

Influence of Nano-fillers on the structure and electrical conductivity of polymer composite films

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Abstract – Polymer composites have established an excellent position among the technologically essential materials because of their wide range of applications. An enormous research interest has been devoted to zinc oxide (ZnO) Nano fillers, due to their exceptional electrical, optical, thermal, mechanical, catalytic and biomedical properties. In the present work, we report a polymer nano-composite system by dispersing ZnO nano powders as fillers in plasticized (PEO+PEMA+NaIO₄) matrix. The formation of nanocomposites and changes in the structural properties of the materials were investigated by X-ray diffraction (XRD). The electrical conductivity measurements of pure and nanocomposite polymer blend films were performed at various temperatures 303 – 373 K using ac impedance technique. The maximum room temperature ionic conductivity of 9.71×10^{-5} S/cm was obtained for the polymer electrolyte membrane with 4% ZnO concentration and exhibited Arrhenius type dependent with temperature.

Key words: Polymer nanocomposites system, XRD, Cole - Cole Plots, Conductivity

1. Introduction

Polymer electrolytes have attracted much attention due to their numerous applications such as rechargeable batteries, sensors, electro chromic devices, super capacitors, fuel cells, smart windows, dye sensitized solar cells etc. [1-6]. Polyethylene oxide (PEO) has been popularly used as the matrix to fabricate solid polymer electrolytes. PEO can dissolve various inorganic salts and transport dissociated ions. Since PEO itself only has C-C, C-O, C-H bonds, the reactivity is exceedingly low and because of this, it is stabilized chemically and also electrochemically [7-10]. The most common polymer in this group is poly (ethyl methacrylate) (PEMA) and because of its high resistance, non-toxic characteristics, surface resistance, optical properties etc.[11-12]. The most important advances in increasing the ionic conductivity of polymer electrolytes were brought into effect by the incorporation of suitable amounts of plasticizers [13]. A plasticizer improves the electrical conductivity of polymer electrolyte by (i) increasing the amorphous content of polymer electrolytes; (ii) dissociating

ion aggregates present in polymer electrolytes; (iii) lowering the glass transition temperature, T_g [14].

The addition of inert inorganic oxide such as Al_2O_3 , TiO_2 and ZnO in polymer electrolyte has become an excellent approach which has attracted considerable attention due to their improved mechanical stabilities, enhanced ionic conductivities and electrolyte/electrode interface stability. It has been known that the increase in conductivity of the composite electrolytes depends up on the concentration and particle size of the inert phases [15].

In this work, we report the composite solid polymer blend electrolytes prepared by the addition of nano sized ZnO particles to PEG plasticized (PEO+PEMA+NaIO₄) system. The purpose of this work is to emphasis the extraordinary effect occurring in the (PEO+PEMA+NaIO₄+PEG)/ ZnO nanocomposites.

2. Experimental

PEG plasticized polymer blend electrolyte films of PEO/PEMA complexed with NaIO₄ at different compositions were prepared by solution cast technique using DMF as solvent. Film of 90 [42.5PEO : 42.5PEMA : 15NaIO₄]: 10 PEG composition was identified as the highest conducting composition at room temperature. The 90[42.5PEO : 42.5PEMA : 15NaIO₄]: 10PEG concentration ratio was fixed and different weight percent of ZnO were added to the total concentration. The composite samples were prepared first by dissolving predetermined amounts of PEO, PEMA, NaIO₄ and PEG in DMF, followed by the addition of ZnO nanoparticles. This solution was stirred at room temperature for approximately 24h until the mixture appeared to be homogeneous. Films were obtained by casting the homogeneous mixture solution on polypropylene dishes. Finally, the films were dried under vacuum for 48h.

The X-ray diffraction studies of these films were performed by means of a SEIFERT X-ray diffractometer system with Ni-filtered Cu $k\alpha$ radiation. The AC conductivity was measured using PSM1700 Impedance Analyzer in the frequency range 1 Hz – 1 MHz and in the temperature range 303–373 K. The activation energies were evaluated from the slope of the plots.

