

# Influence of water absorption on poly-ethylene oxide-based polymer electrolytes complexed with ammonium, sodium and magnesium perchlorates

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The influence of water absorption on polyethylene oxide and its complexes with  $\text{NH}_4\text{ClO}_4$ ,  $\text{NaClO}_4$  and  $\text{Mg}(\text{ClO}_4)_2$  (for O/M = 10 and 3) has been studied. A quantitative estimation of water absorption kinetics has been carried out. The changes in microstructure and thermal behaviour due to water absorption have been studied using X-ray diffraction and thermogravimetric/differential thermal analyses. The electrical conductivity of different films has been measured as a function of relative humidity and explained in terms of the generation of free mobile ions due to water absorption. © 1998 Chapman & Hall

## 1. Introduction

Ionically conducting polymers are of major recent interest due to their technological applications as solid electrolytes in various electrochemical devices [1]. The various properties of polyethylene oxide (PEO)-based polymer electrolytes, such as their thermal behaviour, microstructural and electrical properties, vary widely, depending on the polymer-salt compositions, types of the complexed cations/anions and the temperature. Humidity has also been found to influence drastically these properties of polymer electrolytes, as indicated in a few recent reports on pure PEO [2] and its complexes with  $\text{NH}_4\text{ClO}_4$ ,  $\text{NH}_4\text{I}$ ,  $(\text{NH}_4)_2\text{SO}_4$  [3–5],  $\text{Pb}(\text{CF}_3\text{SO}_3)_2$  and  $\text{Zn}(\text{CF}_3\text{SO}_3)_2$  [6], etc.

The present paper reports an investigation on the influence of humidity on the microstructure, thermal behaviour and electrical properties of PEO-based polymer electrolytes complexed with the perchlorates of different cations  $\text{NH}_4^+$ ,  $\text{Na}^+$  and  $\text{Mg}^{2+}$ . The water uptake kinetics in different polymer films have been estimated quantitatively. The effect of water absorption on microstructure and thermal behaviour have been studied using X-ray diffraction (XRD), differential thermal analysis (DTA) and thermogravimetric analysis (TGA). The electrical conductivity of different films has been evaluated as a function of relative humidity and the variations have been found to be mainly dependent upon the type and concentration of complexed cations in PEO.

## 2. Experimental details procedure

Films (thickness  $\sim 300$ – $400$   $\mu\text{m}$ ) of PEO (Aldrich, molecular weight  $\sim 6 \times 10^5$ ) and its complexes with  $\text{NH}_4\text{ClO}_4$ ,  $\text{NaClO}_4$  and  $\text{Mg}(\text{ClO}_4)_2$  (Fluka) of two compositions, i.e. O/M = 10 and 3, were prepared

using the “solution-cast technique”. The solutions of PEO and salts in dehydrated methanol were mixed in appropriate ratios and thoroughly stirred for  $\sim 10$  h. The mixed solutions were cast on the polypropylene dishes and were allowed to evaporate slowly at room temperature ( $\sim 22^\circ\text{C}$ ) followed by vacuum drying. Finally, the films were heated at  $45$ – $50^\circ\text{C}$  for 3–4 h.

The increase in the weight of polymer films due to water uptake, after exposing them from dry (7%–10% RH) to humid air of RH  $\sim 75$ %– $80$ %, was monitored as a function of time with the help of a microbalance (Cahn, USA).

The XRD patterns of the polymer films stored in a dry atmosphere (RH  $\sim 7$ %– $10$ %) and the films exposed to humid air (RH  $\sim 75$ %– $80$ %) for 12 h, were recorded using an X-ray diffractometer (Rigaku, Japan). The records were taken for  $\text{CuK}_\alpha$  irradiation with the Bragg angles varying from  $5^\circ$ – $50^\circ$  with a scan speed of  $5^\circ \text{min}^{-1}$ . The DTA/TGA of the films were carried out with the help of DTA/TGA instruments (Cahn, USA, model 131). Samples (weighing 20 mg) were heated in a platinum crucible (for DTA) or a quartz crucible (for TGA) at a heating rate of  $10^\circ\text{C min}^{-1}$  in static air.

