

Dielectric Properties of Polyethylene Oxide Doped with NH_4I Salt

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Dielectric parameters were studied over a frequency range from 10 Hz to 335 kHz at room temperature as a function of frequency and salt concentration. Permittivity (ϵ') and dielectric loss (ϵ'') data were fitted in the frequency domain using Yan and Rhodes model in order to estimate the relaxation times for PEO electrolytes. Due to the excellent fitting obtained using this model, PEO/ NH_4I electrolytes can be presented in equivalent circuit as RC in parallel circuits connected in series. Addition of NH_4I salt to PEO host, however, will increase AC conductivity, permittivity and dielectric loss while shortening relaxation time and reduces the melting temperature of PEO electrolytes. This study shows that the relaxation process of these electrolytes is due to viscoelastic relaxation or non-Debye relaxation with two values of relaxation time.

KEY WORDS: Polyethylene Oxide / NH_4I Salt / Electrolytes / Dielectric Relaxation / Relaxation Time / Melting Behavior /

Polymer electrolytes such as PEO play an important role in the development of new energy sources, like solid state batteries, photo-electrochemical solar cells, fuel cells, electrochromic displays and sensors. Up to now, the desired value of electrical conductivity (10^{-3} S/cm) at ambient temperature has not been attained. At the same time, obtaining high ionic conductivity at ambient temperature becomes crucial for the realization of these technological applications.^{1,2} Extensive theoretical and experimental research is necessary in order to explain the theory of ionic conductivity in polymer/salt electrolytes, because this theory is yet in its infancy due to the complex structural nature of polymers. In general, experimental and theoretical research shows that the enhancement of ionic conductivity in polymer/salt electrolytes depend on polymer type, salt type, morphology, nature and size of fillers, degree of crystallinity . . . etc.³⁻⁵ Also, several research works have demonstrated that the addition of an optimum amount of an electrolytic filler greatly enhances the ionic conductivity and affects the bulk properties of the electrolytes.⁵⁻¹⁰ Interesting effects were observed by us on the optoelectrical properties of PS/alum composites.⁵ On the other hand, the dielectric spectra and relaxation processes of electrolyte polymers and polymer electrolytes have been studied before but the dielectric properties especially the relaxation process and the estimation of relaxation time using Yan and Rhodes model for PEO/ NH_4I electrolytes have not been previously reported.¹⁻¹³ When the dielectric material is exposed to an alternating electric field that is generated by applying a sinusoidal voltage the displacement polarization leads to electric oscillations. The orientational polarization is not a resonant process, because the molecular dipoles have inertia. The response of the orientational polarization to a change of the electric field is therefore always retarded. This process is called "dielectric relaxation." The characteristic time constant of such a relaxation process — this is the time for

reaching new equilibrium after changing the excitation is called the relaxation time. It is strongly temperature dependent, because it is closely related to the viscosity of the material. At room temperature, the relaxation times of the orientational polarization in polymers, can reach a few seconds or even hours, days and years, depending on temperature. Real dielectrics also contain charge carriers which can be moved by electric forces between potential walls, formed by non-ohmic or blocking contacts or internal boundaries, *e.g.*, between crystalline and amorphous phases in a semicrystalline material. This leads to a space charge polarization (electrode polarization or Maxwell-Wagner polarization, respectively), which on the other hand is limited by diffusion. These processes are also relaxation processes, and are called charge-carrier relaxations (or conductivity relaxations). In general, dielectric spectroscopy is a powerful tool for the electrical characterization of polymer materials, because it is sensitive to dipolar species as well as localized charges or ions in a material, it determines their strength, their kinetics and their interactions.^{10,14} Additionally, the relaxation time τ of a single Debye relaxation can be determined from both quantities ϵ' and ϵ'' . The physical background is that in the time domain there is of course exactly one response function, consequently, both quantities contain the full information. The relaxation time τ can be determined from the position of the loss maximum or the turning point of the permittivity curve, respectively. In practice, however, it is often difficult to determine ϵ' and ϵ'' because real dielectric spectra are generally broader than the Debye spectrum and their shape is not predefined.^{10,12} However, one of the common models used to study the dielectric properties of dielectric solid materials is Yan and Rhodes model. They assumed a model of solid with well-conducting grains separated by grain-boundary layers of lower conductivity and these grains have different resistivities and grain-boundaries thickness. The equivalent electrical

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circuit for this model was presented as RC in parallel circuits connected in series. The permittivity, ε , for the Yan and Rhodes model is given as:^{15–17}

$$\varepsilon = \varepsilon_{\infty} + \frac{(\varepsilon_0 - \varepsilon_{\infty})}{n} \sum_{n=1}^n \frac{\alpha_n}{1 + \tau_n^2 \omega^2} \quad (1)$$

where $\sum_{n=1}^n \alpha_n = n$ and ε_{∞} : the value of permittivity at higher frequency range, ε_0 : the value of permittivity at lower frequency range, τ_n : relaxation time, and ω : is the angular frequency.

