

DIELECTRIC AND THERMAL PROPERTIES OF PEO DOPED WITH CADMIUM CHLORIDE SALT

Jibril Al-Hawarin^c, Ayman S. Ayesh^{a*} and Rami A. Abdel-Rahem^b

^a Physics Department, College of Science, King Faisal University, Al-Ahssa, Kingdom of Saudi Arabia

^b Chemistry Department, College of Science, King Faisal University, Al-Ahssa, Kingdom of Saudi Arabia

^c Chemistry Department, College of Science, Al Hussein Bin Talal University, Maan, Jordan

Abstract The main aim of this research is to investigate the effect of salt concentration on the dielectric properties (AC (σ_{AC}), permittivity (ϵ'), dielectric loss (ϵ''), and dielectric relaxation process) and melting behavior of polyethylene oxide (PEO)/CdCl₂ complexes. The dielectric study was carried out over a frequency range 10–335 kHz and a temperature range 25–45°C. The AC conductivity, permittivity and dielectric loss of the PEO/CdCl₂ complexes increase with increasing salt concentration and temperature. Also, it was found that the addition of CdCl₂ salt to PEO host reduced the melting temperature of PEO host. Dielectric results reveal that the relaxation process of these complexes is due to viscoelastic relaxation or non-Debye relaxation at room temperature. Additionally, it was found that relaxation behavior remained viscoelastic at different temperatures and salt concentrations.

Keywords: Polyethylene oxide; CdCl₂ salt; Dielectric properties; Dielectric relaxation; Relaxation process; Thermal properties.

INTRODUCTION

Polyethylene oxide polymer plays an important role in the development of new energy sources such as; solid state batteries, photo-electrochemical solar cells, fuel cells, electrochromic displays and sensors. At the same time, obtaining high ionic conductivity at ambient temperature becomes crucial for the realization of these technological applications. Up to date, the desired value of electrical conductivity (10^{-3} S/cm) at ambient temperature has not been achieved^[1,2].

The dielectric properties of PEO with various dissolved salts have been widely investigated^[1–4].

Many investigations have reported that the enhancement of ionic conductivity in polymer/salt complexes depends 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 electrolytic filler greatly enhances the ionic conductivity and affects the bulk properties of the complexes^[3, 6–9]. Interesting effects were observed by us on the optoelectrical properties of polystyrene-alum composite^[3]. Although the dielectric spectra and relaxation processes of electrolyte polymers and polymer complexes have been previously investigated, the dielectric relaxation process for PEO doped with CdCl₂ has not been investigated yet^[1, 2, 10–13]. 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

* Corresponding author: Ayman S. Ayesh, E-mail: dr_ayesh67@yahoo.co.uk

Received February 8, 2011; Revised March 14, 2011; Accepted March 22, 2011
doi: 10.1007/s10118-012-1106-6

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 (*i.e.* electrode polarization or Maxwell-Wagner polarization), which on the other hand is limited by diffusion. These processes are also relaxation processes, and are called charge-carrier relaxations (or conductivity relaxations).

Generally, the electrical characterization of polymer materials is performed by the aid of dielectric spectroscopy which is a powerful tool and sensitive tool to dipolar species as well as localized charges or ions in a material^[10–14].

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 the complex permittivity, ε^* which is equal to the complex electric modulus, M^* according to Ref. [12]:

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

where ε' is the permittivity, ε'' is dielectric loss, M' is the electric modulus, and M'' is electric loss modulus. Large differences 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.

Present work focused on the effects of applied electric field frequency, CdCl_2 concentration (by weight) and temperature on the dielectric properties of PEO/ CdCl_2 complexes such as AC conductivity, permittivity, dielectric relaxation process in addition to the effect of salt content on the melting temperature and melting behavior.

EXPERIMENTAL

Films Preparation

Thin films of CdCl_2 -PEO were prepared by dissolving PEO (Aldrich, M.W. 5×10^6) and CdCl_2 salt in methanol. The solution was mixed for one hour and cast into a stainless-steel ring resting on a Teflon substrate. The solvent was evaporated at 30°C. Samples of different concentration were kept inside a dry vacuumed dissector. The prepared films contain 0 wt%, 5 wt% and 8 wt% CdCl_2 . The film thickness (of 0.1 mm) was measured using a ballended micrometer.

