Research Article

Effect of Plasticizers on Structural and Dielectric Behaviour of [PEO + (NH₄)₂C₄H₈(COO)₂] Polymer Electrolyte

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Improvements in ion transport property of polyethylene-oxide- (PEO-) based polymer electrolytes have been investigated, using different types of plasticizers. The effects of single and coupled plasticizers [i.e., EC, (EC + PC), and (EC + PEG)] on structural and electrical behavior of pristine electrolyte were studied by XRD, SEM technique, and impedance spectroscopy. The electrical conductivity of the best plasticized system was found to be 4×10^{-6} S/cm. Argand plots show dispersive nature of relaxation time or inhomogeneous space charge polarization of plasticized polymer electrolyte.

1. Introduction

Recently, plasticized polymer electrolytes have been extensively used in the electrochemical devices, like secondary batteries, fuel cells, sensors, and smart windows. In order to improve their electrical and electrochemical properties for technical and industrial application, structural modification through plasticized polymer electrolytes is extensively used. Various techniques (like plasticization, copolymerization, etc.) have been adopted to achieve the desired objective of high ionic conduction and better stability of polymer composite electrolytes [1–3]. Large number of host polymer [e.g., polyethylene oxide (PEO), polymethylene methacrylate (PMMA), polypropylene oxide (PPO), polyvinyl alcohol (PVA), polyvinyl formal (PVF), etc.] [4–6] with different alkali and alkaline salts have been investigated in the past four decades. Among these polymers, PEO is the most studied polymeric system. The electrical conductivity of PEO is found relatively low at ambient temperature in comparison to the existing conventional liquid/hybrid electrolytes. The ionic conductivity of polymer electrolyte mainly depends upon (i) crystallinity of the material (ii) simultaneous cation and anion motion, and (iii) the ion-pair formation (anion

complex-cation interaction). To overcome these problems, various approaches have been made to modify the structure of polymer electrolyte in the last three decades. Ammonium adipate (NH₄)₂C₄H₈(COO)₂ contains smaller size cation (H⁺) with larger size anion which can easily dissociate and provide higher protonic conduction [7].

The addition of plasticizers in polymer electrolyte is one of the most effective approaches to improve the mobility of ionic or/and the interfacial interaction among ionic and polar groups in polymer chains. The choice of plasticizer and its concentration can affect film permeability and mechanical properties [8, 9]. The other advantage of plasticization is to modify the polymeric matrix and provide the enhanced conductivity. In general, low molecular weight and high dielectric constant additive, such as polyethylene glycol (PEG), ethylene carbonate (EC), or propylene carbonate (PC) are used to modify the permeability of the polymer film [10]. The addition of plasticizer in polymer matrix tends to decrease the glass transition temperature and increase deformability, viscosity, elasticity, abrasion resistance, and elastic recovery in the electrolyte system. Use of plasticizers also increases the salt-solvating power which leads to an increase in amorphous

content of the polymer matrix and tends to dissociate ion-pairs into free cations and anions thereby leading to an overall enhancement in conductivity. However, many theories have been proposed to account for the mechanism of plasticizer action, which leads to the lowering of processing temperature [11]. The “Lubricity Theory” suggests that the plasticizers act as a lubricant to facilitate movements of the charge carrier over each other, where as the “Gel Theory” considers the disruption of polymer-polymer interaction (Hydrogen bond and Vander Waals or Ionic forces). The “Free Volume Theory” states that a study of plasticization is the way to increase free volume and was useful to clarify the lowering of the glass transition temperature (T_g) by a plasticizer [12–14].

In the present study, we outline the effect of plasticizers that is (single/coupled) (EC, EC + PC and EC + PEG) on electrical properties of $[(\text{PEO})_{0.9} + (\text{C}_6\text{H}_{16}\text{N}_2\text{O}_4)_{0.1}]$ electrolyte that is ionic conduction and ionic behavior (electrical and dielectric response).

