Effect of plasticizers (EC or PC) on the ionic conductivity and thermal properties of the (PEO)$_9$LiTf: Al$_2$O$_3$ nanocomposite polymer electrolyte system

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Abstract A new plasticized nanocomposite polymer electrolyte based on poly (ethylene oxide) (PEO)-LiTf dispersed with ceramic filler (Al$_2$O$_3$) and plasticized with propylene carbonate (PC), ethylene carbonate (EC), and a mixture of EC and PC (EC+PC) have been studied for their ionic conductivity and thermal properties. The incorporation of plasticizers alone will yield polymer electrolytes with enhanced conductivity but with poor mechanical properties. However, mechanical properties can be improved by incorporating ceramic fillers to the plasticized system. Nanocomposite solid polymer electrolyte films (200–600 μm) were prepared by common solvent-casting method. In present work, we have shown the ionic conductivity can be substantially enhanced by using the combined effect of the plasticizers as well as the inert filler. It was revealed that the incorporating 15 wt.% Al$_2$O$_3$ filler in to PEO: LiTf polymer electrolyte significantly enhanced the ionic conductivity [σ_{RT} (max)=7.8×10^{-6} S cm^{-1}]. It was interesting to observe that the addition of PC, EC, and mixture of EC and PC to the PEO: LiTf: 15 wt.% Al$_2$O$_3$ CPE showed further conductivity enhancement. The conductivity enhancement with EC is higher than PC. However, mixture of plasticizer (EC+PC) showed maximum conductivity enhancement in the temperature range interest, giving the value [σ_{RT} (max)=1.2×10^{-4} S cm^{-1}]. It

is suggested that the addition of PC, EC, or a mixture of EC and PC leads to a lowering of glass transition temperature and increasing the amorphous phase of PEO and the fraction of PEO-Li$^+$ complex, corresponding to conductivity enhancement. Al$_2$O$_3$ filler would contribute to conductivity enhancement by transient hydrogen bonding of migrating ionic species with O–OH groups at the filler grain surface. The differential scanning calorimetry thermograms points towards the decrease of T_g, crystallite melting temperature, and melting enthalpy of PEO: LiTf: Al$_2$O$_3$ CPE after introducing plasticizers. The reduction of crystallinity and the increase in the amorphous phase content of the electrolyte, caused by the filler, also contributes to the observed conductivity enhancement.

Introduction

Solid polymer electrolytes are emerging as the most promising electrolyte materials for applications in all-solid-state lithium batteries, super capacitors, fuel cells, dye-sensitized solar cells and other energy storage devices [1–4]. Among the many polymeric electrolyte materials reported so far, poly (ethylene oxide) (PEO) appears to be the most studied candidate to develop solid state electrolytes (SPEs) [5]. This is mainly due to its ability to dissolve salts [LiClO$_4$, LiBF$_4$, LiCF$_3$SO$_3$, NaClO$_4$, Mg (ClO$_4$)$_2$, etc.] well and proper chemical structure to support ion transport [6]. However, the low ionic conductivity of PEO-based electrolytes at ambient temperature has limited their practical applications. To obtain SPEs with improved

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conductivities, many strategies have been attempted, such as the inclusion of cross-linking agents to form networks [7], incorporating low molecular weight organic additives [8–10, 16], and doping with inorganic fillers [11–15]. Among them, the addition of nano-size oxide fillers such as Al_2O_3, TiO_2, SiO_2, ZrO_2, etc., and the addition of low molecular weight plasticizers (ethylene carbonate (EC), propylene carbonate (PC), polyethylene glycol, Double metal cyanide, etc.) to the conventional PEO-salt matrix have been regarded as the most promising methods. However, the incorporation of plasticizers alone would yield polymer electrolytes with enhanced conductivity by reducing crystallinity but with poor mechanical properties. The addition of low molecular weight and high dielectric constant plasticizers shows important intrinsic modifications in the heterogeneous polymer composite such as the enhancement of the amorphous phase content [8], increasing flexibility in the polymeric segments and release of mobile charge carries due to ion dissolution effect. Addition of fillers results in an increase in ionic conductivity of polymeric electrolytes with improved mechanical properties [12]. Though the ceramic-filler-dispersed PEO-lithium salt (LiTf) composite electrolytes exhibit enhanced ionic conductivity, it is still far from the conductivity values required for practical applications. In this respect, the "combined effect" of the plasticizers and ceramic fillers on the electrical and thermal properties of polymer electrolytes reported here will be of great interest. Even though a large number of reports are available in literature on the effect of plasticizers or nano fillers on ionic conductivity enhancement in PEO-based polymer electrolytes, only very few reports are available which discuss the "combined effect" of the plasticizer and the filler [22–27].

