Int. J. Electrochem. Sci., 2 (**2007**) 861 - 871

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Effect of Plasticizer on Structural and Electrical Properties of Polymer Nanocompsoite Electrolytes

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Received: 27 August 2007 / *Accepted:* 7 September 2007 / *Online published:* 5 October 2007

Plasticized polymer nanocomposite electrolytes (PPNCEs) based on Poly (ethylene oxide) + NaI with dodecyl amine modified montmorillonite (DMMT) as the filler and Poly (ethylene glycol) as the plasticizer were prepared by a self-designed tape caster. The effect of plasticization on structural, microstructure, thermal and electrical properties of the PPNCEs were investigated. The changes in the structural and microstructural properties of the materials were investigated by XRD and SEM techniques. Differential scanning calorimetry (DSC) technique was used to study the thermal parameters (i.e., glass transition temperature (T_g) and crystalline melting temperature (T_m)) of the nancomposites. Complex impedance analysis was used to calculate the bulk resistance of the composites. The typical complex impedance spectrum of the samples comprises of a compressed semicircle in the high frequency region (due to the bulk properties) followed by a tail (spike) in the lower frequency region indicating the double layer response at the electrode/sample interface. The maximum conductivity of PPNCE was found to be 1.05×10^{-6} for x=50% of plasticizer (at 40^0C). The effect of plasticizer on the structural and physical properties of polymer nanocomposites was well correlated.

Keywords: Polymer nanocomposite electrolyte; Plasticization, Complex impedance spectroscopy; XRD; Electrical conductivity

1. INTRODUCTION

The polymer electrolytes (polymer-salt complexs) are important for both fundamental understanding of fast ion transport in polymer electrolyte and their potential technological applications in various electrochemical devices [1-6]. The pioneering work of Wright and co-workers [7, 8] motivated researchers to work on solid polymer electrolytes. Later Armand et al. [9] explored the possible applications of these materials for electrochemical devices. As it is well known, solid polymer electrolytes (SPEs) have several advantages over the liquid counterpart such as desirable shape mouldability, free from leakage, mechanical strength and flexibility of design, thereby permitting miniaturization. Unfortunately, SPEs have the inherent problem of low ionic conductivity at ambient temperature that acts as a barrier to their utility when compared with the existing conventional liquid/hybrid electrolytes. The ionic conductivity of SPEs are strongly affected by various factors such as (i) crystallinity of the material, (ii) simultaneous cation and anion motions and (iii) the ion-pair formation (anion complex-cation interaction) [10, 11]. These factors reduce the cationic conductivity, and therefore this act as a barrier for potential applications. To overcome these problems, the realization of single ion conduction is fascinating alternative. Recently, an innovative approach was made to use layered silicate clay (such as montmorillonite, hecrorite, laponoite etc.) based nanocomposite to obtain the mobility of ions in polymeric matrix in a controlled way resulting in single ion conducting polymer nanocomposite electrolytes (PNCEs) [12]. The clay layered silicate nanocomposite could directly affect mobility of cation while reducing the mobility of anion to a negligible limit due to the intercalation of cations into the layered silicate where bulky anion cannot enter into that. This idea has attracted researchers to work on PNCEs to suppress dual ionic motions and ion-pair formation [10, 12]. Some times, it is necessary for organic modification of the clay layers, which makes the hydrophilic surface of montmorillonite (DMMT) as a hydrophobic. The hydrophobic organic modifier facilitates the intercalation of hydrophobic polymer into MMT by reducing the surface energy [13].

Berthier et al. [14] established that the ionic conductivity in polymer electrolytes is related to the amorphous phase of the sample. One of the most successful approaches is to increase the amorphous nature (i.e., reduction of polymer crystallinity) and hence ionic conductivity of SPEs by incorporating suitable plasicizer into the polymer electrolyte. The essence of plasticization is to enhance the conductivity of solid polymer electrolytes using low molecular weight and high dielectric constant additives such as propylene carbonate (PC), ethylene carbonate (EC), polyethylene glycol (PEG) etc. [15, 16]. These additives, increase the amorphous content of the polymer matrix and tend to dissociate ion-pairs into free cations and anions thereby leading to an overall enhancement in conductivity. However, to the best our knowledge, only a very few reports are available in the literature which discuss the combined effect of the filler and the plasticizer on polymer salt complex [17-21]. In view of the above, we have studied the effect of plasticization on the microstructural/structural, thermal and electrical properties of the polymer nanocomposite electrolytes based on poly (ethylene oxide)-NaI system dispersed with dodecyl amine modified montmorillonite (DMMT) as filler and plasticized with polyethylene glycol (PEG_{200}).

