

Investigations on ION Transport and Materials Properties of PEO based KIO₃

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ABSTRACT

Research Study reports synthesis and characterization of potassium (K⁺) ion conducting SPE: (PEO: KIO₃) and NCPE: (70PEO: 30KIO₃) + x SiO₂ films. These films were casted by hot-press technique as well as traditional solution cast method in order to compare the quality of the films. Solution casting of the films could become possible due to the availability of a common solvent which could dissolve both the polymer (PEO) and salt (KIO₃).

The conductivity measurements were done at fixed (5 KHz.) frequency. A comparative studies have been carried out on (PEO: KIO₃) polymer electrolyte films dispersed with nano-sized SiO₂ prepared using a novel hot-press and the solution cast techniques. Fractional dispersal of nano-SiO₂ in to SPE host: (70PEO: 30 KIO₃) + enhanced the room conductivity by more than 3 – fold. The complexation of the salt in the polymer has been confirmed by SEM, XRD, DSC, FTIR studies.

1. Introduction

This paper reflects the synthesis and characterization of another potassium (K⁺) ion conducting SPE: (PEO: KIO₃) and NCPE: (70PEO: 30KIO₃) + x SiO₂ films. These films were casted by hot-press technique as well as traditional solution cast method in order to compare the quality of the films. Solution casting of the films could become possible due to the availability of a common solvent which could dissolve both the polymer (PEO) and salt (KIO₃). The conductivity measurements were done at fixed (5 KHz) frequency. Following the similar line of action, described in the preceding chapter, the highest room temperature conducting SPE film: (70PEO: 30 KIO₃) was identified from the salt concentration dependent conductivity studies. Using this as Ist-phase polymer electrolyte host, NCPE films: (70PEO: 30 KIO₃) + x SiO₂, where x = 0, 1, 3, 5, 7, 10, 12, 15 wt. (%) were casted after dispersing SiO₂ nano-particles (~ 8 nm) as IInd-phase dispersoid. Further, from the SiO₂ – dependent conductivity studies NCPE OCC film was identified.

1.1 STUDIES OF ION TRANSPORT PROPERTY

1.1.1 SALT / DISPERSOID CONCENTRATION DEPENDENCE OF Σ IN SPE & NCPE FILMS

Fig. 1.1 illustrates the plots of room temperature conductivity values as a function of salt concentration for various SPE films: (PEO: KIO₃) prepared by both hot-press and solution cast techniques. It can be clearly noted that salt concentration dependent conductivity variations for both hot-press and solution casted films look almost alike. The conductivity increased rapidly with the addition of salt initially up to 20 wt. (%), then remained almost stable up to 50 wt. (%). A moderate sized σ -maximum could be witnessed at 30 wt. (%) salt for both the hot-press and solution casted films. The initial increase in σ was attributed to the dissociation of KIO₃ salt. The films beyond 50 wt. (%) should slightly lower σ -values and appeared brittle with relatively poor mechanical integrity. The hot-press casted SPE film: (70PEO: 30 KIO₃) exhibited slightly higher σ -value as compared to that of solution casted SPE film. Hence, hot-press technique, which has several procedural merits over the traditional solution cast method, can be preferred for casting polymer electrolyte membranes. The room temperature conductivity of hot-press SPE film: (70PEO: 30 KIO₃), (σ_{rt}) ~ 4.40 × 10⁻⁷ Scm⁻¹, more than two orders of magnitude higher than that of the pure PEO (σ) ~ 3.2 × 10⁻⁹ Scm⁻¹.

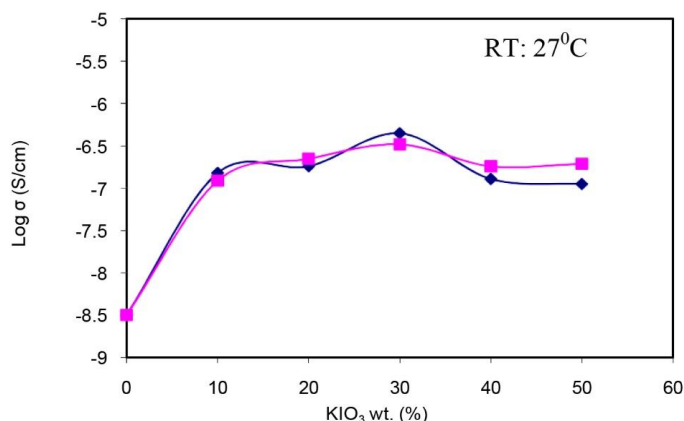


Fig. 1.1: Log σ -x plot for SPE films: (1-x) PEO: x KIO₃, (♦) hot-press, (■) solution cast

