

Effect of plasticizer and fumed silica on ionic conductivity behaviour of proton conducting polymer electrolytes containing HPF_6

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Abstract. The effect of addition of propylene carbonate (PC) and nano-sized fumed silica on the ionic conductivity behaviour of proton conducting polymer electrolytes containing different concentrations of hexafluorophosphoric acid (HPF_6) in polyethylene oxide (PEO) has been studied. The addition of PC results in an increase in ionic conductivity, whereas the addition of nano-sized fumed silica improves mechanical strength of electrolytes along with a small increase in ionic conductivity. It was observed that the simultaneous addition of PC and fumed silica results in electrolytes with optimum value of ionic conductivity and other properties.

Keywords. Polymer electrolytes; ionic conductivity; polyethylene oxide; plasticizer; fumed silica.

1. Introduction

Since the pioneering work of Wright *et al* (1973) and Armand *et al* (1978), solid polymer electrolytes containing lithium salts have been widely studied (Armand 1987; Gray 1991; Scrosati 1993; Morita *et al* 1998). Proton conducting polymer electrolytes containing various inorganic acids and ammonium salts have also been studied (Armand *et al* 1990; Lassegues 1992; Chandra *et al* 2000; Kumar and Sekhon 2002; Sekhon *et al* 2007). Study of polymer electrolytes based on different polymers such as poly(ethylene oxide) (PEO), poly(methylmethacrylate) (PMMA), poly(vinylidene fluoride) (PVdF), poly(vinyl chloride) (PVC) and poly(acrylonitrile) (PAN), etc has been the subject of great interest in recent years due to their potential applications in rechargeable batteries, fuel cells, sensors, supercapacitors, electrochromic display devices, etc (Armand *et al* 1979; Weston and Steele 1982; Owen 1989; Scrosati 1993; Gray 1997). Amongst these polymers, PEO can dissolve high concentrations of a wide variety of dopants (Armand *et al* 1979). However, due to the large crystallinity, high ionic conductivity at room temperature has not been achieved (Armand *et al* 1979; Quartarone *et al* 1998). At present, special interest has been focused on the development of polymer electrolytes having high ionic conductivity at ambient temperature because of their practical applications. Amorphous phase has been generally reported to be the high conducting phase in these polymer electrolytes (Berthier *et al* 1983). To enhance ionic conductivity, various approaches such as using salts with large anions, polymer blends, plasticizers, composite materials, etc have been used in different polymer electrolytes (Cowie 1987; Armand *et al* 1990; Gray 1991; Abraham 1993; Croce *et al* 1998; Appetecchi *et al* 2000;

Forsyth *et al* 2002; Kumar and Sekhon 2002; Kumar 2004; Sekhon *et al* 2007; Pradhan *et al* 2009). Enhancement in ionic conductivity by about two orders of magnitude has been observed for plasticized polymer electrolytes. The addition of high dielectric constant plasticizer dissociates some ion aggregates into free ions which lead to an enhancement in ionic conductivity. However, the addition of large concentration of plasticizer leads to poor mechanical strength of plasticized polymer electrolytes. The composite polymer electrolytes obtained by adding insulating matrix to polymer electrolytes have been proposed by Weston and Steele (1982). However, the ionic conductivity of composite polymer electrolytes is not large enough as required for practical applications. An improvement in mechanical properties of different nanocomposite polymer electrolytes has also been observed by different workers (Pitawala *et al* 2008; Sharma and Sekhon 2009; Ramesh *et al* 2010). Therefore, the development of polymer electrolytes with high ionic conductivity and good mechanical strength will be required for their use in different applications.

In the present work, the effect of simultaneous addition of both plasticizer and insulating matrix on the properties of PEO-based polymer electrolytes containing hexafluorophosphoric acid (HPF_6) has been studied.

