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Effect of PMMA dispersion on electrolytic properties of PEO:NH_4ClO_4

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The ionic conductivity, dielectric constant and X-ray diffraction (XRD) studies are reported on the solution casted film of [xPEO + (100-x) PMMA]:NH_4ClO_4 for x= 0-100 weight percent. The NH_4ClO_4 crystallizes out in the films with large amounts of polymethyl methacrylate (PMMA). However, addition of a small amount of PMMA in PEO: NH_4ClO_4 matrix enhances the ionic conductivity. The thermally activated conductivity variation is explained in terms of the electrolyte dissociation theory.

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Keyword: Ionic conductivity, Dielectric constant, X-ray diffraction

1. Introduction

Polyethylene oxide (PEO) in particular is an exceptional polymer which dissolves high concentrations of a wide variety of salts to form polymeric electrolytes [1-2]. Interest began in this field after the pioneering studies of materials based on alkali metal salts complexed with polyethylene oxide (PEO) [3-5]. PEO complexed with a large number of salts of different cations (e.g. Li^+, Na^+, Ag^+, NH_4^+ etc.) have been the subject of most ion transport studies in polymer electrolytes because of low glass transition temperature (T_g) value of PEO and ease of film formation by solution cast technique. However, the complex PEO films always turn out to be partially crystalline and therefore the maximum room temperature conductivity which could be attained was limited to ~ 10^{-5} S cm^{-1}. Attempts have been made by using copolymers to modify the crystalline nature of the complexed PEO by blending with low mass oligomers or solvents by copolymerization, addition of plasticizers and semiconducting nanoparticles etc. [6-10]. PEO:NH_4ClO_4 is well studied system by Chandra et al [11] which shows are non-compatibility, limited range of salt complexation, phase separation. This paper is an attempt to study the structural and transport property modifications introduced by addition of PMMA in PEO base proton conducting polymers. The system chosen is PEO:NH_4ClO_4 in which different amounts of PMMA have been added. Poly(methyl methacrylate) (PMMA) is a transparent thermoplastic, often used as a lightweight or shatter-resistant alternative to glass. Chemically, it is the synthetic polymer of methyl methacrylate. The material was developed in 1928 in various laboratories, and was first brought to market in 1933 by the Rohm and Haas Company, under the trademark Plexiglas.

PMMA is an economical alternative to polycarbonate (PC) when extreme strength is not necessary. Additionally, PMMA does not contain the potentially harmful bisphenol-A subunits found in polycarbonate. It is often preferred because of its moderate properties, easy handling and processing, and low cost. The non-modified PMMA behaves in a brittle manner when loaded, especially under animpact force, and is more prone to scratching than conventional inorganic glass. However, the modified PMMA achieves very high scratch and impact resistance.

It has been reported [12] that in PEO: NH_4ClO_4 system, by free volume measurement, the conductivity variation is more affected by the change in the number of charge carriers available. In the present study it has been shown that PMMA does not complex well with NH_4ClO_4, albeit addition of small weight ratios in the PEO complex leads to conductivity enhancement. At higher concentration of PMMA, the conductivity drops. Further, it is found that NH_4ClO_4 salt crystallizes out of the PEO:PMMA blend when weight percent of PMMA is more than 20 %. The temperature dependent conductivity pattern has been explained by the simple electrolyte dissociation model. The enhancement in the number of charge carriers have been sought out as the prime factor for the enhancement of the conductivity.

2. Experimental details

For preparation of solution casted films, polymers (PEO and PMMA) were purchased from Aldrich co., USA and used as procured. Films of PEO: NH_4ClO_4 and (PEO+PMMA): NH_4ClO_4 were prepared in different composition ratios by solution cast technique by dissolving the desired amounts of the components in acetonitrile and slowly evaporating the solution in polypropylene Petri dishes at room ambient. The films were finally dried under vacuum for complete removal of solvent traces. The XRD studies were carried out by Rigaku Rotaflex diffractometer. For all electrical characterization, either side of the films were coated with aluminum using a vacuum coating unit (HHV, 12C).