The room temperature ( $\sim 26^\circ\text{C}$ ) electrical conductivity of different films was measured at 1 kHz using the Hioki (Japan) LCR HI TESTER (model 3520-01) Vacuum-evaporated aluminium was used as electrodes, having an area of  $\sim 0.785 \text{ cm}^2$ .

## 3. Results and discussion

### 3.1. Water uptake

The change in mass of the films of PEO and its complexes have been carried out as a function of time after exposing them from a dry (7%–10% RH) to an open humid atmosphere (75%–80% RH). Fig. 1

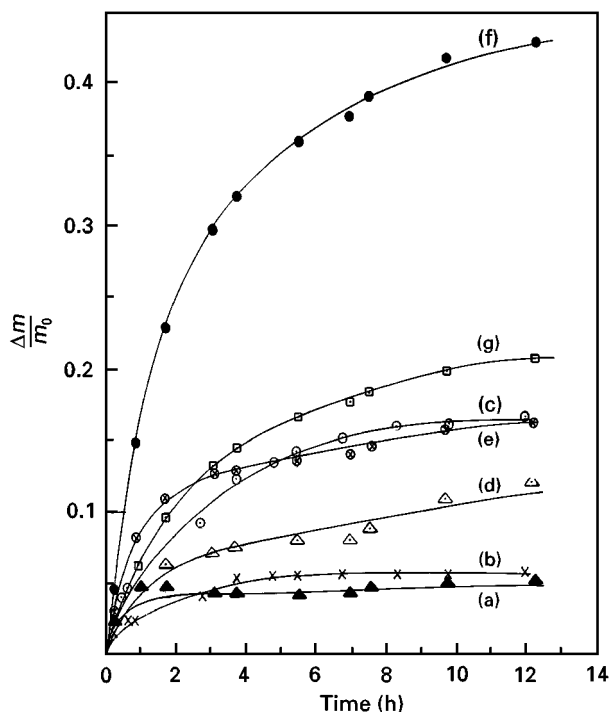


Figure 1 The relative increase of mass ( $\Delta m/m_0$ ) versus time plots after exposing the films of (a) PEO, PEO +  $\text{NH}_4\text{ClO}_4$  of O/ $\text{NH}_4^+$  ratio (b) 3 and (c) 10, PEO +  $\text{NaClO}_4$  of O/Na ratio (d) 3 and (e) 10, and PEO +  $\text{Mg}(\text{ClO}_4)_2$  of O/Mg ratio (f) 3 and (g) 10, in a humid atmosphere of RH  $\sim 75\%$ – $80\%$ .  $m_0$  is the initial mass measured at 7%–10% R.H.

shows the relative increase in mass due to water absorption as a function of time. The increase in mass,  $\Delta m$ , of the films can be expressed as [7]

$$\Delta m = m_0 [1 - \exp(-kt)] \quad (1)$$

where  $m_0$  is the initial mass of the films stored in a dry atmosphere and  $k$  is the rate constant of water uptake. The variations in  $\ln(1 - \Delta m/m_0)$  versus time have been found to be linear (Fig. 2) which shows that the rates of water uptake follow the “first order kinetics”. The water uptake by each film is initially faster up to a certain time, thereafter it becomes slower (Fig. 1) and hence two linear slopes have been observed in  $\ln(1 - \Delta m/m_0)$  versus time plots (Fig. 2). The corresponding two rate constants  $k_1$  and  $k_2$  for different films are listed in Table I. In each film, the value of rate constant  $k_1$  (Table I) has been observed to be substantially greater than  $k_2$ . This indicates that the rate of water absorption is higher up to a certain level, thereafter, the water absorption capacity of each film is lowered and hence the rate of absorption becomes quite slow.

