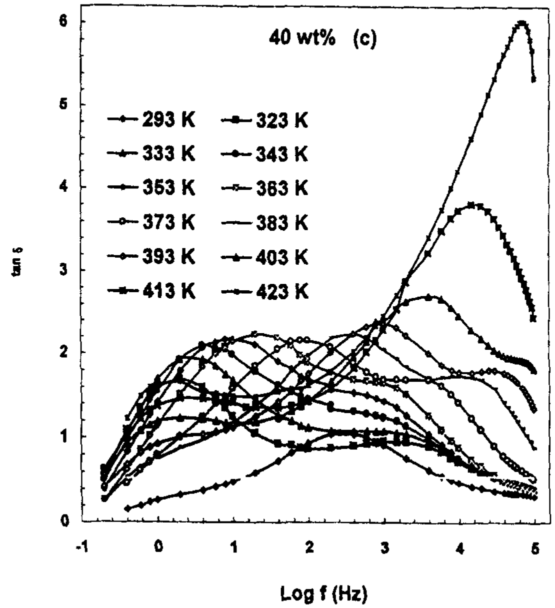

FIGURE 5 (Continued).

component involving the motions of the side groups of the polymer together with the local motion of the salt molecules, *i.e.*, β-relaxation [17]. These processes do not relax all the mean square dipole moments of these dipolar units, so the remainder are relaxed by a second, low frequency process whose mechanism will resemble that for α- process of other amorphous polymers such as poly (vinyl acetate) and poly (ethylene terephthalate) [14]. Moreover, in semicrystalline polymers, the loss curves due to the micro-Brownian motion of chain molecules in an amorphous phase show a remarkable broadening as the temperature is reduced to the vicinity of glass transition, T_g, as shown in Figure 5c. Moreover, on doping, a shift in the peak position has been observed. This shift could be attributed to hindering of the internal rotation of the side groups by hydrogen bonding [17].

The values of the characteristic relaxation time (τ) of all samples, were determined from the peak frequency (f_m) in the tan δ against log f plots at different temperatures, $\omega\tau = 1$, where ω is the angular frequency equal to $2\pi f_m$, where f_m being the frequency (corresponding to the peak) in Hz. Hence, the following formula was used to estimate the values of τ

$$\tau = 1/2\pi f_m \tag{1}$$

Plots of ln τ against 1/T for all samples are shown in Figure 6. These plots are linear, indicating that τ obeys the Arrhenius relationship

$$\tau = \tau_0 \exp(E_a/kT) \tag{2}$$

where τ_0, E_a and k are defined as the pre-exponential factor, the activation energy and Boltzmann's constant, respectively. The activation energy values were calculated and the results revealed that, as the thiourea concentration increased, the activation energy increased. The values of activation energies were 1.3, 1.37 and 1.57 eV for pure PVA, low and high doped samples, respectively. In addition, the values of relaxation time are listed in Table I. Hence, we can say that the broad asymmetric loss curves and the relatively high activation energy are

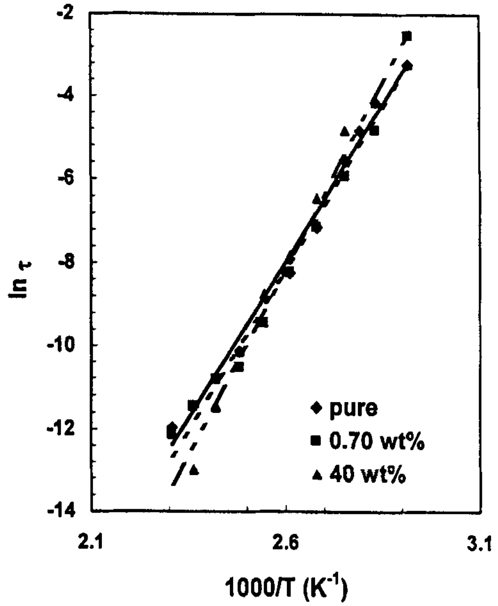

FIGURE 6 Arrhenius plots of (a) pure PVA, (b) low doped sample and (c) high doped sample.