Dielectric Measurements

Dielectric measurements were carried out using an HP 4194A-impedance analyzer over the frequency range 10 Hz–335 kHz and temperature range from 25°C to 45°C. Before each measurement, temperature was raised up to 100°C and then slowly cooled to reduce the effect of humidity. The capacitance “C” and the loss tangent “tanδ” 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. Disk shaped specimens were cut from the composite sheets (0 wt%, 5 wt%, and 8 wt% CdCl_2) and placed between the copper plates (10 mm diameter) of a test sample holder placed in a shielded cell (designed for this purpose) and located inside the oven. The two leads of the holder were connected to the terminals of the impedance analyzer^[3].

Differential Scanning Calorimetry (DSC)

The thermal analysis of the samples was studied using a Metler DSC FP85. The DSC experiments were run at a heating rate of 10 K/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

Dielectric Properties

The dielectric parameters (permittivity (ϵ'), dielectric loss (ϵ'') and AC conductivity (σ_{AC})) of the prepared CdCl_2 -PEO films were calculated from capacitance “C” and the loss tangent “ $\tan\delta$ ” data obtained from the HP 4194A-impedance analyzer over the frequency range from 10 Hz to 335 kHz and temperature range from 25°C to 45°C. The AC conductivity (σ_{AC}) was calculated according the following equation:

$$\sigma_{AC} = \epsilon'' \omega \epsilon_0 \quad (2)$$

where ω is the angular frequency, and ϵ_0 is the absolute permittivity of free space. The results obtained which are related to ϵ' , ϵ'' and σ_{AC} are presented graphically in Figs. 1(a), 1(b) and 1(c) respectively. Figures 2(a), 2(b) and 2(c) show the variations of the dielectric parameters (ϵ' , ϵ'' and σ_{AC}) for 8 wt% CdCl_2 -POE complex as a function of applied frequency at different temperature values.

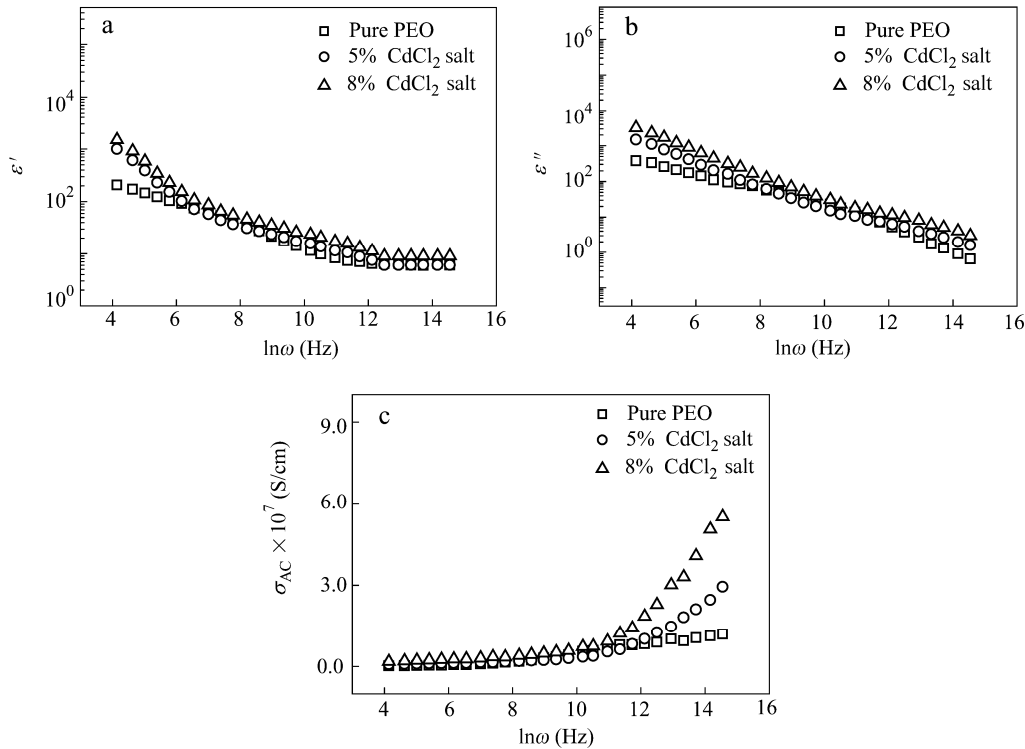


Fig. 1 (a) Permittivity, (b) dielectric loss and (c) AC conductivity as a function of frequency and salt concentration for CdCl_2 -PEO samples

