Influence of nano filler on conductivity in PEO-PMMA-AgNO$_3$ polymer blend

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The electrical conductivity of plasticized PEO-PMMA-AgNO$_3$ polymer blend films with different concentrations of nano-filler (Al$_2$O$_3$) has been studied. The polymer electrolyte films have been prepared by solution cast technique and characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR) and differential scanning calorimetry (DSC). Electrical properties of polymer films have been investigated by using complex impedance spectroscopy in the frequency range 2 MHz-100 Hz from 303 to 373 K. The variation of ionic conductivity with nano-filler concentration is discussed.

Keywords: Nano-filler, Polymer blend, DSC, Conductivity

1 Introduction

Solid polymer electrolytes are being attractive materials since more than two decades due to their potential applications in electrochemical devices as well as in the field of solid state batteries, super capacitors, photonics and optoelectronics. In recent years, blending of polymers provides a useful way to produce materials with a desirable combination of properties unavailable with a single polymer. This technique is a quicker and simple way of preparing and controlling the physical properties of individual polymer just by compositional change instead of synthesizing a new polymer. Hence, a polymer blend system based on PEO-PMMA has been taken as host polymer for the present study as PEO is still an active polymer host for polymer electrolytes.

The addition of plasticizer yields polymer electrolytes with enhanced conductivity but the main disadvantage of plasticized polymer electrolyte is the leakage of liquid from the films and/or loss of mechanical properties. Johan et al. suggested that the dispersion of nano-fillers in polymer electrolytes results into improved electrical, thermal and mechanical properties of the polymer materials.

The polymer blend PEO-PMMA forms a good blend system and it seems that Ag$^+$-ion conducting in this blend system is hardly seen. Therefore, the effect of lower concentrations of nano-fillers (Al$_2$O$_3$) on electrical properties of silver ion conducting polymer blend system as PEO-PMMA-PEG-AgNO$_3$ has been investigated.

2 Experimental Details

In the present investigation, PEO (Mw = 3×10$^5$, Alfa Aesar), PMMA (Mw= 3.5×10$^5$, Alfa Aesar), PEG (Mw= 4000, Loba Media) polymers were used for the preparation of polymer electrolytes. Nano-filler, Al$_2$O$_3$ with the particle size < 50 nm was obtained from Sigma-Aldrich. PEO and PMMA were taken in 50:50 weight percentage which were optimized in our previous report and the concentration of PEG plasticizer and silver salt AgNO$_3$ was kept fixed as 5 wt% each with respect to the total concentration of PEO and PMMA. Acetonitrile was used as common solvent for polymer films.

The polymer samples are prepared according to: (PEO$_{50}$-PMMA$_{50}$)-5 wt% PEG-5 wt% AgNO$_3$-x wt% Al$_2$O$_3$ where x is varied from 1 to 5 in steps of 1 with respect to the total concentration of PEO and PMMA.

Desired amount of PMMA was dissolved and stirred in a beaker using acetonitrile solvent for 24 h at 323 K. PEO, silver nitrate salt and PEG plasticizer were dissolved in a separate beaker at room temperature and stirred for 4-5 h. After complete dissolution, both the solutions were mixed and a desired amount of nano-filler was added to this mixed solution and again stirring was carried out at room temperature for another 10 h. Thus, obtained solution was poured in Teflon Petri dish and left to evaporate the solvent slowly at room temperature. The resulting film was then also dried in an oven at 313 K to ensure the removal of the solvent traces and the dried films
were peeled off from the Petri-dish. The obtained films were stored in dark desiccators to prevent any contamination from moisture and/or light. The thickness of polymer blend films was found to be in the range 100-150 μm.

X-ray diffraction (XRD) measurement was carried out using monochromatic Cu-Kα radiation (=1.5418Å) in X-ray diffractometer (Brucker NSZ, model D8) in the range 10°-50° at a scan rate of 2 min. Differential scanning calorimetry (DSC) of the polymer films was performed using SII EXSTAR-6000 from room temperature to 363K with a scanning rate of 10 K/min in N₂ atmosphere. FT-IR spectra of the samples were obtained in the range 4000-400 cm⁻¹ using single beam FT-IR 4100 JASCO model by directly mounting in the sample holder in transmission mode.

The electrical properties of the polymer films have been investigated using complex impedance spectroscopy technique. Impedance spectroscopy was carried out using the impedance gain/phase analyzer (SOLARTRON 1260) interfaced to a computer in the frequency range 10 Hz-1 MHz at different temperatures. For the impedance measurements, the polymer electrolyte films were sandwiched between two silver electrodes of radius 1 cm under spring pressure in a temperature controlled furnace. The obtained impedance plots were fitted using Z view 2 program developed by Solartron Analytical.

3 Results and Discussion

XRD patterns are carried out to find the complexation of salt with polymer host in prepared polymer films. XRD patterns of polymer nano-composites are shown in Fig. 1, which clearly depicts the presence of diffraction peaks corresponding to pure PEO indicating the presence of semi-crystalline phase of PEO. The prominent crystalline peaks at 19° and 23° of pureⁱ³ PEO in the prepared polymer films are observed to be less intense due to the incorporation of nano-fillers as well as plasticization. The blending effect of PEO-PMMA cannot be ignored in the polymer films indicating reduction in degree of crystallinity of pure PEO (Fig. 1). The relative intensities of X-ray peaks are gradually decreased by increasing the nano-filler concentration, which is an indication of reduction of crystalline phase in polymer films. However, at 5 wt% of Al₂O₃, the intensity of XRD peaks increases as compared to other polymer film specimen. Figure 2 shows the plot of variation of melting temperature (T_m) with nano-

filler concentration. With the increment of nano-filler concentration, the melting or semi crystalline-amorphous phase transition temperature i.e., T_m of PEO in polymer films shifts towards the lower temperature side up to Al₂O₃-4 wt%. Beyond this concentration, the values of T_m increase. The observed decrease in T_m values with nano-filler concentration indicates weakening of intermolecular interactions.