2. EXPERIMENTAL PART

2.1. Materials Preparation

Plasticized polymer nanocomposite electrolyte (PPNCE) films were prepared using a self-designed tape caster. The commercially available Polyethylene oxide (PEO) (M/S Aldrich, M. W.~ $6x10^5$), NaI (M/S Merck India Ltd, Mumbai India) and dodecyl amine modified Na^+-montmorillonite

(DMMT) and poly ethylene glycol (PEG) (M/S Aldrich, M. W. = 200) were used for preparation of PPNCEs. The details procedure for modification of montmorillonite is reported elsewhere [22]. An appropriate ratio of PEO and NaI was dissolved in dehydrated acetonitrile, and the mixed solution was stirred thoroughly for 12 h to allow polymer-salt complexation. Previously optimized ratio (5 wt %) [23] of the ceramic filler DMMT was then added to the complex solution and further stirred for 12 h. Finally, different concentrations of the plasticizer by wt. (wt.% of PEG in relation to PEO) were added followed by continuous stirring for 12 h. Then it was casted using a self-designed tape caster of desirable thickness and allowed to dry slowly at room temperature followed by vacuum drying. At the end, the films were heated at ~40^0C for 3-4 h to remove residual solvents, if any so as to get freestanding thin films of the PPNCEs. The entire operation was carried out in an inert atmosphere inside a glove box. The sample composition may be represented as: $(PEO)_{25}$-NaI+5wt.% DMMT + x wt.% PEG (x = 0, 5, 10, 20, 30, 40 and 50).

2.2. Materials Characterization

The x-ray diffraction (XRD) pattern of the PNCEs films was recorded at room temperature using an x-ray powder diffractometer (Rigaku Miniflex) with CuK_α radiation (λ=1.5405A^0) in a wide range of 2θ (Bragg angles) ($2^0 \leq 2\theta \leq 30^0$) at a scan speed of 0.5^0 minute^{-1}. The surface morphology of the plasticized composite polymer electrolytes (PCPEs) were obtained using a computer-controlled scanning electron microscope; SEM, (JOEL–JSM, model 5800F). The film surfaces were gold coated prior to being scanned under high-resolution field emission gun scanning electron microscope. Thermal analysis was carried out using differential scanning calorimeter (Shimadzu, DSC-50) with a low temperature measuring head and liquid nitrogen as coolant. About 10 mg of samples were crimped in alumina pans inside the glove box (under argon atmosphere) and transferred to DSC cell for measurement. The samples in alumina pans were stabilized by slow cooling to –100^0C and then heated to 150^0C at 10^0C/minute. Al_2O_3 powder was used as reference material. The impedance data were collected using a computer-controlled impedance analyzer (HIOKI LCR Hi TESTER Model: 3532) in the frequency range of 100 Hz to 1MHz. The impedance spectra/data of the cell SS | PCPE | SS, (SS stands for stainless steel), were recorded using an input signal of amplitude 100mV at different temperatures (room temperature to 150^0 C). The impedance spectrum was used to evaluate the bulk d. c. conductivity and other related parameters of PPNCEs.

