Effect of Various Plasticizers Concentration on the Conductivity of Solid-State Poly (Ethylene Glycol)-Polyurethane/Polymethylmethacrylate-$LiClO_4$ Electrolyte

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Abstract

Herein, we report the modification of poly (ethylene glycol)-polyurethane-polymethylmethacrylate (PEG-PU-PMMA) solid polymer electrolyte using different low molecular weight plasticizers (PEG_{400}, PEG_{600} and dibutyl sebacate (DBS)) at various concentrations (5, 10, 15 and 20 wt%) through solution-casting method. The formation of plasticized polymer electrolyte, its structural properties and thermal stability are confirmed by FT-IR, SEM, XRD and TGA. The effect of various plasticizers and their concentrations on the ionic conductivity (σ), activation energy (E_a), enthalpy (ΔH), entropy (ΔS) and diffusion coefficient (D) of polymer electrolyte are studied in detail. The highest ionic conductivity of 0.180 x 10^{-3}S cm^{-1} at 313 K is observed for PEG-PU-PMMA solid polymer electrolyte with20wt% PEG400 plasticizer which is attributed to its high dielectric constant and low molecular weight.

Keywords:Solid polymer electrolytes, Plasticizers, Polyurethane, Ionic conductivity, Polyethylene glycol.

1. Introduction

The solid polymer electrolytes (SPE) have achieved tremendous attention in recent decades due to their widespread applications in fuel cells, solar cells, batteries, chemical sensors and electrochemical capacitors. Nevertheless, poor ionic conductivity of these electrolytes as compared to the existing conventional liquid/hybrid electrolytes limits their application.As a result, significant effort has been made to improve the electrolyte's ionic conductivity and its potential technical uses in a variety of electrochemical devices. [1-6]The crystallinity of the material, simultaneous cation and anion movements, and ion-pair formation, among other parameters, all have a significant impact on the ionic conductivity of SPE. [7,8]Various techniques of altering the structure and morphology of polyether hosts have been investigated to increase electrolyte efficiency. [9-10]The reduction of polymer chain crystallization to promote polymer chain mobility and an increase in charge carrier concentration are the two most important approaches to boost the ionic conductivity of the SPE. The suppression of crystallization of polymer chains to improve polymer chain mobility can be attained by (i) block copolymerization, [11](ii) cross-linking (UV, gamma, chemical), (iii) co-polymerization, [12] (iv) comb like copolymerization (side chains and dendrite polymers), [13](v) polymer blending, [13-17](vi) addition of liquid plasticizers etc.[14], [17-19] which assists the formation of interpenetrating polymeric network (IPN). [20-22]

Among these modifications IPN formation is the most effective strategy for reducing the crystallinity, enhancing the mechanical strength and increasing the dimensional stability. [23-24]Though, the IPN formation decreases the micro phase separation and increases the mechanical strength, it results in decreased conductivity of the polymer electrolyte.We investigated the influence of nano filler concentration on the conductivity of the solid-state poly (ethylene glycol)-polyurethane/poly methylmethacrylate system and showed the system's practicality as a solid polymer electrolyte in earlier works. [25]Experimental results of the above- mentioned system did not exhibit an enhancement in conductivity that is high enough for further applications. In our present study we have made an attempt to enhance the conductivity of the polymer system by incorporating different low molecular weight plasticizers. These low molecular weight plasticizers with high dielectric constant ensured proper dissociation of the charges and provided a liquid-like environment within the polymer matrix, which facilitates ion transport. We have also studied how plasticizers and their concentration affect the ionic conductivity, activation energy, enthalpy, entropy and diffusion coefficient of the solid polymer system. In this context, we chose dibutyl sebacate, poly ethylene glycol (PEG400 MW), and poly ethylene glycol (PEG600MW) as plasticizers because they can dissolve lithium salt via coordination with the oxygen functional group present in these plasticizers, and as they have a higher dielectric constant and lower molecular weight. [26]