2. Experimental

Plasticized polymer nanocomposite electrolyte films were prepared using phase inversion technique. The polyethylene oxide [(PEO) (M.W. 6×10^5 , ACROS organics)] and Ammonium adipate ($\text{C}_6\text{H}_{16}\text{N}_2\text{O}_4$) (Rankem, India) of AR grade were used for the synthesis of composite polymer electrolyte (CPE). The stoichiometric ratio of PEO and vacuum dried ($\text{C}_6\text{H}_{16}\text{N}_2\text{O}_4$) was dissolved in deionized (DI) water at 40°C and mixed together. This solution was stirred for 12 h continuously. This gelatinous polymer solution was finally casted in polypropylene petri dish. The solution casted film was finally dried at room temperature in a constant humidity condition ($\text{RT} = 30^\circ\text{C}$ and $\text{RH} = 60\%$) for obtaining free standing films of CPE. To study the effect of plasticizer, we have used different concentrations of the plasticizer by wt (%) of EC, PC, and PEG, respectively. Following systems were synthesized for further studies:

- (a) ES-1 $(\text{PEO})_{0.9} + (\text{C}_6\text{H}_{16}\text{N}_2\text{O}_4)_{0.1}$,
- (b) ES-2 $[(\text{PEO})_{0.9} + (\text{C}_6\text{H}_{16}\text{N}_2\text{O}_4)_{0.1}]_{0.99} : [\text{EC}]_{0.01}$,
- (c) ES-3 $[(\text{PEO})_{0.9} + (\text{C}_6\text{H}_{16}\text{N}_2\text{O}_4)_{0.1}]_{0.99} : [\text{EC} + \text{PC}]_{0.01}$,
- (d) ES-4 $[(\text{PEO})_{0.9} + (\text{C}_6\text{H}_{16}\text{N}_2\text{O}_4)_{0.1}]_{0.99} : [\text{EC} + \text{PEG}]_{0.01}$.

Structural behavior of $[(\text{PEO})_x + (\text{C}_6\text{H}_{16}\text{N}_2\text{O}_4)_{1-x}]$: plasticizer_y, where $y = 0$ and 0.10] system was studied with XRD, SEM, and IR spectroscopic investigations. The XRD pattern was recorded between $2\theta = 15\text{--}60^\circ$ at room temperature using Phillips X-pert diffractometer. The SEM image was obtained by JOEL, EPMA model JXA-8100. The stub was coated with graphite to a thickness of $50 \text{ \AA}$ under vacuum using JEOL high vacuum evaporator. The coated samples were randomly scanned, and photographs were taken by EPMA. The infrared spectrum was recorded on Perkins Elmer IR spectrophotometer in a range of $4000\text{--}400 \text{ cm}^{-1}$. The electrical conductivity was evaluated using

FIGURE 1: XRD pattern of different polymer electrolyte systems.

complex impedance plot obtained by computer controlled Hioki (JAPAN)-LCZ HI Tester (model 3520-01) in the frequency range of 1 Hz to 100 KHz. The other dielectric parameters, modulus spectra (real and imaginary part), and a.c. conductivity were derived from impedance spectroscopic data. Mobility of the mobile ionic species was evaluated using the dielectric parameters.

3. Result and Discussion

XRD pattern of polymer electrolytes $[(\text{PEO})_x + (\text{C}_6\text{H}_{16}\text{N}_2\text{O}_4)_{1-x}]$: plasticizer_y, where $y = 0$ and 0.10] are shown in Figure 1. Two strong diffraction peaks at $2\theta = 19^\circ$ (120) and 23° (112) (i.e., characteristic peak of PEO) are recorded in all composite electrolyte samples. A comparative look of XRD pattern shows that the plasticized composite electrolytes have relatively sharper peak at 19° and more broadness of 23° peak with respect to the pristine sample. This change indicates the polymer-salt-plasticizer interaction as well as the decrease in crystalline behaviour of the composite electrolyte. The increase in amorphosity supports the high conductivity in PCPE. W-H plot, shows that the size of the average crystallites is decreasing $\text{ES-2} (29 \text{ nm}) > [\text{ES-3}] (27 \text{ nm}) > [\text{ES-4}] (24 \text{ nm})$. This effect clearly reveals that the addition of plasticizer in the pristine electrolyte affects the viscosity ratio and it controls the particle size.