Using this SPE composition: (70PEO: 30 KIO₃) as Ist-phase polymer electrolyte host, Nano- Composite Polymer Electrolyte (NCPE) membranes: [70PEO: 30 KIO₃] + x SiO₂, have been casted by hot-press as well as solution casting methods. SiO₂ nano-particles have been dispersed in fractional amount (x in wt. (%)) as IInd-phase dispersoid, as already mentioned. SiO₂-concentration dependent conductivity plots, measured at room temperature for different hot- press/solution casted NCPE films, are shown in Fig. 1.2. 'Log σ - x' plot for hot-press NCPE film exhibited two conductivity maxima at x = 7 & 12 wt. (%) as usual while for solution casted NCPE film a single σ -maximum

appeared at x = 10 wt. (%). However, the conductivity of NCPE film for x = 7 wt. (%) of SiO₂ was relatively high as compare to others. Hence, NCPE film: (70PEO: 30 KIO₃) + 7SiO₂, with room temperature conductivity (σ_{rt}) $\sim 1.00 \times 10^{-6} \text{ Scm}^{-1}$, has been identified as NCPE OCC (Optimum Conducting Composition) film. An enhancement of approximately 3-fold in the room temperature conductivity of SPE host has been obtained in NCPE OCC film simply by dispersing SiO₂ nano-particles. Moreover, this film appeared relatively more stable / flexible mechanically.

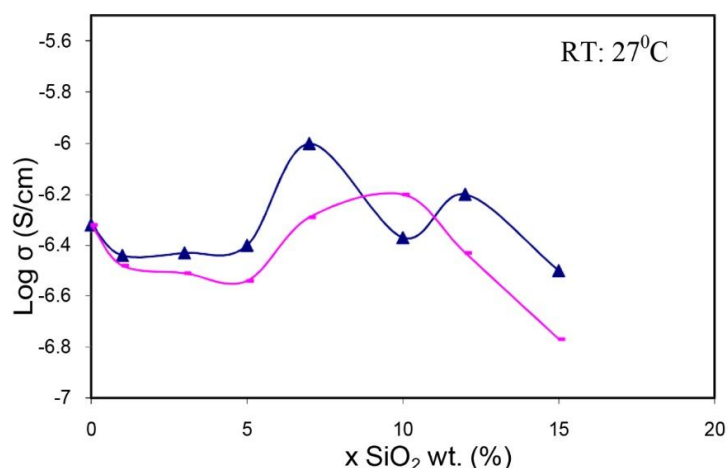


Fig. 1.2: Log σ -x plot for NCPE films: (70PEO:30KIO₃) + x SiO₂; (▲) hot-press, (●) solution cast

The room temperature conductivity values for pure PEO and SPE host/NCPE OCC films, prepared by both hot-press / solution cast methods, are listed in Table 1.1 along with the activation energy (E_a), total ionic transference number (t_{ion}) and cationic transport number (t_+) values (to be discussed

later). It can be noted that as a consequence of SiO₂ dispersal, t_+ improved substantially.

Table 1.1: Room temperature (27°C) values of ionic conductivity (σ) for pure PEO, hot- press/solution casted SPE/NCPE film along with activation energy (E_a), ionic transference number (t_{ion}) and cationic transport number (t_+).

Film	σ (Scm ⁻¹)	E_a (eV)	t_{ion}	t_+
Pure PEO	3.2×10^{-9}	-	-	-
Hot-pressed: SPE host: (70PEO: 30 KIO ₃)	4.40×10^{-7}	0.17	0.94	0.28
NCPE OCC: (70PEO: 30 KIO ₃) + 7SiO ₂	1.00×10^{-6}	0.25	0.97	0.34
Solution casted: SPE host: (70PEO: 30 KIO ₃)	1.25×10^{-7}	0.26	0.94	0.27
NCPE OCC: (70PEO: 30 KIO ₃) + 10SiO ₂	2.95×10^{-7}	0.21	0.97	0.32