2. Results and Discussion

2.1. FT-IR Spectroscopy

Figure 1 shows the FT-IR spectra of PU, PU-x-PEG400, PU-x-PEG600, and PU-x-DBS (x=5 wt%, 10 wt%, 15 wt%, and 20 wt%). [27]The axial stretching vibration of the OH group of PEG is attributed to the IR band at 3658 cm^{-1}, followed by the peak of the N-H stretching vibration of polyurethane at 3458 cm^{-1}, and the C-H stretching vibration of the CH and CH_2 group in PMMA, PEG, PU, and castor oil at 2923 cm^{-1} and 2952 cm^{-1}, respectively. Peak at 1752 cm^{-1} is a result of free C=O group in polyurethane's amide group. At 1785 cm^{-1}, the C=O functionality of PMMA coexisted with the polyurethane free carbonyl group amide group.The IR-spectra of composite films of different plasticizers shows a lowering of the intensity of the peak at 1752 cm^{-1} with increase in different plasticizer concentrations and shows a minimal hypochromic shift. [28]This anomalous behavior is attributed to the interaction between plasticizer and polymer matrix.

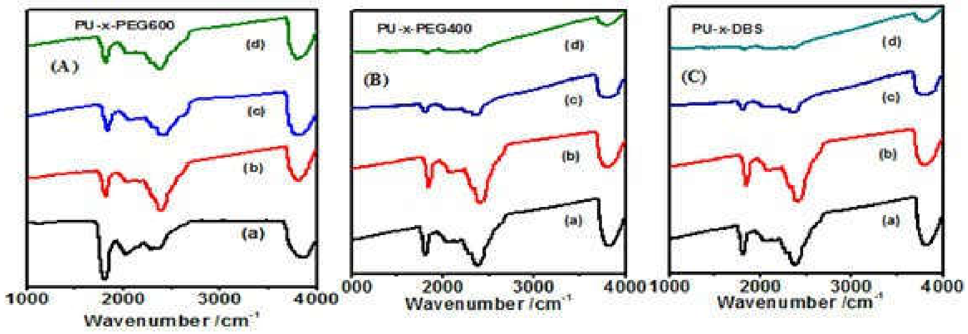

Figure 1.FT-IR plots of the (A) PU-x-PEG600 (B) PU-x-PEG400 (C) PU-x-DBS (a.5wt%, b.10 wt%, c. 15 wt%, d. 20 wt%).

2.2 SEM

As shown in **Figure 2**, the scanning electron micrographs of PU-x-PEG400, PU-x-PEG600, and PU-x-DBS confirms the presence of PEG-PU and PMMA phases. [29]From the SEM images, it is well visible that with the addition of more amount of plasticizer the surface of the polymer matrix became smoother which clearly indicates the good interaction between polymer matrix and the plasticizer.

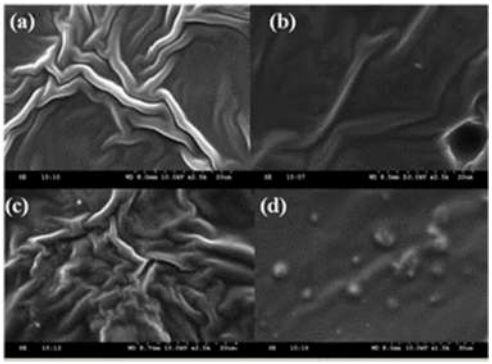

Figure 2.SEM images of (a) PU, (b) PU- 20wt% -PEG600, (c) PU- 20Wt% -PEG400, (d) PU-20wt% -DBS.

2.3 XRD

Figure 3 shows XRD patterns of PU-x-PEG400, PU-x-PEG600 and PU-x-DBS with different wt% of corresponding plasticizers. Absence of peak corresponding to the plasticizer can also be observed from the XRD spectra.[30]The broad peak at 2θ value of 18° – 20° seems to be a characteristic response of amorphous nature of the polyurethane which is akin to the XRD images already obtained from the previous studies. [25]However, with greater wt% of plasticizer, the peak widens, resulting in the composite material becoming more amorphous.