2. Experimental

Polyethylene oxide (PEO) (Aldrich, av. mol. wt 5×10^6), hexafluorophosphoric acid (HPF_6) (Aldrich), propylene carbonate (PC) (Merck) and fumed silica (Aldrich) with an average particle size, 7 nm, have been used as the starting materials. Polymer electrolytes have been prepared by the solution casting method using methanol as solvent. PEO, HPF_6 and PC taken in stoichiometric ratio, were dissolved

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in methanol and stirred for 8–10 h to obtain a clear solution. Subsequently, nano-sized fumed silica was incorporated/dispersed into a polymer matrix under vigorous stirring to form nanocomposite polymer electrolytes. Obtained viscous solution was then poured into polypropylene dishes kept under dry atmosphere and the solvent was allowed to evaporate slowly. Free standing films of polymer electrolytes so obtained were dried under vacuum at 45 °C for 24 h. Films of PEO:HPF₆ polymer electrolytes having compositions in weight percent, viz. (100:0), (95:5) and (90:10), etc were prepared by solution casting method. Films of plasticized and plasticized-nanocomposite polymer electrolytes were prepared by adding *y* wt% PC and (*y* + *z*) wt% (PC and fumed silica concentration) of total weight (90 PEO–10 HPF₆ + *y*PC + *z* fumed silica). The ionic conductivity of polymer electrolytes was measured by complex impedance spectroscopy using computer interfaced Hioki 3532-50 LCR HiTester in 40 Hz–5 MHz frequency range. The conductivity was also measured at different temperatures in 25–100 °C temperature range by keeping the sample holder containing polymer electrolyte in a temperature controlled furnace. FTIR spectra of different polymer electrolytes were recorded with computer interfaced Shimadzu 8400S FTIR spectrometer at room temperature in 400–4000 cm⁻¹ wavenumber range. Crystalline/amorphous nature of different polymer electrolytes was studied by X-ray diffraction using Philips analytic X-ray diffractometer (by using copper as a source of K_α radiation having a wavelength of 1.5415 Å). Thermal properties of different polymer electrolytes were studied by DSC/TGA with Perkin Elmer Pyris Diamond system in different temperature ranges at a heating rate of 10 °C/min under nitrogen atmosphere. Morphology of different polymer electrolytes was studied by Hitachi S-4700 scanning electron microscope at an accelerating voltage of 10 kV.

3. Results and discussion

3.1 Conductivity

3.1a Conductivity vs acid concentration: The ionic conductivity of polymer electrolytes having composition, PEO-*x* (wt%) HPF₆, was measured at different concentrations of HPF₆ and conductivity of PEO (~10⁻⁹ S/cm) has been observed to increase by three orders of magnitude (~10⁻⁶ S/cm) with the addition of HPF₆. Maximum ionic conductivity of 8.8 × 10⁻⁶ S/cm is obtained at 25 °C for electrolytes containing 10 wt% HPF₆ (figure 1). Initially, with an increase in HPF₆ concentration, free charge carrier concentration increases which results in an increase in conductivity, as also observed by Srivastava *et al* (1995) for PEO–NH₄SCN system. However, at higher acid concentrations, the conductivity does not increase at the same rate, which may be explained to be due to the formation of neutral ion aggregates. Figure 1 also shows variation of ionic conductivity of polymer electrolytes having composi-

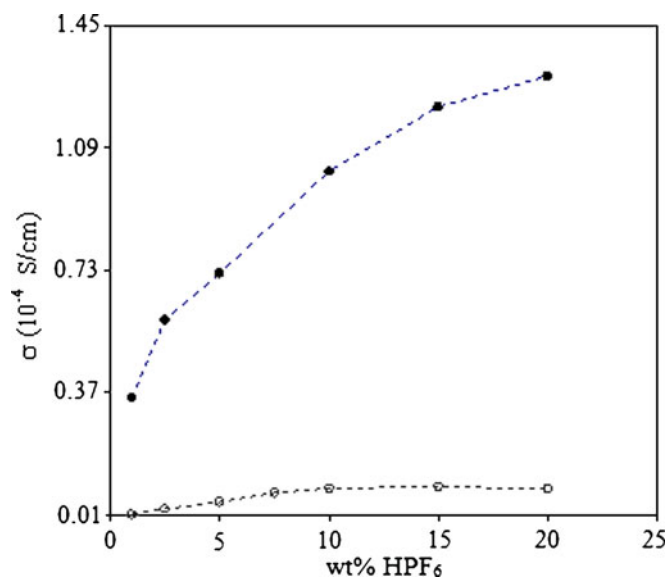


Figure 1. Variation of conductivity with HPF₆ concentration for polymer electrolytes having composition PEO-*x* wt% HPF₆ (a) and PEO-32 wt% PC-*x* wt% HPF₆ (b).