For polymeric materials, the loss factor term is a combination of two processes: (a) viscoelastic relaxation due to the dipolar relaxation, where these dipoles are permanent dipoles present on the side chains of the polymer backbone and (b) conductivity relaxation, this process due to translational diffusion of ions which causes conduction. McCrum *et al.* found a mathematical procedure in order to resolve the viscoelastic process from the conductivity by taking the inversion value of complex permittivity, ε^* , which is equal to complex electric modulus, M^* :

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

where ε' : permittivity, ε'' : dielectric loss, M' : electric modulus, and M'' : electric loss modulus. Large differences exist between the properties of viscoelastic relaxations and the properties of conductivity relaxations present in the polymers. Viscoelastic relaxations exhibit a distribution of relaxation times, while conductivity relaxations have only single relaxation time and it corresponds to the Debye model.¹⁰

The main aim of present work is to study effect of NH₄I salt doping on the dielectric properties, dielectric relaxation process and melting behavior of PEO polymer. The variation of dielectric parameters (permittivity (ε'), dielectric loss (ε'') and AC conductivity (σ_{AC})) with the applied electric field frequency and salt concentration at room temperature are presented and studied. Determination of relaxation time values using Yan and Rhodes is also reported. Furthermore, McCrum *et al.* mathematical procedure is used in this study in order to resolve the viscoelastic relaxation process from the conductivity relaxation process. Finally, the effect of NH₄I salt doping on the melting behavior of PEO is also studied.

EXPERIMENTAL

Films Preparation

Thin films of Polyethylene oxide (PEO)/NH₄I were prepared by dissolving PEO (Aldrich, M_w 5×10^6) and Ammonium iodide (NH₄I) (Aldrich) in methanol. The solution was mixed for one hour and casted into a stainless-steel ring resting on a teflon substrate. The solvent was evaporated at 30 °C. The prepared samples contain 0, 3, 5 and 8 wt% NH₄I were kept

inside vacuumed dissector. The film thickness was measured by using a ballended micrometer and it was of 0.1 mm.

Dielectric Measurements

Dielectric measurements were carried out using a HP 4194A-impedance analyzer over the frequency range 10 Hz–335 kHz at room temperature. The capacitance “C” and the loss tangent “tan δ ” were obtained directly from the bridge from which the conductivity (σ), permittivity (ε') and dielectric loss (ε'') were calculated. Calibration (short and open) of the impedance analyzer was done before the measurements. Additionally, samples were heated up to 100 °C and slowly cooled to room temperature before each measurement in order to evaporate unexpected water inside sample. Disk shaped specimens were cut from the prepared sample sheets (0, 3, 5, and 8 wt% NH₄I) and placed between the copper plates (10 mm diameter) of a test sample holder placed in a shielded cell designed for this purpose. The two leads of the holder were connected to the terminals of the impedance analyzer.⁵

Differential Scanning Calorimetry (DSC)

The melt behavior of the samples was studied using a Mettler DSC FP85. The DSC experiments were run at a heating rate of 10 °C/min with nitrogen purged at a flow rate of 10 mL/min. The melting temperature of the samples was calibrated by using a standard sample of indium at the same rate. Each sample was carefully prepared and measured out to have approximately the same weight (5 ± 0.2 mg).

