International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064
Impact Factor (2012): 3.358

Investigation of Characterization of (PEO+ $NaClO_3$+Plasticizer) Based Polymer Electrolytes

T. Sreekanth

Assistant Professor, Department of Physics, Jawaharlal Nehru Technological University Hyderabad College of Engineering Nachupally (Kondagattu), Karimnagar District, Telangana State, India

Abstract: ***Ion conducting solid state polymer electrolytes has been prepared by using poly (ethylene oxide) (PEO), $NaClO_3$ salts and plasticizer (Dimethyle Formamide [DMF]). (PEO+$NaClO_3$+plasticizer) various polymer electrolyte compositions were prepared in the Wt% ratios (90:10), (80:20) and (70:30) by using solution – casting technique where methanol as solvent. Several experimental techniques such as X-ray diffraction, Infrared (IR) and differential scanning calorimetry (DSC) studies have been employed to determine the complexation of the salt and polymer in the polymer electrolyte.***

Keywords: Polymer, poly (ethylene oxide), plasticizer, X-ray diffraction, differential scanning calorimetry

1. Introduction

At present, an extensive quantity research work have been reported on solid electrolytes due to the technological advantages, such as long self life, extreme miniaturization and a wide a wide – temperature range of operation. These solids show appreciable high ionic conductivities at their operating temperatures. These solids are known as "super ionic solids" and they find wide application in fuel cells, gas sensors, electrochemical display devices and solid state batteries. Due to these facts, research work on solid state electrolytes is timely an interdisciplinary area in contemporary science, calling upon the proficiency on chemists, physicists and material science and engineers [1-4].

Earlier most of the reports were mad on lithium based polymer electrolytes and only few reports have been observed on sodium based polymer electrolytes. Keeping these aspects in view, the author prepared (PEO+$NaClO_3$+plasticizer) polymer electrolytes by using solution casting technique. The complexation of the PEO, $NaClO_3$ salts and plasticizer (Dimethyle Formamide [DMF]) was examined by using X-ray diffraction (XRD), Infrared (IR) and differential scanning calorimetry (DSC) studies.

2. Experimental

Poly (ethylene oxide) (PEO) (Aldrich, M.W. $6X10^5$) and various compositions of (PEO+$NaClO_3$+plasticizer) polymer electrolytes were prepared in the Wt% ratios (90:10), (80:20) and (70:30) by solution-casting technique by using methanol as solvent. The solutions were stirred for 15-20 hr, were cast on polypropylene dishes, and were evaporated slowly at room temperature. Finally, the films were dried thoroughly at 10^{-3} Torr [5]. 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 λ = 1.5406 Å). The infrared spectrum of polymer electrolyte films was recorded on a Perkin Elmer FTIR spectrophotometer [Model 1605] in the range of 1000 – 4000 cm^{-1}. DSC (TA 2010 instrument) was used to study the melting temperatures of the polymer electrolyte films [6].

3. Results and Discussion

3.1 X-ray diffraction (XRD) analyses

X-ray diffraction (XRD) patterns of pure PEO, $NaClO_3$ and plasticizer are shown in Figure 1. A comparison of the diffraction spectra of complexed PEO with that of pure PEO and $NaClO_3$ reveals the following details:

a) XRD pattern obtained in the 2θ range of 10^o to 30^o, where the complexed PEO films to be less intense than those for the pure PEO films, which indicates that the addition of $NaClO_3$ to the polymer causes a decrease in the degree of crytallinity of the polymer PEO.
b) Peaks corresponding to the uncomplexed PEO are also present, on one those of the $NaClO_3$, in complexed PEO films, showing the simultaneous presence of both crystalline uncomplexed and complexed PEO [7].
c) For the higher concentration of $NaClO_3$ salt in the polymer, no sharp peaks were observed, which indicates the dominant presence of an amorphous phase.

Therefore, the XRD pattern clearly indicates a complexation between the $NaClO_3$ salt and the PEO polymer.

3.2 IR studies

The complexation of pure PEO, $NaClO_3$ and plasticizer has been extensively studied using vibrational spectroscopic studies [8].The IR spectra of pure PEO, $NaClO_3$ and PEO complexed with $NaClO_3$ are shown in Figure 2 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 $NaClO_3$.

a) The intensity of the aliphatic C-H stretching vibrational band observed around 2897.1 cm^{-1} in PEO decreases with increasing concentration of $NaClO_3$ salt in the polymer.
b) The width of the C-O Stretching band observed around 1095.2 cm^{-1} in PEO also showed an increase with an increase of $NaClO_3$ in the polymer.
c) Several new peaks around 4329.6, 4002.0, 2363.4 and 1280.8 cm^{-1} have been observed in complexed PEO.