tion, PEO-32 wt% PC-*x* wt% HPF₆ vs HPF₆ concentration. An enhancement in ionic conductivity by two orders of magnitude (~10⁻⁴) has been observed with an increase in HPF₆ concentration, reaching maximum ionic conductivity of 1.02 × 10⁻⁴ S/cm at 10 wt% HPF₆. From figure 1, it has been observed that plasticized polymer electrolytes containing PC have higher ionic conductivity than unplasticized (PEO-HPF₆) polymer electrolytes at all concentrations of HPF₆. The higher ionic conductivity of plasticized polymer electrolytes is generally due to the higher dielectric constant and plasticizing nature of PC. The increase in ionic conductivity of different polymer electrolytes containing plasticizers is also related to an increase in the amorphous phase, which is reported to be the high conducting phase in polymer electrolytes (Berthier *et al* 1983).

Figure 2 shows variation of ionic conductivity of 90 PEO:10 HPF₆ and 90 PEO:10HPF₆-32 wt% PC as a function of fumed silica concentration. Increase in ionic conductivity for (PEO-HPF₆-fumed silica) nanocomposite polymer electrolytes has been observed by a small amount as compared to (PEO-HPF₆-PC-fumed silica) plasticized-nanocomposite polymer electrolytes (figure 2). On the other hand, ionic conductivity at higher concentrations of fumed silica decreases because excessive dispersion of fumed silica particles impedes the movement of ions. Maximum ionic conductivities of 1.93 × 10⁻⁵ and 6.89 × 10⁻⁴ S/cm at room temperature have been observed for nanocomposite polymer electrolytes containing 4 wt% fumed silica and both 32 wt% PC as well as 4 wt% fumed silica, respectively. An improvement in the mechanical properties of nanocomposite polymer electrolytes has also been observed visually.

3.1b Conductivity vs temperature: Dependence of ionic conductivity on temperature in the range of 25–125 °C for

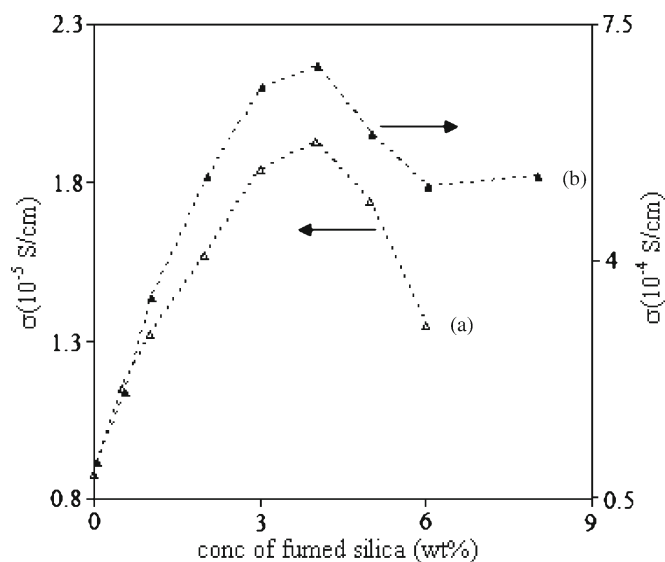


Figure 2. Variation of conductivity with fumed silica concentration for polymer electrolytes having composition 90 PEO:10HPF₆-z wt% fumed silica (a) and 90 PEO:10HPF₆-32 wt% PC-z wt% fumed silica (b).

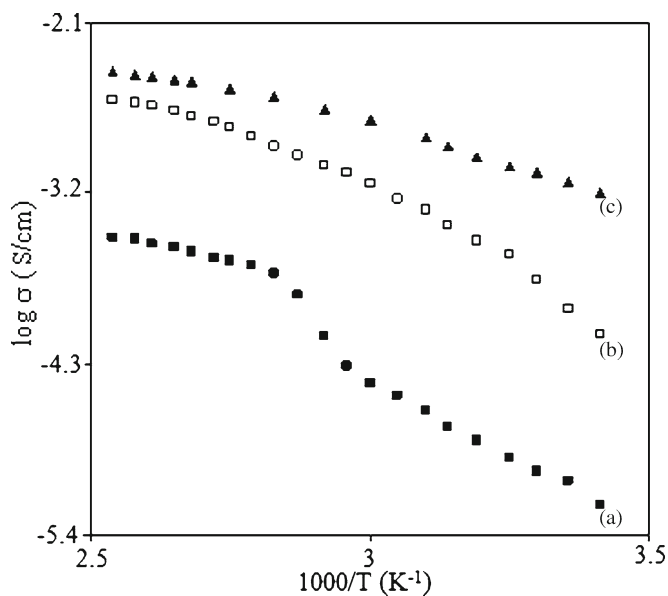


Figure 3. Variation of log conductivity with reciprocal temperature for 90 PEO:10HPF₆ (a), 90 PEO:10HPF₆-32 wt% PC (b) and 90 PEO:10HPF₆-32 wt% PC-4 wt% fumed silica (c).