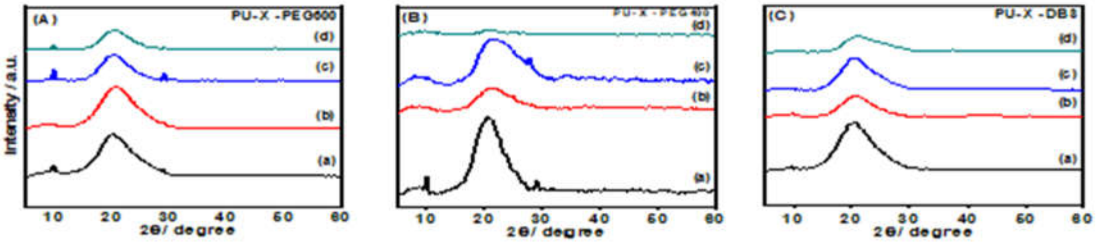

Figure 3.XRD Plots of the (A) PU-x-PEG600, (B) PU-x-PEG400 and (C) PU-x-DBS (x= 5, 10, 15, 20 wt%).

2.4 Thermo gravimetric analysis(TGA)

The thermal stability of the experimental specimens at various temperatures was determined by examining the various weight loss stages (**Figure 4**) of the TGA curve, which comprise of three distinct phases of sample degradation. Within the temperature range of 220℃-335℃, degradation was observed within the soft polymeric chain present in polyurethane (**Table1**), followed by the scissoring of the chains in PMMA within the temperature gap of 340^0C-380^0C. Finally, a large weight loss observed at 385℃ and 470℃ correspond to the decomposition of hard segments of polyurethane. [25, 27]As an essence of the TGA analysis it is obvious that there is a decrease in the stability of the composite films as the wt% of plasticizers increases and the amount of polymer degraded increased in composite films compared to PU.

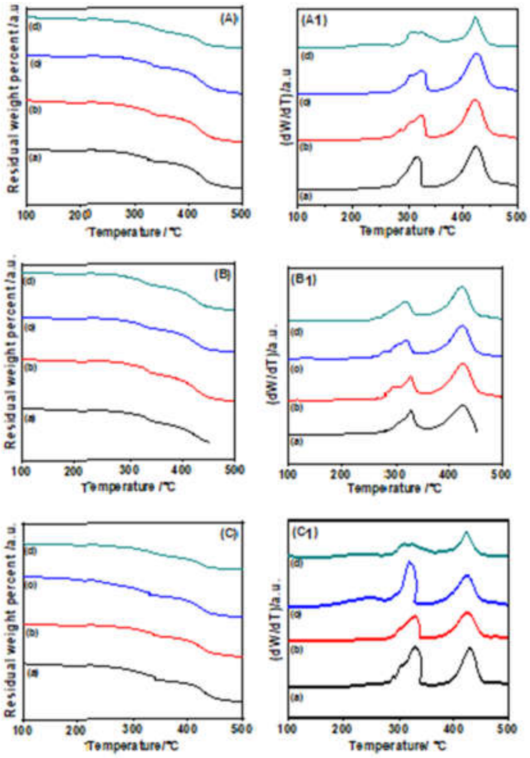

Figure 3.TGA images of (A) PU-x-PEG600, (B) PU-x-PEG400, (C) PU-x-DBS& A_1, B_1, C_1 are DTA curves (a. 5 wt% b. 10 wt% c. 15 wt% d. 20 wt%).