1.1.1 TEMPERATURE DEPENDENT CONDUCTIVITY STUDIES

The conductivity as a function of temperature has been measured on SPE and NCPE OCC films prepared by both the hot-press and solution cast methods. As already, mentioned, σ -

measurements were carried out at a fixed frequency (5 kHz). Fig. 1.3 shows 'log σ - 1/T' plots for hot-press SPE: (70PEO: 30 KIO₃) & NCPE OCC: (70PEO: 30 KIO₃) + 7 SiO₂ films as well as for solution casted SPE: (70PEO: 30 KIO₃) & NCPE: (70PEO: 30 KIO₃) + 10 SiO₂ films. Akin to 'log σ - 1/T' variations

reported earlier in the preceding chapter, the conductivity of all SPE/NCPE films increased linearly with the increase in the temperature followed by a slight upward change in the slope at (T_m) ~ 65°C then increased linearly again afterwards. As before, this upward change in all 'log $\sigma - 1/T$ ' has been attributed to the usual semi-crystalline - amorphous phase transition in PEO which has also been observed in DSC studies (discussed later). The straight-line portion of 'log $\sigma - 1/T$ ' plot

below ' T_m ' can be expressed by the Arrhenius equation: $\sigma = \sigma_0 \exp(-E_a/kT)$. The activation energy (E_a) values involved in the thermally activated $E_a \sim 0.17$ conductivity processes have been computed by least square linear fitting of the data. & 0.25 eV for hot-pressed SPE & NCPE OCC film and $E_a \sim 0.26$ & 0.21 eV for solution casted SPE & NCPE films have been obtained respectively, as listed in Table 1.1.

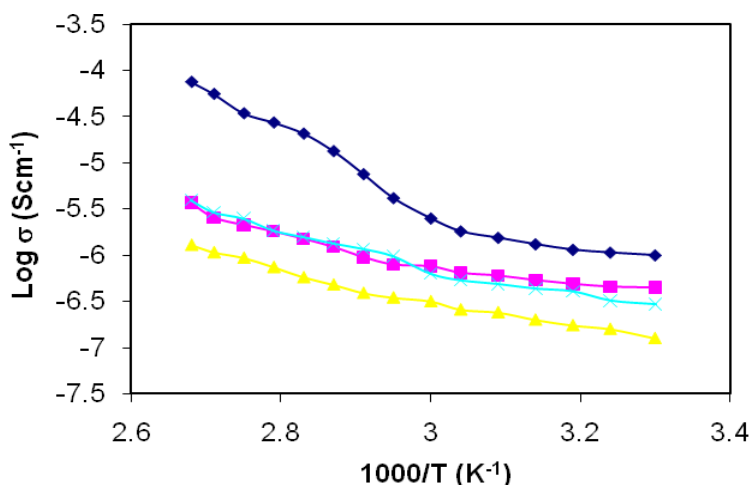


Fig. 1.3: 'Log $\sigma - 1/T$ ' plots for polymer electrolyte membranes: (70PEO: 30KIO₃) + x SiO₂: (SPE) x = 0 (x) and (NCPE OCC) x = 7(♦) (hot-press); (SPE) x = 0 (▲) and (NCPE) x= 10 (x) (solution cast).

1.1.2: TOTAL IONIC TRANSFERENCE (t_{ion}) AND CATIONIC TRANSFERENCE (t_+) NUMBER MEASUREMENT IN SPE AND NCPE OCC FILMS

The total ionic transference number (t_{ion}) in SPE/NCPE films, prepared by both hot-press and solution cast method, have been determined by the d.c. polarization TIC method. Fig. 1.4 shows a typical TIC plot for NCPE OCC film: (70PEO: 30KIO₃) + 7SiO₂. Similar plots were obtained for other SPE and NCPE films. From these TIC 'current-time' plots, the values of $t_{ion} \sim 0.94$ and 0.97 were obtained for SPE and NCPE film materials respectively, as listed in Table 1.1. One can note that dispersal of SiO₂ improved the t_{ion} value slightly in both NCPE films. t_{ion} values are very close to unity hence, it can be stated that the conduction process in these electrolytes is predominantly due to ions only and the electronic contribution to

the overall electrical conductivity is negligibly small. For electrochemical device applications of the polymer electrolyte, the cationic transference number (t_+) is more relevant. Hence, the cation (K^+) transport number (t_+) in the present SPE/NCPE films has also been evaluated using combined ac/dc technique of Evans et al. Data obtained from the complex impedance plots and polarization saturation current plots as before, t_+ values for SPE/NCPE films, prepared by both hot-press and solution cast methods have been determined and listed in Table 4.1. Fig. 1.5 and 1.6 respectively depicts typical complex impedance ($Z'-Z''$) plot before/after polarization and current versus time plot for NCPE OCC films: (70PEO: 30 KIO₃) + 7SiO₂. For other SPE/NCPE film samples the plots look almost alike.

