Polyethylene oxide based sodium ion conducting composite polymer electrolytes dispersed with $\text{Na}_2\text{SiO}_3$

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Received 3 February 1999

A composite polymer electrolyte based on polyethylene oxide (PEO): NaI system dispersed with sodium metasilicate ($\text{Na}_2\text{SiO}_3$) has been reported. The structural, thermal and electrical behaviour of the materials have been characterised using optical microscopy, X-ray diffraction, differential scanning calorimetry and impedance spectroscopy. A maximum electrical conductivity of $\approx 10^{-4}$ S cm$^{-1}$ at 45°C and 1.2 x $10^{-3}$ S cm$^{-1}$ at 100°C has been achieved with the dispersion of the adduct, $\text{Na}_2\text{SiO}_3$. The temperature dependence of the conductivity follows an Arrhenius type plots before and after the melting temperature ($T_m$) of PEO in the composite materials.

1 Introduction

A large number of solid polymeric electrolytes with appreciably high ionic conductivity have been investigated in the last three decades by complexing polar polymers [e.g., Polyethylene Oxide (PEO), Polypropylene Oxide (PPO) etc.] having strong solvating ability with a number of alkali, alkaline and transition metal salts (e.g. LiClO$_4$, LiI, Mg(ClO$_4$)$_2$, NaClO$_4$, NaI, AgNO$_3$, etc.)$^{1,2}$ These materials are of prime technological importance because of their high prospects of application as electrolytes in various electrochemical devices like high energy density batteries, fuel cells, sensors, memory devices, electrochromic display devices, supercapacitors etc.$^{1,2}$

Recently, particular attention has been devoted to introduce some structural modifications in polymer electrolytes in order to increase their electrical conductivity and to improve their thermal, mechanical and electrochemical properties. Various techniques have been adopted to achieve the above mentioned desirable changes in the polymer electrolyte structure such as plasticization by adding plasticizers like EC, PC, PEG etc., copolymerisation by blending the polymer electrolytes with high glass transition temperature ($T_g$) polymers.

Recently, a new class of polymer electrolyte referred as “composite polymer electrolytes (CPEs)” has attracted much attention$^{6,15}$ These polymer electrolytes are dispersed with ceramic/inorganic or high molecular weight organic fillers with an aim to enhance electrical conductivity and to improve thermal, mechanical and electrochemical stability of the polymer films.

The present paper reports a new composite polymer electrolyte: PEO + NaI system dispersed with sodium metasilicate ($\text{Na}_2\text{SiO}_3$). The effect of using a new dispersoid on morphology, electrical, thermal and mechanical behaviour of the composite system has been studied using different experimental techniques like optical microscopy, X-ray diffraction, DSC analysis, impedance analysis and conductivity measurements. The changes in the morphology and structure of the composite polymer electrolyte system are studied by optical microscopy and X-ray diffraction. The electrical conductivity has been evaluated from complex impedance plots and interpreted as a function of composition and temperature of the materials. The results on the temperature dependence of the conductivity has been correlated with the semi-crystalline to amorphous phase transition in the composite system as observed by DSC studies.

2 Experimental Procedure

The composite polymer electrolyte films (300-500µm thick) of different dispersoid ($\text{Na}_2\text{SiO}_3$) compositions for a fixed ratio (O/Na = 25) of PEO and NaI were prepared using the standard “solution-cast technique.” The commercial PEO (Aldrich, M.W. $\approx 6 \times 10^6$), NaI and $\text{Na}_2\text{SiO}_3$ (Fluka) were used as received after drying without further purification. The calculated ratios of
PEO and NaI were dissolved in anhydrous methanol separately. The solutions were then mixed and stirred thoroughly for ~12 hours. After that, different weight percentages of Na$_2$SiO$_3$ were added to the solutions and further stirred for 10-12 hours. The mixed solutions were then cast in polypropylene dishes and allowed to evaporate slowly at room temperature (~25°C) followed by vacuum drying.

In the process of synthesis, the PEO and NaI molar ratio was maintained at 25:1 and the amount of Na$_2$SiO$_3$ dispersed is expressed as a weight percent (wt. %) with respect to the polymer matrix (PEO) present in the system. The composition of the material can precisely be expressed as (PEO)$_{25}$ NaI + x % Na$_2$SiO$_3$.

The optical micrographs of the different compositions of the composite polymer electrolytes were taken by LEITZ make optical microscope (LABORLUX model).

The XRD patterns of the films were recorded at room temperature (25°C) using CuK$_\alpha$ irradiation with X-ray diffractometer (Rigaku, Japan).

The differential scanning calorimetry (DSC) of the different composite films have been done using a PERKIN ELMER DSC-4 unit for the temperature range -100°C to 250°C at a heating rate of 10°C min$^{-1}$ in static nitrogen atmosphere.

The complex impedance spectroscopic studies (bulk electrical conductivity) of different composite films have been carried out as a function of temperature and composition with the help of computer controlled LCR HI TESTER (model 3520-01), HIOKI (Japan). The impedance measurements were done on the cell: SS | polymer electrolyte | SS, for a frequency range varying from 40 Hz to 100 kHz with a signal level of 20 mV (SS stands for stainless steel).

3 Results and Discussion

The optical micrographs of (PEO)$_{25}$ NaI + x % Na$_2$SiO$_3$, with increasing concentration (value of x) are shown in Fig. 1. The distinct spherulites are observed in the pure polymer complex (x = 0 %) which indicate its lamellar crystalline microstructure (Fig. 1a).