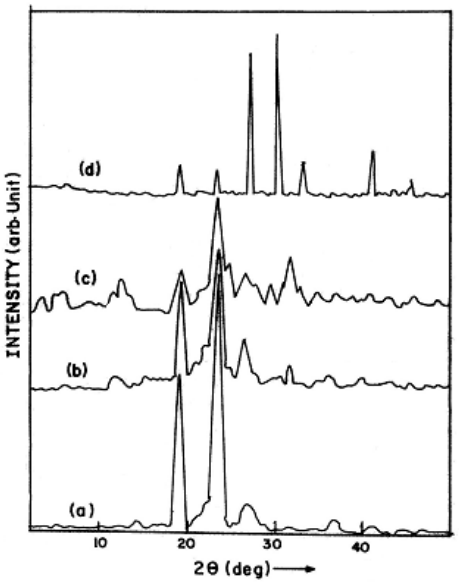

Figure 1: X-ray diffraction spectra of (a) Pure PEO (b) (PEO+$NaClO_3$+plasticizer) (90:10), (c) (PEO+$NaClO_3$+plasticizer) (70: 30) and (d) $NaClO_3$ salt.

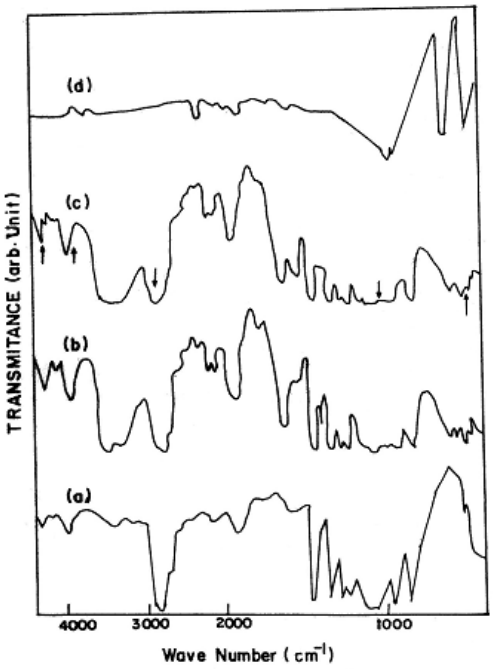

Figure 2: IR spectra of (a) Pure PEO, (b) (PEO+$NaClO_3$+plasticizer) (90: 10), (c) (PEO+$NaClO_3$+plasticizer) (70: 30) and (d) $NaClO_3$ salt

The appearance of new peaks along with changes in existing peaks (and / or their disappearance) in the IR spectra directly indicates the complexation of $NaClO_3$ with PEO. If the cations of $NaClO_3$ 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 [9], suggests the coordination / complexation of the salt with the polymer PEO.

Table 1: various vibrational bands observed in the IR spectra of PEO, (PEO+$NaClO_3$+plasticizer) (90:10), (PEO+$NaClO_3$+plasticizer) (70: 30) and $NaClO_3$.

Pure PEO (cm-1)	*(PEO+$NaClO_3$ +plasticizer) (90:10) (cm^{-1})*	*(PEO+$NaClO_3$ +plasticizer) (70: 30) (cm^{-1})*	*$NaClO_3$ (cm^{-1})*
470.6	520.5	849.1	970.4
843.9	1076.7	1282.2	1542.7
951.7	1454.4	1457.7	1702.4
1117.7	1650.6	1644.9	1891.9
1237.7	1964.4	1958.2	2365.7
1279.6	2930.2	2906	3567.8
1349.3	3442.7	3494	3650.3
1464.9	4008.2	3992.2	3750.4
1628.9	4332.5	4329	
1807.4			
1960			
1267.1			
2237.6			
2355.1			
2872.2			
3448.1			
4003.4			
4329.5			

3.3 Studies of Differential Scanning Calorimetry (DSC):

Figure 3 shows the differential scanning calorimetry (DSC) curves of pure PEO and various compositions of complexed PEO. At 70°C an endothermic peak corresponding to the melting temperature (T_m) of the pure PEO was observed. With the addition of $NaClO_3$ to pure PEO, the melting temperature (T_m) slightly shifted towards lower temperatures [6 & 9]. The details of the melting temperatures (T_m) of pure PEO and various compositions of (PEO+$NaClO_3$+plasticizer) are presented in the Table 2.

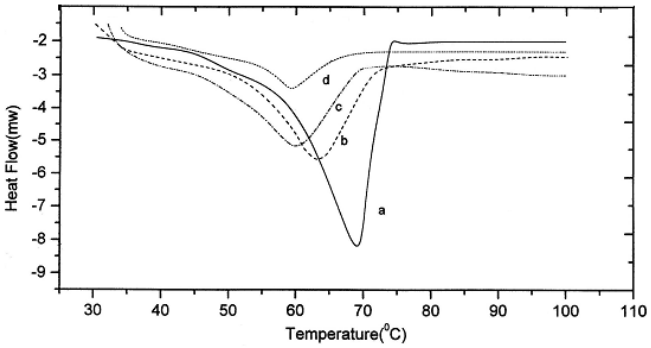

Figure 3: DSC curves of (a) Pure PEO, (b) (PEO+$NaClO_3$+plasticizer) (90:10), (c) (PEO+$NaClO_3$+plasticizer) (80:20) and (d) (PEO+$NaClO_3$+plasticizer) (70:30).