RESULTS AND DISCUSSION

Electrical Properties

AC conductivity (σ_{AC}), permittivity (ε'), and dielectric loss (ε''), of the prepared PEO/NH₄I electrolytes with NH₄I concentration 0, 3, 5, and 8 (wt%) were calculated from capacitance “C” and the loss tangent “tan δ ” data obtained from the HP 4194A-impedance analyzer over the frequency range from 10 Hz to 335 kHz at room temperature. The AC conductivity (σ_{AC}), was calculated according the following equation:

$$\sigma_{AC} = \varepsilon'' \omega \varepsilon_0 \quad (3)$$

where: ω : angular frequency and ε_0 : absolute permittivity of free space. The results obtained which are related to ε' , ε'' and σ_{AC} are presented graphically in Figure 1A, 1B and 1C respectively. It is clear that σ_{AC} value for PEO/NH₄I increases by increasing the salt concentration, as shown in Figure 1C. The observed increase in conductivity with salt content is due to :NH₄⁺ migration transporting the oxygen, salt elements and impurities existing in the salt filler. This motion leads to higher electrical conduction in the filled electrolytes. On the other hand, the increase of AC conductivity with frequency, this attributed to the increase of ions and impurities mobilities at higher frequency range.⁵ Also, NH₄I salt enhances the polar character of PEO host as shown in Figure 1A and 1B. Similar effects were observed by other researches in PEO/salt complexes.^{1,2,18–21}

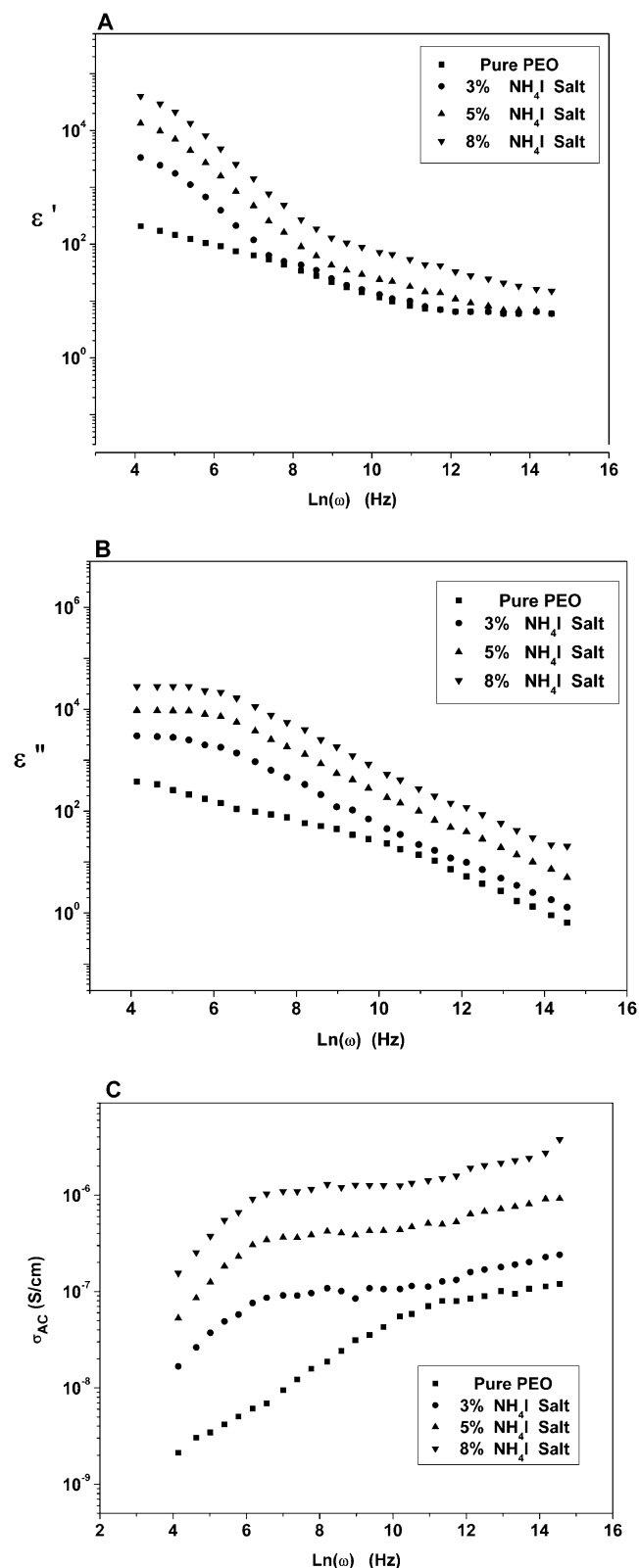


Figure 1. (A) Permittivity, (B) dielectric loss and (C) AC conductivity as a function of frequency and salt concentration for PEO/NH₄I electrolytes.