IR spectra of materials vary according to their compositions and show the occurrence of the complexation and interaction between the various constituents. The vibrational assignments of pure PEO, PMMA are fairly reported in literature⁴⁻⁸. In pure PEO, CH₂ scissoring mode at 1454 cm⁻¹, CH₂ wagging mode at 1353 cm⁻¹, CH₂ twisting mode at 1276 cm⁻¹, C-O-C vibration mode at 941 cm⁻¹ and CH₂ rocking at 844 cm⁻¹ are observed. In pure⁸ PMMA, the peaks at 1721, 1433 and 1137 cm⁻¹ are assigned to C=O stretching, CH₃ stretching and –OCH₃ stretching vibrations, respectively. The band at 986 cm⁻¹ is attributed to the symmetrical stretching of the C-O bond in the C-O-C linkage of PMMA. The
vibration band at 750 cm$^{-1}$ is assigned to CH rocking vibration$^{10}$ of PMMA.

In the present system, the shifts in the pure PEO and PMMA IR spectra (Fig. 3) may be due to the interactions between the carbonyl carbon atoms of PMMA and the oxygen atoms$^{14}$ of PEO. The vibration bands at lower frequency region i.e., at 745, 845 and 966 cm$^{-1}$ of PEO and PMMA appeared only in 1 wt% of nano-filler and found to be absent in rest of the samples. The stretching frequency at 1721 cm$^{-1}$ corresponding to C=O of pure PMMA is shifted and gets broadened. Its intensity decreases with the addition of nano-filler in polymer film specimen. The shift observed in the carbonyl stretching frequencies of the complexes confirms the complex formation$^{14}$. Stretching vibrations of methoxy-group and wagging mode of CH$_2$ of pure PMMA and PEO are absent in polymer nano-composites. The intensity of different vibrational bands in IR spectra of the polymer films decreases with nano-filler concentration up to Al$_2$O$_3$-4 wt% in polymer nano-composites while increase in intensity and sharpness of IR bands are again seen in the film with 5 wt% of nano-filler. Thus, the FTIR spectra establish the complexation of Ag-salt, PEO and PMMA in the prepared polymer electrolytes films.

Complex impedance spectroscopy is a useful method to investigate the electrical properties of materials. A complex impedance plot for various Al$_2$O$_3$ concentrations in polymer blend films at 323 K is shown in Fig. 4. The obtained semicircles are found to be depressed, i.e., its center lying below the real axis which means, the relaxations of ions are non-Debye in nature in the present system$^{19}$. It is clear from the impedance plot that the intercept of the low frequency arc on the real axis shifts towards the origin with the increase of nano-filler concentration, i.e., the bulk resistance (calculated from the low frequency intercept on the real axis) of the polymer film decreases with nano-filler concentration whereas an increase in bulk resistance at Al$_2$O$_3$-5 wt% is observed. The values of the ionic conductivity are calculated from the bulk resistance values using the geometrical dimensions of polymer films.

As mentioned in our earlier report$^{12}$, the conductivity of the un-doped system i.e., PEO-PMMA-PEG-AgNO$_3$ was observed in the range 10$^{-9}$ S/cm. To study the effect of nano-filler on ionic conductivity, the polymer blend was doped with nano-fillers. Figure 5 shows the variation of ionic conductivity of polymer system with nano-filler concentration. An enhancement in ionic conductivity with nano-filler concentration with a maximum at 4 wt% of Al$_2$O$_3$ is observed. The variation in conductivity at different nano-filler concentration has

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**Fig. 3** — FT-IR spectra of (PEO$_{50}$-PMMA$_{50}$-5PEG)-5 AgNO$_3$-$x$ (Al$_2$O$_3$), $x=1$ to 5 wt%.

**Fig. 4** — Complex impedance spectra of different concentrations of nano-filler polymer films at 323 K.

**Fig. 5** — Variation of ionic conductivity with nano-filler concentration.
been reported by many researchers in PMMA as well PEO based polymer electrolyte systems\textsuperscript{20,21}. Ekanayake et al.\textsuperscript{22,23} reported the increased ionic conductivity with the addition of nano-fillers resulting into high conducting pathways for migration of ions enhancing cation transport. Johan et al.\textsuperscript{24} reported the enhancement in conductivity with CuO nano-filler due to increase in the amorphous phase caused by the modification of the host polymer. The retarding effect in conductivity after 4 wt% of Al\textsubscript{2}O\textsubscript{3} nano-filler is attributed to the conglomeration of excessive nano-filler reaching a threshold which makes the long polymer chains immobilized leading to a decrease in the conducting pathways. This maximum shows the balance between the opposing forces: increase in free volume as well as chain flexibility and decreasing polymer segmental mobility. The observed drop in conductivity at 5 wt% is also found to be in good agreement with the XRD and DSC results.

4 Conclusions
XRD and IR results of prepared PEO-PMMA-PEG-AgNO\textsubscript{3}-Al\textsubscript{2}O\textsubscript{3} polymer nano-composites confirm the complexation of silver salt in host polymer blends. The influence of the nano-filler Al\textsubscript{2}O\textsubscript{3} in PEO-PMMA-PEG-AgNO\textsubscript{3} polymer electrolyte films shows an enhancement in ionic conductivity with nano-filler up to Al\textsubscript{2}O\textsubscript{3}-4 wt.%.

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References