3. Results and Discussion

3.1 x-ray diffraction studies

Fig.3.1 shows the comparative profiles of the XRD patterns of ZnO doped solid polymer electrolytes. The diffraction peaks observed for 2θ values at 19.5° and 23.6° in sample 1 were found to be less intense in sample 2, 3 and 4. This indicated that the addition

of ZnO nanoparticles caused a decrease in the degree of crystallinity of the film and a dominant presence of the amorphous phase. This amorphous nature resulted in greater ionic diffusivity with high ionic conductivity as amorphous polymers have flexible backbone [16]. The broadening of the characteristic peaks in sample1 at 19.5° and 23.6° is due to incorporation of nanoparticles in the polymer lattice [17]. New peaks were also observed at 34.2° , 37.4° , 41.8° , 53.3° , 60.9° , 68.7° due to the presence of ZnO nano crystallites in the polymer electrolytes [18].

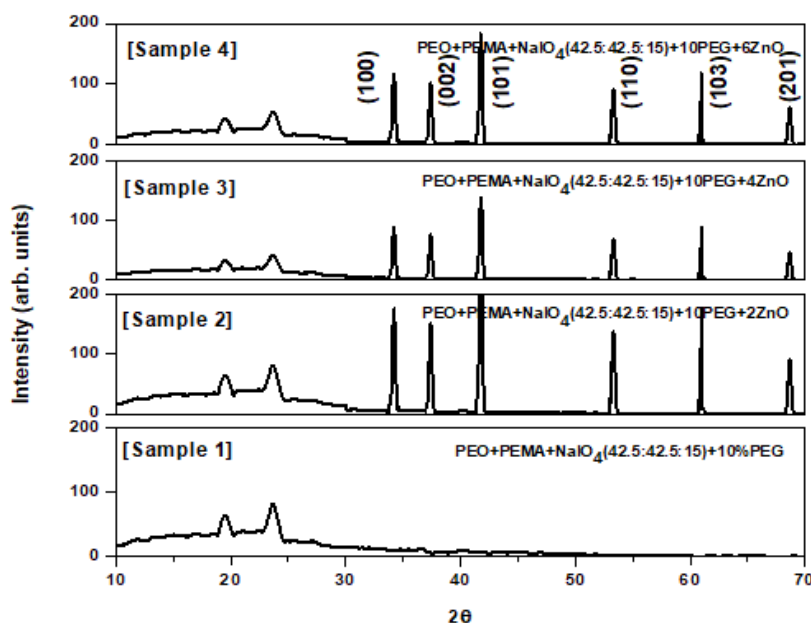


Fig. 3.1 XRD patterns of $90[42.5\text{PEO}+42.5\text{PEMA}+15\text{NaIO}_4] : 10\text{PEG}+x \text{ ZnO}$, where $x = 2, 4$ and $6 \text{ wt}\%$ composite electrolytes

3.2 AC impedance studies

Typical impedance plots (Z' vs Z'') for $90[42.5\text{PEO}+42.5\text{PEMA}+15\text{NaIO}_4] : 10\text{PEG} + x\text{ZnO}$ where $x=2,4\&6 \text{ wt}\%$ composite electrolytes at different temperatures ($303 - 373 \text{ K}$) are shown in Fig 3.2 which showed a normal impedance behaviour such as a depressed semicircular portion followed by a spike (residual tail), is characteristic of a blocking double-layer capacitance. In the complex impedance representation, the low frequency response appears as an inclined spike and such a spike is characteristic of a blocking double-layer capacitance (C) whose magnitude can be estimated from any position on the spike using the equation : $Z'' = 1/2\pi fC$, where f is the frequency and C is the capacitance at the frequency f . The high frequency semicircle corresponds to the bulk response of the films. We directly read the resistance of the electrolyte (R_b) from the intercept of the impedance spectrum on the

Z' real axis. The conductivity can then be calculated from: $\sigma = L/(R_bA)$, where L is the thickness of the electrolyte film and A represents the electrode area.