Table1 TGA data

Plasticizer	5 wt%	10 wt%	15 wt%	20 wt%
PEG-600	329.0°C	326.13°C	322.0°C	320.41°C
PEG-400	327.89°C	324.0°C	312.69°C	308.35°C
DBS	340.6°C	336.0°C	331.53°C	323.66°C

2.5 DSC measurements

Figure 5 shows the DSC curves of PU-x-PEG400, PU-x-PEG600 and PU-x-DBS with different weight percentage of plasticizers in the temperature range of -150 °C to 150 °C. Two distinct glass transition temperatures (T_g) values clearly reveal the presence of two phases.The endothermic peak around 50ºCisdue to the melting of PEO. [30]The pre polymer PU has two T_g values at -22^{0}c and 115^{0}c are attributed to the PEG-PU phase and PMMA phase respectively. After the formation of IPN with plasticizers, the T_g of two phases of plasticized polymer shifted inward i.e., T_g corresponding to PU-PEG is shifted from -22 °C to -37 ºCand T_g corresponding to PMMA is shifted from 115ºC to 97 ºC (PMMA). Consequently, an increase in the conductivity is expected. [31]Furthermore, PU-20wt%-PEG400 composite has prominent shift of T_g value from 115 ºC to 98.48 ºCfor PMMA phase and from -22 ºCto -42.65 ºCfor PU-PEG phase which supports the conductivity studies of the electrolytes.

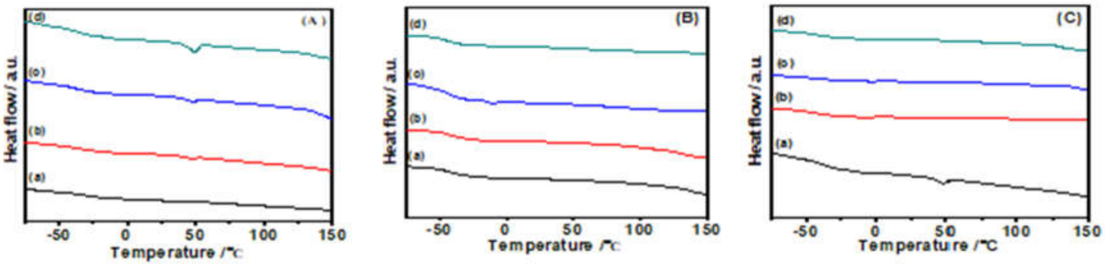

Figure 5.DSC images of (A) PU-x-PEG600, (B) PU-x-PEG400 (C) PU-x-DBS (a.5wt%, b. 10 wt%, c.15wt%, d. 20 wt %).

2.6 Impedance spectroscopy

The Nyquist plots for polymer electrolytes with various wt% of plasticizer are shown in **Figure 6** within a temperature range of 40°C to 90°C, within the frequency range from 1 MHz to 1 Hz. The plots show the presence of semicircular arcs in the high frequency range, which are indicative of bulk electrolyte properties, and they reveal information about bulk Resistance (R_b) and bulk Capacitance (C_b), which are caused by Li^+ ion migration and dielectric polarization of the SPE film, respectively. [32]The plots also show a non-vertical spike at low frequency range due to electrode-electrolyte interface property. The diameter of the semicircular arc continues to decrease with increasing temperature and plasticizer content, showing enhanced conductivity of the SPE, according to the plots. The rise in conductivity with increasing temperature is due to thermal activation of charge carriers, which tends to increase the free volume thereby creating more unoccupied sites for ion mobility, hence improved conductivity. [25, 33]The rise in conductivity with plasticizer concentration (**Figure 7**) is attributable to the fact that the amorphous character of the electrolyte and charge dissociation increase as the concentration of low molecular weight plasticizer increases. [34-36]As a result, rise in conductivity is due to a larger concentration of charge carriers and rapid polymer chain motion (**Figure 8**).In addition, we have also seen from the plot that the conductivity increases up to 20 wt% of plasticizer concentration and beyond that there is no considerable increase in conductivity and reaches a saturation value. Further, it is also observed that, among three plasticizers, rise in conductivity is more with PEG400, which is due to its higher dielectric constant. [37]