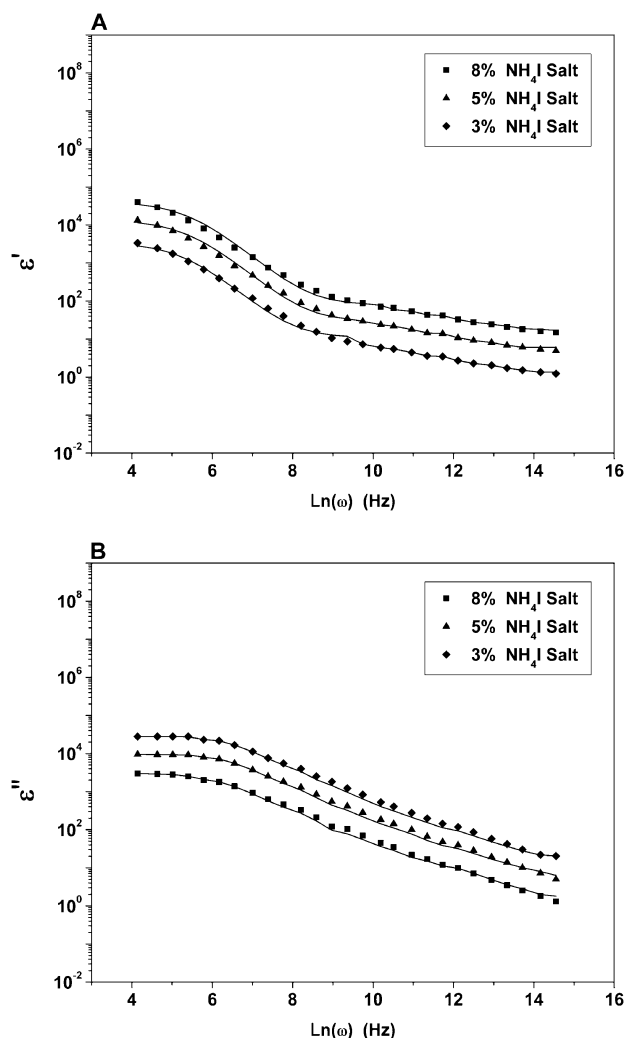


Figure 2. (A) Permittivity and (B) dielectric loss of PEO/NH₄I electrolytes as a function of frequency and NH₄I concentration; for experimental data (symbol curves) and for theoretical data (dark-solid curves).

Dielectric Permittivity and Relaxation Time

Figure 2A shows the permittivity values of PEO/NH₄I electrolytes as a function of frequency and NH₄I concentration. The increasing of permittivity value with salt concentration can be attributed to the reorientation of permanent dipoles, ions diffusions and Maxwell-Wagner polarizations.^{10,11,14}

A computer program was performed in order to determine the best fitting between experimental values of permittivity and dielectric loss for PEO/NH₄I electrolytes and theoretical values obtained from different models commonly used in dielectric researches.^{11,22} The best model found was Yan and Rhodes model.¹⁵⁻¹⁷ From eq 1, the theoretical permittivity data and also dielectric loss data for each composite were determined from the best fitting obtained with experimental data. The obtained results are presented graphically in Figure 2A and 2B respectively. Relaxation parameters obtained from the best fittings were: $n = 2$, $\alpha_1 = 1$ and $\alpha_2 = 1$. The values of ϵ_∞ and ϵ_0 were obtained from experimental data at higher and lower frequency range respectively. The

Table I. Relaxation times for the PEO/NH₄I electrolytes (calculated from ϵ' data)

Samples: NH ₄ I (wt %)	Relaxation time (s)	
	τ_1	τ_2
3	4.40×10^{-3}	8.60×10^{-3}
5	3.80×10^{-3}	8.30×10^{-3}
8	3.70×10^{-3}	8.10×10^{-3}

Table II. Relaxation times for the PEO/NH₄I electrolytes (calculated from ϵ'' data)

Samples: NH ₄ I (wt %)	Relaxation time (s)	
	τ_1	τ_2
3	1.50×10^{-3}	1.30×10^{-3}
5	1.40×10^{-3}	1.00×10^{-3}
8	1.33×10^{-3}	0.95×10^{-3}

relaxation time τ_1 and τ_2 for each electrolytes was estimated by these fittings. The obtained values of relaxation time (τ_1 and τ_2) for each NH₄I concentration are listed in Tables I and II. It is clear that the values of relaxation time for electrolytes slightly decreases with increasing NH₄I concentration. The present work strongly supported our earlier reported data.⁵ In other words, from the assumption suggested by Yan and Rhodes model, we can say that, PEO/NH₄I electrolytes can be presented in equivalent circuit as RC in parallel circuits connected in series.^{5,15,23}

Relaxation Process. Two analysis procedures were followed in order to recognize if that the relaxation process is due to viscoelastic relaxation or due to ionic conductivity relaxation.