TABLE I Parameters of the dielectric relaxation of all samples

T (K)	*Pure PVA* τ (*sec*), n, W_m (eV)	0.7 *wt*% τ (*sec*), n, W_m (eV)	40 *wt*% τ (*sec*), n, W_m (eV)	*Thiourea* τ (*sec*), n, W_m (eV)
293	5.30×10^{-4}, 0.82, 0.85	7.96×10^{-2}, 0.55, 0.34	7.96×10^{-5}, 0.55, 0.33	–
323	7.90×10^{-4}, 0.64, 0.47	7.96×10^{-2}, 0.52, 0.35	7.96×10^{-2}, 0.48, 0.32	1.59×10^{-1}, 0.752, 0.67
333	1.59×10^{-1}, 0.74, 0.68	1.59×10^{-1}, 0.51, 0.35	7.96×10^{-2}, 0.47, 0.33	–
343	3.90×10^{-2}, 0.71, 0.62	7.96×10^{-2}, 0.53, 0.38	3.98×10^{-2}, 0.46, 0.33	–
353	1.50×10^{-2}, 0.67, 0.57	7.96×10^{-3}, 0.45, 0.33	1.59×10^{-2}, 0.43, 0.32	7.96×10^{-5}, 0.488, 0.36
358	7.90×10^{-3}, 0.63, 0.51	–	–	–
363	3.90×10^{-3}, 0.60, 0.47	2.60×10^{-3}, 0.43, 0.33	7.96×10^{-3}, 0.36, 0.29	–
373	5.30×10^{-4}, 0.58, 0.46	7.96×10^{-4}, 0.41, 0.33	1.59×10^{-3}, 0.30, 0.27	–
383	2.60×10^{-4}, 0.38, 0.32	2.60×10^{-4}, 0.23, 0.25	3.98×10^{-4}, 0.27, 0.27	7.96×10^{-5}, 0.030, 0.20
393	–	7.96×10^{-5}, 0.07, 0.22	1.59×10^{-4}, 0.27, 0.28	–
403	3.98×10^{-4}, 0.15, 0.25	2.65×10^{-5}, 0.05, 0.22	3.98×10^{-5}, 0.23, 0.27	–
413	–	1.99×10^{-5}, 0.04, 0.22	1.06×10^{-5}, 0.17, 0.26	7.96×10^{-5}, 0.004, 0.21
423	1.06×10^{-5}, 0.04, 0.23	1.06×10^{-5}, 0.04, 0.23	2.27×10^{-6}, 0.15, 0.25	–
433	6.36×10^{-6}, 0.02, 0.22	5.30×10^{-6}, 0.03, 0.23	–	–

strongly indicative of cooperative relaxation [18]. In this mechanism it is envisaged that a dipole may reorientate only with the cooperation of a large region of surrounding molecules. This type of process, which may be observed for amorphous polymers and simple molecular glasses, generally occurs at or slightly above the glass transition temperature, T_g.

Figure 7 shows the variation of ε'' as a function of temperature at fixed frequencies, for pure PVA sample. Existence of three peaks have characterized this behaviour. It was observed that these peaks are frequency dependent. The first one is observed at lower temperature and corresponds to local relaxation process, *i.e.*, β-relaxation. This low-temperature peak may be attributed to the carbonyl local conformational motion in the chain. The second one is related to the glass-rubber transition of the amorphous phase, where its position is located around the glass transition temperature of PVA ($T_g = 358$ K) [19]. It is attributed to large-scale conformational rearrangements of the main chains in the amorphous region, *i.e.*, α-relaxation.

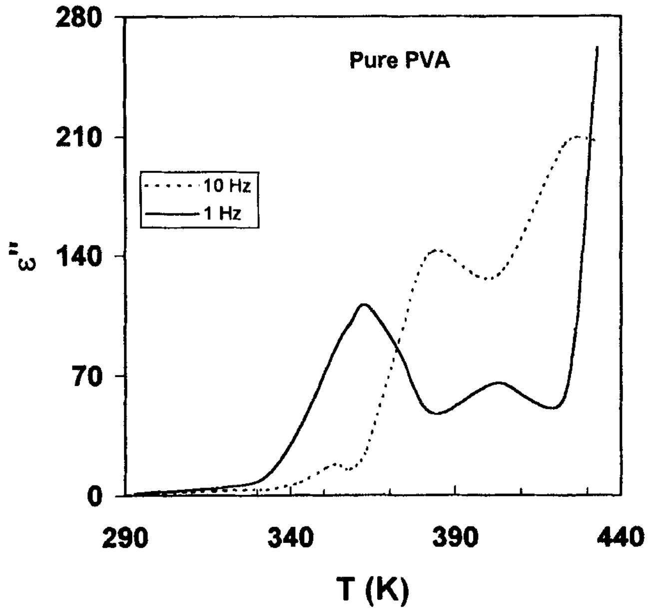

FIGURE 7 Isochronal plot of (ε'') *versus* temperature T at different frequencies, (a) at 1 Hz and (b) at 10 Hz.

