

STUDY OF CHARACTERIZATION OF (PEO+KClO₄) POLYMER ELECTROLYTE SYSTEM

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Abstract

Solid state polymer electrolytes have been prepared by using poly (ethylene oxide) (PEO) and KClO₄ salt in the Wt% ratios of (90:10), (80:20) and (70:30) by solution – casting technique by using methanol (water-free) as solvent. The complexation of pure PEO with KClO₄ salts has been extensively studied using IR studies. In the Differential Scanning Calorimetry (DSC) curves it observed that, pure PEO melting temperature (T_m) slight shift towards lower temperature is due to the addition of KClO₄ salt to the polymer. XRD data for these films clearly confirm the complexation between the KClO₄ salt and the polymer PEO. The d-values calculated from the X-ray diffraction of pure PEO and various compositions of KClO₄ complexed films are clearly indicate the complexation of PEO and KClO₄.

Keywords: Polymer electrolytes, IR studies, differential scanning calorimetry, X-ray diffraction.

1. INTRODUCTION

Polymer electrolytes are emerging key technology resulting from the complexation of low-lattice energy salts with solvating polymers, have generated over the past decade a widespread and sustained interest with in the scientific community [1-3]. The solid polymer electrolytes are easy to fabricate as soft films of only a few microns and their flexibility permits interfaces with solid electrodes, which remain intact, when the device is in use. This makes the application and development of all electrochemical devices possible. In the present study, our interest is in the preparation and characterization of polymer films. As per the literature available, there are various methods to prepare good quality polymer films. Some excellent reviews [4-7] are available in the literature on the methods of preparation of good polymer films.

For the past several years extensive studies have been performed on the ionic conductivity of certain kinds of ion containing polymers. These ion-containing polymers show a relatively high ionic conductivity and have a potential application as solid electrolytes. Such electrolytes have mainly been based on the alkali metal salt systems and application to high batteries, fuel cells etc. therefore, (PEO+KClO₄) polymer electrolytes have been prepared and its characterization has been studied.

2. EXPERIMENTAL

Poly (ethylene oxide) (PEO) (Aldrich, M.W. 4×10^5) and various compositions of (PEO+KClO₄) polymer electrolytes were prepared in the Wt% ratios (90:10), (80:20) and (70:30) by solution – casting technique by using methanol (water-free) as solvent. The solutions were stirred for 15-20 hr, were cast using polypropylene dishes, and were evaporated slowly at room temperature. Finally, the films were dried thoroughly at 10^{-3} Torr [8]. X-ray diffraction (XRD) analyses of all the samples were carried out by using a SIEMES / D 5000 X-ray diffractometer (Cu K _{α} radiation $\lambda = 1.5406 \text{ \AA}$). The infrared spectrum of polymer electrolyte films was recorded on a PERKIN ELMER FTIR spectrophotometer [Model 1605] in the range of 450-4500 cm⁻¹ with scans 16 cm⁻¹ / sec. DSC (TA 2010 instrument) was used to study the melting temperatures of the polymer electrolyte films [9].

3. RESULTS AND DISCUSSION

3.1 IR Studies

The complexation of pure PEO with various salts has been extensively studied using vibrational spectroscopic studies [10]. The IR spectra of pure PEO, KClO₄ and PEO complexed with KClO₄ are shown in Fig.1 and the vibrational bands observed in this system are given in the Table - 1. The following differences in the spectral features have been observed on comparing the spectra of complexed PEO with pure PEO and KClO₄.

- The intensity of the aliphatic C-H stretching vibrational band observed around 2897.1 cm^{-1} in PEO decreases with increasing concentration of KClO_4 salt in the polymer.
- The width of the C-O Stretching band observed around 1095.2 cm^{-1} in PEO also showed an increase with an increase of KClO_4 in the polymer.
- Several new peaks around 4329.6 , 4002.0 , 2363.4 and 1280.8 cm^{-1} have been observed in complexed PEO.