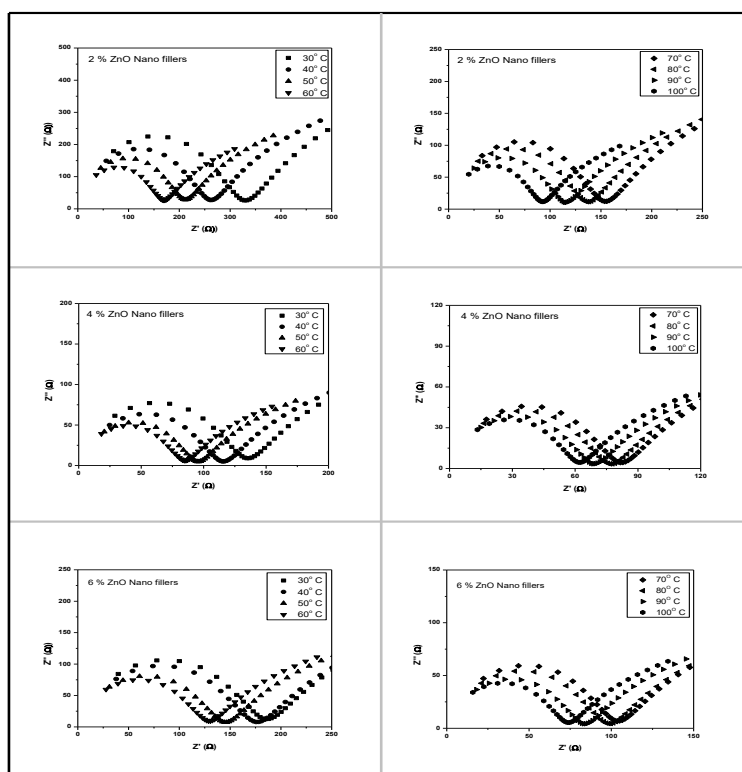


Fig 3.2. Impedance (Cole-Cole) plots of 90[42.5PEO+42.5PEMA+15NaIO₄] : 10PEG+xZnO polymer blend films at different temperatures

3.3 ZnO Composition dependence of conductivity

Fig 3.3 shows the variation of conductivity as a function of concentration of ZnO of polymer electrolyte system. From the figure it clear that the conductivity increases with increase in the concentration of ZnO upto 4 wt%. For further increase in the concentration of ZnO (6 wt%), the conductivity becomes decreased. This is because of the fact that ZnO particles tend to impede Na⁺ ionic movement by acting as mere insulators [19]. The conductivity data of all samples are given in Table 1.

From the table 1, it was observed that the enhancement of conductivity is achieved in ZnO dispersed polymer electrolytes. ZnO nano particles, being relatively small in size compared to polymer molecules, penetrate into the polymer matrix and establish attractive forces between nanoparticles and chain segments. These attractive forces reduce the cohesive forces between the polymer chains and increase the segmental mobility, thus enhancing conductivity.

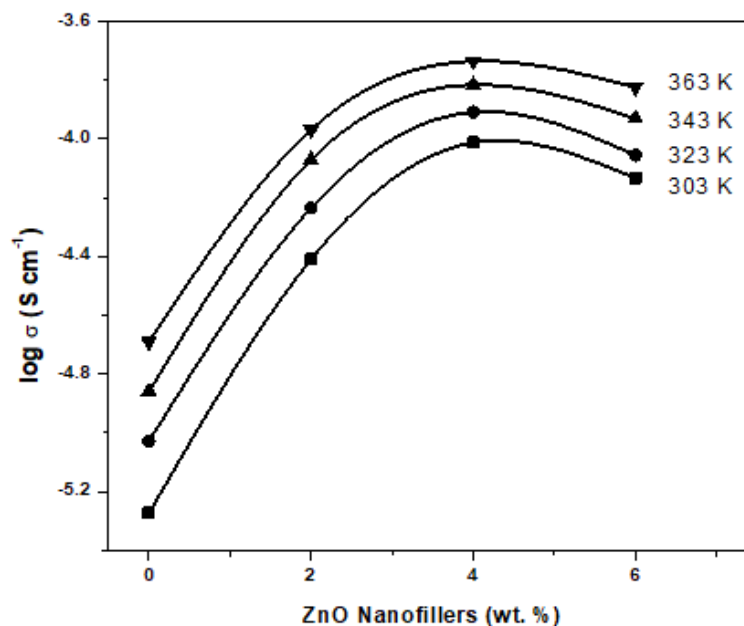


Fig 3.3 Conductivity as function of concentration of ZnO added to 90[42.5PEO+ 42.5PEMA+15NaIO₄]:10PEG+xZnO at different temperatures

Table 1. Conductivity data of 90[42.5PEO+42.5PEMA+15NaIO₄]:10PEG+xZnO polymer blend electrolyte system at different temperatures