different polymer electrolytes has been studied and the variation is shown in figure 3. Sharp increase in the ionic conductivity of PEO-HPF₆ at about 65 °C corresponds to the semicrystalline to amorphous phase transition of PEO (Papke *et al* 1981). For polymer electrolytes containing PC and fumed silica, almost a linear variation in ionic conductivity as a function of temperature has been observed, which shows Arrhenius type thermally-activated behaviour (table 1). Activation energies have been calculated for ion transport below

Table 1. Thermal data for different polymer electrolytes.

Sample (electrolyte system)	T_m (°C)	ΔH_m (Jg ⁻¹)	χ_c (%)
PEO	74	209.0	100
90 PEO:10 HPF ₆	72	107.0	51
90 PEO:10 HPF ₆ -32 wt% PC	69	96.8	46
90 PEO:10 HPF ₆ -32 wt% PC-4 wt% fumed silica	64	89.6	42

and above the melting temperature and are presented in table 2. Decrease in activation energy (from 0.194 to 0.085 ± 0.002 eV) for the polymer electrolytes containing PC and fumed silica implies a decrease of the energy barrier to ion transport which in turn facilitates fast ion movement in polymer electrolytes. From the above results, it is revealed that plasticized-nanocomposite polymer electrolytes have higher ionic conductivity and smaller activation energy as compared to other electrolytes.

3.2 FTIR studies

The complexation of PEO with HPF₆, presence of free ions, ion aggregates and their dissociation with the addition of PC have been observed by FTIR and spectra of some samples in the selected region is shown in figure 4. Peaks at 560, 730 and 820 cm⁻¹ are assigned to the presence of free PF₆⁻ anions. The shoulder at 860 cm⁻¹ is attributed to the presence of ion aggregates. Peaks in the region 850–1450 cm⁻¹ corresponds to -C-O-C- stretching and deformation mode. Some important peaks related to PEO and PC have also been assigned by our group previously (Sharma and Sekhon 2006a, b). Peaks at about 1020, 1080 and 1150 cm⁻¹ related to -C-O-C- symmetric and asymmetric stretching vibrations and doublet at 1343 and 1360 cm⁻¹ related to swinging vibrations of CH₂ group are characteristics of crystalline PEO phase (Li and Hsu 1984). With the addition of HPF₆ to PEO, some new peaks along with a shift in the position of existing peaks of PEO confirms the polymer-salt complexation. With the addition of PC in polymer electrolytes, shoulder at 860 cm⁻¹ disappears due to the dissociation of ion aggregates. These FTIR results are in agreement with the ionic conductivity results (figure 1) as the dissociation of ion aggregates with the addition of PC enhances the free ion concentrations and hence ionic conductivity. With the addition of PC and fumed silica, changes in the frequencies of -C-O-C- vibrations of PEO may be due to the weakening of interaction between ether oxygen of PEO and HPF₆ and an increase in PEO flexibility which leads to further increase in ionic conductivity. It is also observed from FTIR spectra that peaks at around 1000–1150 cm⁻¹ corresponding to the crystalline PEO phase disappeared and doublet (at 1343 and 1360 cm⁻¹) changes to a single sharp band at around 1350 cm⁻¹ (due to swinging vibration of C-H in CH₂ in amorphous phase of PEO).

3.3 XRD studies

Figure 5 shows X-ray diffraction patterns for different polymer electrolytes. Addition of plasticizer PC to PEO-HPF₆ has been observed to result in an increase in the amorphous content. Diffractogram of PEO shows main characteristic peaks at $2\theta = 19$ and 23° . With the addition of HPF₆ in PEO, new characteristic peaks are also observed at $2\theta = 42$, 43.5 , 49 , 51 and 72° , which are due to the presence of HPF₆ and PEO-HPF₆ complex formation. Peaks corresponding to HPF₆ (spectra not shown) and PEO-HPF₆ disappear with the addition of PC and fumed silica. The decrease in the intensity and significant broadening in PEO peaks at $2\theta = 19$ and 23° indicates a decrease in the crystallinity with the addition of PC and fumed silica. These results are in agreement with the ionic conductivity results.