The water uptake by pure PEO is quantitatively minimal compared to the uptake by films of PEO complexes (Fig. 1). The maximum water absorption has been found particularly in the films of PEO +  $\text{Mg}(\text{ClO}_4)_2$  systems, showing their greater hygroscopic nature than the sodium and ammonium complexes of PEO. In addition to this, the absorption of water is also affected by the salt concentration in PEO matrices. The water absorption capacity of PEO +  $\text{Mg}(\text{ClO}_4)_2$  complexes increases with increasing salt concentrations (Fig. 1f, g), in contrast to sodium and ammonium complexes, where water absorption

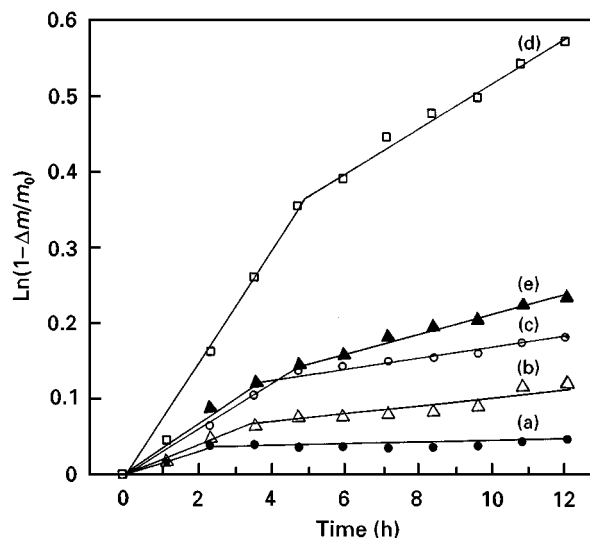


Figure 2 The  $\ln(1 - \Delta m/m_0)$  versus time plots for the films of (a) PEO, PEO +  $\text{NaClO}_4$  of O/Na ratio (b) 3 and (c), 10, and PEO +  $\text{Mg}(\text{ClO}_4)_2$  (d) 3 and (e) 10 after exposing them to a humid atmosphere of R.H.  $\sim 75\%$ – $80\%$ .  $m_0$  is the initial mass measured at 7%–10% R.H.

TABLE I The values of rate constants of water uptake for different polymer films.

Polymer systems	O/M	$k_1$ ( $\text{s}^{-1}$ )	$k_2$ ( $\text{s}^{-1}$ )
PEO (pure)	—	$8.0 \times 10^{-6}$	$2.5 \times 10^{-7}$
PEO + $\text{NH}_4\text{ClO}_4$	10	$8.1 \times 10^{-6}$	$1.5 \times 10^{-6}$
	3	$3.0 \times 10^{-6}$	$2.5 \times 10^{-7}$
PEO + $\text{NaClO}_4$	10	$2.4 \times 10^{-5}$	$1.7 \times 10^{-6}$
	3	$1.0 \times 10^{-5}$	$1.1 \times 10^{-6}$
PEO + $\text{Mg}(\text{ClO}_4)_2$	10	$1.1 \times 10^{-5}$	$2.9 \times 10^{-6}$
	3	$4.2 \times 10^{-5}$	$6.5 \times 10^{-6}$

capacity decreases for higher salt concentrations (Fig. 1b–e).

### 3.2. Microstructure and thermal behaviour

Fig. 3a and b show the typical XRD patterns of PEO +  $\text{NaClO}_4$  (O/Na = 10) system recorded for the film (a) stored in a dry (low humidity) atmosphere (RH  $\sim 7\%$ – $10\%$ ), and (b) exposed to a humid atmosphere (RH  $\sim 79\%$ ) for 12 h. The disappearance of all the peaks in the humid atmosphere indicates the drastic change in the lamellar microstructure of the PEO complexes due to water absorption. The following additional changes have also been observed from the experimental XRD data of PEO and its complexes (Table II).

1. The  $d$  values and Scherrer length,  $L$ , corresponding to the peaks of polymer complexes and excess uncomplexed salts in PEO with  $\text{NaClO}_4$  and  $\text{NH}_4\text{ClO}_4$  (O/M = 3) films, have been found to be reduced after exposure to a humid atmosphere (Table II). This indicates the reduction in their crystallite sizes due to water absorption. In contrast, the film of PEO +  $\text{NH}_4\text{ClO}_4$  of ratio O/ $\text{NH}_4^+$  = 10 shows an increase in these values (Table II), indicating swelling of crystallites of the polymer complex.