In the present work, we have examined the electrical and thermal properties of the polymer electrolyte $(PEO)_9LiTf$ dispersed with nano-size ceramic filler (Al_2O_3) and plasticized with PC, EC, and a mixture of EC and PC (EC+PC). In a previous study, we have reported that the optimized ratio of 15 wt.% of Al_2O_3 resulted the maximum ionic conductivity enhancement at ambient temperature for the same electrolyte.

Experimental

Materials and sample preparation

PEO (molecular weight 4×10^6), Lithium Triflate (LiTf), Al_2O_3 (pore size 5.8 nm, 150 mesh, neutral), EC (purity of 99%) and PC (anhydrous, purity of 99.7%) purchased from Aldrich, were used as starting materials. Prior to use, PEO was vacuum dried at 50 °C for 24 h whereas salt (LiTf) and ceramic powder (Al_2O_3) were vacuum dried for 24 h at

120 °C and 200 °C, respectively. The polymer and salt concentration ratio was fixed at 9:1 and the optimized amount of ceramic powder added was 15% of the total weight of the PEO_9LiTf. The optimized ratio (50 wt.%) of plasticizer (EC, PC, or mixture of EC and PC) were mixed with the polymer–salt–filler solutions. The anhydrous acetonitrile was used as the solvent. All the weightings were done inside the glove box and the solution was magnetically stirred at room temperature for at least 24 h, until a homogeneous solution was obtained. The resulting slurry was cast on a Teflon support and then left nearly for 24 h in order to let the solvent slowly evaporate. All the polymer electrolyte films were finally dried under vacuum for 24 h before use.

Measurements

The complex impedance measurements were carried out on disc-shaped samples sandwiched between two stainless steel (S/S) electrodes of 13 mm diameter, using a computer-controlled Schlumberger SI 1260 impedance analyzer in the 1 Hz to 10 MHz frequency range. The temperature of the samples was varied from room temperature to 100 °C in 10 °C intervals on heating. DSC thermograms were obtained using a Mettler Toledo DSC 30 differential scanning calorimeter. The glass transition temperature (T_g), crystallite melting temperature (T_m), and melting enthalpy (ΔH_m) of different samples were extracted from these thermograms. Thermal measurements ware carried out at a heating rate of 10 °C min^{-1} from −120 °C to 120 °C in the heating cycle. A flow of nitrogen gas was maintained over the perforated pan to avoid any contact with atmospheric moisture.
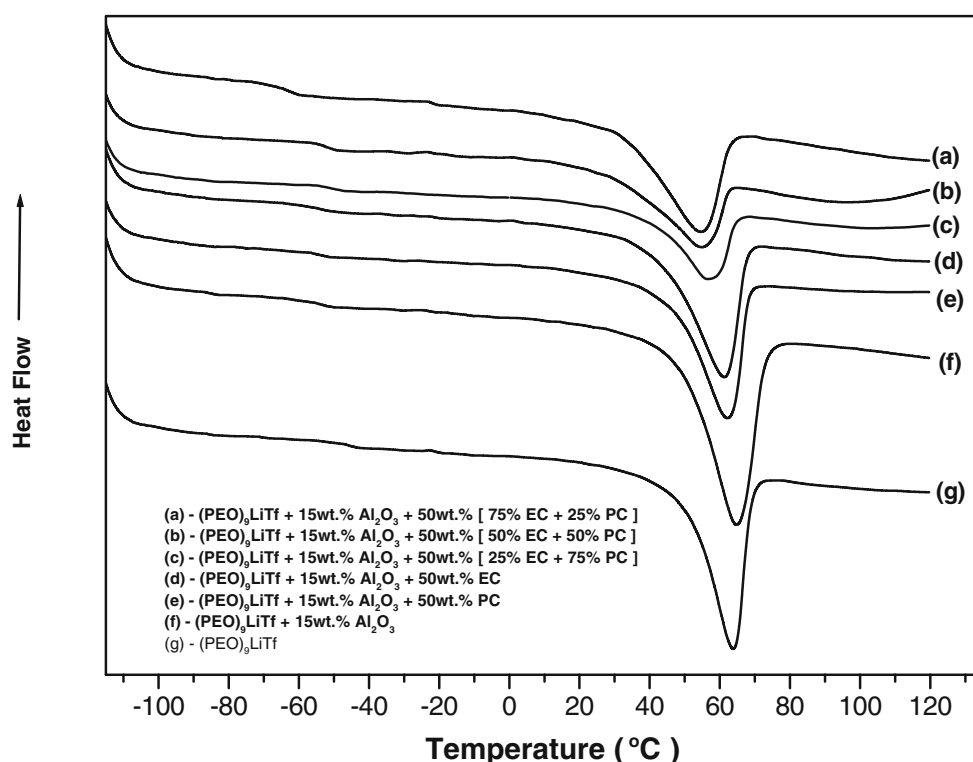
Results and discussion