Electrical Conductivity Measurements

The dependence of the conductivity on frequency at fixed temperatures is shown in Figure 8. As can be seen, firstly for pure PVA, at low temperatures the AC conductivity increases with frequency, whereas at temperatures higher than about T ~ 393 K, a plateau is observed, namely σ is approximately independent of frequency in a frequency region which extends to higher frequencies with increasing temperature. The conductivity values at the plateau increase with increasing temperature. Similar behaviour has been observed in the relatively low doped sample (figure not shown), the plateau region started at T ~ 403 K. However, higher concentration of salts and its distribution throughout the polymer matrix will change the local electric field and, therefore, the electrical properties as shown in Figure 8b [20]. Hence, the plateau region has disappeared for highly doped sample. Moreover, the general behaviour is that of the universal power

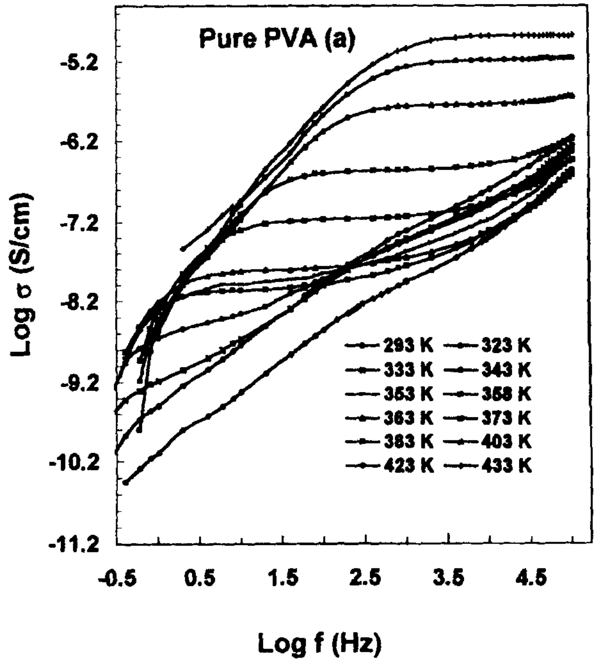

FIGURE 8 Plots of log σ *versus* log f at different temperature for the samples (a) pure PVA and (b) highly doped sample.

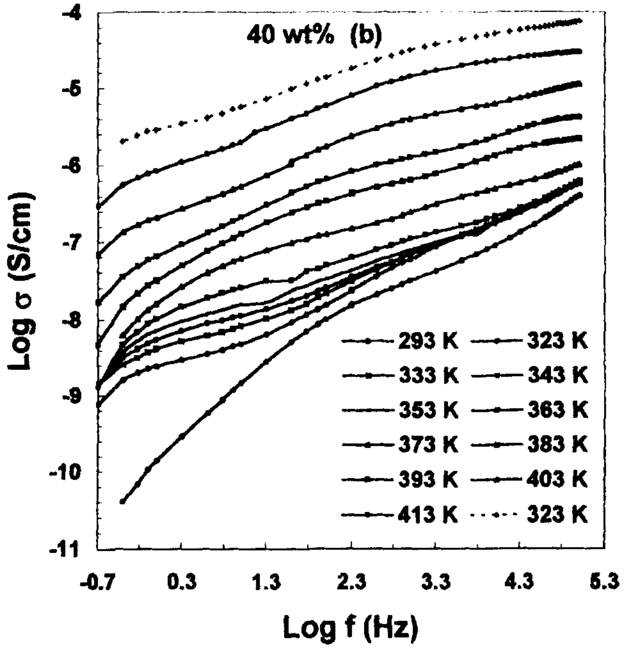

FIGURE 8 (Continued).

law [21, 22]:

$$\sigma = \sigma_0 + A\varpi^n \tag{3}$$

where σ is the real part of AC conductivity, σ_0 in most cases is found to be temperature dependent only, while in this case it depends on both the temperature and the frequency. A is a constant depending on temperature and n is an exponent. Many publications in the polymer field have presented results qualitatively similar to such behaviour, where electronic and/or ionic hopping models were taken into account [23, 24]. It was observed that, Eq. (3) could not be fitted successfully to the experimental data of Figure 8 over the whole frequency range. From the graph, the values of n has been evaluated from the experimental $\log\sigma$ *vs.* $\log f$ curves at high frequency range as a function of temperatures and are listed in Table I.