Procedure 1. Argand plots of M'' vs. M' can be obtained according to the following equation:

$$\left\{ M' - \frac{(M_U + M_R)}{2} \right\}^2 + (M'')^2 = \left(\frac{M_U - M_R}{2} \right)^2 \quad (4)$$

where M_U and M_R represents electric modulus values at high frequency, unrelaxed state and at low frequency, relaxed state. Mohamed *et al.*¹⁰ showed that, if Argand plot (M'' vs. M') has semicircular behavior (according to eq 4), then the relaxation is due to conductivity relaxation process, if not, then it is due to viscoelastic relaxation. In the present work, the values of M' and M'' were determined for all samples at the domain frequency by substituting both permittivity (ϵ') and dielectric loss (ϵ'') values in eq 2, where:

$$M' = \frac{\epsilon'}{(\epsilon'^2 + \epsilon''^2)}$$

$$M'' = \frac{\epsilon''}{(\epsilon'^2 + \epsilon''^2)}$$

The obtained results are presented graphically in Figure 3 (for pure PEO) and Figure 4 (for the electrolytes). It is clear that for all PEO/NH₄I electrolytes, the plot do not exactly follow semicircular behavior which is mean that in all cases the relaxation process is due to viscoelastic relaxation.¹⁰

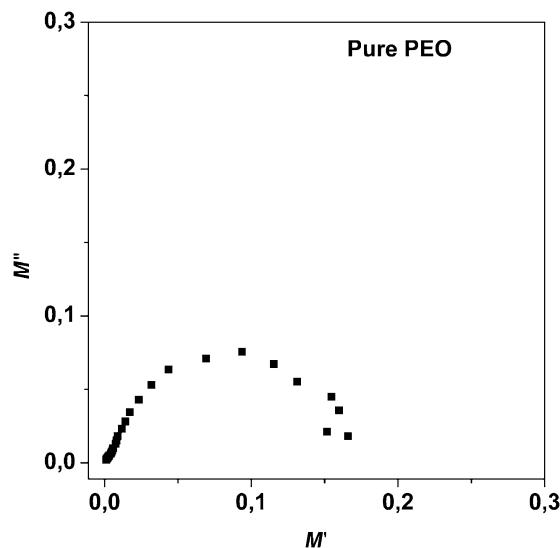


Figure 3. Argand plots of pure PEO.

Procedure 2. Ambrus *et al.*²⁴ assumed that the conduction is purely due to the diffusion of ions and independent of viscoelastic relaxation and they presented the electrical modulus in terms of time, frequency and modulus.

$$M = M_s \left\{ \frac{(\tau_\sigma \omega)^2}{1 + (\tau_\sigma \omega)^2} \right\} + i M_s \left\{ \frac{\tau_\sigma \omega}{1 + (\tau_\sigma \omega)^2} \right\} = M' + i M'' \quad (5)$$

where $M_s = \frac{1}{\epsilon_0}$. τ_σ is the relaxation time.

Mohomed *et al.*¹⁰ and Ambrus *et al.*²⁴ reported that Johari and Pathmanathan, together with others, have stated that conductivity relaxations in ionic conductors exhibit single relaxation times. Starkweather *et al.*²⁵ and Mohamed *et al.*¹⁰ showed that, in case of ionic relaxation, plots of $\log M''$ vs. $\log M'$ vs. \log frequency will reveal slopes of 1 and 2, respectively.

According to the assumptions and results reported by the mentioned authors, in the present work, the values of M' and M'' are presented graphically for 3, 5, and 8 (wt %) NH₄I electrolytes as $\log M''$ vs. \log frequency and $\log M'$ vs. \log frequency. The obtained results are different from those obtained by Starkweather *et al.*²⁵ and Mohamed *et al.*¹⁰ The behavior of curves are different and all slope values are less than 1 for both cases, as shown in Figure 5 and Figure 6 for the 8 (wt %) NH₄I sample. The results obtained from analysis procedures 1 and 2 indicate that, at the domain frequency range, the relaxation process for all PEO/NH₄I electrolytes is due to viscoelastic relaxation process and not due to ionic conductivity relaxation process. In other words, the relaxation process in case of PEO/NH₄I electrolytes is non-Debye relaxation.