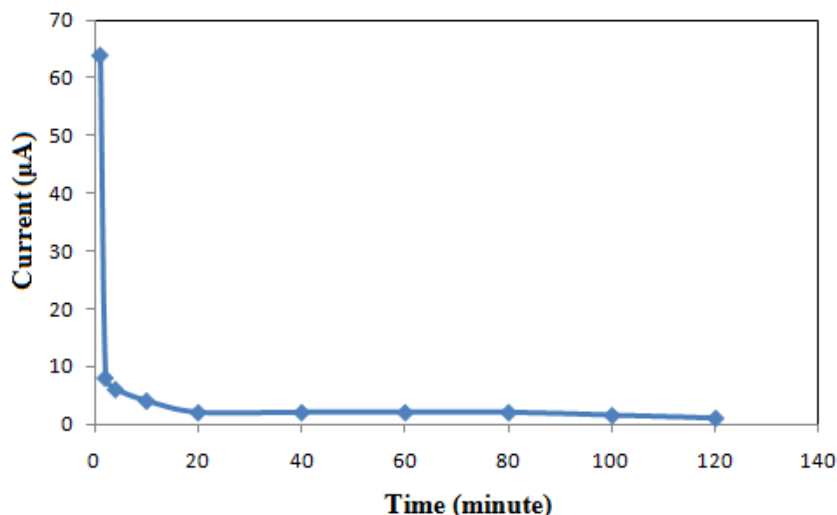


Fig. 1.4: Variation of polarizing current as a function of time in a typical cell: SS/NCPE OCC/SS

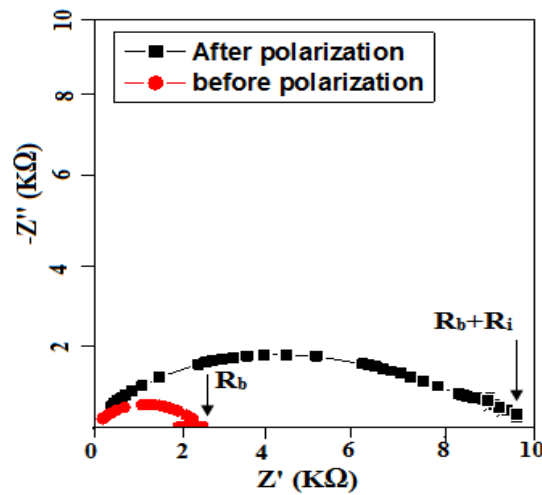


Fig. 1.5: Complex Impedance ($Z'-Z''$) plots before and after polarization of the cell K//NCPE OCC film//K.

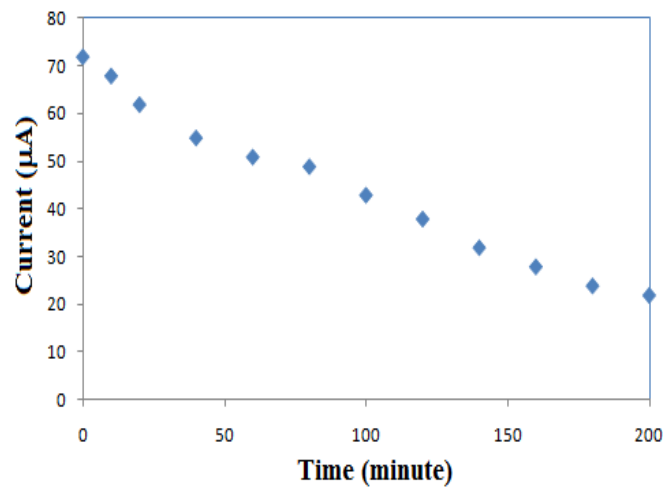


Fig. 1.6: Current versus time plot for the cell K//NCPE OCC film//K.