Infra red spectrum of pristine and PCPE with different plasticizers (EC, EC + PC, or EC + PEG) electrolyte films are shown in Figure 2. The absorption peak of $(\text{NH}_4)_2\text{C}_4\text{H}_8(\text{COO})_2$ shows various peaks between 4000 cm^{-1} and 400 cm^{-1} . Some peaks related to skeleton vibration of salt with deformation mode of C–CN and bending vibrations of N=N=N are appeared in the lower wave number region (upto 600 cm^{-1}). In ES-1 $[\text{PEO}-(\text{NH}_4)_2\text{C}_4\text{H}_8(\text{COO})_2]$ electrolyte film, the absorption peak

FIGURE 2: The infrared spectrum of different electrolyte system.

at 3502 cm^{-1} is due O–H stretching vibration. The peaks at 2894 , 2236 , and 1945 cm^{-1} related to the C–H stretching vibration, C–C stretching in PEO, and asymmetric C=C=C stretching vibration are recorded, respectively. After the doping of salt in PEO matrix, few new peaks at 1720 , 1274 cm^{-1} were observed due to C=O stretching vibration of $(\text{NH}_4)_2\text{C}_4\text{H}_8(\text{COO})_2$ in polymer chain. Furthermore, addition of salt in polymer the peaks at 1303 and 1400 cm^{-1} were shifted toward higher wave numbers 1342 cm^{-1} and 1465 cm^{-1} due to polymer salt complexation. Similarly, the peak at 1035 cm^{-1} is shifted to 1054 cm^{-1} . The peaks at 943 , 840 , 734 , 690 , 578 , and 534 cm^{-1} were assigned to C–H deformation vibration in PEO, CH_2 rocking vibration, and C–C skeleton vibration of polymer chain.

In the plasticized polymer electrolyte system, ethylene carbonate (EC) gives new absorption peaks at 1382 cm^{-1} and 3490 cm^{-1} related to characteristic peak of EC. It shifts the peak at 2172 cm^{-1} towards lower wave number side that is 2162 cm^{-1} . The shift in $(\text{NH}_4)_2\text{C}_4\text{H}_8(\text{COO})_2$ peak (1303 cm^{-1} and 1400 cm^{-1}) at higher wave number indicates C=C=C bending vibration with higher frequency. The peak at 3502 cm^{-1} of O–H vibration is disappearing in the presence

of EC, which indicates the removal of O–H vibration in electrolyte system. The presence of plasticizer increases the frequency of vibration of polymer chain and facilitates more flexibility.

Propylene carbonate (PC) as plasticizer in pristine electrolyte shows few new absorption peaks at 2694 , 2858 , 1697 , and 1243 cm^{-1} related to characteristic peak of PC. The combination of EC and PC in the pristine polymer electrolyte shows a minor shift with respect to their individual peaks. In this case, the reappearance of –OH-related peak took place which is an indication of interaction of PC in the electrolyte matrix. The other combinations of poly ethylene glycol (PEG) with ethylene carbonate (EC) give some new peaks at 2086 , 1984 , 1741 , 1631 , 1249 , and 1297 cm^{-1} . These peaks are related with the presence of PEG in the plasticized electrolyte. The reappearance of C–C stretching vibration peak at 1097 cm^{-1} is an indication of main chain vibration in the presence of PEG. The new peaks at 1631 , 1741 , and 1984 cm^{-1} are CH deformation vibration, CH_2 symmetric deformation vibration, and C=O stretching vibration of PEG. The peak at 2858 cm^{-1} of ES-1 of N–H stretching vibration with small increment in wave number is indicating highly frequent vibration. The addition of plasticizer in the electrolyte provides more flexible path for the ionic conduction in electrolyte system. Such type of complexation can also be seen in XRD pattern of plasticized polymer electrolyte.

The SEM images of ES-1, that is, $[(\text{PEO})_{0.9} + (\text{C}_6\text{H}_{16}\text{N}_2\text{O}_4)_{0.1}]$ electrolyte system with different plasticizers were recorded to assess the morphology of electrolyte system (shown in Figure 3). In ES-1, several heterogeneous distributions of polycrystalline domain are observed. The addition of plasticizers drastically changes the microstructure of the pristine electrolyte. It clearly shows heterogenous morphology with modified crystalline domain. The addition of plasticizers with electrolyte results in an the induced delay in phase relation or lower surface energy. A comparative look of SEM images of plasticized system with pristine electrolyte provides more smoothness with more grains. The film plasticized with combination of (PEG + EC) has a higher degree of surface smoothness and smaller pin hole due to enhanced flexibility. The plasticizer is believed to act as a spacer between molecules of polymer by forming links with them. It was mentioned that dipole interaction occurs between polar groups in the plasticizer. In films with EC + PC, smooth and better structure was obtained. But EC + PEG containing film gives more smooth morphology of films and enhancement in visible grains. The developments of grains are very useful for interfacial contact between the polymer and salt. The plasticized film with EC + PEG has a higher degree of surface smoothness and smaller pinhole in the cross section.