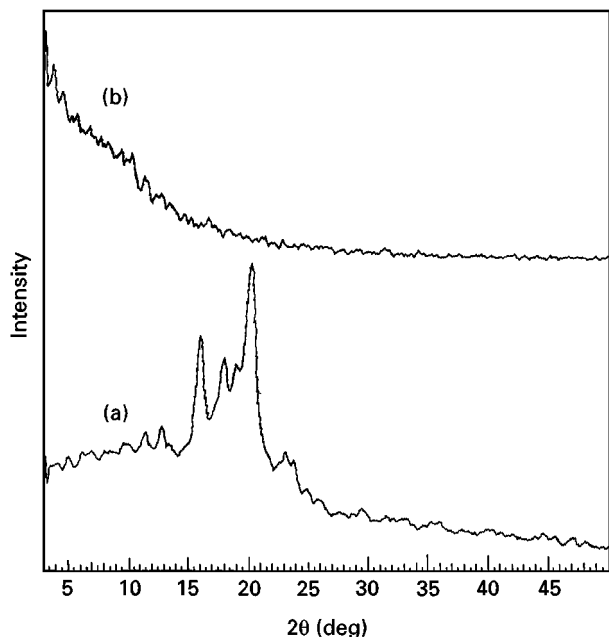


Figure 3 XRD patterns of PEO + NaClO<sub>4</sub> (O/Na = 10) film (a) stored in dry (low humidity) air of R. H. ~7%–10%, and (b) exposed to humid air of R.H. ~79%.

2. The shifts and splitting of XRD peaks have also been observed due to water absorption. For example, in the PEO + NaClO<sub>4</sub> (O/Na = 3) system, the peak at  $2\theta = 21.6^\circ$  (in a dry atmosphere) has been split into two peaks at  $2\theta = 20.9^\circ$  and  $22.2^\circ$  (in a humid atmosphere).

3. No substantial change was observed in XRD data for pure PEO due to change in humidity, thus showing the least effect on its microstructure.

4. The films of PEO + Mg(ClO<sub>4</sub>)<sub>2</sub> were extremely hygroscopic and hence they are difficult to handle for XRD studies.

The TGA/DTA results for dry and humid samples of pure PEO and its complexes are shown in Fig. 4a and b. A small weight loss was observed for humid PEO up to 210 °C, attributed to evolution of the absorbed water content. The larger weight loss due to decomposition has been found to be the same for both dry and humid PEO after 210 °C (Fig. 4a (i, ii)). The decomposition of PEO complexes begins at relatively higher temperatures for both dry and humid samples. A marginal temperature difference of  $\pm 5^\circ\text{C}$  has been observed in the decomposition temperature due to water absorption in humid samples. The initial weight loss in each humid PEO complex films up to 150–175 °C is attributed to the release of absorbed water.

The melting temperature of pure PEO is independent of atmosphere, as indicated in DTA studies by Shodai *et al.* [8]. However, the dependence of dry and humid air can be seen from DTA studies on PEO complexes shown in Fig. 3b. The following changes in DTA curves have been observed due to water absorption in PEO complexes.

1. The endothermic peaks between 70 and 100 °C corresponding to the melting temperature of dry samples of PEO + NaClO<sub>4</sub> (O/Na = 10) and PEO + NH<sub>4</sub>ClO<sub>4</sub> (O/NH<sub>4</sub><sup>+</sup> = 10 and 3) are overlapped by exothermic peaks observed in this temperature range due to release of absorbed water.

2. The endothermic peak corresponding to the high-temperature melting point  $T_m$  of PEO + NaClO<sub>4</sub> (O/Na = 10) has been found to shift from 206 °C to 236 °C, whereas  $T_m$  has been found to be

TABLE II X-ray diffraction data of PEO and its complexes in dry and humid atmospheres