3. RESULTS AND DISCUSSION

The x-ray diffraction (XRD) pattern of plasticized polymer nanocomposite electrolyte (PPNCE) films with different concentrations of PEG are compared in Fig. 1. The XRD patterns comprise of characteristic peaks of DMMT at ~5^0, polymer (PEO) at 2θ ~ 19^0 and 23^0 and broad hump at peak position of PEO for PPNCE films with different plasticizer concentration. The distance between the clay sheets is given by the d_{001} reflection of DMMT. The d_{001} values for different plasticizer concentration is close to 17.5 Å (for 2θ~5^0) compared to 12 Å found for host silicate (hydrated sample containing a monolayer of H_2O). These pattern, therefore, suggest the formation of nanocmposite, where polymer-salt complex have been intercalated between the nanometric gallery of the montmorillonite. It is observed that the addition of plasticizer brings substantial changes in XRD pattern of PPNCEs films. The shift in (001) peak position of MMT towards the lower with increase in intensity was observed with increase in plasticizer concentration. This indicates the increase in the gallery height of montmorillonite suggesting intercalation of more polymer salt complex. Also, the characteristic peaks of PEO shifts towards the lower angle side with significant broadening on addition of plasticizer. This shift towards the lower angle side indicates an increase in interplaner spacing of the (100) plane. It is possibly due to the incorporation of the small plasticizer molecule in to the interplaner spacing of the matrix, but for (010) plane it remains nearly constant. The structural

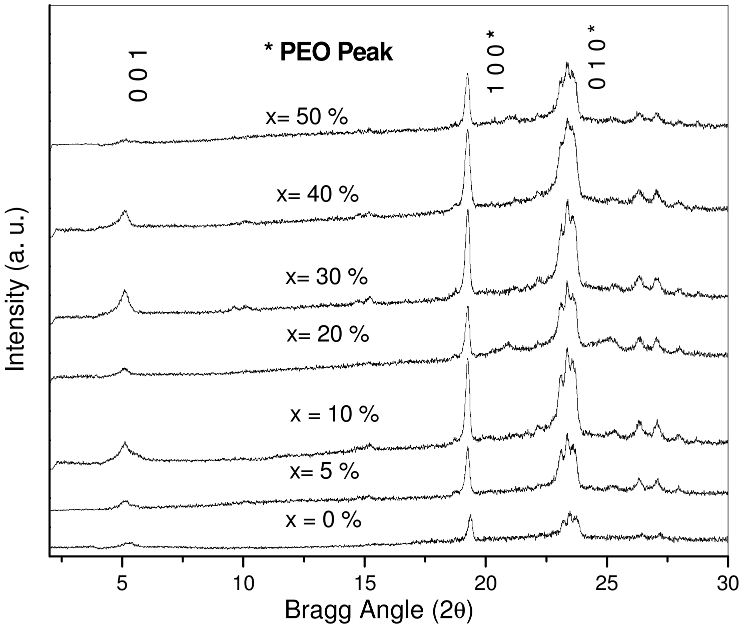


Figure 1. Comparison of XRD patterns of $(PEO)_{25}$–NaI+ 5 wt % DMMT + x wt% of PEG_{200}, with different concentration of PEG (x).

Table 1. Some parameters calculated form XRD data of $(PEO)_{25}$–NaI+ 5 wt % DMMT + x wt% of PEG_{200}, with different PEG concentration.

PEG Concentration	MMT (001) Peak		PEO Peak (100)	
	d_{001} (Å)	L (nm)	d_{100} (Å)	L (nm)
0%	16.92	12.3	4.58	42
10%	17.23	12.51	4.61	42.6
20%	17.38	10.1	4.6	42.1
30%	17.35	17.9	4.61	40.7
40%	17.38	19.5	4.60	33.6
50%	17.04	11.8	4.61	40.8

parameters calculated for (001) and main PEO (1 0 0) peak are given in Table-1. Comparison of the crystallite size (L) calculated from Scherre's equation for 100 peak of PEO for different concentration of plasticizer exhibits that the crystallite size decreases on increasing plasticizer concentration. These observations suggest an enhancement in the degree of disorder and amorphocity in the polymeric films on plasticization [19].