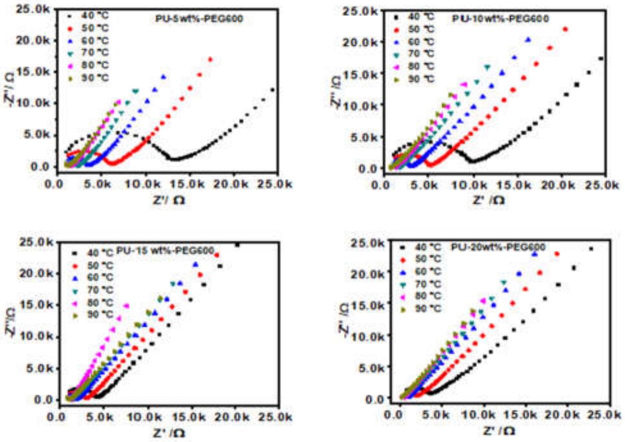

Figure 6. Nyquist plot of PU-plasticizers with different weight percent of PEG600plasticizers from 40 °C to 90 °C.

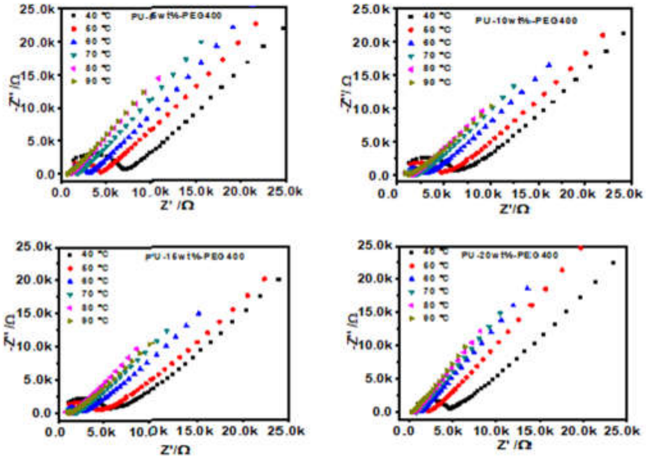

Figure 7. Nyquist plot of PU-plasticizers with different weight percent of PEG400 plasticizers from 40 °C to 90 °C.

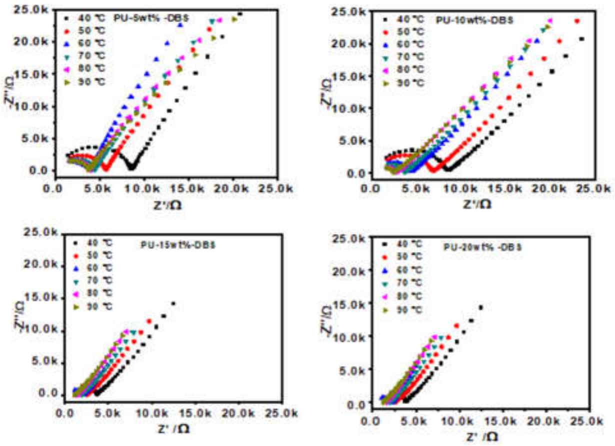

Figure 8. Nyquist plot of PU-plasticizers with different weight percent of dibutyl sebacate plasticizers from 40 °C to 90°C.

2.7 DC Conductivity studies

Figure 9 demonstrates how bulk ionic conductivity (σ) changes with temperature for plasticized SPE with varying amounts of plasticizers. The Bulk resistance (R_b) determined by the intersection of a semicircular arc with the real axis in a Nyquist plot at high and low frequencies is used to determine the ionic conductivity of SPE. Using the following equation, conductivity of the resultant SPE is determined from this R_b. R_b was calculated from the intersection of a semicircular arc with the real axis in a Nyquist plot at high and low frequencies to determine the bulk ionic conductivity of the SPE. The reciprocal of bulk resistant ($1/R_b$) i.e., ionic conductivity was determined from equation (1).

$$\sigma = L/R_bA \qquad (1)$$

where L = thickness; A= area of the SPE, respectively.