3.4 DSC/TGA studies

DSC/TGA thermograms were recorded for different polymer electrolytes to study the effect of HPF₆, PC and fumed silica upon crystallinity (%) of PEO and thermal stability. For PEO, endothermic peak at 74°C corresponds to the melting point (T_m) of PEO as shown in figure 6. A decrease in the melting temperature of PEO-HPF₆ ($T_m = 72^\circ\text{C}$) and PEO-HPF₆ containing PC and fumed silica ($T_m = 64$ – 69°C) has been observed indicating a decrease in crystallinity. This is due to the interaction between polymer and fumed silica particles which reduces the amount of crystalline phase of polymer into amorphous phase to some extent and hence enhancing the ionic conductivity (Choi and Shin 1997). The values of enthalpy of melting (ΔH_m) and % crystallinity (% χ_c) have been calculated assuming PEO to be 100%

Table 2. Activation energies for different polymer electrolytes.

Sample (electrolyte system)	Activation energies (eV)		σ (S/cm) at 25°C
	Region I $T < T_m$	Region II $T < T_m$	
90 PEO:10HPF ₆	0.194 ± 0.002	0.116 ± 0.002	8.80×10^{-6}
90 PEO:10HPF ₆ -32 wt% PC	0.143 ± 0.002		1.02×10^{-4}
90 PEO:10HPF ₆ -32 wt% PC-4% fumed silica	0.085 ± 0.002		6.89×10^{-4}

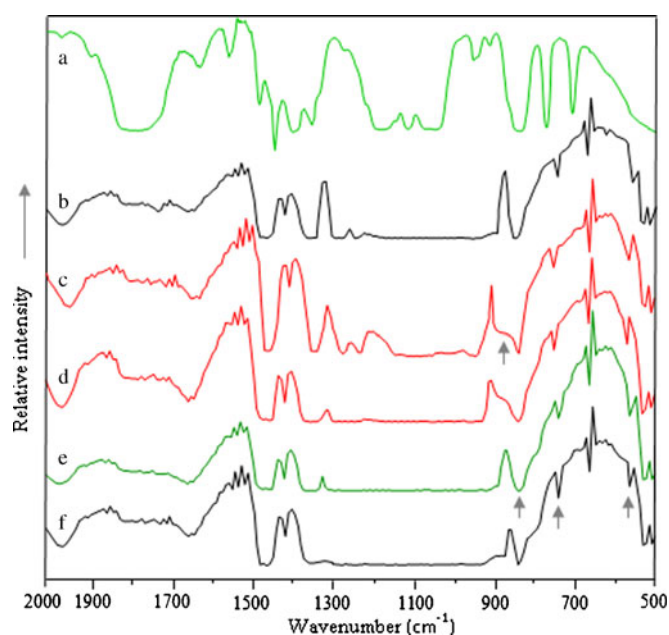


Figure 4. FTIR spectra of PEO (a), PEO containing 5 wt% (b), 10 wt% (c), HPF₆, 90 PEO:10HPF₆ containing 19 wt% (d), 32 wt% (e) and PC and 90 PEO:10HPF₆-32 wt% PC containing 4 wt% fumed silica (f) in 500 – 2000 cm^{-1} region.