It is clear that AC conductivity (σ_{AC}) values for $CdCl_2$ -PEO films increase by increasing salt concentration and temperature as shown in Fig. 1(c) and Fig. 2(c) respectively. The observed increase in the conductivity with salt content is due to salt elements motion and impurities existing in the salt filler. This motion leads to higher electrical conduction in the polymer electrolytes. On the other hand, the increase in the AC conductivity at high frequency range could be attributed to the increase in the mobility of the ions and impurity species^[5]. Also, it is clear that addition of $CdCl_2$ salt to PEO host will enhance the polar character of PEO host as shown in Fig. 1(a) and 1(b). Similar effects were also observed by other researches in PEO/salt complexes^[1, 2, 15–18].

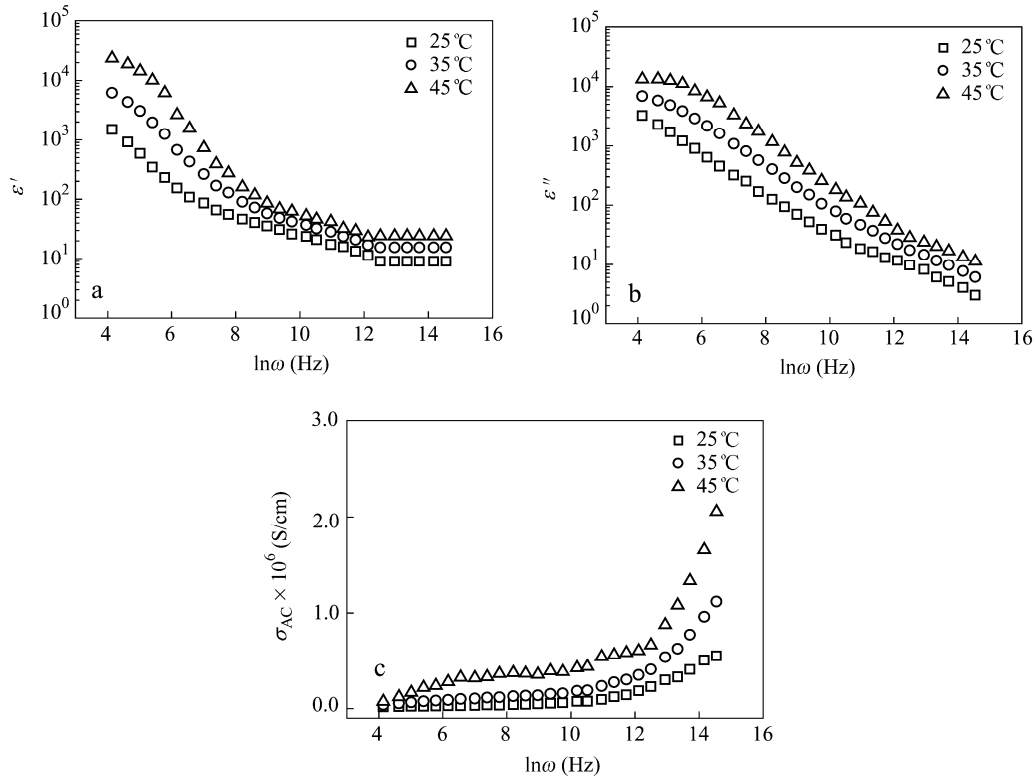


Fig. 2 (a) Permittivity, (b) dielectric loss and (c) AC conductivity as a function of frequency and temperature for the 8 wt% $CdCl_2$ -PEO sample

Figures 2(a), 2(b) and 2(c), indicate that as the temperature increases (below the melting temperature of PEO), the dielectric constant, dielectric loss and AC conductivity all increase. The obtained results indicate the contribution of the segmental motion of polymeric chains. Such a motion will also lead to an enhancement in the conductivity of PEO-salt complex. Similar result was previously reported for PEO-salt mixed system^[19].