Thermal properties

Figure 1 and Table 1 show the DSC thermograms of polymer electrolyte samples with different filler and plasticizer contents.

The T_g and the T_m obtained in this work is shown in Fig. 1. These values closely agree with the values reported in literature for PEO-LiTf polymer electrolyte systems [19, 24]. The T_g and T_m values for the $(PEO)_9LiTf$ electrolyte obtained in this work are −45.8 °C and 65 °C, respectively. After incorporating 15 wt.% Al_2O_3 to the $(PEO)_9LiTf$ electrolyte, T_g and T_m have decreased to −52.7 °C and 64.6 °C, respectively. This observation suggests that the decrease of crystallinity of $(PEO)_9LiTf$ electrolyte mainly occurs through the Lewis acid–base interactions between the ether O of PEO chain and Lewis

Fig. 1 DSC thermograms of different composite polymer electrolytes

Legend inside figure:

(a) - (PEO)$_9$LiTf + 15wt.% Al$_2$O$_3$ + 50wt.% [75% EC + 25% PC]
(b) - (PEO)$_9$LiTf + 15wt.% Al$_2$O$_3$ + 50wt.% [50% EC + 50% PC]
(c) - (PEO)$_9$LiTf + 15wt.% Al$_2$O$_3$ + 50wt.% [25% EC + 75% PC]
(d) - (PEO)$_9$LiTf + 15wt.% Al$_2$O$_3$ + 50wt.% EC
(e) - (PEO)$_9$LiTf + 15wt.% Al$_2$O$_3$ + 50wt.% PC
(f) - (PEO)$_9$LiTf + 15wt.% Al$_2$O$_3$
(g) - (PEO)$_9$LiTf

acid sites on surface of filler [12]. After introducing the plasticizers to the (PEO)$_9$LiTf + 15 wt.% Al$_2$O$_3$ composite electrolyte, the T_g and T_m have decreased further. The maximum decrease is shown for the composition (PEO)$_9$LiTf + 15 wt.% Al$_2$O$_3$ + 50 wt.% [75% EC + 25% PC]. For this sample, the T_g has decreased to −62.2 °C, and the T_m to 53.2 °C. ΔH_m has decreased from 78.21 to 38.32 Jg^{-1}.

Figure 2, shows variation of T_g and room temperature (25 °C) ionic conductivity with different plasticizer content. As the T_g is related to the segmental flexibility of the host polymer and the disordered structure [19, 25], the result may be related to a possible enhancement in the segmental flexibility of polymeric chains of the electrolyte due to the addition of plasticizer [24, 26]. The maximum conductivity is obtained for the composition exhibiting the minimum T_g,

suggesting that the major contribution to the ionic conductivity enhancement comes from the structural modifications caused by the combined effect of the filler and the plasticizer.

Figure 3 shows variation of T_m and room temperature (25 °C) ionic conductivity with different plasticizer compositions. The T_m is attributed to the melting of PEO-rich crystalline phase [21]. The plasticizer-added electrolyte, with composition (PEO)$_9$LiTf + 15 wt.%Al$_2$O$_3$ + 50 wt.% [75% EC + 25% PC], shows the lowest T_m and the maximum conductivity enhancement. It is evident that the addition of plasticizer increases the amorphous phase content of the polymer. The overall result suggests that the polymer chains become more flexible and the lithium ion motion taking place in the amorphous phase is facilitated compared to the unplasticized sample [25].