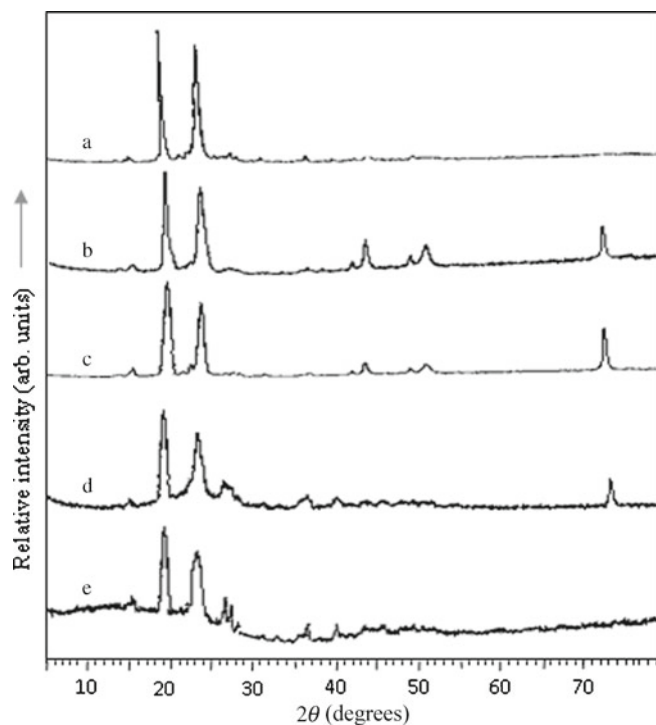


Figure 5. XRD pattern of PEO (a), 90 PEO:10 HPF₆ (b), 90 PEO:10HPF₆-19 wt% PC (c), 90 PEO:10HPF₆-32 wt% PC (d) and 90 PEO:10HPF₆-32 wt% PC-4 wt% fumed silica (e).

crystalline and results are listed in table 1 for different polymer electrolytes. The decrease in the value of ΔH_m and $\% \chi_c$ with the addition of fumed silica particles indicates increase in volume fraction of amorphous phase (Croce *et al* 1998; Scrosati *et al* 2000). TGA curve (figure 7) indicates no weight loss up to 200 °C and a gradual weight loss has

been observed up to 300 °C. Above this temperature, there is a rapid weight loss which could be due to the degradation of polymer electrolytes. Higher thermal stability has been observed for polymer electrolytes containing both PC and fumed silica as shown in figure 7.

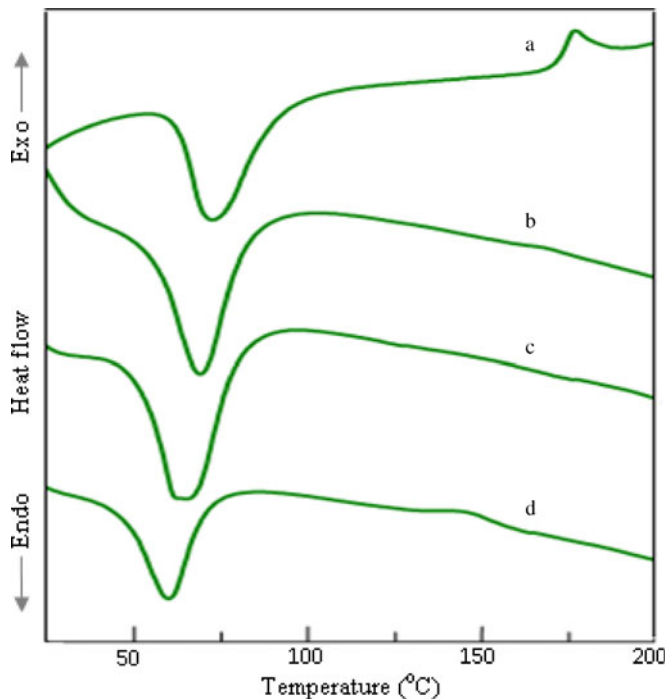


Figure 6. DSC plots for PEO (a), 90 PEO:10HPF₆ (b), 90 PEO:10HPF₆-32 wt% PC (c) and 90 PEO:10HPF₆-32 wt% PC- 4 wt% fumed silica (d).

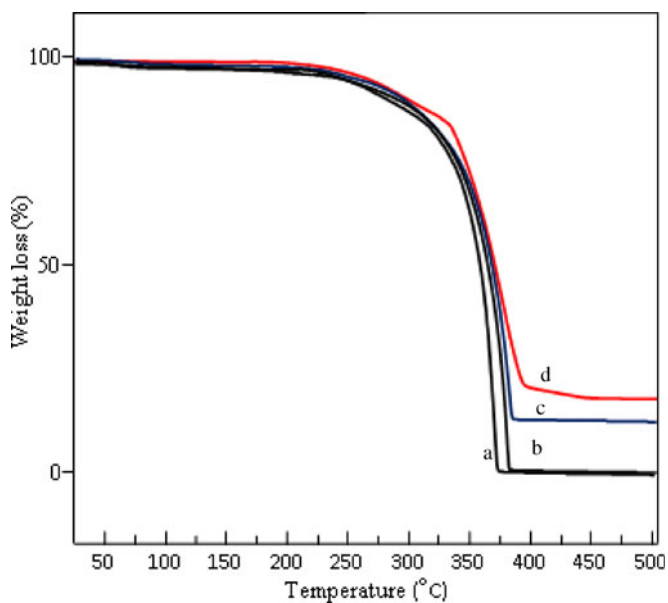


Figure 7. TGA plots for PEO (a), 90 PEO:10HPF₆ (b), 90 PEO:10HPF₆-32 wt% PC (c) and 90 PEO:10HPF₆-32 wt% PC- 4 wt% fumed silica (d).