1.2 Materials Property Studies

Fig. 1.7 (a-d) shows SEM micrographs for solution cast and hot-pressed polymer electrolyte films: (70PEO: 30 KIO₃) + xSiO₂ (where x = 0 SPE; x = 10 and 7, NCPE and NCPE OCC films). The surface morphological pictures indicated almost

uniform distributions of salt as well as SiO₂ particles in these films. However, the micrographs of hot-pressed films show no spherulites texture, this may be due to the reason that during the process of film casting by applying a sudden pressure at relatively high temperature ~ 70°C.

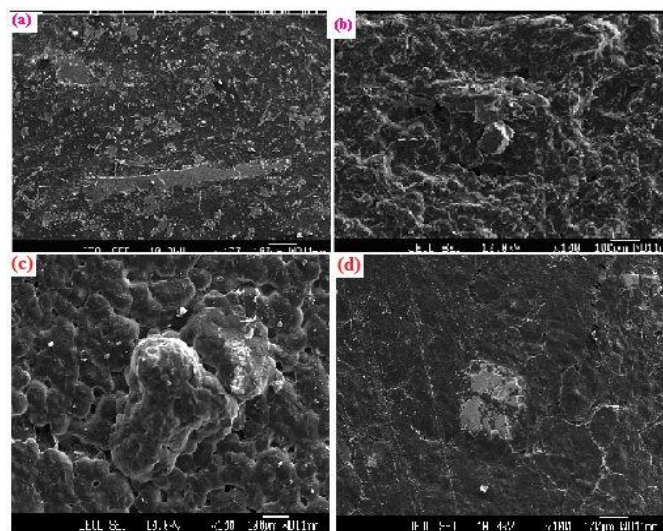


Fig.1.7 (a-d): SEM surface morphology of polymer electrolyte membranes: (70PEO:30KIO₃) + xSiO₂ (a) (SPE) x = 0 and (b) (NCPE) x = 10 % SiO₂ (solution casted), (c) (SPE) x = 0 and (d) (NCPE OCC) x = 7 % (hot-press).

Find sufficient time to grow a lamellar structure. The X-ray diffraction (XRD) patterns of pure PEO, solution cast and hot-pressed polymer electrolyte films: (70PEO: 30 KIO₃) + x SiO₂ (where x = 0 for SPE; x = 10 and 7 for NCPE and NCPE OCC films) are illustrated in Fig. 1.8. On a closer inspection, one can note that all the main peaks of PEO although appeared but affected as a result of complexation of salt and dispersion of SiO₂ - particles. The main two peaks of PEO at around ~ 19° and 23° remained almost intact even after complexation of salt

in PEO (in SPE) and dispersal of SiO₂ (in NCPE). However, the intensity of PEO main peaks decreased substantially specially in NCPE film. This is indicative of decrease in degree of crystallinity and / or increase of amorphousity in PEO. Fig. 1.9 shows comparative FTIR spectra for the films of pure PEO, PEO-salt complexed SPEs and SiO₂ dispersed NCPEs prepared by both hot-press and solution cast method. Following distinctive features can be extracted from these spectral responses.