Table 1 Thermal properties (T_g, T_m, and ΔH_m) of different CPEs obtained from DSC plots

Composite polymer electrolyte	T_g (^{0}C)	T_m (^{0}C) Peak value	Melting enthalpy ΔH_m (Jg^{-1})
(PEO)$_9$LiTf	−45.8	65.0	78.21
(PEO)$_9$LiTf + 15 wt.% Al$_2$O$_3$	−52.7	64.6	64.38
(PEO)$_9$LiTf + 15 wt.% Al$_2$O$_3$ + 50 wt.% PC	−53.4	61.5	58.72
(PEO)$_9$LiTf + 15 wt.% Al$_2$O$_3$ + 50 wt.% EC	−53.6	60.3	54.68
(PEO)$_9$LiTf + 15 wt.% Al$_2$O$_3$ + 50 wt.% [25% EC + 75% PC]	−53.8	56.7	44.74
(PEO)$_9$LiTf + 15 wt.% Al$_2$O$_3$ + 50 wt.% [50% EC + 50% PC]	−55.1	54.5	40.51
(PEO)$_9$LiTf + 15 wt.% Al$_2$O$_3$ + 50 wt.% [75% EC + 25% PC]	−62.2	53.2	38.32

Fig. 2 Relationship between T_g and σ_{RT} as a function of different plasticizer content for $(PEO)_9LiTf + 15$ wt.% Al_2O_3 CPE
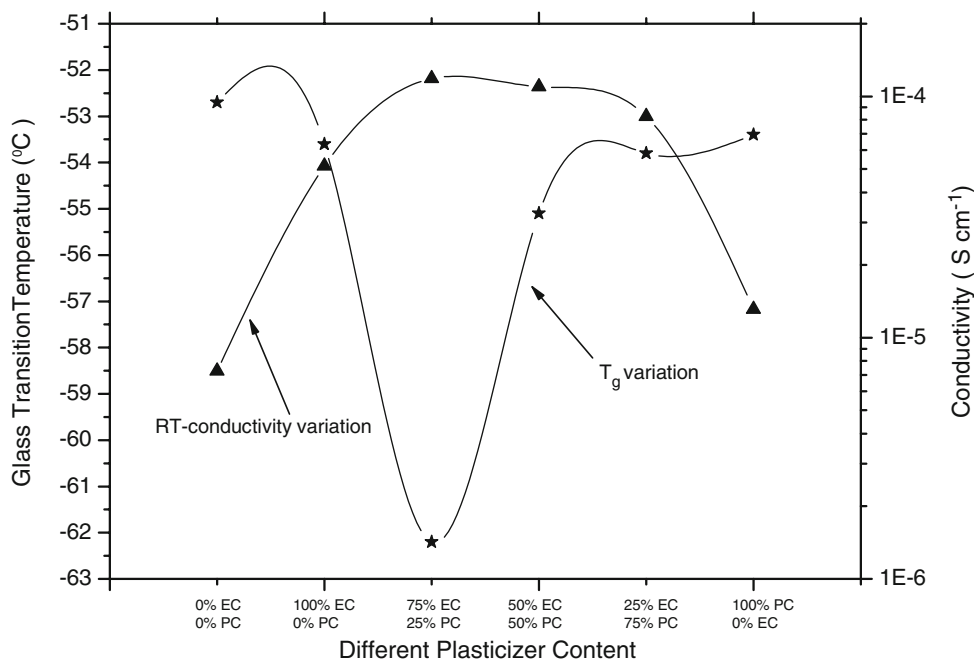
The increase of the amorphous phase content can be clearly seen by calculating the relative percentage of crystallinity (χ_c) for the electrolyte samples studied. The Table 2 shows χ_c of different samples and their ionic conductivity values at room temperature. The relative percentage of crystalline PEO, χ_c, can be calculated using the equation, $\chi_c = \Delta H_m^{sample} / \Delta H_m^*$, where ΔH_m^* is the heat of fusion of PEO [26]. It can be clearly seen that in Table 2, χ_c decreases due to the filler as well as the plasticizer. This is a good evidence to estimate the enhancement of volume fraction of the amorphous phase caused by the

modification of the polymer–salt matrix after the addition of the plasticizer.