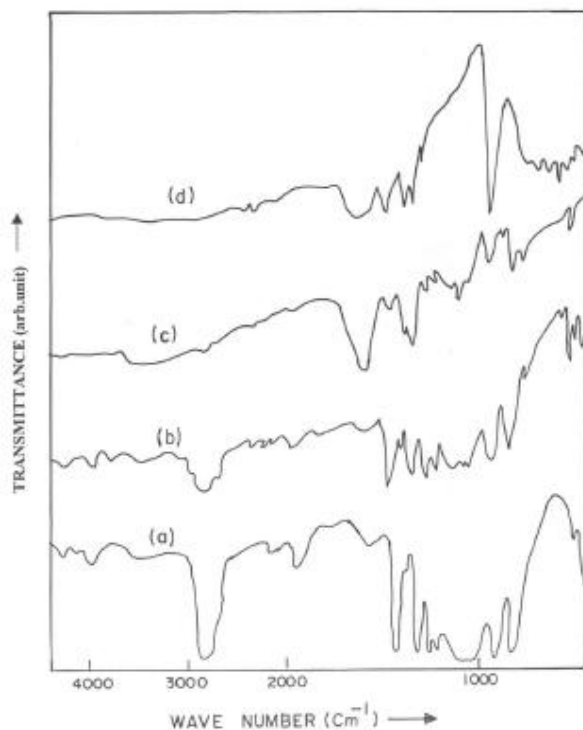


Fig 1 IR Spectra (a) Pure PEO, (b) [PEO + KClO_4] (80:20), (c) [PEO + KClO_4] (70:30) and (d) KClO_4

Table – 1 Various vibrational bands observed in the IR-Spectra of pure PEO, (PEO+ KClO_4) Polymer electrolyte and KClO_4 salt.

Pure PEO Cm^{-1}	PEO+ KClO_4 (80:20) Cm^{-1}	PEO+ KClO_4 (70:30) Cm^{-1}	KClO_4 Cm^{-1}
470.6	849.6	529.1	585.1
843.9	961.2	770.2	949.5
951.7	1096.4	839.0	1296.2
1117.7	1231.5	960.2	1343.2
1237.7	1278.5	1108.6	1396.0
1279.6	1337.3	1351.8	1484.2
1349.3	1469.0	1595.9	1642.8
1464.9	1960.1	3471.5	2355.1
1628.9		2855.7	

1807.4			
1960.0			
2167.1			
2237.6			
2355.1			
2872.2			
3448.1			
4003.4			
4329.5			

The appearance of new peaks along with changes in existing peaks (and / or their disappearance) in the IR spectra directly indicates the complexation of KClO_4 with PEO. If the cations of KClO_4 get coordinated with the ether oxygen of PEO, the spectral changes are expected to be in the COC stretching and deformation ranges. The decrease in the width of 1095.2 cm^{-1} band, which is assigned to COC symmetrical and asymmetrical stretching [11-16], suggests the coordination / complexation of the salt with the polymer PEO.

3.2 Differential Scanning Calorimetry (DSC)

The Differential Scanning Calorimetry (DSC) curves of pure PEO and PEO complexed with KClO_4 for various compositions are shown in Fig.2. An endothermic peak is observed at 70°C , which corresponding to melting temperature of pure PEO. The slight shift in the melting point T_m , towards lower temperature is due to the addition of KClO_4 salt to the polymer. Similar result on PEO complexed system has also been reported by earlier workers [17-19].