The variations of a.c. conductivity (σ) with frequency for different plasticizers are shown in Figure 4(a). In pristine polymer electrolyte, the conductivity of the system due to dissociation of salt facilitates the free charge carriers/ions which enhances ionic conduction in electrolytes [15]. Incorporation of plasticizers in the pristine electrolyte system provides better mechanical strength as well as higher conductivity.

FIGURE 3: The SEM image of (a): ES-1, (b): ES-2, (c): ES-3, and (d): ES-4 polymer electrolyte systems.

FIGURE 4: (a) The variations of a.c. conductivity with frequency at room temperature. (b) The variations of conductivity with temperature for different polymer electrolyte systems.

TABLE 1: Transport parameters for different electrolyte systems.

Electrolyte system	σ (S·cm ⁻¹)	n (cm ⁻³)	μ (cm ² v ⁻¹ s ⁻¹)	D (cm ² s ⁻¹)
(PEO) _{0.9} + (C ₆ H ₁₆ N ₂ O ₄) _{0.1}	1.87×10^{-7}	1.32×10^{13}	0.88×10^{-1}	2.29×10^{-3}
[(PEO) _{0.9} + (C ₆ H ₁₆ N ₂ O ₄) _{0.1}] _{0.99} : [EC] _{0.01}	1.09×10^{-7}	2.19×10^{13}	0.31×10^{-1}	0.81×10^{-3}
[(PEO) _{0.9} + (C ₆ H ₁₆ N ₂ O ₄) _{0.1}] _{0.99} : [EC + PC] _{0.01}	0.15×10^{-7}	3.26×10^{13}	0.27×10^{-1}	7.18×10^{-3}
[(PEO) _{0.9} + (C ₆ H ₁₆ N ₂ O ₄) _{0.1}] _{0.99} : [EC + PEG] _{0.01}	4.37×10^{-7}	0.93×10^{13}	2.93×10^{-1}	7.59×10^{-3}

This enhancement in conductivity is possibly due to better percolation path. In (EC + PC) and (EC + PEG), combination of plasticizer shows better effect than pristine/and with single plasticizer. The reason behind this is that PEG polymer adopts a random coil configuration in solution, acting as if it was a sphere with an effective radius. The highest conductivity in this case was also explained as the more solubility of the system which facilitates more linear H-bond (extra) in the system which provides the extra percolation path for the mobile charge carriers. It has been also reported by other workers that the frequency-dependent conductivity and relaxation dynamics are both sensitive to the motion of charge species and dipoles of the polymer electrolyte [16, 17]. The temperature-dependent conductivity of pristine and plasticized polymer electrolyte is shown in Figure 4(b). In pristine electrolyte system, conductivity increases with temperature linearly up to 70° then suddenly jumps and again increases regularly up to 100°C. But in other three plasticized systems, a.c. conductivity linearly increases with temperature. The trend of conductivity is ES-1 < ES-2 < ES-3 < ES4 valid from room temperature to 373 K. The plots of $\log \sigma$ versus $10^3/T$ are found to be linear a limited temperature range and well fit in the Arrhenius equation

$$\sigma_T = \sigma_0 \exp\left(\frac{-E_a}{KT}\right), \quad (1)$$

where σ_0 is the preexponential factor, E_a is the activation energy, K is the Boltzmann constant, and T is the absolute temperature. The activation energy (E_a) of each system was calculated from the slop of the curve shown in Figure 4(b). The increase in conductivity with temperature is also explained by the Rice and Roth model [18] that expresses the ionic conductivity σ as

$$\sigma = \frac{2}{3} \left[\frac{(Ze)_2}{KBT_m} \right] n E_a \tau \exp\left(\frac{-E_a}{KT}\right), \quad (2)$$

where Z is valency, m the mass of the conducting ion, e electronic charge, and τ is time of flight between the sites. Using (2), number of charge carriers (n), ionic mobility (μ), and diffusion coefficient (D) can be identified.