Dielectric 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'' versus M' can be obtained from the following equation:

$$\left\{ M' - \frac{(M_v + M_R)}{2} \right\}^2 + (M'')^2 = \left(\frac{M_v - M_R}{2} \right)^2 \quad (3)$$

where M_v and M_R represent electric modulus values at high (the un-relaxed state) and low frequency (the relaxed state). Mohamed *et al.*^[12] showed that, if Argand plot (M'' versus M') has semicircular behavior 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 from Eq. (1) and Eq. (3) at different salt concentrations and temperatures for CdCl_2 -PEO samples. The obtained results are presented graphically in Figs. 3 and 4.

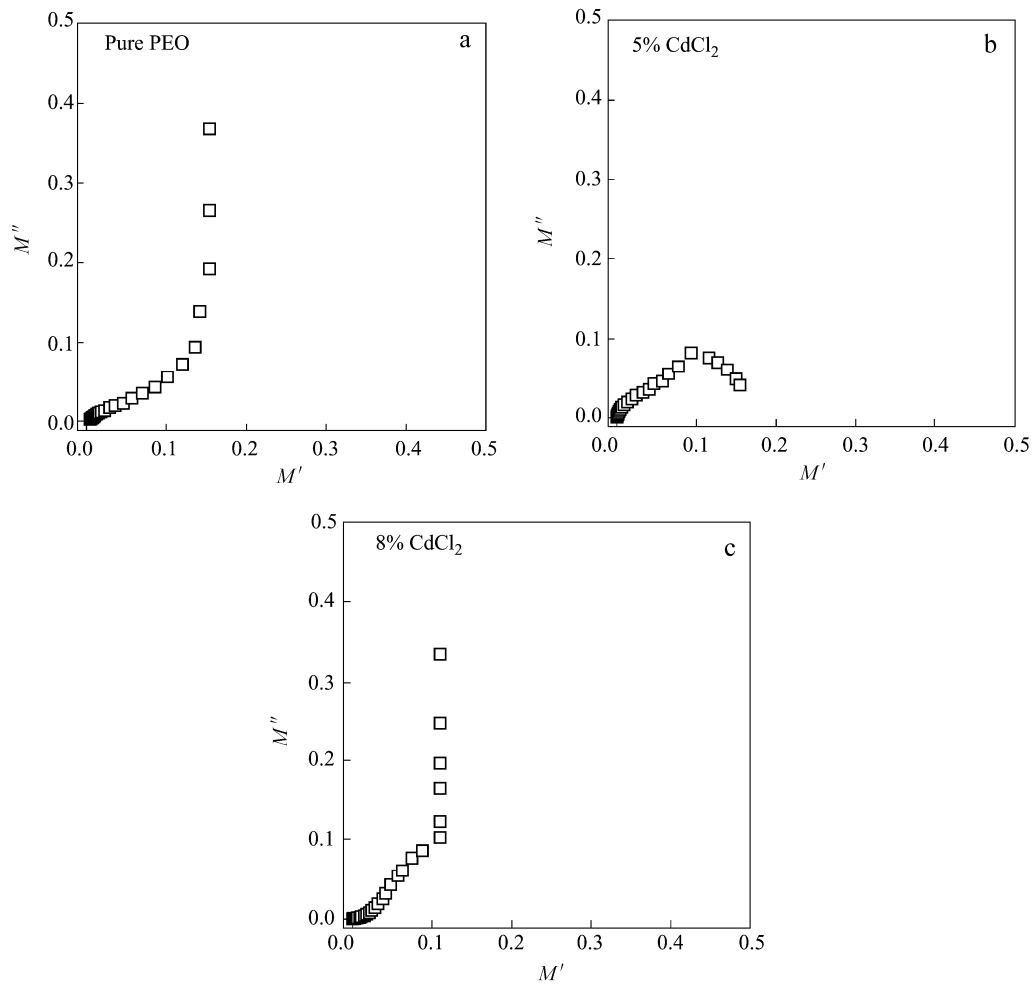


Fig. 3 Argand plots of CdCl_2 -PEO samples at different salt concentration

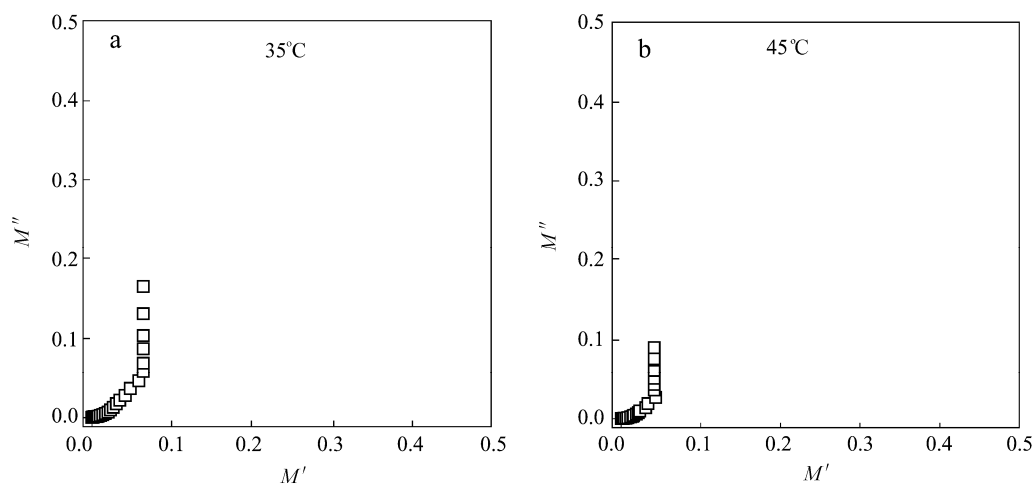


Fig. 4 Argand plots of the 8 wt% CdCl_2 -PEO sample at different temperatures

The results obtained in Figs. 3 and 4 indicate that for all CdCl_2 -PEO mixed systems, the plots do not follow semicircular behavior which means that the relaxation is a viscoelastic one and this relaxation remains viscoelastic in spite of changing the salt concentration and temperature^[10], consequently, this relaxation is non-Debye relaxation. The variations in the relaxation process behavior could be attributed to the existence of the following factors which might be responsible for these changes^[20]: (a) segmental mobility of polymer chains, (b) thermal expansion of PEO host and salt disrupting the chains of contacting nanoclusters.