It is seen from **Figure 9** that conductivity increases with increase in concentration of plasticizers and temperature and a high conductivity of 0.180×10^{-3} S cm^{-1} is found at 313 K in PU-x-PEG400. The fact that the conductivity of electrolytes increases as the concentration of plasticizers rises is explained above.In addition, we estimated the activation energies (ΔE) of the produced polymer electrolytes using the well-known formula

$$\sigma = \sigma_0 \exp(\Delta E / K_B T) \qquad (2)$$

which are listed in **Table 2**. It can be seen from the table that ΔE values fell as temperature increased. Greater ion mobility and hence increased conductivity are indicated by a drop in ΔE value.Further we have also observed that activation energy is very less for PEG400 indicating it is having very less energy barrier for ion movement and hence is an effective plasticizer for enhancing the conductivity.

Table 2 DC Conductivity, activation energy, entropy, enthalpy and diffusion coefficient of PU- PEG600, PU-PEG400 and DBS with different weight percentage of plasticizers from RT to 363K.

Sample name	**Conductivity Range (S cm^{-1})**	**ΔE ($kJ\ mol^{-1}$)**	**ΔS ($kJ\ mol^{-1}$)**	**ΔH ($kJ\ mol^{-1}$)**	**Diffusion coefficient ($cm^2\ sec^{-1}$)**
PU- 5wt%- PE-600	$0.650 x 10^{-4}$ to $0.615 x 10^{-3}$	20.12204	-21.9995	43.53343	$1.06 x 10^{-4}$ to $2.07 x 10^{-4}$
PU-10wt%-PEG600	$0.859 x 10^{-4}$ to $0.951 x 10^{-3}$	18.73452	-23.4208	40.3386	$3.34 x 10^{-4}$ to $9.81 x 10^{-4}$
PU-15wt%-PEG600	$0.194\ x 10^{-3}$ to $0.699 x 10^{-3}$	17.37485	-23.5915	37.20789	$2.48 x 10^{-4}$ to $7.96 x 10^{-4}$
PU-20wt%-PEG600	$0.224 x 10^{-3}$ to $2.487 x 10^{-2}$	11.10285	-29.1446	22.76606	$3.66 x 10^{-3}$ to $6.98 x 10^{-3}$
PU-5wt%-PEG400	$0.136 x 10^{-3}$ to $0.684 x 10^{-3}$	21.1701	-20.2957	45.94666	$1.06 x 10^{-3}$ to $7.76 x 10^{-3}$
PU-10wt%-PEG400	$0.154 x 10^{-3}$ to$0.692\ x 10^{-3}$	14.46794	-26.6299	30.51446	$1.59 x 10^{-4}$ to $3.23 x 10^{-3}$
PU-15wt%-PEG400	$0.118 x 10^{-3}$ to$0.589\ x 10^{-3}$	14.03154	-27.1028	29.50955	$1.95 x 10^{-3}$ to $4.01 x 10^{-3}$
PU-20wt%-PEG400	$0.180 x 10^{-3}$ to $2.412 x 10^{-2}$	13.53552	-27.3104	28.36745	$1.83 x 10^{-3}$ to $5.06 x 10^{-3}$
PU-5wt%- DBS	$0.985 x 10^{-4}$ to $0.220 x 10^{-3}$	10.65996	-30.225	21.74618	$1.91 x 10^{-5}$ to $7.94 x 10^{-5}$
PU-10wt%- DBS	$0.100 x 10^{-3}$ to $0.355 x 10^{-3}$	9.358987	-30.5762	18.75056	$4.77 x 10^{-4}$ to $1.54 x 10^{-3}$
PU-15wt%- DBS	$0.226 x 10^{-3}$ to $0.731 x 10^{-3}$	9.291477	-30.6372	18.59518	$8.63 x 10^{-6}$ to $2.21 x 10^{-5}$
PU-20wt%- DBS	$0.227 x 10^{-3}$ to $0.742 x 10^{-3}$	6.83277	-33.5941	12.93384	$8.21 x 10^{-6}$ to $4.74 x 10^{-5}$