Table 2: Melting temperature (T_m) of PEO and complexed polymer electrolyte systems obtained from DSC studies.

Polymer electrolyte	*Melting temperature (T_m) °C*
Pure PEO	70
(PEO+$NaClO_3$+plasticizer) (90:10)	64
(PEO+$NaClO_3$+plasticizer) (80:20)	60
(PEO+$NaClO_3$+plasticizer) (70:30)	59

4. Conclusions

Ion conducting (PEO+$NaClO_3$+plasticizer) solid-state polymer electrolytes were fabricated by using the solution casting method. The complexation of the polymer and salt was confirmed by using XRD Infrared (IR) and differential scanning calorimetry (DSC) studies. At 70°C, an endothermic peak was observed in DSC study corresponding to the melting temperature (T_m) of pure PEO. With the addition of $NaClO_3$ to pure PEO, the melting temperature (T_m) was slightly shifted towards lower temperature. The decrease in the melting temperature (T_m) is attributed as an increment in the amorphous content of the polymer is due to the addition of the salt and plasticizer to the polymer. Future scope of study is using these polymer electrolytes a variety of devices can be fabricated such as fuel cells, sensors, electrochemical display devices, smart windows, photochemical cells etc.

References

[1] D. F. Shriver, B. L. Papke, M. A. Ratner, R. Doppon, T. Wong and M. Brodwin, "Structure and ion transport in polymer-salt complexes", *Solid Sate Ionics,* (5) pp. 83-88, 1981.
[2] D. F. Shriver and M. A. Ratner, "Ion Transport in Solvent-Free Polymers" Chem. Rev., (88), pp, 109, 1988.
[3] M. B. Armand,"Polymer Electrolytes" Ann. *Rev. Mater. Sci.,* (16), pp. 245-261, 1986.
[4] T. Sreekanth, International Journal of Engineering Research and Applications, "Preparation and Characterization of (PEO+NaClO3) Based Polymer Electrolyte System and Its Application as an Electrochemical Cell", (4), pp. 29-32, 2014.
[5] M. Jaipal Reddy, T. Sreekanth, and U.V. Subba Rao, "Study of the plasticizer effect on a (PEO+$NaYF_4$) polymer electrolyte and its use in an electrochemical cell", Solid Sate Ionics. (126), pp. 55-63, 1999.
[6] M. Jaipal Reddy, Peter P. Chu, T. Sreekanth, and U. V. Subba Rao, "PEO: KIO_3 Polymer Electrolyte System- Its Application to Solid State Electrochemical Cell", Journal of Materials Science: Materials in Electronics, (12), pp. 153-156, 2001.
[7] T. Sreekanth, M. Jaipal Reddy, S. Ramalingaiah, U. V. Subba Rao, "Ion-conducting polymer electrolyte based on poly (ethylene oxide) complexed with $NaNO_3$ salt-application as an electrochemical cell" Journal of Power Sources, (79), pp. 105-110, 1999.
[8] T Sreekanth, M Jaipal Reddy, S Subramanyam, U. V Subba Rao, "Ion Conducting Polymer Electrolyte Films Based on (PEO+KNO_3) System and Its Application as an Electrochemical Cell", Materials Science and Engineering: B, (64), pp. 107-112, 1999.
[9] H. Yang, R. Huq and G. C. Farrington, "Conductivity in PEO-based Zn(II) polymer electrolytes", Solid State Ionics (40-41 Part 2), pp. 663-665, 1990.

Author Profile

Dr T Sreekanth is born and brought up in Mahabubnagar town of Telangana State. He has completed his schooling at Model Basic High School Mahabubnagar. He obtained graduation (B.Sc.) and post graduation (M.Sc.) from Osmania University, Hyderabad with fist division. In 2002, He was awarded doctoral degree from Osmania University, Hyderabad under the guidance of Prof. U. V. Subba Rao, with thesis entitled as *"Polymer electrolyte thin films and their applications"*. He has tremendous academic credentials to his credit with over 13 years of teaching and research experience. He has several International and national publications to his credit. He has also attended various International and national Conferences. He was organized several National Conference and Workshops. He is also author for four B. Tech Books namely *Soli State Physics and Engineering Physics etc.,* published by S. Chand & Company, New Delhi. His area of interest includes Solid State Physics, Materials Science and Nanotechnology. At present He is working as Assistant Professor and Head, Department of Physics, JNTUH College of Engineering, Nachupally (Kondagattu), Karimnagar district of Telangana State, India. Presently four research scholars are working under his guidance. Dr Sreekanth is life member of MRSI and MISTE.