Procedure 2: Ambrus *et al.* 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^[21]. Johari and Pathmanathan together with others have reported that the conductivity-relaxations in ionic conductors exhibit a single relaxation time^[10, 20]. Starkweather Jr. *et al.*^[21] and Mohamed *et al.*^[12] showed that, in case of ionic relaxation, plots of $\lg M''$ versus $\lg(\text{frequency})$ and $\lg M'$ versus $\lg(\text{frequency})$ 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 0 wt%, 5 wt%, and 8 wt% CdCl_2 samples and for 8 wt% CdCl_2 sample at 35°C and 45°C as $\lg M''$ versus $\lg(\text{frequency})$ and $\lg M'$ versus $\lg(\text{frequency})$. The obtained results are different from those obtained by Starkweather Jr. *et al.*^[22] and Mohamed *et al.*^[12]. It is clear from Figs. 5, 6, 7 and 8 that the behavior of 8 wt% CdCl_2 -PEO is not similar and all curves have slope values less than unity.

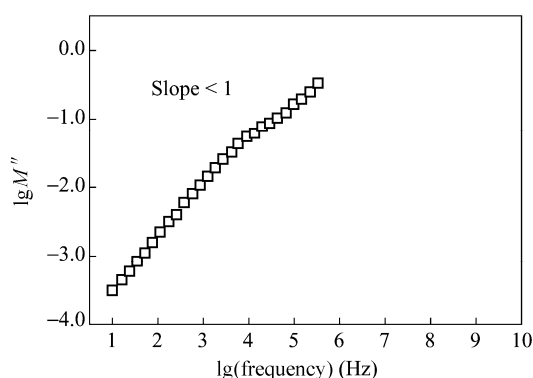


Fig. 5 $\lg M''$ versus $\lg(\text{frequency})$ for the 8 wt% CdCl_2 -PEO sample at 25°C

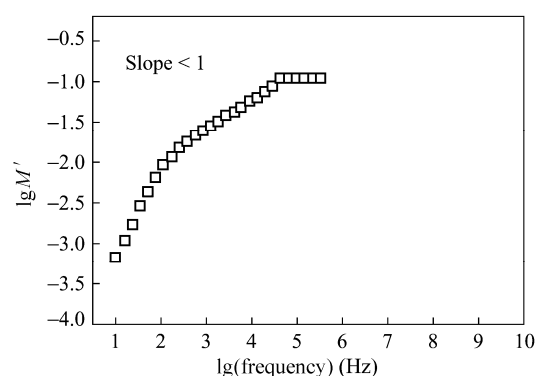


Fig. 6 $\lg M'$ versus $\lg(\text{frequency})$ for the 8 wt% CdCl_2 -PEO sample at 25°C