Polymer systems	O/M	Dry (RH ~ 10%)				Wet (RH ~ 75–80%)				
		2θ (deg.)	d (nm)	I/I <sub>0</sub>	L (nm)	2θ (deg.)	d (nm)	I/I <sub>0</sub>	L (nm)	
PEO + NaClO <sub>4</sub>	10	15.9	5.5694	87.09	8.075					
		17.9	4.9514	57.54	9.104					
		18.8	4.7163	42.23	6.708					
		20.1	4.4141	100.00	7.372					
	3	9.3	9.5018	100.00	16.880	9.6	9.2055	100.00	5.779	
		20.5	4.3289	54.29	11.970	20.4	4.3499	67.90	10.210	
		21.6	4.1109	35.75	12.230	20.9	4.2469	83.53	3.380	
						22.2	4.0011	67.90	5.294	
PEO + NH <sub>4</sub> ClO <sub>4</sub>	10	13.4	6.6023	26.26	11.707	14.7	6.0212	82.58	11.862	
		15.9	5.5694	60.26	11.826	15.4	5.7491	39.97	16.222	
		18.8	4.7163	100.00	6.398	17.6	5.0351	67.05	11.800	
		19.4	4.5718	73.36	13.890	18.1	4.8971	100.00	8.189	
	3	12.3	7.1902	85.91	13.915	17.4	5.0925	9.30	6.185	
		18.5	4.7921	98.56	9.153	18.2	4.8704	10.85	8.936	
		19.0	4.6671	83.52	9.160	18.7	4.7413	14.08	2.693	
		19.4	4.5718	100.00	6.389	24.9	3.5730	48.91	37.134	
		46.5	1.9514	48.25	27.265	46.6	1.9474	100.00	25.656	
PEO	Pure	16.3	5.4336	100.00	8.150	15.8	5.6044	42.38	20.400	
		16.9	5.2420	47.94	20.470	16.4	5.4007	100.00	8.190	
		19.7	4.5028	30.67	13.570	20.6	4.3088	98.22	6.290	
		20.7	4.2875	82.80	5.440					