Differential Scanning Calorimetry

The DSC melting thermograms of pure PEO, 3%, 5% and 8% NH₄I electrolytes are shown in Figure 7. It can be seen that the melting temperature (T_m) reduces from 65.46 °C (for pure PEO) up to 50.34 °C (for 8% NH₄I) as NH₄I salt increases from

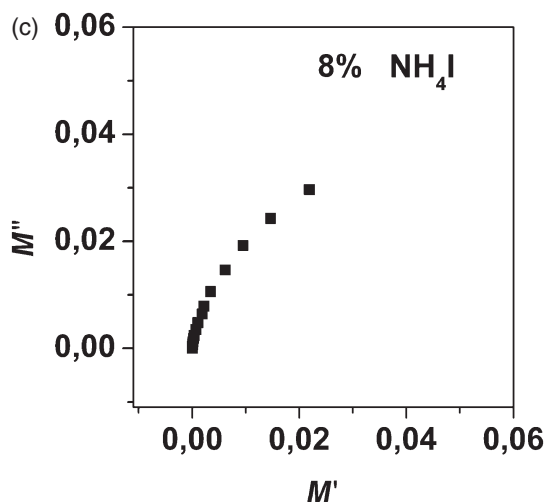
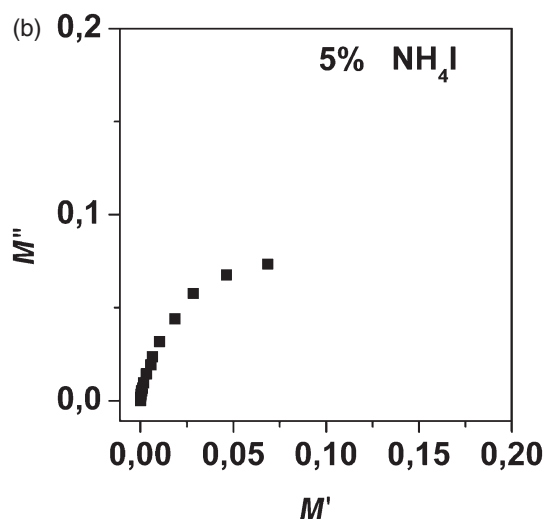
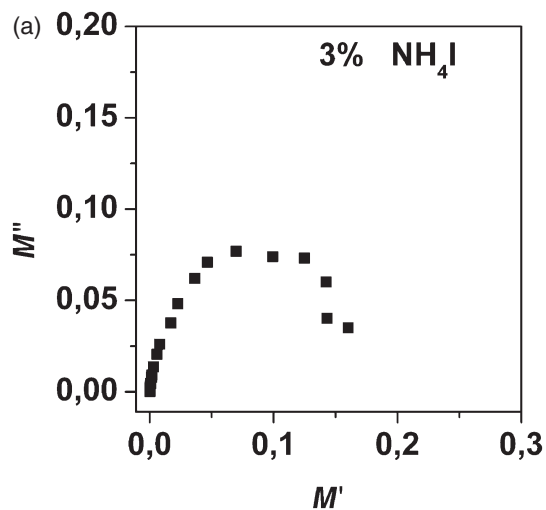


Figure 4. Argand plots of PEO/NH₄I electrolytes.

0% to 8%. (by weight), see Figure 7. Also it can be seen from Figure 7 that addition of the NH₄I, the DSC traces become broader. This is due to the crystal sizes obtained. At higher

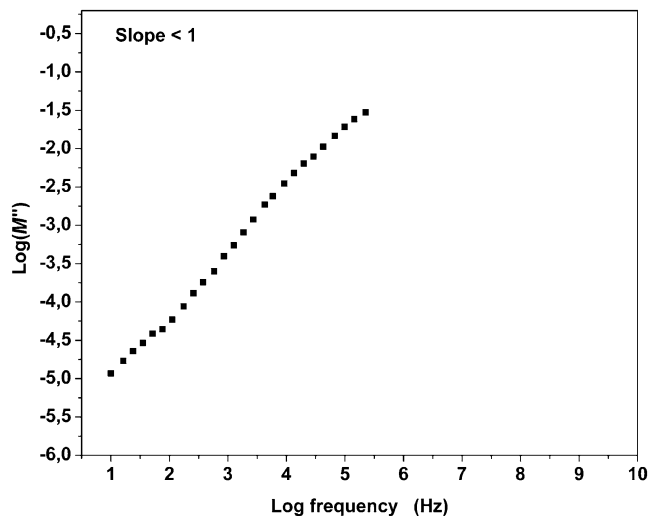


Figure 5. Log M'' vs. Log frequency for the 8 (wt%) NH₄I sample.