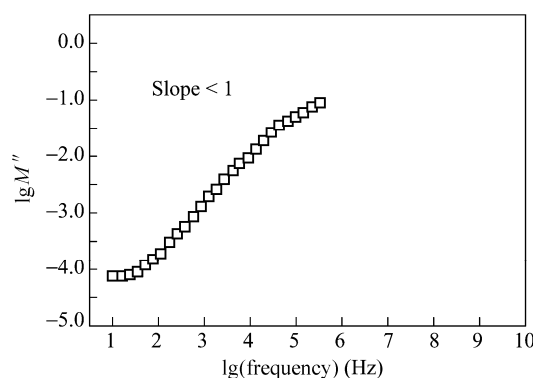


Fig. 7 $\lg M''$ versus $\lg(\text{frequency})$ for the 8 wt% CdCl_2 -PEO sample at 45°C

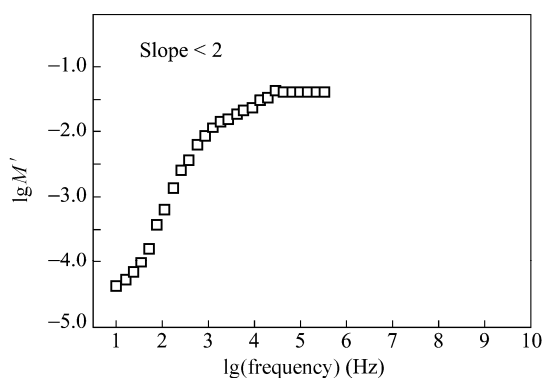


Fig. 8 $\lg M'$ versus $\lg(\text{frequency})$ for the 8 wt% CdCl_2 -PEO sample at 45°C

The results obtained from first and second analysis procedures indicate that at the domain frequency range the relaxation process for all CdCl₂-PEO samples is due to viscoelastic relaxation process and not due to ionic conductivity relaxation process. In other words, the relaxation process in case of CdCl₂-PEO is non-Debye relaxation.

The values of relaxation time were estimated using Yan and Rhodes model^[23, 24] for CdCl₂-PEO electrolytes at room temperature and domain frequency range. The relative permittivity (ϵ') according to Yan and Rhodes model, is given as^[23, 24].

$$\epsilon' = \epsilon'_{\infty} + \frac{(\epsilon'_0 - \epsilon'_{\infty})}{n} \sum_{n=1}^n \frac{\alpha_n}{1 + \tau_n^2 \omega^2} \quad (4)$$

where $\sum_{n=1}^n \alpha_n = n$ and ϵ'_{∞} is the value of permittivity at higher frequency range, ϵ'_0 is the value of permittivity at lower frequency range, τ_n is the relaxation time, and ω is the angular frequency. The details of using this model to determine the relaxation time values from the best fitting with the experimental data were explained by us for several times^[23, 24]. However, the relaxation parameters that were obtained from the best fittings are $n = 2$, $\alpha_1 = 1.2$ and $\alpha_2 = 0.8$. The values of ϵ_{∞} and ϵ_0 were obtained from experimental data at higher and lower frequency ranges respectively. The relaxation time τ_1 and τ_2 were estimated from these fittings for each CdCl₂-PEO electrolyte. The obtained relaxation time values are listed in Table 1. It is clear that relaxation time values decrease with increasing salt content. The obtained results indicate that the dielectric relaxation process in these CdCl₂-PEO electrolytes at the domain frequency is not a single relaxation process at room temperature. Such a conclusion was also reported in our previous studies^[23, 24].