Measurement of bulk conductivity was done by complex impedance method, using computer controlled CH instrument (USA). The impedance measurements were carried out in the frequency range 10 Hz to 1 MHz. The conductivity value (σ) was calculated using the relation $\sigma = \frac{1}{R_b} x \frac{l}{A}$; where R_b is the bulk impedance obtained from the intercept in Z'-Z" plot, l and A are the thickness of the film and area of electrode coated on the film. The dielectric constant values have been calculated using the complex impedance data obtained at 1 MHz. Total ionic transference numbers of the complexed films were determined by Wagner's polarization method [13]. A small dc voltage was applied across the sample and the current was monitored. Using the initial and final (after complete polarization) current values, the transference number was calculated as

$$t_{ion} = \frac{i_{initial} - i_{final}}{i_{initial}}.$$

3. Results and discussion

Solution casted pure PEO films have been found to be partially crystalline [14-16]. On the contrary pure PMMA film gives excellent amorphous nature. Fig. 1 (a) shows the XRD pattern of solution casted PMMA films with 20 wt% of NH_4ClO_4. Interestingly, it shows partially crystalline nature with sharp peaks superimposed on a hallow. These peaks were assigned to the NH_4ClO_4 crystallites getting formed in the polymer matrix. For comparison the XRD of pure NH_4ClO_4 powder is given in Fig. 1 (b). Visually the PMMA: NH_4ClO_4 film was coarse and many crystals were seen sitting at the surface. The morphology of the NH_4ClO_4 crystallizing out as observed by an optical microscope (Fig. not shown here) which shows that the smaller crystals are rod like but the larger crystals were highly strained showing step like growth. The present study clearly indicates that NH_4ClO_4 has low solubility in PMMA. Therefore, PMMA: NH_4ClO_4 system is not expected, as such to yield high ionic conductivity compositions. In fact, our conductivity studies show that the conductivity of PMMA: NH_4ClO_4 complexes was less than 10^{-8} S cm^{-1} which is the minimum limit of our measurement. It may be pointed out that PEO is known to form complexes with a large number of alkali metal salts over extended composition ranges. The amorphous region (black portion) is assumed to be more conducting region [16]. Considering this aspect along with the amorphicity achievable in pure PMMA films, we attempted to form blends of PMMA+PEO: NH_4ClO_4 and to study their ion transport properties. The following compositions have been synthesized

[xPEO + (100-x)PMMA]: NH_4ClO_4

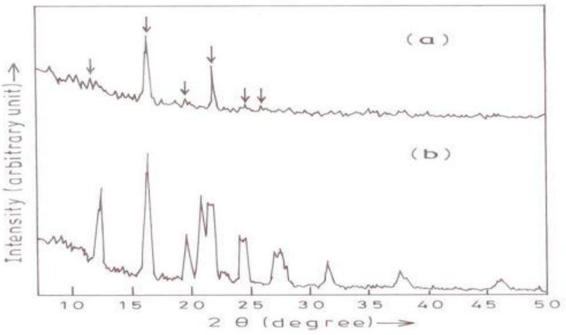

Fig. 1. The recorded XRD patterns of (a) solution casted PMMA: NH_4ClO_4 (80:20) and (b) pure NH_4ClO_4.

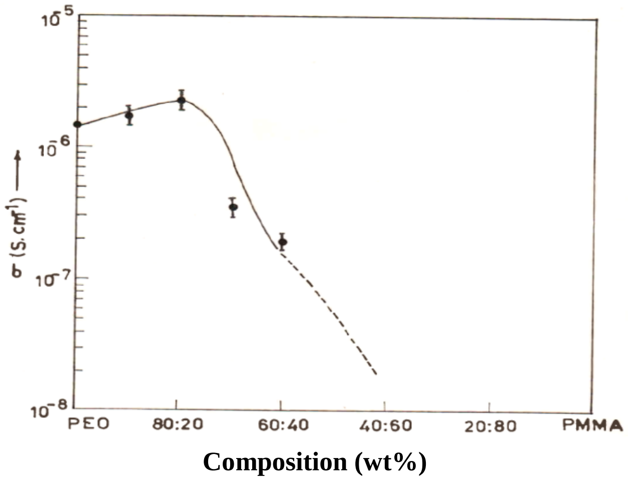

Fig. 2. Variation of ionic conductivity (σ) with composition (wt%) in PMMA+ PEO:NH_4ClO_4 polymer electrolyte system.