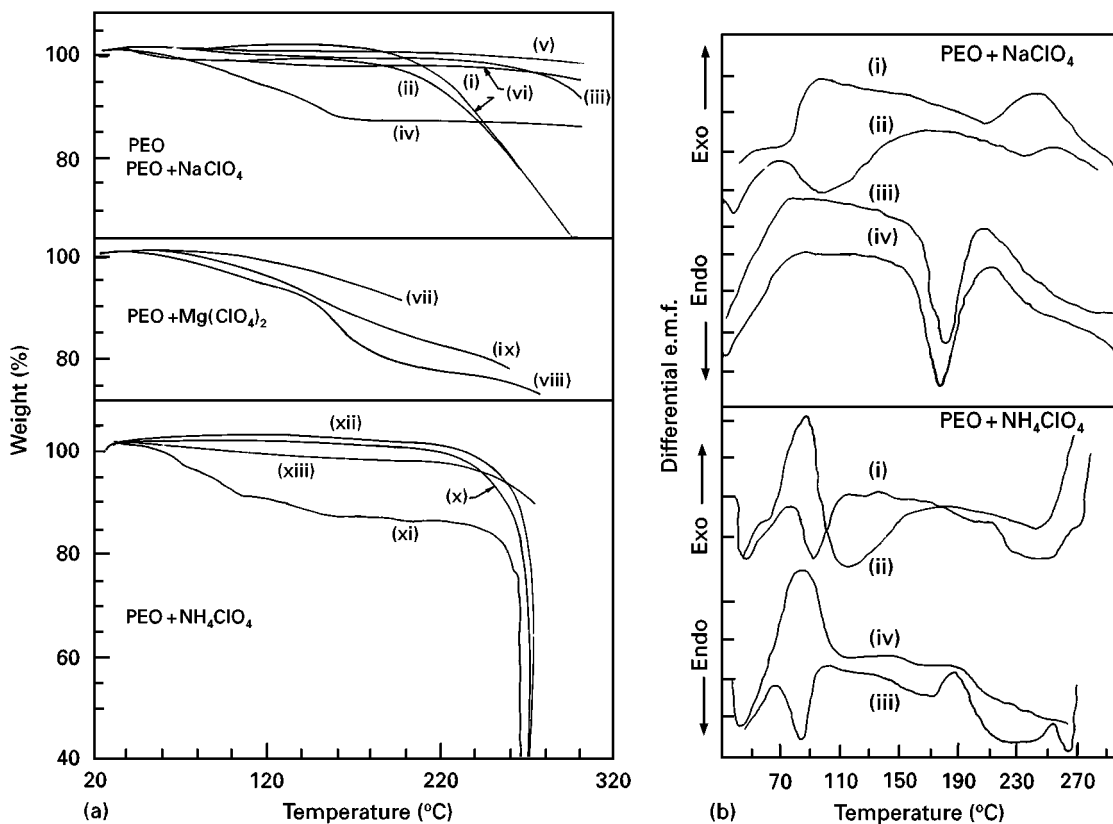


Figure 4(a) TGA traces of the films. Pure PEO: (i) dry and (ii) humid. PEO + NaClO<sub>4</sub> systems: O/Na ratio = 10, (iii) dry and (iv) humid; O/Na = 3, (v) dry and (vi) humid. PEO + Mg(ClO<sub>4</sub>)<sub>2</sub> systems: O/Mg ratio = 10, (vii) dry and (viii) humid; O/Mg = 3, (ix) dry. PEO + NH<sub>4</sub>ClO<sub>4</sub> systems; O/NH<sub>4</sub><sup>+</sup> ratio = 10, (x) dry and (xi) humid; O/NH<sub>4</sub><sup>+</sup> = 3, (xii) dry and (xiii) humid. (b) DTA traces. PEO + NaClO<sub>4</sub> systems: O/Na = 10, (i) dry and (ii) humid; O/Na = 3, (iii) dry and (iv) humid and PEO + NH<sub>4</sub>ClO<sub>4</sub> systems: O/NH<sub>4</sub><sup>+</sup> ratio = 10, (i) dry and (ii) humid; O/NH<sub>4</sub><sup>+</sup> = 3, (iii) dry and (iv) humid.

reduced from 182 °C to 175 °C in the case of the film of ratio O/Na = 3, due to water absorption (Fig. 4b (i)–(iv)). The shifts observed in the melting peaks are attributed to the initial change in morphology of the complex films due to water uptake.

### 3.3. Electrical conductivity

Fig. 5 shows the variation of  $\sigma/\sigma_0$  with respect to per cent RH, where  $\sigma$  is the room-temperature conductivity and  $\sigma_0$  is the conductivity of the polymer complexes measured at ~7% RH. The value of  $\sigma_0$  of the PEO + NH<sub>4</sub>ClO<sub>4</sub> system has been found to be  $6.4 \times 10^{-9} \text{ S cm}^{-1}$  for O/NH<sub>4</sub><sup>+</sup> = 10 and  $4.0 \times 10^{-10} \text{ S cm}^{-1}$  for O/NH<sub>4</sub><sup>+</sup> = 3. On increasing the humidity from 7% to 73% RH, the ratio  $\sigma/\sigma_0$  increases approximately 1000 times for both the low and high NH<sub>4</sub>ClO<sub>4</sub> concentrations in PEO (Fig. 5c, d). In the PEO + NaClO<sub>4</sub> system, the  $\sigma_0$  values have been observed to be  $1.5 \times 10^{-5} \text{ S cm}^{-1}$  for O/Na = 10 and  $1.6 \times 10^{-8} \text{ S cm}^{-1}$  for O/Na = 3. The increase in  $\sigma/\sigma_0$ , as a function of RH values, is found to be approximately 3000 times higher for the high NaClO<sub>4</sub> concentration in PEO (Fig. 5a), whereas it is quite small (~1.5 times higher) in the case of low concentration of NaClO<sub>4</sub>, i.e. O/Na = 10 (Fig. 5b).

The increase in conductivity due to water absorption has been explained as follows. The <sup>1</sup>H NMR

report by Lauenstein *et al.* [6] indicates that all the absorbed water molecules are bound to the polymer chains and/or to the cations and, hence, molecular mobility of the polymer increases with increasing water content. This increase in polymer chain mobility is attributed to the increase in conductivity of polymer electrolytes. Another explanation for the increase in the conductivity of polymer electrolytes due to water absorption has been suggested by Wendsjo *et al.* [9]. According to them, the coordination between oxygen of PEO and the cations is weakened due to the presence of absorbed water, and hence it produces an increasing number of free mobile ions to enhance the conductivity of polymer complexes.