Table 1. Relaxation times for the CdCl₂-PEO electrolytes

CdCl ₂ content (wt%)	Relaxation time (s)	
	τ_1	τ_2
0	4.80×10^{-3}	8.90×10^{-3}
5	3.65×10^{-3}	8.40×10^{-3}
8	3.50×10^{-3}	7.90×10^{-3}

Differential Scanning Calorimetry, DSC

The DSC thermograms for pure PEO, 5 wt%, and 8 wt% CdCl₂-PEO mixed systems are shown in Fig. 9(a). It can be seen that the melting temperature (T_m) for pure PEO is 64.5°C. Addition of 8 wt% CdCl₂ to PEO host reduces the melting temperature to 53.0°C. Also it can be seen from Fig. 9 that the DSC traces become broader in the presence of CdCl₂ salt. This is due to the crystal sizes obtained. At higher concentration of CdCl₂ 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 sharper due to perfect crystals^[25]. Additionally it is expected in the present work that the physical bond between the PEO chains decreases with increasing CdCl₂ salt.

Bhattacharyya *et al.*^[26] have investigated the effect of KI/I₂ salts on the structure and melting behavior of PEO using XRD and DSC. They showed the formation of complete amorphous complex and they reported that DSC results were also confirmed the amorphous nature of the polymer electrolyte. The same conclusion with the same system was also reported by Kalaignan *et al.*^[27]. Furthermore, Kelly *et al.*^[28] studied the system containing PEO doped with lithium salts and reported that partial replacing of the high molecular weight polymer by a low molecular weight PEO led to an increase in the solubility of the crystalline polymer-salt as well as lowering the effective melting and glass transition temperatures of the polymer. Although in our study a fixed molecular weight of PEO was used but changing the molecular weight of PEO might lead to the same result as obtained before^[28]. The homogeneity of CdCl₂ in PEO matrix might be investigated through colligative properties

relation^[29]:

$$\Delta T_m = -iK_m \cdot m \quad (5)$$

where ΔT_m is the change in melting temperature of PEO, i is the Vant Hoff factor, K_m is the melting constant and m is the concentration in mol/kg unit. Figure 9(b) shows a linear correlation between $-\Delta T_m$ and m with a slope (iK_m) equal to 24.1 K·kg/mol, indicating the validity of equation (5) and the homogeneity of the prepared samples.

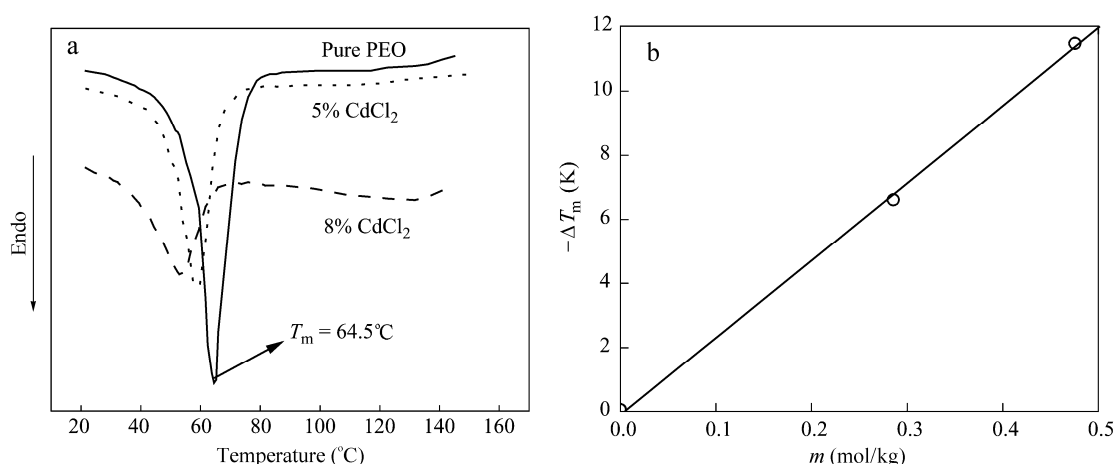


Fig. 9 (a) DSC thermograms for CdCl₂-PEO samples; (b) The linear fitting of PEO-CdCl₂ according to equation (5)

CONCLUSIONS

The dielectric properties of PEO films doped with CdCl₂ were investigated as a function of frequency and salt concentration. The AC conductivity of these complexes increases with increasing salt concentration and temperature. On the other hand, addition of salt to PEO host increases the permittivity values and enhances the polar character of PEO host. Also, temperature enhances the ionic conductivity of the CdCl₂-PEO mixed system and this could be attributed to that conductivity is governed by the motion of the polymeric chains. Results obtained from electric modulus reveal that the relaxation process occurred in these complexes is due to viscoelastic relaxation with more than a single value of relaxation time and consequently this relaxation is non-Debye relaxation. Besides, the values of relaxation time were estimated using Yan and Rhodes model and it was found that there were two values of relaxation time. The relaxation time values decrease with salt content. Finally, addition of CdCl₂ salt to PEO host decreases the melting temperature of PEO in addition to the increasing of imperfect polymer crystals.