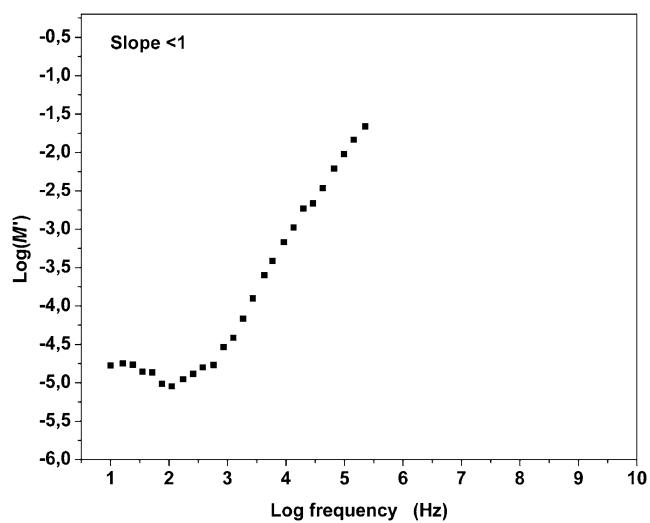


Figure 6. Log M' vs. Log frequency for the 8 (wt%) NH₄I sample.

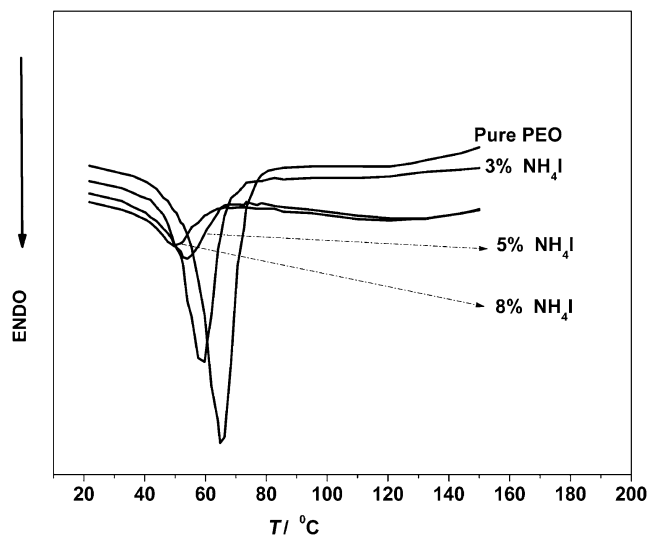


Figure 7. DSC thermogram for PEO/NH₄I electrolytes.

concentration of NH₄I, a lot of PEO crystals with different sizes are formed in the sample. The crystals with smaller size, have lower melting temperature. Therefore, the sample of 8 wt % salt, has a broad melting peak due to the imperfect polymeric crystals, while for pure PEO sample the melting peak is more sharp due to perfect crystals.²⁶

Additionally it is expected in the present work that the physical bond between the PEO chains decreases with increasing NH₄I salt.

CONCLUSIONS

Films of PEO doped with NH₄I salt were prepared. The dielectric properties of these films were investigated at room temperature (above the T_g of PEO) as a function of frequency and salt concentration. AC conductivity of these electrolytes, however, increases with increasing salt concentration. On the other hand, addition of salt to PEO host increases the permittivity values and enhances the polar character of PEO host. Results obtained from Yan and Rhodes model and electric modulus reveals that PEO/NH₄I electrolytes can be presented in equivalent circuit as RC in parallel circuits connected in series and also that the relaxation process occurred in the PEO/NH₄I electrolytes is due to viscoelastic relaxation with two values of relaxation time and consequently this relaxation is non-Debye relaxation. The values of relaxation time decrease with increasing of salt concentration. Finally, addition of NH₄I salt to PEO host decreases the melting temperature and increasing of imperfect polymer crystals.

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