Ionic conductivity

Figure 4 shows the temperature dependence of ionic conductivity (σ) of different solid polymer electrolyte compositions $(PEO)_9LiTf$, $(PEO)_9LiTf + 15$ wt.% Al_2O_3, $(PEO)_9LiTf + 15$ wt.% $Al_2O_3 + 50$ wt. % plasticizer. According to Fig. 4, incorporating 15 wt.% Al_2O_3 ceramic filler into the PEO-LiTf complex significantly enhanced the

Fig. 3 Relationship between Tm and σ_{RT} as a function of different plasticizer content for.$(PEO)_9LiTf + 15$ wt.% Al_2O_3 CPE

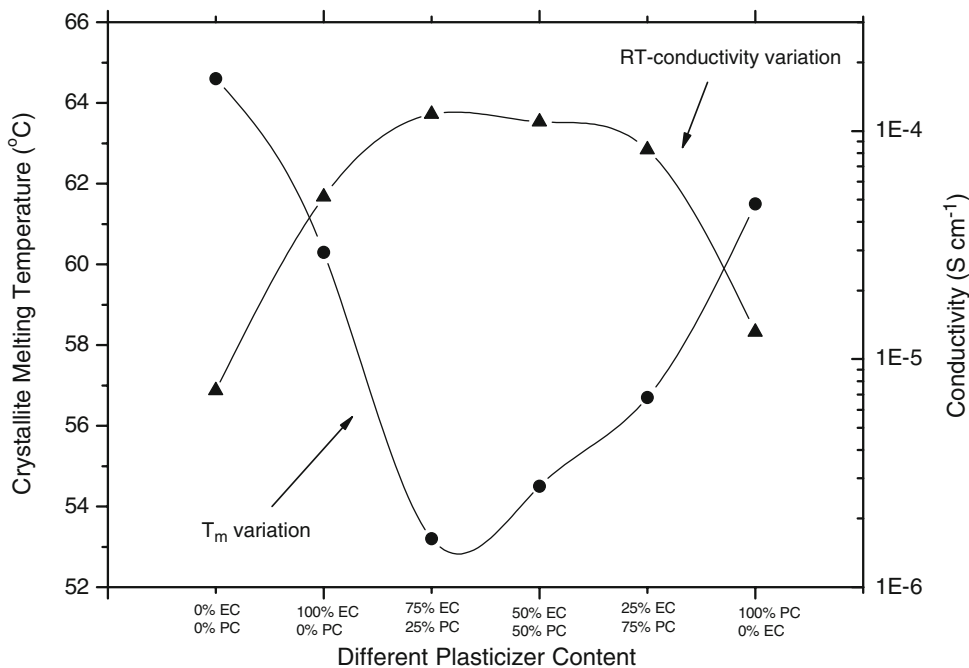**Table 2** Relative percentage of crystallinity (χ_c) of different CPEs and their ionic conductivity values at room temperature (25 °C)

$$\chi_c = \left[\Delta H_m^{\text{sample}} / \Delta H_m^* \right] \times 100,$$
$$\Delta H_m^* = 162 \text{ Jg}^{-1}$$

Composite polymer electrolyte	χ_c (%)	σ_{RT} (max)/S cm^{-1}
(PEO)$_9$LiTf	48.28	6.70×10^{-7}
(PEO)$_9$LiTf + 15 wt.% Al$_2$O$_3$	39.74	7.81×10^{-6}
(PEO)$_9$LiTf + 15 wt.% Al$_2$O$_3$ + 50 wt.% PC	36.24	1.29×10^{-5}
(PEO)$_9$LiTf + 15 wt.% Al$_2$O$_3$ + 50 wt.% EC	33.75	4.98×10^{-5}
(PEO)$_9$LiTf + 15 wt.% Al$_2$O$_3$ + 50 wt.% [25% EC + 75% PC]	27.62	8.25×10^{-5}
(PEO)$_9$LiTf + 15 wt.% Al$_2$O$_3$ + 50 wt.% [50% EC + 50% PC]	25.01	1.08×10^{-4}
(PEO)$_9$LiTf + 15 wt.% Al$_2$O$_3$ + 50 wt.% [75% EC + 25% PC]	23.65	1.21×10^{-4}