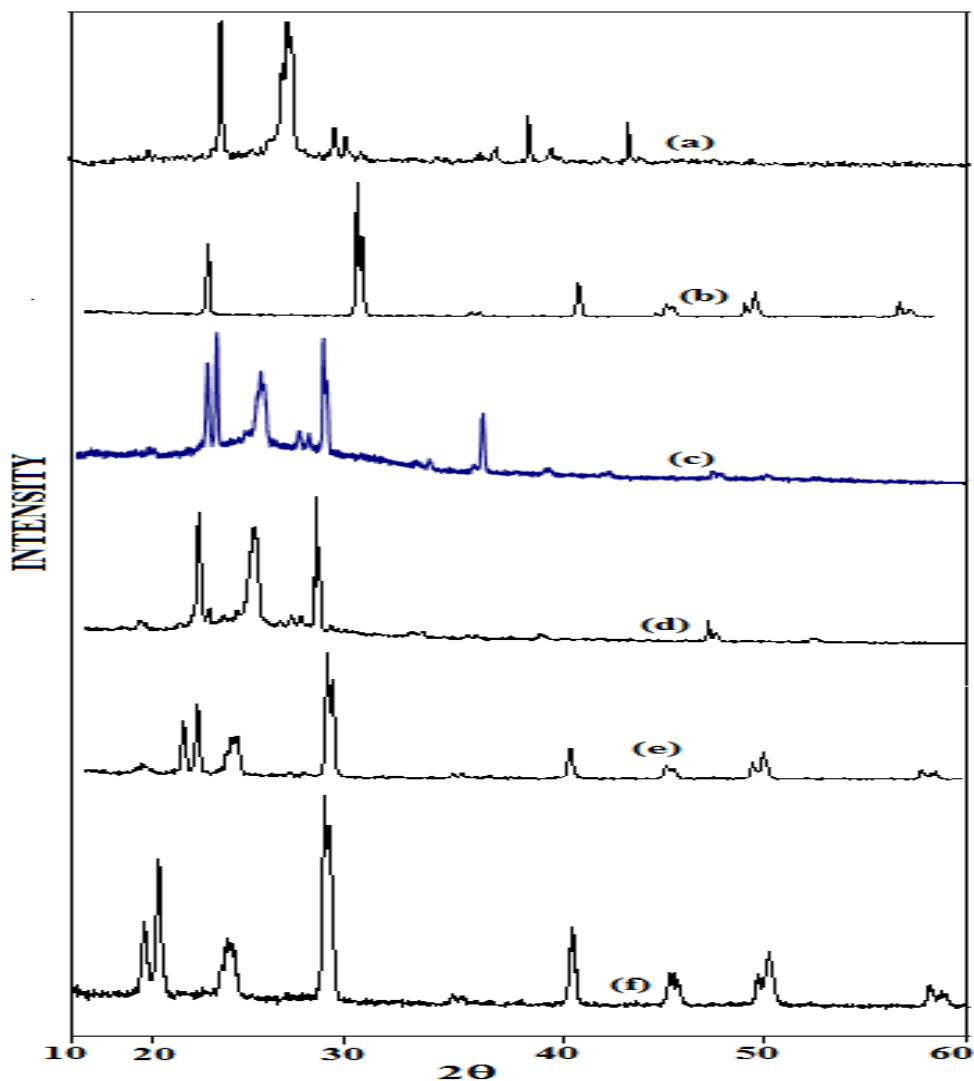


Fig. 1.8: X-ray diffraction patterns for (a) pure PEO, (b) pure KIO₃; (c) SPE film: (70PEO: 30 KIO₃), (d) NCPE OCC: (70PEO: 30KIO₃) + 7SiO₂ (hot-pressed); (e) SPE film: (70PEO: 30 KIO₃), (f) NCPE OCC: (70PEO: 30KIO₃) + 10 SiO₂ (solution casted film).

The C-H stretching bands of at 2900-2800 cm⁻¹, broad vibrational bands corresponding to symmetric / anti-symmetric C-O-C stretching modes around 1100-1000 cm⁻¹; gauche (OC-CO) conformation in between 900-800 cm⁻¹ etc. are all present in the spectra of SPE & NCPE OCC films. However, slight variations in the shapes occurred which is indicative of the complexation of salt in the polymer. No substantial changes could be noticed due to the presence of SiO₂ filler particles which may probably be due to its dispersal in the fractional amount. Differential Scanning Calorimetry (DSC) thermograms

of polymer electrolyte films: (70PEO: 30 KIO₃) + x SiO₂, where x = 0 (SPE) and 10 (NCPE) (solution cast) and x = 0 (SPE) and 7 (NCPE OCC) (hot-press) as well as pure PEO are shown in Fig. 1.10. All the DSC responses depict the existence of dominant endothermic peak ~ 65-70°C which corresponds to semi-crystalline-amorphous phase transition and/or melting temperature (T_m) of PEO. However, slight shifts in the peak position could be noticed which may be due to complexation of salt KIO₃ in PEO.