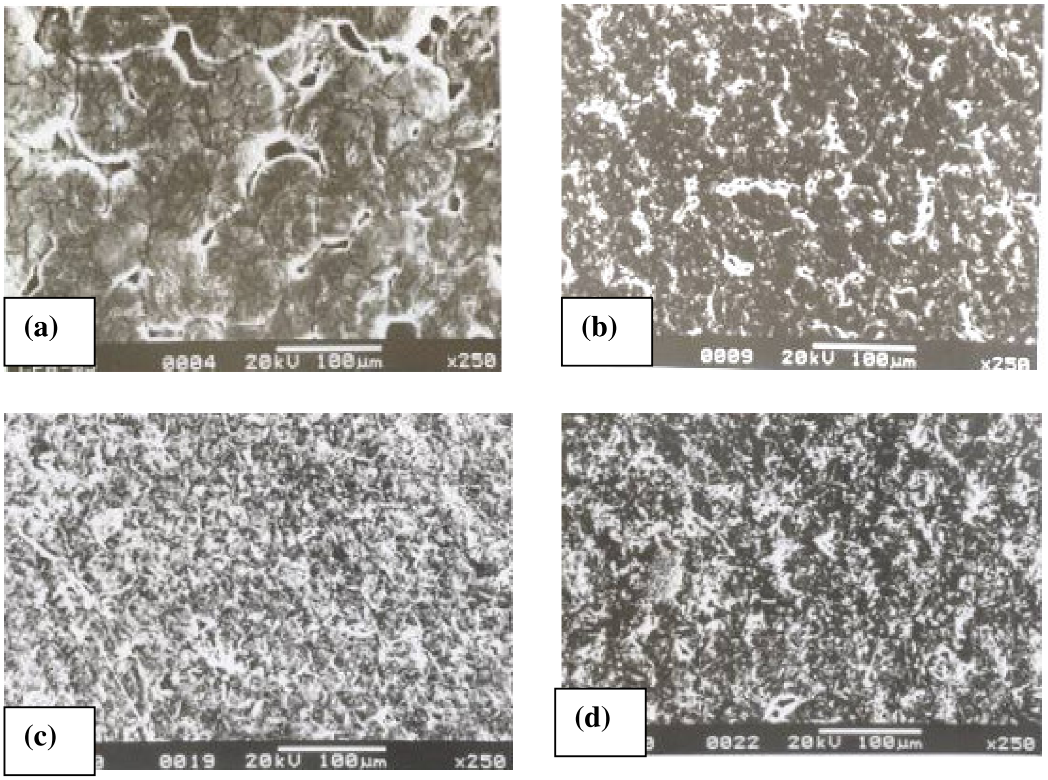
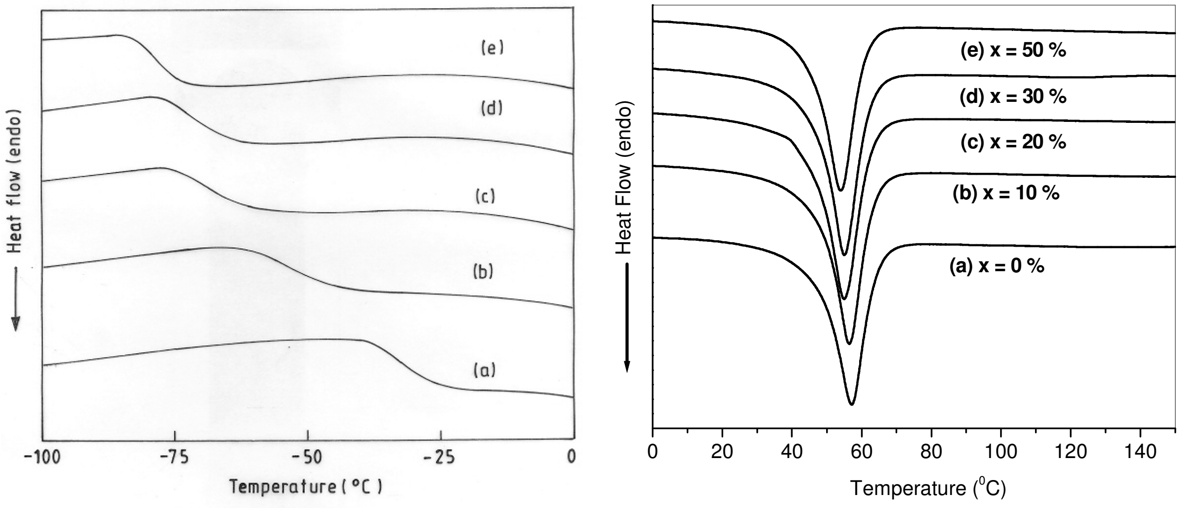


Figure 2. SEM micrographs of PPNCEs thin films of $(PEO)_{25}$-NaI+5wt.% DMMT + x wt.% PEG_{200} with different concentration of x.(i.e., (a) x= 0, (b) x=10, (c) x=20, and (e) x = 50)).