The ionic conductivity is represented by

$$\sigma = \sum n_i e_i \mu_i, \quad (3)$$

where n_i , e_i , and μ_i are the charge carriers density of ionic charge of the i th ion, respectively. In general, an increase of ionic conductivity of the complex system is due to an increase of number of mobile charge carriers introduced/produced in the material with a change of constituent concentration. The calculated values of these constants are given in Table 1. On the basis of the transport parameters, calculated by Rice and Roth model, it is interesting to observe that the combination of plasticizers provide a better medium for mobility in the matrix. The plasticized polymer electrolyte (namely, ES-4 with conductivity 4E-6) is found to be the highest mobility. The number of charge carriers is even low for this electrolyte. Here, it is clear that the highest conductivity is due to higher mobility of ionic species.

The frequency-dependent a.c. conductivity at different temperatures of all four electrolytes (namely, ES-1, ES-2, ES-3, and ES-4) is shown in Figure 5(a) and their scaling behaviour in Figure 5(b). In Figure 5(a) conductivity increases with frequency at different temperatures ($T = 35^\circ\text{C}$, 45°C , 55°C , 70°C , and 85°C). In all cases, the conductivity pattern shows a frequency independent plateau, with an indication of electrode polarization. Scaling of a.c. conductivity is an important feature for the polymer electrolyte. The a.c. conductivity follows scaling law [19]

$$\frac{\sigma}{\sigma_0} = F\left(\frac{f}{f_0}\right); \quad (4)$$

$$f(x) \cong 1 + x^n,$$

where f_0 is the characteristics frequency, but arbitrarily determined frequency, and x is % of salt concentration. All the measured conductivity data with respect to frequency at different temperatures were scaled according to $f_0 = \sigma_0 T$ and shown in Figure 5(b). In the first two electrolyte systems (ES-1: PEO with ammonium adipate salt) (ES-2: Pristine with EC plasticizer), the scaled plot is scattered, but in the other two cases (with combination of plasticizer EC + PC and EC + PEG) the data collapse almost in single master curve. This suggests that in later cases, the relaxation mechanism is independent of temperature, and it also represents their ion-hopping motion behavior. Slight dispersion in the higher frequency regime is possibly due to enormous diffusion phenomenon. The relative dielectric constant ϵ' determines the maximum energy that can be stored in

FIGURE 5: (a) The variations of a.c. conductivity with frequency at different temperatures. (b) Variation of scaled a.c. conductivity with respect to scaled frequency for different electrolyte systems.

FIGURE 6: Variation of the dielectric constant (ϵ') with frequency and temperature of pristine and plasticized electrolytes.

the material. However, the relative loss factor ϵ'' evaluates the absorption of electrical energy by a dielectric material that is subjected to an alternating electromagnetic field. Furthermore, the dissipation factor $\tan \delta = \epsilon''/\epsilon'$ determines the absorbance of electromagnetic field in material. The relaxation can be seen in dielectric materials particularly in polymer electrolytes when they are subjected to an a.c. electric field. The electronic and ionic relaxations are correlated to very high rapid oscillations of weak dipoles, but after plasticization of polymer electrolytes, these dipoles relaxations subsequently appear at near audio frequencies. This relaxation arises from the facts that free charges/ions were present due to doping of salt in polymer. These free charges/ions are mobiles in the applied magnetic field. Further, these free carriers are then blocked at interface

between the two media of different conductivity and permittivity. An interfacial or Maxwell-Wagner-Sillars (MWS) polarization can occur depending on the frequency of applied field. This type of polarization can be seen in heterogeneous or multiphase system/composite system at high temperature and low frequency region. However, it is difficult to discriminate between MWS relaxations and d.c. conduction. The MWS effect has been found to be possibly responsible for the low frequency and high temperature dielectric losses in composites system of dispersion of fillers in polymer matrix or by copolymerization or by the addition of low molecular weight polymer in host matrix. This type of relaxation has been studied by various groups of researchers. The dielectric constant (ϵ') and loss (ϵ'') of pristine and plasticized electrolytes are shown in Figures 6 and 7. These