3.5 SEM

SEM photographs of different polymer electrolytes are shown in figure 8. Presence of spherulites in PEO-HPF₆ is

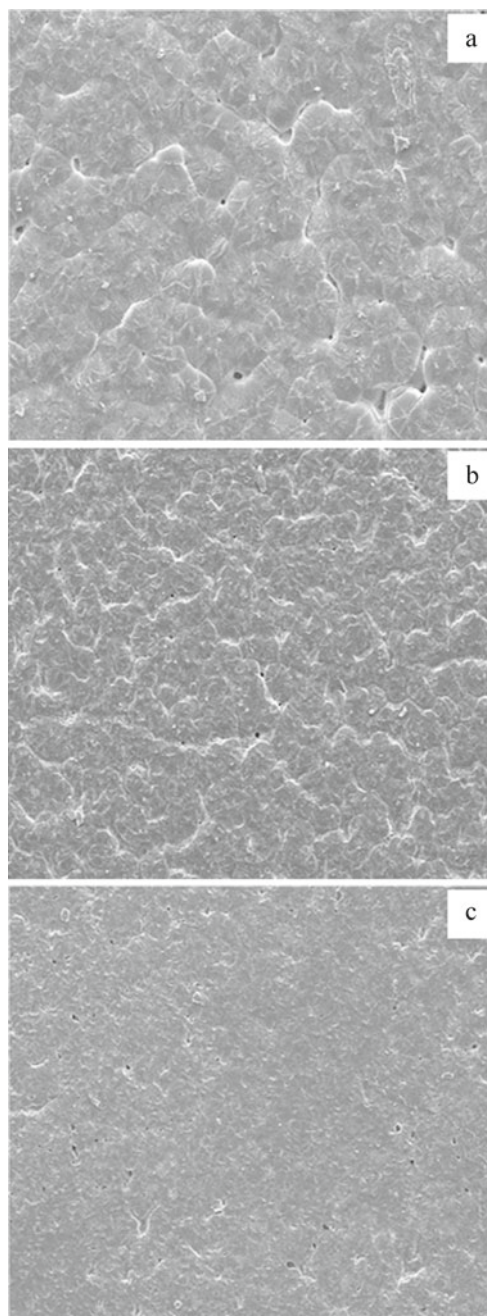


Figure 8. SEM photographs of 90 PEO:10HPF₆ (a), 90 PEO:10HPF₆-32 wt% PC (b) and 90 PEO:10HPF₆-32 wt% PC- 4 wt% fumed silica (c).

due to the existence of crystalline domains. Dark boundaries observed between spherulites show presence of partial amorphous phase. Improvement of surface morphology from rough to smooth surface is observed for polymer electrolytes containing PC and fumed silica. The appearance of pores due to entrapment of PC and fumed silica particles in polymer electrolytes is related to the reduction in crystallinity which leads to an enhancement in the amorphous content and hence ionic conductivity.

4. Conclusions

Ionic conductivity of PEO-based polymer electrolytes has been enhanced with the incorporation of PC and fumed silica. Highest ionic conductivity of 6.89×10^{-4} S/cm and lowest activation energy of 0.085 ± 0.002 eV has been obtained for polymer electrolytes containing both PC as well as fumed silica (plasticized-nanocomposite polymer electrolytes). FTIR results reveal polymer-salt complexation, presence of ion aggregates and their dissociation with the addition of PC. XRD and DSC results indicate that the amorphous content of polymer electrolytes increases with the addition of PC. Visual observations and TGA plots suggest that mechanical strength as well as thermal stability of plasticized-nanocomposite polymer electrolytes remain fairly high along with high value of ionic conductivity. Smooth surface morphology observed from SEM photographs for polymer electrolytes containing PC indicates a decrease in the crystallite size which results in an increase in the amorphous content of polymer electrolytes and hence ionic conductivity.

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