The contribution to conductivity, from the carrier movement (carrier movement between and within the defect wells) at different temperatures are different, thereby resulting in the decrease of n with increase of temperature. Hence, it was observed that n decreases slightly at low temperature and sharply at high temperature. In addition, the decrease of the exponent n with increasing temperature because the measured $\sigma(\omega)$ conductivity at lower frequencies increases more rapidly with temperature. From Table I, we can say that from room temperature to nearly 358 K region, the values of n in the range from 0.85 to 0.6 points to Jonscher's "universal dielectric response" in the regime of hopping localized charge carriers [25]. The variation in the exponent n reflects the change in the nature of the conduction process with change in temperature and composition. In addition, n is predicted to have temperature dependence and the magnitude of n at any temperature is determined by the binding energy (W_m) of the charge carrier by $W_m = 6kT/(1-n)$ [26, 27]. W_m is the energy difference between the ground state of the potential well, and the ionized state (*i.e.*, the charge carrier localized state). The values of all parameters

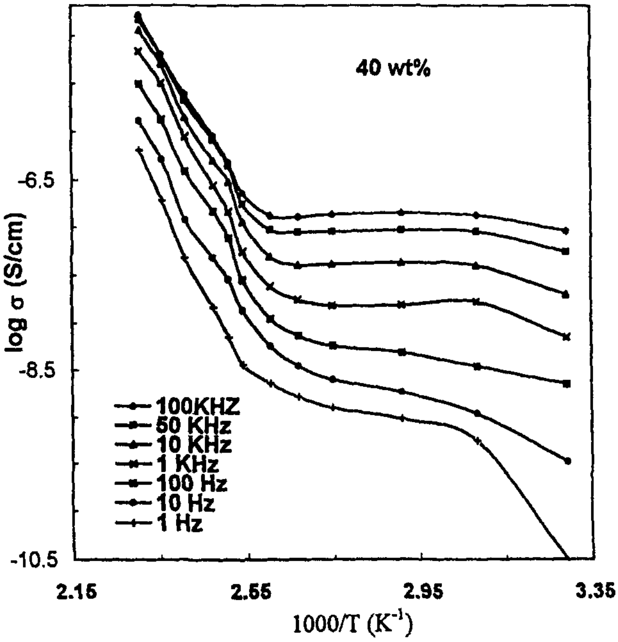

FIGURE 9 Plots of logσ *versus* 1000/T for highly doped sample at different frequencies.

TABLE II The values of activation energies for all samples at different frequencies according to Eq. (4)

f(HZ)	*Pure PVA* E_a *(eV)*	0.7 *wt%* E_a *(eV)*	40 *wt%* E_a *(eV)*	*Thiourea* E_a *(eV)*
1 Hz	0.31	0.11	0.82	0.55
10 Hz	0.23	0.06	0.74	0.54
100 Hz	1.54	0.26	0.71	0.54
1 kHz	1.12	0.51	0.71	0.53
10 kHz	1.01	0.51	0.69	0.48
50 kHz	0.82	0.488	0.65	0.40
100 kHz	0.69	0.47	0.63	0.34

characterizing the samples such as τ, n and W_m are estimated and listed in Table I.

In order to obtain a better insight into the electrical transport in the polymer-complex, it is rewarding to analyse the AC properties over a large range of frequencies. These AC measurements are expected to provide information about the conduction mechanism below and above the glass transition temperature. Figure 9 illustrates the Arrhenius plot $\log\sigma$ *vs.* 1/T, at different frequencies, according to the following equation

$$\sigma = \sigma_0 \exp(-E_a/kT) \tag{4}$$

The highly doped sample was taken as a representative curve. Two regions are observed in these plots: (i) a low-temperature region where the slope is small and (ii) a high-temperature region with steeper slope. The results in this Figure 9 suggest that there is a change in the transport mechanism in the temperature region of the glass transition temperature at about T ~ 363 K. It was observed that, as the frequency increases the activation energy decreased. These values of activation energy are calculated as a function of frequency and listed in Table II.

CONCLUSION

X-ray study revealed that thiourea salt increased the crystillinity of PVA. The dielectric properties of thiourea-PVA complexes have been studied in a wide frequency range from 0.2 Hz to 100 kHz and temperature (293 to 433 K). The experimental data were presented in isothermal and isochronal plots to stress special aspects of the dielectric behaviour. It was found that the dielectric constant decreases with an increase of frequency for all samples. This agrees with the Maxwell-Wagner double layer model. The values of the exponent n, suggest that the hopping mechanism dominates at lower temperature (from room temperature to nearly glass transition temperature). Different modes of relaxation such as β and α-relaxations have been obtained in the isochronal plot. The Arrhenius plot of the AC conductivity at the different frequency measurements, suggests that there is a change in the conductivity mechanism around the region of the glass transition temperature.

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