The weight ratio of the total polymer [xPEO + (100-x) PMMA] and NH_4ClO_4 was always kept 80:20 percent while x was varied [chosen as 100, 90, 80, -- 0). The composition dependence of conductivity is shown in Fig. 2. As indicated earlier, the conductivity of pure PMMA complexed with NH_4ClO_4 (i.e. x = 0) as well as compositions in which PMMA was more than 40%, the conductivity was less than the measurable limit of ~ 10^{-8} S cm-^{1}. an interesting point to note is the conductivity enhancement effect which have been introduced by addition of small amounts of PMMA. The conductivity (σ) of pure PEO: NH_4ClO_4 is 1.5×10^{-6} S cm-^{1}. There is an increase of the conductivity by nearly 70 % which may be due to the effect of PMMA in changing the overall crystalline nature of PEO:NH_4ClO_4 complex. Although the order of conductivity is low as far as device is concerned but it is quite comparable with the values reported in literature for polymer electrolyte based batteries. It is known that PMMA remains dispersed all over the film and shows a separate phase in polymer blends [17]. We extend this report in our system i.e. the PMMA remains dispersed in the PEO: NH_4ClO_4 matrix. This system can therefore be considered as a multiphase system in which PMMA is dispersed in the ion conducting PEO:NH_4ClO_4 matrix. The insulating PMMA dispersed in the PEO: NH_4ClO_4 ion conducting polymer matrix is similar to the composite systems reported by Chandra et al [18,19]. In that case the increase in conductivity with the addition of PMMA and then a decrease after achieving a maximum can be explained in terms of the percolation theory [20]. In all systems mentioned, the conductivity, unlike to the insulator-insulator composites, shows a maxima below 50:50 composition.

The addition of small amount of PMMA in the PEO : NH_4ClO_4 does not alter the ionic nature of the conductivity though it shows enhancement in the conductivity values as discussed above.

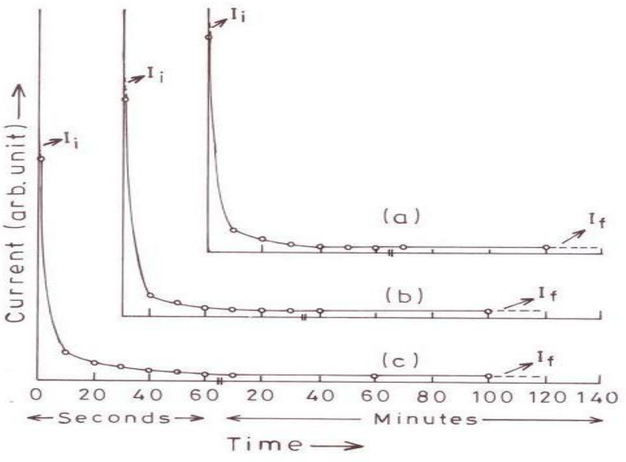

Fig. 3. Current vs time graph in PMMA+ PEO:NH_4ClO_4 polymer electrolyte system using Wagner polarization method.

Current versus time curves obtained in the Wagner's polarization experiment carried out on samples with different amounts of PMMA are shown in Fig. 3. The values of total ionic transference numbers, as calculated from the measured values of I_i and I_f from the Fig. 3 are more than 0.98 for each case. Fig. 4 shows the temperature dependence of conductivity of the highest conductivity composition i.e. (80PEO:20PMMA)+NH_4ClO_4. The conductivity shows a sudden jump near 60 ^{0}C corresponding to the melting temperature (T_m) of PEO and its crystalline complex. The conductivity could not be measured beyond 100 ^{0}C because the films became soft. The temperature dependence of conductivity in the limited temperature range of 30-60 ^{0}C could be assigned to Arrhenius type behavior. In order to sort out the possible reason causing this rise in the conductivity near T_m of PEO, attempts have been made to study the change in the number of charge carriers and their mobility.