Fig. 2 shows scanning electron micrographs of PPNCE films (PEO_{25}-NaI+5 wt % DMMT+x wt% PEG) for different value of x. Comparison of the surface morphology of PPNCEs show a marked change in the surface properties and texture of the nanocomposite polymeric thin films on addition of plasticizer. On addition of plasticizer, it is observed that there is a decrease in the spherulite size and for higher concentration, it no longer exist. The surface roughening and crystalline texture appear to be decreases gradually, which results into the appearance of smooth texture of the surface on increasing plasticizer concentration. These changes may be attributed to the effect of plasticization resulting in the reduction of crystallinity of host polymer (i.e., polyethylene oxide) and subsequent enhancement in the overall amorphous fraction in the material [24].

Fig.3 shows the DSC traces of $(PEO)_{25}$–NaI+ 5 wt % DMMT + x wt% of PEG_{200}, with different value of x in the temperature range of -100^0C to 0^0C (A)and 0 to 150^0C (B) respectively. The DSC pattern shows a step change (Fig. 3 (A)) attributed to glass transition temperature (T_g) of the PNCEs. The step change in DSC curve is followed by a predominant endothermic peak (T_m) (Fig. 3 (B)) appearing in the temperature range of 50-60^0C. The endothermic peak is due to the melting of crystalline PEO. The thermal parameters (T_g and T_m) calculated from the DSC curves are tabulated in Table-2. The glass transition temperature was obtained at the mid point of the step changes of curve and the melting temperature was determined at the peak temperature of the melting endotherm. It is observed that both T_g and T_m decrease on plasticizer addition. The addition of plasticizer helps in increasing the local chain flexibility by lowering the T_g. As we know, the increase in chain flexibility is a measure of the ability of a chain to rotate about the chain bonds. A decrease in the value of T_g helps in easy movement of the polymer chains as a result an increase in the conductivity is expected [15].



(A) (B)

Figure 3. (A) Variation of DSC pattern in the temperature range –105^{0}C to 0^{0}C with different concentration (x) of PEG (a) x = 0%, (b) x = 10%, (c) x = 20% (d) x = 30% and (e) x = 50%. (B) Variation of DSC pattern in the temperature range 0^{0}C to 150^{0}C with different concentration (x) of PEG (a) x = 0%, (b) x = 10%, (c) x = 20%, (d) x = 30% and (e) x = 50%.

Table 2. Comparion of T_g (^{0} C) and T_m (^{0} C) polymer nanocomposite thin films for different value of x.

PEG concentation (x)	T_g (^{0} C)	T_m (^{0} C) Peak
0	-32.17	57.36
5	-37.75	58.20
10	-51.68	56.63
20	-67.93	55.14
30	-69.54	54.91
50	-76.90	54.04

Fig. 4 represents the complex impedance spectrum of PPNCE films $(PEO)_{25}$-NaI+5wt.% DMMT + xwt.%PEG_{200} (x = 0, 5, 10, 20, 30 and 40) for various concentrations of PEG_{200}. The impedance spectrum comprises of a distorted semicircular arc in the high frequency region followed by a spike in the lower frequency region. The high frequency semicircle is due to the bulk properties and the low frequency spike is due to the material and electrode interface properties of the nanocomposites. The intercept of the semicircle with the real axis (Z') in the low frequencies region gives rise to the bulk (ionic) resistance (R_b) of the materials [1]. Generally, equivalent circuit is used for the analysis of impedance spectroscopy because it is simple and can provide the complete picture of the system. [25]. The flattening/broadening of semicircle and the tilting of the spike can only be explained by incorporating a constant phase element (CPE) in equivalent circuit (Fig.4). This CPE replacing the capacitors in the circuit is nothing, but a leaky capacitor, which has an intermediate characteristic between a resistor and a capacitor [26, 27]. The analysis and fitting of the impedance data according to the equivalent circuit (as shown in Figure) can be accomplished by a commercially available computer software Z SimpWin [28]. The solid line (representing fitting of the experimental data) shows that there is good agreement between the experimental data and the proposed equivalent circuit. The bulk resistance is obtained on fitting the experimental data using the equivalent circuit by the software. It is found that the bulk resistance decreases with increase in plasticizer concentration.