The dark boundaries observed between the spherulites represent the partial amorphous phase of the complexed polymer. The morphological texture of the films is seen to change appreciably upon gradual addition of the additive, Na$_2$SiO$_3$. These changes distinctly appear in the Fig.1(b and c). The addition of even 1 wt % of the additive, Na$_2$SiO$_3$, changes the spherulitic texture of the polymer film, substantially. The size of the spherulites have been found to be drastically reduced (Fig.1b). The presence of several dark spots have also been noticed on further addition of the additives (Fig. 1c). This indicates that the films are in a composite phase with homogeneous distribution of the additive throughout the films. The similar observations have been obtained by us in the (PEO)$_{25}$ NaClO$_4$ + x % Na$_2$SiO$_3$ composite system$^{12}$.

The X-ray diffraction patterns of (PEO)$_{25}$ NaI + x % Na$_2$SiO$_3$ for different values of x are shown in the Fig. 2. A comparative study of the peaks indicates that the PEO peak positions are observed at 2θ = 16° and 19°. 

![Optical micrographs of (PEO)$_{25}$ NaI + x % Na$_2$SiO$_3$ with x = 0 % (a), 1 % (b) and 15 % (c)](image)
These peaks get shifted at 2θ~14.5° and 18.5°. The shift remains almost the same for all the compositions of the additive ranging from values \( x = 0 \% \) to \( x = 20 \% \). So this shift may be attributed to the complexation of NaI with PEO chains. Further, the distinct peaks start appearing at 2θ~11°, 11.5°, 12° and 14° which have been attributed to the additive, Na₂SiO₃, as a separate phase. This separate phase of Na₂SiO₃ dispersed in the polymer films has also been observed in the optical micrographs Fig. 1 (b and c). So, XRD data also indicate changes in the crystalline morphology of PEO complex on addition of Na₂SiO₃ resulting into semi-crystalline structure.

The DSC curves of (PEO)₂₅ NaI + x % Na₂SiO₃ with different wt% of Na₂SiO₃ is shown in Fig. 3. The pure complex (PEO)₂₅ NaI shows a predominant endothermic peak at ~69°C and two step changes owing to glass transition temperatures at \( T_{g1} \sim -48°C \) and \( T_{g2} \sim -15°C \) (Fig. 3a). The \( T_{g2} \) is assigned to the un-complexed PEO which does not change with the addition of the adducts. While, \( T_{g1} \) which can be assigned to the complexed PEO, shows a marked shifts in its position. The peaks observed at ~69°C are assigned to the crystalline melting of un-complexed PEO, which remain unaffected with the compositional changes.

Further, two small endothermic peaks also appear for different wt % of Na₂SiO₃ over a range of temperature ~100 °C to 150 °C. The intensity of the peak at ~100°C increases with increasing concentration of Na₂SiO₃ which indicates that this peak is associated with the additive material which can be assigned to the dehydration of water trapped with the additive material Na₂SiO₃·H₂O. It is difficult to assign the peaks observed at ~145 °C.

The variation in the electrical conductivity (measured at 45 °C) of the composite polymer electrolyte films as a function of composition (i.e. Na₂SiO₃ content) is shown in the Fig. 4. The electrical conductivity (of \( 10^{-6} \) S cm⁻¹) remains almost constant over a wide range of composition up to 15 wt % of the adduct, Na₂SiO₃. Thereafter, the conductivity starts decreasing with increasing concentration of the dispersoid. This is possibly due to the increase of \( T_{g2} \) of the composites with increase in the adduct concentration, as observed in DSC results (Fig. 3). In addition, the mechanical stability of the composite materials has also been found to increase with increasing concentration of the adduct.

The temperature dependence of the conductivity i.e., \( \sigma \) vs. \( 1/T \) plots of (PEO)₂₅ NaI + x % Na₂SiO₃ is shown in the Fig. 5. The plots indicate a sudden jump in conductivity for each composition after melting temperature of PEO, \( T_m \) (~69 °C as observed in DSC). This has been explained on the basis of semicrystalline to amorphous phase transition. The almost linear variation
in conductivity as a function of temperature follows apparently an Arrhenius type thermally activated process before and after $T_m$. The conductivity $\sigma$ may be expressed as:

$$\sigma = \sigma_0 \exp \left( -\frac{E_a}{kT} \right)$$

where, $\sigma_0$ is the pre-exponential factor, $E_a$ is activation energy and $k$ is the Boltzmann constant.

4 Conclusion

The composite polymer electrolyte films of composition $(\text{PEO})_{25} \text{NaI} + x \% \text{Na}_2\text{SiO}_3$ ($x = 0$ to 25 wt %) show reasonably good conductivity with substantial improvement in their mechanical stability. The dispersed phase composite nature of the materials with homogeneous distribution of the additive is indicated by optical microscopy and XRD studies. The temperature dependence of conductivity shows an Arrhenius type thermally activated process before and after melting temperature, $T_m$ of the materials.

Acknowledgement

Authors acknowledge the financial support of the Department of Science & Technology (New Delhi) under the project sanction No. SP/SS/05/94. Our grateful thanks are extended to the Head, Forestry Department, NERIST and Dr C L Sharma (Forestry Department, NERIST) for providing the facility of Optical Microscopy.

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