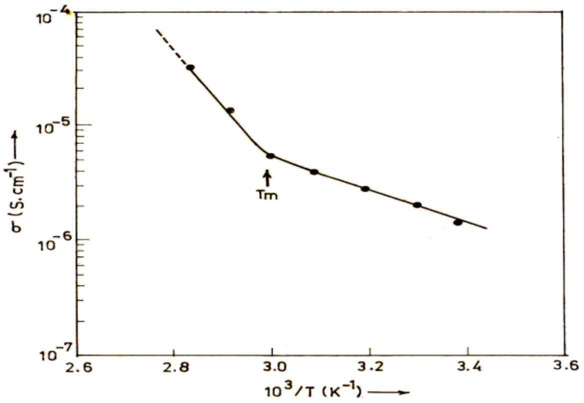

Fig. 4. Temperature dependence plot of a typical (80PEO:20PMMA) + NH_4ClO_4 polymer electrolyte film.

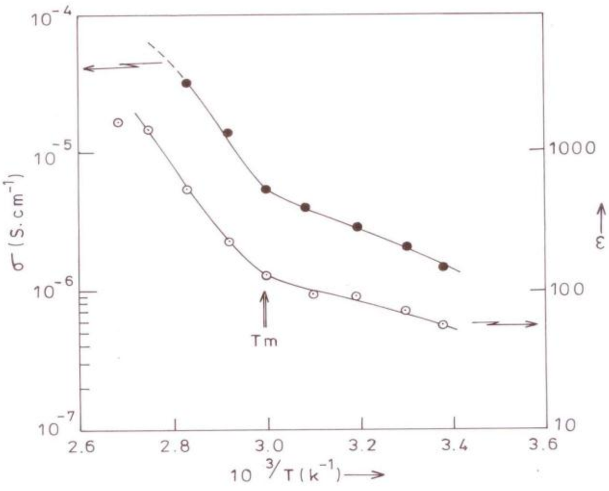

Fig. 5. The dielectric constant (ε) and conductivity (σ) vs temperature plot in PMMA + PEO:NH_4ClO_4 polymer electrolyte system.

We could not succeed in measuring the mobility of the charge carriers by the Transient Ionic Current (TIC) measurements. Since according to dissociation theory [21] the number of dissociation ions 'n' is given as

$$n = n_0 \exp(-U/2\varepsilon kT)$$

where U is the dissociation energy of the salt, ε is the dielectric constant of the medium and n_0 is the total number of charge carriers. This implies that if ε increases, the number of charge carrier (n) would also increase, which in turn will enhance the conductivity. With this idea, the dielectric constant ε of the highest ionic conductivity composition (80:20) have been measured at 65 kHz with varying temperature. Fig. 5 shows the variation in ε with temperature for the maximum conductivity composition. The variation of ε has a direct and exact correlation between ε and σ have been earlier reported in PEO and PMMA based systems [22-24]. The higher dielectric constant value indicates an increase in free ion concentration, by the dissociation of ion aggregates, which enhances conductivity [25]. Adopting the value of U from earlier reports we have calculated (n/n_0) with $10^3/T$. The variation in (n/n_0) is shown in Fig. 6. A jump could be seen at the T_m. At higher temperature (~90 ^{0}C) more than 95 % charge carriers become available for conduction whereas at room temperature only 40% were free. The results of Fig. 5 and 6 confirm that the temperature dependence variation in the conductivity is governed by the number of charge carriers and the carrier mobility has almost no effect (or very less effect) on the conductivity. The prime factor is the number of mobile charge carriers which become available due to possible dissociation of more and more salt molecules with increasing temperature. This results is in agreement with the results of the free volume and positron annihilaton studies in PEO:NH_4ClO_4 systems [12]. Knowing the facts about PMMA system some literature are also exist in which researchers are applied it in battery application [26,27].

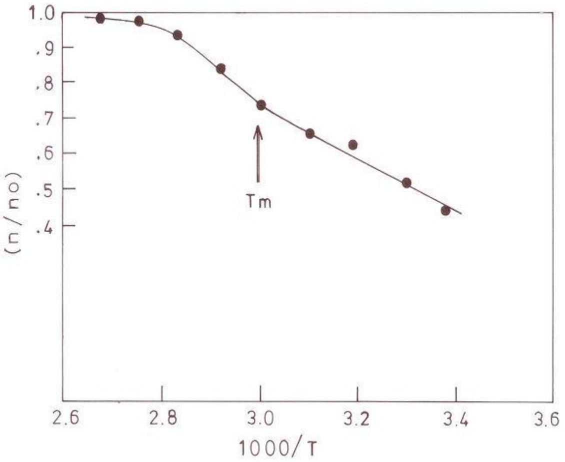

Fig. 6. The variation of n/n_0 vs $10^3/T$ plot in PMMA+PEO:NH_4ClO_4 polymer electrolyte system.