FIGURE 7: Variation of the dielectric loss (ϵ'') with frequency and temperature of pristine and plasticized electrolytes.

curves give a peculiar nature of the polymeric substance due to low frequency dispersion. The high value at low frequency region is an indication of electrode polarization. It can be deduced that plasticizers with high dielectric constant allows greater dissolution of the electrolyte salt resulting in an increased number of charge carriers. The apparent role of plasticizer in a host polymer is to change the viscosity of electrolyte and assist in the dissociation of the salt thereby increasing the number of charge carriers. The value of real and imaginary part of dielectric relaxation shows a regular

increase in the plasticized sample relative to the pristine electrolyte. This increase in ϵ' and loss ϵ'' value is directly based on the production of more charge carriers/dipoles in the matrix. The variation of (ϵ') and (ϵ'') with different frequency does not provide any new insight. But the temperature-dependent tangent loss variation clearly gives a single peak at 363 K in the pristine electrolyte system (Figure 8(a)), whereas the plasticized systems show two peaks (Figures 8(b), 8(c), and 8(d)). The new peak appears at the lower temperature side near

FIGURE 8: Variation of the temperature-dependent tangent loss of pristine and the plasticized electrolyte system.

10 K frequency and becomes relatively intense in EC, (EC + PC) then (EC + PEG) systems. The peak at the higher frequency region is due to β relaxation peak of the host polymer, and second peak may infer that plasticizer EC or EC/PC or PEG has dissociated more salt and generated more ions. The increase in intensity of peak is related to the more salt dissociation/dissolution in the two plasticizers. The Argand plots between the real and imaginary part of

the dielectric relaxation for all the four systems (pristine and plasticized) were presented in Figure 9. All the curves are incomplete half semicircles. The incomplete half semicircle in all the curves cannot be explained by Debye-Model (i.e., single relaxation time) and suggest multiple relaxation times in the electrolyte system. The formation of shapes as ellipsoid in these system is due to various factors like hopping nature, space charge polarization, or inhomogeneously of

FIGURE 9: The Argand plots between the real and imaginary parts of the dielectric relaxation for different electrolyte systems.

structure. It also explains the poly dispersive nature of the dielectric relaxation of the pristine and PCPEs (ES-2, ES-3, and ES-4). The master curve representation of various dielectric parameters (ϵ^* , σ^* , M^* and $\tan \delta$) with frequency is shown in Figure 10 for pristine (marked as "A" in Figure 10) and best conductive plasticized electrolytes ES-4 (marked as "B" in Figure 10). From Figure 10, it is obvious that relative permittivity and tangent loss decrease with

increasing frequency. The parameters like a.c. conductivity and modulus spectra increase with frequency. A comparative look of $\tan \delta$ plot indicates the shift of peak position towards the lower frequency side with respect to pristine electrolyte. In the same plot other parameters like σ^* , M^* , and ϵ^* recorded some specific changes in plasticized sample with respect to the pristine system. In plasticized sample (ES-4), a clear intercept is observed in the real and imaginary part

FIGURE 10: The master curve representation of various dielectric parameters (ϵ^* , σ^* , M^* , and $\tan \delta$) with frequency for ES-1 and ES-4 plasticized electrolytes.

of scaled value of σ^* , M^* , and ϵ^* on frequency level, and it is noted as relaxation frequency. This intersection is also an indication of better ionic conduction relaxation mechanism.

4. Conclusion

A group of plasticized polymer nanocomposite electrolytes were prepared and characterized. Effect of plasticization on dielectric behaviour, electrical conductivity, and other physical property was clearly visible on the pristine electrolyte. XRD study emphasizes that the increase of amorphous content is relatively high after plasticization. The better electrical conductivity depends on the combination of plasticizers. The maximum conductivity was obtained with (EC + PEG). The addition of PEG modifies the matrix and provides an excellent path for conduction. This enhancement in electrical conductivity of the films agrees well with the changes in the local microstructure/structure on plasticizer addition. Scaled curve shows single transport mechanism of ion conduction in the plasticized polymer electrolytes.

Acknowledgments

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