ionic conductivity. The room temperature ionic conductivity of the (PEO)$_9$LiTf + 15 wt.% Al$_2$O$_3$ sample was 7.8×10^{-6} S cm^{-1}. The discontinuity of the $\sigma \sim 1/T$ curve around T_m has diminished for the filler-added electrolyte. The ionic conductivity has enhanced also in the amorphous state above T_m due to the presence of the filler. The addition of PC, EC, or a mixture of EC and PC to the (PEO)$_9$LiTf + 15 wt.% Al$_2$O$_3$ electrolyte resulted in a further conductivity enhancement. The conductivity enhancement with 50 wt.% EC is higher than that with 50 wt.% PC. However, the sample with a mixture of plasticizers showed the maximum conductivity enhancement, for the composition (PEO)$_9$LiTf + 15 wt.% Al$_2$O$_3$ + 50 wt.% [75% EC + 25% PC] with a room temperature conductivity value of σ_{RT}

(max)$= 1.2 \times 10^{-4}$ S cm^{-1}. This result shows that the ionic conductivity of the plasticized electrolyte is two order of magnitude higher than unplasticized one with (PEO)$_9$LiTf + 15 wt.% Al$_2$O$_3$.

The effect of the plasticizers in enhancing the conductivity of PEO-based polymer electrolytes is well known [10, 16]. The role played by the plasticizer may involve several factors such as the viscosity and the dielectric constant of the plasticizer, polymer–polymer and polymer–plasticizer interactions and ion–plasticizer coordination [10]. The structure and the molecular weight of the plasticizer would influence these factors. The plasticizer can interrupt polymer–polymer interactions by occupying the inter and intra-chain free volume which will, in turn, influence the

Fig. 4 Variation of the ionic conductivity of both plasticizer and filler-free, only filler-added and both plasticizer and filler-added polymer electrolytes with inverse temperature
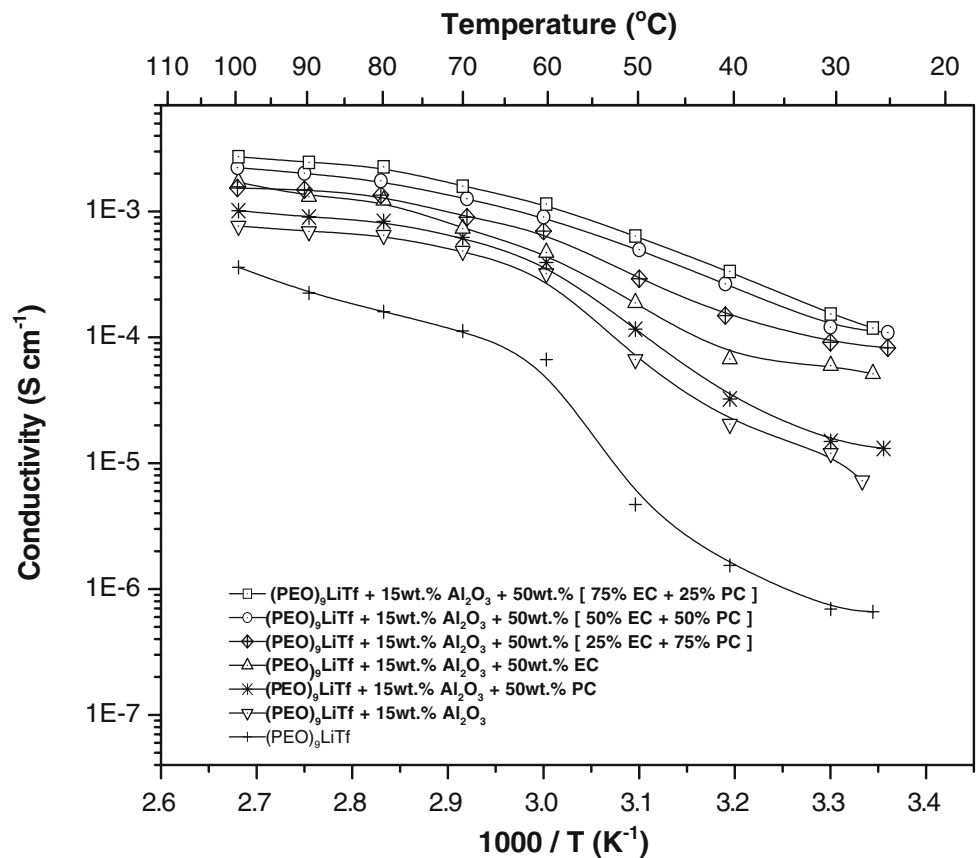
glass transition temperature of the polymer. The presence of the plasticizer would, therefore, reduce the fraction of the crystalline PEO and the fraction of the crystalline PEO-Li$^+$ complexes in the system giving rise to an increase in the amorphous phase content as evidenced by an decrease in T_g. The associated increase in the segmental flexibility of polymer chains would contribute to the conductivity enhancement. Results of infrared (IR) studies by Frech et al. [16] on plasticized PEO-LiCF$_3$SO$_3$ electrolyte have clearly shown that the fractions of the crystalline phases of pure PEO and PEO$_9$LiCF$_3$SO$_3$ complex gradually vanishes with increasing PC content. The interconnected regions of amorphous, plasticized PEO with dissolved salt become ionically conducting pathways. Although we have not made any experimental observations, we expect a similar mechanism to operate in our plasticized, filler-added PEO-based polymer electrolytes reported here.