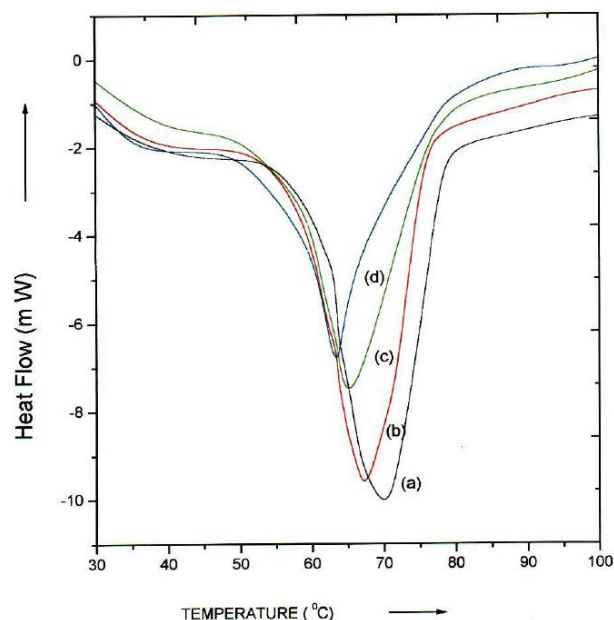


Fig 2 DSC Curves (a) Pure PEO, (b) [PEO + KClO_4] (90:10), (c) [PEO + KClO_4] (80:20) and (d) [PEO + KClO_4] (70:30)

Table – 2 Melting temperature of PEO and (PEO+KClO₄) polymer electrolyte systems obtained from DSC studies.

Polymer electrolyte system	Melting Temperature (T _m) °C
Pure PEO	70
PEO+KClO ₄ [90:10]	68
PEO+ KClO ₄ [80:20]	65
PEO+ KClO ₄ [70:30]	63

Table – 3 The d-Values calculated from the X-RD Spectra of pure PEO and various compositions of KClO₄ complexed films.

Pure PEO		PEO+ KClO ₄ (80:20)		PEO+ KClO ₄ (70:30)		KClO ₄	
2θ	d	2θ	d	2θ	d	2θ	d
15.092	5.8657	13.498	6.5545	11.317	7.8123	3.135	28.1560
19.203	4.6181	14.981	5.9089	14.878	5.9496	4.910	17.9831
23.352	3.8062	19.118	4.6385	17.081	5.1867	14.774	5.9910
25.258	3.5231	21.169	4.1934	19.244	4.6083	17.610	5.0322
26.326	3.3825	23.359	3.8050	21.228	4.1820	18.398	4.8183
26.920	3.3093	26.149	3.4050	23.428	3.7940	19.116	4.6390
32.497	2.7529	26.985	3.3014	25.163	3.5361	19.943	4.4485
35.454	2.5291	30.986	2.8837	26.399	3.3733	21.087	4.2096
36.310	2.4721	32.788	2.7291	27.116	3.2858	22.099	4.0190
39.735	2.2665	35.353	2.5368	27.87	3.1855	23.314	3.8123
		36.163	2.4818	35.629	2.5178	24.348	3.6527
		39.647	2.2714	36.326	2.4711	26.199	3.3986
		45.153	2.0064	39.767	2.2648	26.982	3.3018
		50.027	1.8217	45.338	1.9986	27.828	3.2032
		53.967	1.6976	45.42	1.9110	31.071	2.8759
				54.006	1.6965	32.552	2.7484
				56.369	1.6309	35.124	2.5528
						36.260	2.4754
						39.689	2.2691
						45.360	1.9977
						47.361	1.9178
						48.646	1.8702
						50.093	1.8195
						54.061	1.6949
						56.175	1.6360
						63.666	1.4604

3.3 X-ray Diffraction

PEO complexation with various salts has been extensively studied using X-ray diffraction and vibrational spectroscopic studies [11 - 16]. The X-ray diffraction (XRD) pattern of pure PEO, KClO₄ complexed PEO and KClO₄ are given in Fig. 3.2. A comparison of the diffraction spectra of complexed PEO with that of pure PEO and KClO₄ reveals the following differences.