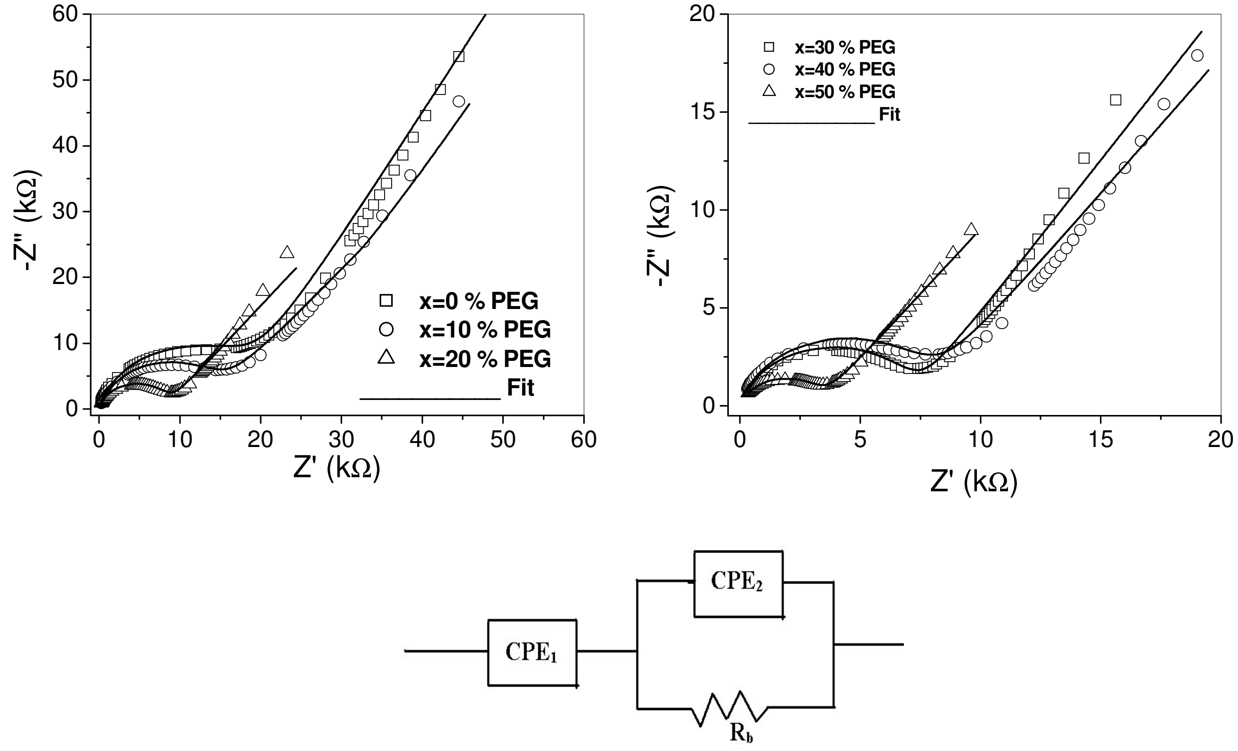


Figure 4. Complex impedance spectrum of $(PEO)_{25}$-NaI+5wt.% DMMT + xwt.%PEG_{200} (x = 0, 5, 10, 20, 30, 40 and 50). The solid line represents the fitting of the experimental data in accordance with the equivalent circuit.