The role played by the alumina filler in enhancing conductivity can be explained on the basis of experimental evidence from our work as well as from reports by previous workers [4, 11–15, 17–21]. As evidenced from the present work (Fig. 2), the presence of the filler would contribute to the lowering of T_g and increasing the volume fraction of the amorphous phase possibly by modifying the host polymer structure. A dominant contribution to the conductivity enhancement below T_m should possibly be due to this effect. However, the filler has enhanced the conductivity also in the amorphous phase above T_m pointing towards the existence of a second mechanism associated with the filler particles. At this stage, we can only speculate on this based on observations suggested by other workers on similar systems [13, 28, 29]. As suggested by Wieczorek et al. [29], this mechanism possibly results from Lewis acid–base type interactions of migrating ionic species with O–OH surface groups on alumina grains. These interactions would be able to provide transient hopping sites and conducting pathways for migrating ions contributing to enhanced conductivity. The overall effect of the plasticizer and the filler, as described above would lead to a considerable conductivity enhancement in the filler-added, plasticized polymer electrolyte system.

The addition of plasticizers to PEO-based polymer electrolytes is usually accompanied by some major draw backs, such as the loss of mechanical properties and deterioration of the electrolyte–lithium metal interface. Although no quantitative measurements have been made with regard to mechanical properties, we have observed by mechanically stretching the electrolyte membranes that the addition of alumina filler has yielded mechanically stronger films. Thus, the plasticized electrolyte appears to have "regained" the loss of mechanical strength due to the incorporation of the alumina filler which has "reversed" the molding effect of the plasticizer.

With regard to the interfacial properties of the polymer electrolyte films, we have, again, not made any measurements. However, the work reported by Appetecchi et al. [15] on several PEO-based polymer electrolytes have shown that the passivation effect on lithium metal electrode could also be reduced by incorporating ceramic fillers. Authors have attributed this to the "trapping" of traces of residual reaction products by ceramic powders. It is possible to expect a similar mechanism to operate in the case of plasticized polymer electrolytes as well. However, these beneficial effects may be somewhat less in the plasticized system due to the increased amorphous phase content in the electrolyte.

Conclusions

The incorporation of both Al$_2$O$_3$ nano filler along with a mixture of the plasticizers, EC and PC, in to the (PEO)$_9$LiTf solid polymer electrolyte has led to significantly enhanced ionic conductivities with the composition (PEO)$_9$LiTf: 15 wt.% Al$_2$O$_3$:50.wt.% (75% EC + 25% PC) exhibiting the highest room temperature (25 °C) conductivity value of 1.2×10^{-4} S cm^{-1}. According to the results of DSC thermograms, the conductivity enhancement is largely caused by the reduced glass transition temperature and PEO crystallite melting temperature due to the presence of the filler and the plasticizer. An additional mechanism directly associated with alumina grains is evidently responsible for a further contribution to conductivity enhancement as seen from the conductivity increase in the amorphous phase above T_m due to the filler. A possible explanation to this effect could be the availability of extra hopping sites for migrating ionic species due to the formation of transient H-bonding with O–OH groups at filler surface.

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