Polymer blend electrolyte system(wt%)	Conductivity (Scm ⁻¹)			
	303 K	323 K	343 K	363 K
90[42.5PEO+42.5PEMA +15NaIO ₄]:10PEG	5.33 X 10 ⁻⁶	9.35 X 10 ⁻⁶	1.38 X 10 ⁻⁵	2.04 X 10 ⁻⁵
90[42.5PEO+42.5PEMA +15NaIO ₄]:10PEG+2ZnO	3.89 X 10 ⁻⁵	5.82 X 10 ⁻⁵	8.48 X 10 ⁻⁵	1.07 X 10 ⁻⁴
90[42.5PEO+42.5PEMA +15NaIO ₄]:10PEG+4ZnO	9.71 X 10 ⁻⁵	1.23 X 10 ⁻⁴	1.52 X 10 ⁻⁴	1.83 X 10 ⁻⁴
90[42.5PEO+42.5PEMA +15NaIO ₄]:10PEG+6ZnO	7.34 X 10 ⁻⁵	8.79 X 10 ⁻⁵	1.17 X 10 ⁻⁴	1.49 X 10 ⁻⁴

3.4 Temperature dependence of conductivity and activation energy

Fig 3.4 shows the variation of log conductivity with inverse absolute temperature for 90[42.5PEO+42.5PEMA+15NaIO₄]:10PEG+xZnO where x =2, 4 & 6 wt% solid polymer

electrolytes. From the plot, it was observed that, in the temperature range of study, the conductivity increased with temperature and followed Arrhenius behavior throughout the region [20]. The activation energies were evaluated from the slope of these plots ($\log \sigma$ vs $1000/T$) and the values are given in Table 2. From the table, it is clear that the activation energy decrease with an increase in the concentration of ZnO upto 4 wt%. After the increase in the concentration of ZnO (6 wt%) the activation energy slightly increases. This is because of the decrease in the electrical conductivity of 6 wt% ZnO added polymer electrolyte films.

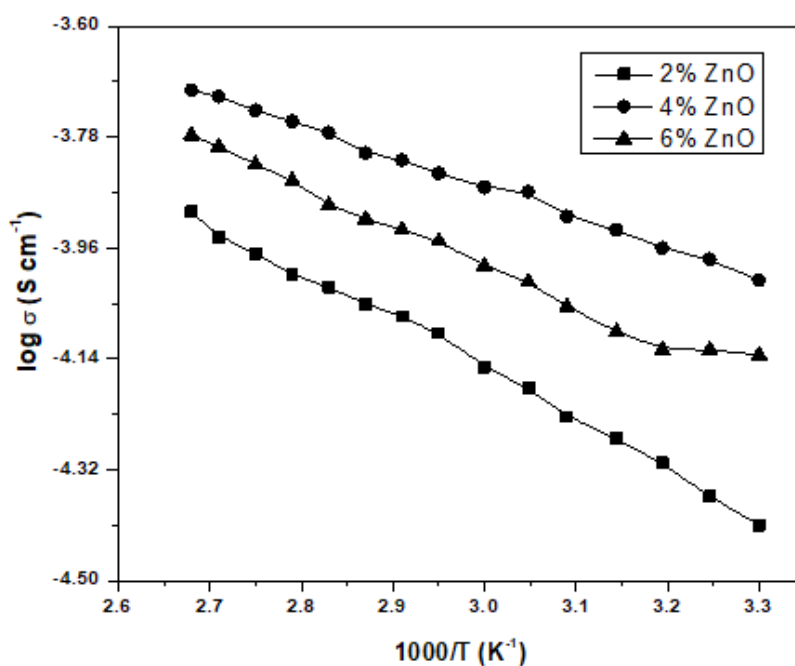


Fig 3.4 Temperature – dependent conductivity of 90[42.5PEO+42.5PEMA+5NaIO₄]:10PEG+ xZnO composition polymer electrolytes

Table 2. Activation energies of (PEO+PEMA+NaIO₄+PEG+ZnO) polymer blend electrolytes

POLYMER ELECTROLYTE	ACTIVATION ENERGY
90[42.5PEO+42.5PEMA+15NAIO ₄]: 10PEG+2ZNO	0.15
90[42.5PEO+42.5PEMA+15NAIO ₄]: 10PEG+4ZNO	0.11
90[42.5PEO+42.5PEMA+15NAIO ₄]: 10PEG+6ZNO	0.13

4. Conclusions

A new plasticized PEO/PEMA+NaIO₄ based nanocomposite electrolytes containing nano sized ZnO particles have been synthesized. Complexation of the polymer matrices have been ascertained by XRD analysis. In the 90[42.5PEO:42.5PEMA:15NaIO₄]:10PEG + xZnO polymermatrix electrolytes, the addition of a small amount of ZnO particles enhances the ionic conductivity of 90[42.5PEO:42.5PEMA:15NaIO₄]:10PEG by ten times at room temperature. The results obtained above could be further optimized by a proper choice of the morphology of the ceramic filler and the processing.

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