The value of σ_{dc} of the plasticized composite polymer electrolyte was evaluated from complex impedance spectra and expressed as a function of plasticizer concentration at 40^0C. It is observed that the σ_{dc} increases monotonically with increase in PEG concentration (Fig. 5). The maximum conductivity was found to be $1.05x10^{-6}$ for x=50% plasticizer. An enhancement in conductivity by one order of magnitude is observed on plasticiztaion when compared to that of the nanocomposite (plasticizer free, x=0%) polymer electrolyte films has been observed.

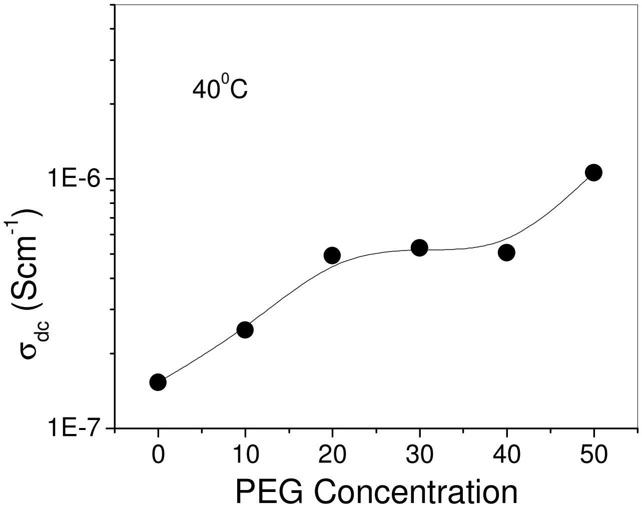


Figure 5. Variation of d. c. conductivity (40^{0}C) as a function of plasticizer concentration

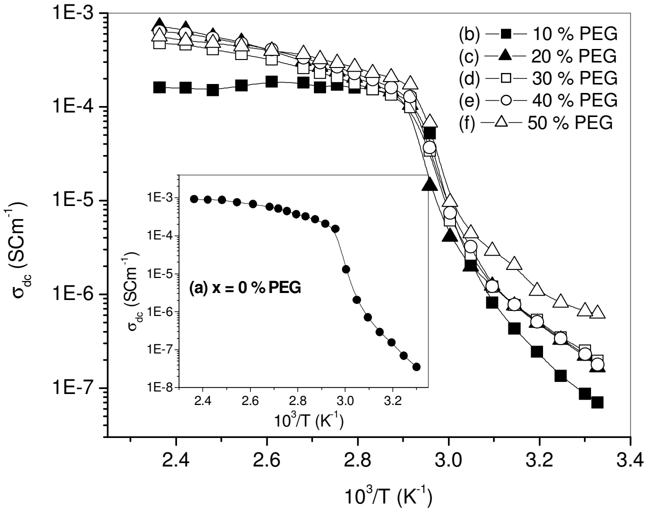


Figure 6. Variation of d. c. conductivity as a function of temperature with different concentration (x) of PEG (a) x = 0%, (b) x = 10% (c) x = 20%, (d) x = **3**0% and (d) x = 50%.

Fig. 6 shows the variation of d. c. conductivity of PPNCEs as a function of temperature (logσ vs 10^3/T) for different concentration of PEG. The variation of conductivity indicates that the conductivity increases with rise in temperature. The temperature dependence of conductivity of electrolyte films exhibit a typical VTF (Vogel-Tamman-Fulcher) behaviour as expressed by an empirical relation:

$$\sigma = \sigma_0 \exp \frac{[-E_a]}{k_\beta [T - T_0]} \qquad \text{.......................(i)}$$

where σ_0 is the pre exponential factor, k_β = Boltzmann constant, E_a is the activation energy and T_0 is a reference temperature identified as the equilibrium glass transition temperature which is usually 50K lower than that of the glass transition temperature (T_g).