From Eyring equation (3), a linear relationship is obtained using the plot of ln ($\sigma h / K_B$ T) vs 1000/T. The enthalpy (ΔH) and entropy(ΔS) of the electrolyte has been determined by calculating the slope and intercept of following equation.[38]

$$R ln\,(\frac{\sigma h}{kT}) = \frac{-\Delta H}{T} + \Delta S \qquad \textbf{(3)}$$

Where ‘h’ is Planck's constant (6.626 x 10^{-34} J s^{-1}), and k_B is Boltzmann constant, respectively (values are given in the **Table 2**). From the calculated values we observed that there is no significant relation between the Ea, ΔH and ΔS with the variation in the concentration of plasticizers.

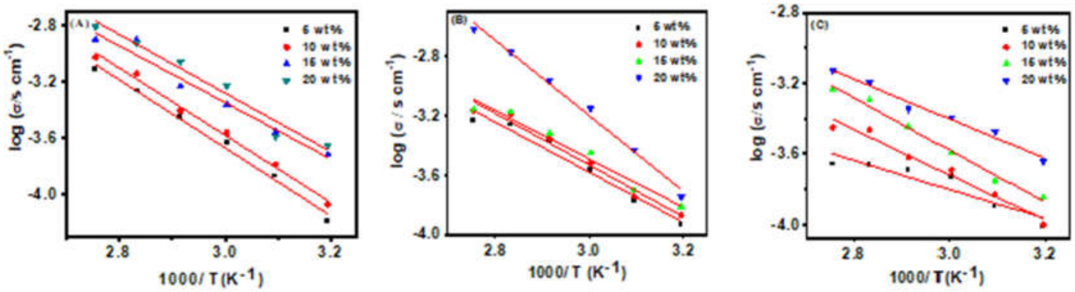

Figure 9. Arrhenius plots of PU-x wt% Plasticizers with different weight percentages (A) PU-x-PEG600 (B) PU-x-PEG400 (C) PU-x-DBS (x= 5, 10, 15, 20 wt %).

2.8 Determination of Diffusion Coefficient

The mobility of cations and anions in a SPE can be determined in terms of diffusion coefficient. It is difficult to quantify the exact amount of ionic mobility of the charge carrier in polymer system, because most of them are bounded as ion pairs or clusters. The Trukhan model is the most appropriate method to determine the total charge carrier concentration in polymer electrolyte system. The Trukhan model basically describes the mobility of charge carriers and helps to determine the diffusion coefficient and mobility charge concentration with respect to loss tangent (tan δ) values (**Figure 10**).

$$D = \frac{2\pi . f^{max} . L^2}{32.(\tan \delta)^3_{max}}$$

(4)

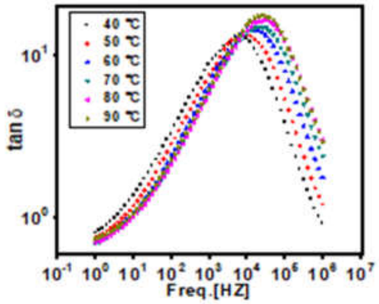

Figure 10.tanδ as a function of perturbation frequency for different temperatures for PU-15wt%-PEG600.