5. Conclusion

Addition of small amount of PMMA in PEO:NH_4ClO_4 complex enhances the conductivity and addition of higher amounts of PMMA leads to crystallization of NH_4ClO_4 salts out of the polymeric matrix. The temperature dependence of the conductivity and dielectric constant are consistent with the proposed electrolyte dissociation model. The enhancement in conductivity with temperature is assigned to the increase in the number of charge carriers and not to the mobility.

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References

[1] J. Plocharski, W. Wieczorek, J, Przyluski, K. Such, Appl Phys A **49**, 55 (1989).
[2] J. R. MacCallum, C. A. Vincent ed Polymer Electrolyte Reviews (London, Elsevier) (1987).
[3] P. V. Wright, Br. Polym. J. **7**, 319 (1975).
[4] D. E. Fenton, J. M. Parker, P. V. Wright, Polymer **14,** 589(1973).
[5] M. A. Ratner, D. F Shriver, Chem. Rev. **88,** 109 (1988)
[6] J. Zhang, X. Huang, H. Wei, J. Fu, Y. Huang, X. Tang, J Appl Electrochem **40**, 1475 (2010).
[7] B. K. Money, K. Hariharan, Appl Phys A **88**, 647 (2007).
[8] P. K. Singh, A. Chandra, J. Phys. D: Appl. Phys. **36,** L93 (2003).
[9] K. K. Maurya, N. Srivastava, S. A. Hashmi, S. Chandra, J. Mat. Sci. **27**, 6357 (1992).
[10] A. Chandra, P. K. Singh, S. Chandra, Solid State Ionics **154-155**, 15 (2002).
[11] S. A. Hashmi, A. Kumar, K. K. Maurya, S. Chandra, J Phys. D: Appl. Phys. **23**, 1307 (1990).
[12] B. Halder, R. M. Singru, K. K. Maurya, Phys. Rev. B **54**, 714 (1996).
[13] J. B. Wagner, C. Wagner, J Chem. Phys. **26**, 1597 (1957).
[14] P. K. Singh, H. W. Rhee, S. K. Tomar, R. K. Nagarale, Journal of Thermoplastic Composite Materials **23**, 227 (2010).
[15] I. F. Hakem, J. Lal, Appl Phys A **74**, 616 (2002).
[16] M. J. Reddy, P. P. Chu, Electrochimica Acta **47**, 1189 (2002).
[17] T. Mani, R. Mani, J. R. Stevens, Solid State Ionics **60**,113 (1993).
[18] P. K. Singh, A. Chandra, National Academy Science Letters: India **25**, 286 (2002).
[19] S. Chandra, S. K. Tolpadi, S. A. Hashmi, J. Phys.: Condens. Matter **1**, 9101 (1989).
[20] J. Maier, Prog. Solid St. Chem. **23**,171 (1995).
[21] R. E. Baker, C. R. Thomas, J Appl. Phys. **35**, 3203 (1964).
[22] P. K. Singh, R. K. Nagarale, B. Bhattacharya, Journal of Applied Polymer Science **118**, 2976 (2010).
[23] L. M. Clayton, A. K. Sikder, A. Kumar, M Cinke, M. Meyyappan, T. G. Gerasimov, J. P. Harmon, Adv. Funct. Mater. **15**, 101(2005).
[24] L. Othman, K. W. Chew, Z. Osman, Ionics **13**, 337 (2007).
[25] S. S. Sekhon, B. S. Lalia, J. S. Park, C. S. Kim, K. Yamada, J. Mater. Chem. **16**, 2256 (2006).
[26] X. H. Flora, M. Ulaganathan, R. S. Babu, S. Rajendran Ionics **18,** 731 (2012).
[27] W. Z. Liang, T. Z. Yuan, G. Xin, X. J. Jun, Acta Phys Chim Sin **18**, 272 (2002).

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