Further, a greater number of low-mobility ion pairs/aggregates is possible to be present in the electrolytes of high NaClO<sub>4</sub> concentration, which decreases in number due to water absorption giving more free ions [9]. Hence, the increase in  $\sigma/\sigma_0$  is found to be more in the electrolytes of ratio O/Na = 3 as compared to that of the ratio O/Na = 10. In contrast, the difference in  $\sigma/\sigma_0$  versus % RH curves for the PEO + NH<sub>4</sub>ClO<sub>4</sub> systems are observed to be quite small for both low and high salt concentrations. From the optical microscopic studies of PEO complexes of high NH<sub>4</sub>ClO<sub>4</sub> concentrations, it has been observed that the excess NH<sub>4</sub>ClO<sub>4</sub> crystallizes in localized regions of the PEO matrix [10]. These small crystals are possibly not dissociated by the water

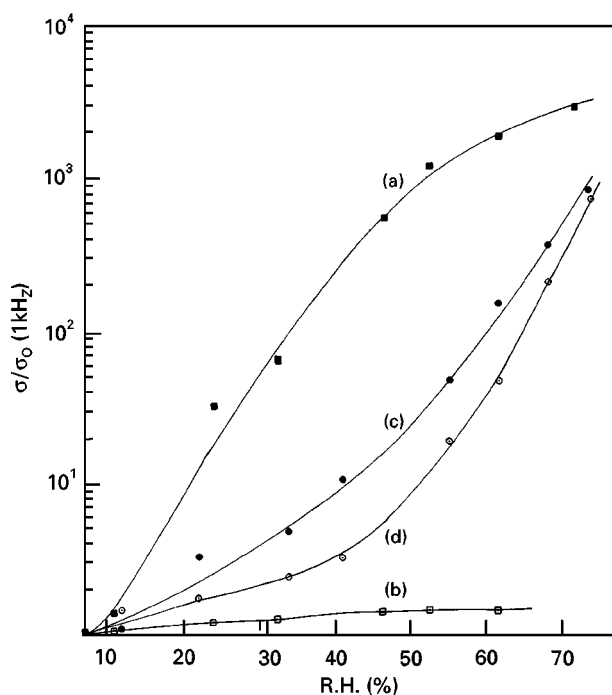


Figure 5 The relative increase in room temperature ( $\sim 26^\circ\text{C}$ ) conductivity of different polymer electrolyte films as a function of the relative humidity. (■, □) PEO + NaClO<sub>4</sub>, O/Na = (■) 3, (□) 10; (○, ●) PEO + NH<sub>4</sub>ClO<sub>4</sub>, O/NH<sub>4</sub><sup>+</sup> = (○) 3, (●) 10.

absorption to give additional free ions to enhance the conductivity.

#### 4. Conclusions

The results show that a substantial absorption of water occurs in PEO complexes and the amount and rate of water absorption strongly depends on the types of complexed cations and their concentrations. Studies also show that the absorbed water plays a significant role in changing the thermal behaviour, structural and electrical properties of the PEO complexes. On the basis of various structural, thermal and electrical studies, mentioned above, the following conclusions have been drawn.

1. The disappearance of XRD peaks after exposing the PEO + NaClO<sub>4</sub> film (O/Na = 10) to a humid atmosphere indicates a drastic change in lamellar microstructure of the PEO matrix. The changes in  $d$  values and Scherrer lengths,  $L$ , for other cationic complexes also support the drastic structural change in the polymer.

2. A comparative study of TGA/DTA of the dry and wet polymer complexes depicts a substantial shift in the melting temperature,  $T_m$ , and dissociation temperature.

3. The electrical conductivity of the polymer complexes increases with increase in relative humidity. The increase in conductivity also depends on the types of complexed cations and their concentrations. The conductivity increase due to water absorption has been explained on the basis of the increase in molecular mobility of the polymer chain and the generation of free mobile cations due to weakening of the coordination between ether oxygen of PEO and the cations.

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