Aforementioned diffusion coefficient equation is depending on maximum of tanδspectra, the sample thickness L and the frequency value at which the tanδ is maximum. By substituting a maximum value in above equation, the diffusion coefficient wasevaluated(values are given in the **Table 2**). [39-42]

3. Conclusion

In this work our main goal is the modification of IPN of two polymers PMMA and PEG-PU by addition of plasticizers (PEG600, PEG400, and DBS) with various weight percentage to achieve better electrolytic conduction of the Li cation in the solid polymer matrix. We got a good response of maximum ionic conductivity 0.180 x 10^{-3}S cm^{-1} SPE using 20wt% -PEG400 plasticizer measured by the impedance spectrometry analysis at 313K. This may be due to increase in amorphous nature of the composite upon the addition of plasticizer some surface morphology changes i.e., has been noted by the XRD and DSC measurement and T_g values found to be shifted to the lower temperature region comparatively. The ΔE values obtained from Arrhenius plots indicated the increased mobility as well as the ionic conductivity of the electrolyte at high plasticizer concentration. The entropy (ΔS), and enthalpy (ΔH) of polymer electrolytes are estimated by using Eyring equation and the results showed no significant relation among the E_a, ΔH and ΔS with the change in plasticizer concentrations.

Experimental section

Materials

Diphenylmethane diisocyanate (MDI), poly ethylene glycol (PEG ~4000Mw) and N, N-dimethyl aniline (DMA) were obtained from Merck, India. Benzoyl peroxide (BPO) and castor oil (CO) (BSS grade) were purchased from SD. Fine-Chem. Ltd., India. Methyl methacrylates, Lithium perchlorate ($LiClO_4$) dibutyl sebacate, poly ethylene glycol (PEG~400 MW & 600 MW) dibutyl sebacate plasticizer (DBS), Acetonitrile and Tetrahydro-Furan (THF) were procured from Rankem, India.

Synthesis of PEG-PU/PMMA-$LiClO_4$/ Plasticizers

Semi-IPN of PEG-PU/PMMA-$LiClO_4$ with PEG-PU and PMMA weight ratio of 60/40 and ethylene glycol (EO)/Li mole ratio of 10 was synthesized following our previous report [25]. Poly (ethylene glycol)-polyurethane (PEG-PU) polymer network was synthesized maintaining -OH/-NCO ratio of 1: 0.8. Initially, C=O (O-H value ~2.6) and the required amount of MDI solution in THF were taken in a round-bottomed flask, degassed, and stirred in inert atmosphere (N_2 atmosphere) for an hour at room temperature. To this pre polymer, a solution of PEG (Monomer-I), methyl methacrylate (Monomer-II) and $LiClO_4$ in THF along with BPO (initiator) and catalyst (DMA) were added. After 4 h of reaction, required amount of plasticizer [Dibutyl Sebacate (DBS)] was added. This solution was stirred for 12 hour and then casted on to a Teflon petri dish. This was allowed to dry at room temperature for 24 h followed by oven curing at 60 °C for another 24 h to obtain a free-standing film of ~0.5 mm thickness. Same procedure was used for the synthesis of polymer electrolytes with other plasticizers (PEG 400 MW) and (PEG~600 MW) and was labeled as PU-x-PEG400, PU-x-PEG600, PU-x-DBS (where x is the weight percent of PEG-400, PEG-600 and DBS added) for further discussion.

Characterizations

AC Impedance measurements were carried out in the frequency between 1Hz to 1 MHz in the temperature range of 40 °C to 90 °C on a ZIVE SP2 electrochemical workstation, ZIVE LAB, using an indigenously designed sample holder. The disk-shaped polymer films were sandwiched between two spring-loaded stainless steel (SS) blocking electrodes. X-ray diffraction (XRD) patterns were taken in reflection mode on a Rigaku MiniFlex tabletop X-ray diffractometer using a Cu Kα source. DSC (differential scanning calorimetry) thermograms were obtained by HITACHI DSC7020 calorimeter (TA instruments) in the temperature range of -150 °C to 150 °C at a heating rate of 2 °C min^{-1}. Thermogravimetric analysis (TGA) was performed using TGA HITACHI TG/DTA 7300 (TA instruments) in the temperature range of 30 °C to 500 °C at a heating rate of 10 °C min^{-1}under nitrogen atmosphere. FT-IR (Fourier transform infrared) spectra were recorded using a BRUKER ALPHA T (spectrometer with frequency range from 4000 cm^{-1} to 400 cm^{-1}).

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