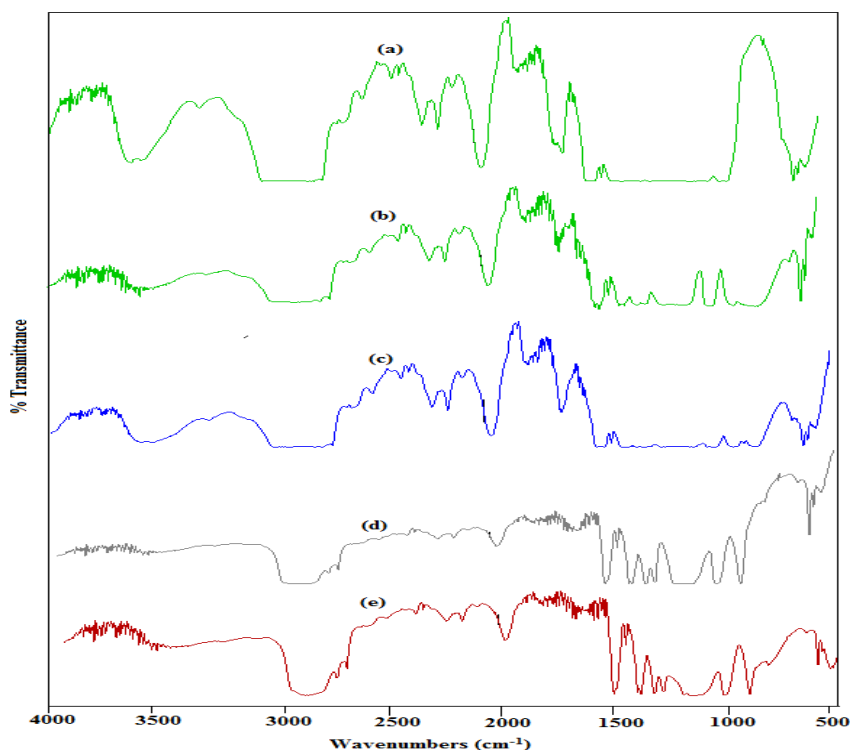


Fig. 1.9: Comparative FTIR spectra for the films: (a) pure PEO, (b) (70PEO: 30 KIO₃)², (c) (70PEO: 30 KIO₃) + 7SiO₂ (hot-press) and (d) (70PEO: 30 KIO₃), (e) (70PEO: 30 KIO₃) + 10SiO₂ (solution cast).

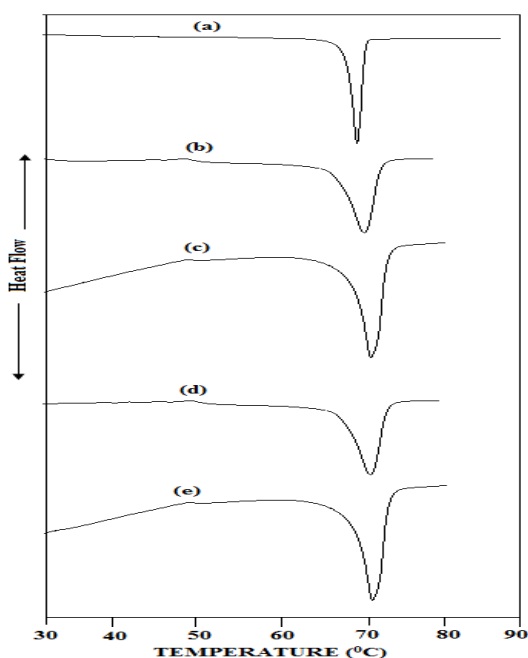


Fig. 1.10: DSC thermograms for (a) pure PEO and polymer electrolyte films: (70PEO: 30KIO₃) + x SiO₂. (b) x = 0 (SPE), (c) = 7% (NCPE OCC) (hot-presses); (d) x = 0 (SPE), x = 10 % (NCPE) (solution cast).

1.3 Conclusion

A comparative studies have been carried out on (PEO: KIO₃) polymer electrolyte films dispersed with nano-sized SiO₂ prepared using a novel hot-press and the solution cast techniques. Fractional dispersal of nano-SiO₂ in to SPE host: (70PEO: 30 KIO₃) + enhanced the room conductivity by more than 3 – fold. The complexation of the salt in the polymer has been confirmed by SEM, XRD, DSC, FTIR studies. The hot-press technique which is the least expensive / solvent-free/dry procedure can be preferred over the solution cast method. The

total ionic transport number measurements in film materials indicated that they are predominantly ion conducting medium with both cation and anion movements. The total ionic transference number has been found in the range ~ 0.94-0.97, hence, they can be suitably used for electrochemical device fabrications. However, the cation potassium (K⁺) transport number, measured separately using combined ac/dc technique, was found to be t₊ = 0.28 and 0.34 for hot-pressed SPE/NCPE OCC films respectively, which needs to be improved further.

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