Fig. 7 shows the variation of glass transition temperature (T_g), crystalline melting temperature (T_m) as a function of plasticizer concentration. The variation of T_g and T_m has been correlated with the electrical conductivity for different concentration of plasticizer. Addition of plasticizer decreases the value of T_g and T_m and increase the conductivity of the materials. It is believed that plasticizers are basically low molecular weight organic solvents (mostly liquid), added to a polymer matrix to modify its physical properties such as flexibility (by lowering the glass transition temperature), microstructure, viscosity/internal friction etc. Further, plasticizer molecules are relatively small in size as compared to that of polymer host molecule, and hence can easily penetrate into the polymer matrix, causing an interaction between plasticizer molecule and polymer chain molecules. This may reduce the cohesive forces operating between the polymer chains resulting in an increase in the chain segmental mobility. The overall result is an increase in the conductivity of polymer nanocomposite electrolyte on the addition of plasticizers [19, 29].

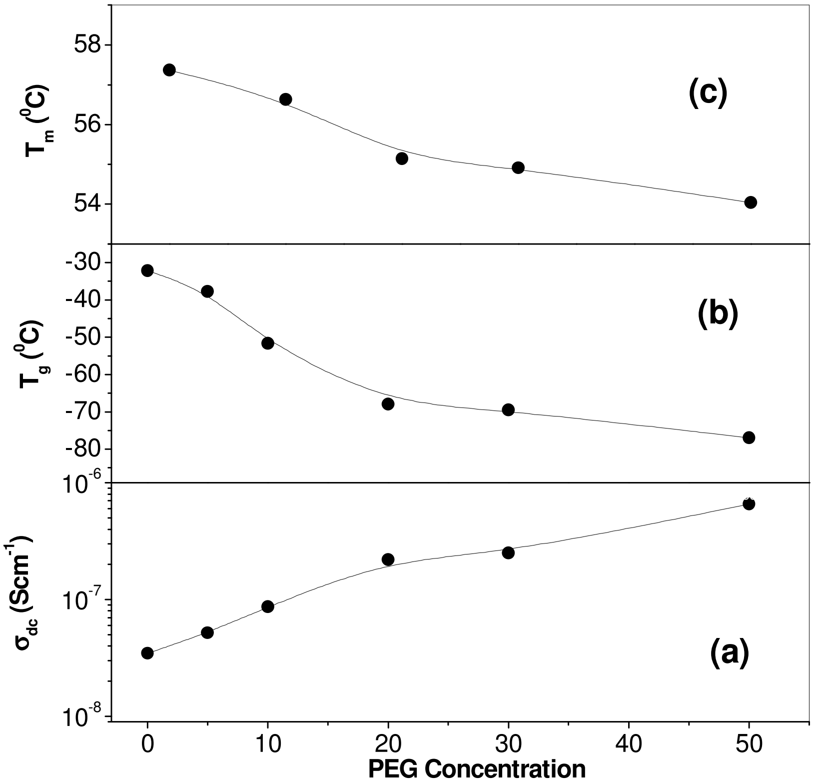


Figure 7. Effect of PEG concentration on (a) d. c. conductivity, (b) glass transition temperature (T_g) and (c) malting temperature (T_m) of PPNCEs system of $(PEO)_{25}$-NaI+5 wt.% DMMT+ x wt.% PEG

4. CONCLUSIONS

A group of plasticized polymer nanocomposite electrolytes having heterogeneous combination (polymer-salt-filler-plasticizer) was prepared and characterized. The effect of plasticization on electrical conductivity and other physical properties was also investigated. The change in the surface morphology and increase in the amorphous content on addition of plasticizer were observed. Both T_g and T_m of PPNCEs were found to be decreased on increasing plasticizer concentration. The electrical conductivity was studied using a. c. impedance spectroscopy was found to be dependent on plasticizer concentration. A substantial enhancement in the electrical conductivity, by one order of magnitude of the PPNCEs was observed as compared to polymer nanocomposite electrolyte (x=0% PEG) films without any plasticizer. This enhancement in electrical conductivity of the PCPE films agrees well with the changes in the local microstructure/structure on plasticizer addition. The temperature dependence of conductivity behavior obeys VTF pattern.

ACKNOWLEDGEMENTS
We are thankful to Prof. S. K. Srivastava, Department of Chemistry, I. I. T. Kahargapur-721302-India for some help in experimental work.

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