ACKNOWLEDGMENTS The authors thank Dr. Bassam Sewlleh (Chemistry department, university of Jordan) for his cooperation.

REFERENCES

- 1 Ahmad, A., Saq'an, S., Ramadin, Y. and Zihlif, A., J. Thermoplast. Compos. Mater., 2006, 19(5): 531
- 2 Dygas, J., Misztal-Faraj, B., Florjaczky, Z., Krok, F., Marzantowicz, M. and Zygado-Monikowska, E., Solid State Ionics, 2003, 157(1-4): 249
- 3 Saq'an, S., Ayes, A., Zihlif, A., Martuscelli, E. and Ragosta, G., Polym. Test., 2004, 23(7): 739
- 4 Singh, P. and Chandra, A., J. Phys. D: Appl. Phys., 2003, 36: L93
- 5 Sunandana, C. and Kumar, P., Bull. Mater. Sci., 2004, 27(1): 1

- 6 Armand, M., Solid State Ionics, 1983, 9-10 (part 2): 745
- 7 Saraswathi, R., Gerard, M. and Malhotra, B., J. Appl. Polym. Sci., 1999, 74(1): 145
- 8 Tajitsu, Y., J. Mater. Sci., 1996, 31(8): 2081
- 9 Wright, P., Br. Polym. J., 1975, 7(5): 319
- 10 Botros, S., Eid, M. and Nageeb, Z., J. Appl. Polym. Sci., 2006, 99(5): 2504
- 11 Madbouly, S. and Otaigbe, J., Polymer, 2007, 48(14): 4097
- 12 Mohomed, K., Gerasimov, T., Moussy, F. and Harmon, J., Polymer, 2005, 46(11): 3847
- 13 Narula, A., Singh, R. and Chandra, S., Bull. Mater. Sci., 2000, 23(3): 227
- 14 Frübing, P., Krueger, H., Goering, H. and Gerhard-Multhaupt, R., Polymer, 2002, 43(9): 2787
- 15 Duan, Y., Halley, J., Curtiss, L. and Redfern, P., J. Chem. Phys., 2005, 122: 054702
- 16 Kalogeras, I., Stathopoulos, A., Vassilikou-Dova, A. and Brostow, W., J. Phys. Chem. B, 2007, 111(11): 2774
- 17 Ramadin, Y., Saq'an, S., Eid, A., Ahmad, M. and Zihlif, A., J. Thermoplast. Compos. Mater., 2000, 13(6): 497
- 18 Walls, H., Fedkiw, P., Zawodzinski Jr, T. and Khan, S., J. Electrochem. Soc., 2003, 150: E165
- 19 Polizos, G., Shilov, V. and Pissis, P., J. Non-Cryst. Solids, 2002, 305(1-3): 212
- 20 Ayesh, A.S., Chinese J. Polym. Sci., 2010, 28(4): 537
- 21 Ambrus, J., Moynihan, C. and Macedo, P., J. Phys. Chem., 1972, 76(22): 3287
- 22 Starkweather Jr, H. and Avakian, P., J. Polym. Sci. Part B: Polym. Phys., 1992, 30(6): 637
- 23 Ayesh, A., J. Thermoplast. Compos. Mater., 2008, 21(4): 309
- 24 Ayesh, A.S., Polym. J., 2009, 41(8): 616
- 25 Saq'an, S., Ayesh, A. and Zihlif, A., Opt. Mater., 2004, 24(4): 629
- 26 Bhattacharyya, A.J., Middy, T. and Tarafdar, S., Phys. Rev. B, 1999, 60(2): 909
- 27 Kalaighan, G.P. and Kang, M.S., Solid State Ionics, 2006, 177(11-12): 1091
- 28 Kelly, I., Owen, J. and Steele, B., J. Power Sources, 1985, 14(1-3): 13
- 29 Petrucci, R.H., Harwood, W.S., Herring, F.G. and Madura, J.D., "General chemistry: principles and modern applications", Macmillan, New York, 1993, p. 85