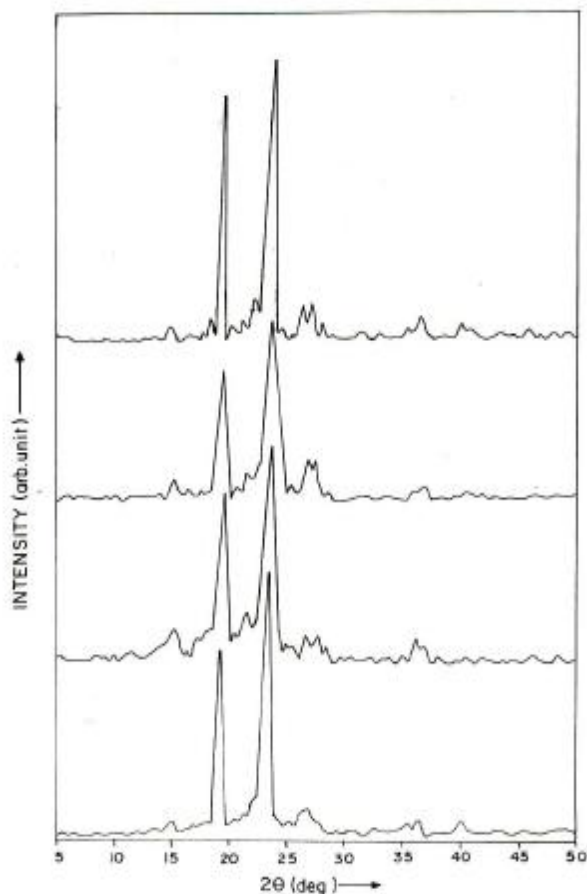


Fig 3 X-ray diffraction pattern (a) Pure PEO, (b) [PEO + KClO₄] (80:20), (c) [PEO + KClO₄] (70:30) and (d) KClO₄.

- i) The diffraction peaks observed between $2\theta = 10^\circ$ and 30° are found to be less intense in complexed PEO films compared to pure PEO films. This indicates that the addition of KClO₄ salt to the polymer causes a decrease in the degree of crystallinity of the polymer PEO.
- ii) Peaks corresponding to the uncomplexed PEO are also present together with that of KClO₄ in complexed PEO films showing the simultaneous presence of both crystalline uncomplexed and complexed PEO. Earlier workers [20 - 25] have reported similar results on PEO complexed systems.
- iii) Almost no sharp peaks were observed for higher concentration of the KClO₄ salt in the polymer, indicating the dominant presence of an amorphous phase.

Thus, the XRD data for these films clearly confirm the complexation between the KClO₄ salt and the polymer PEO. The d-values calculated from the X-ray diffraction of pure PEO and various compositions of KClO₄ complexed films are given in Table - 3, which clearly indicates the complexation.

4. CONCLUSIONS

The IR spectra recorded in these films showed several vibrational bands at various wave numbers. Several new bands have appeared and some bands have disappeared in the IR spectra of complexed films due to the addition of salts to the polymer. The intensity of certain bands observed in polymer showed a decrease with an increase in the concentration of the salts added to the polymer. A decrease in the width of certain bands has been observed due to the addition of salts. Due to the addition of salts to the polymer, several vibrational bands have been found to be shifted from their positions.

DSC studies in these polymer electrolyte films have shown the presence of an endothermic peak at 70°C which corresponds to the melting temperature T_m of the polymer PEO. A slight shift in the melting point, T_m towards lower temperature has been observed due to the addition of salt to the polymer.

A comparison of the X-ray diffraction spectra of complexed PEO films with that of uncomplexed PEO showed a decrease in the intensity of the diffraction peaks in complexed films. This is due to a decrease in the degree of crystallinity of the polymer due to the addition of the salt, indicating the salvation of the salt with the polymer. Peaks corresponding to the uncomplexed PEO are also present in complexed films, showing the simultaneous presence of both crystalline uncomplexed and complexed PEO. Almost no sharp peaks have been observed for higher concentrations of the added salts, showing the dominant presence of an amorphous phase. Thus, the results of IR, XRD and DSC have confirmed the polymer-salt complexation.

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BIOGRAPHIES



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