



Structural, electrical and thermal properties of nanocomposite polymer electrolytes PCL : ZnTr : Fe₂O₃ for applications in energy storage power devices

A. C. Ganeshkumar^{1*} S. Austin Suthanthiraraj²

¹Department of Physics, Dr. Ambedkar Government Arts College, Chennai-600039,

²Department of Energy, University of Madras, Guindy Campus, Chennai-600025,

*Corresponding author, e-mail : acganeshkumhar@gmail.com

Abstract

A new nanocomposite polymer electrolyte based on poly (caprolactone) (PCL)-ZnTr dispersed with ceramic filler (Fe₂O₃) have been studied for their ionic conductivity and thermal properties. The incorporation of nanofillers will yield polymer electrolytes with enhanced conductivity and mechanical properties. Nanocomposite solid polymer electrolyte films (80–100 μm) were prepared by common solvent-casting method. It was revealed that the incorporating 7 wt.% Fe₂O₃ filler into PCL: ZnTr polymer electrolyte significantly enhanced the ionic conductivity [$\sigma_{RT}(\max)=2.7 \times 10^{-5} \text{ S cm}^{-1}$]. It is suggested that the addition of nanofillers leads to a lowering of glass transition temperature and increasing the amorphous phase of PCL and the fraction of PCL-Zn⁺ complex, corresponding to conductivity enhancement. The differential scanning calorimetry thermograms points towards the decrease of T_g, crystallite melting temperature, and melting enthalpy of PCL: ZnTr: Fe₂O₃ nanocomposite polymer electrolyte after introducing plasticizers. The reduction of crystallinity and the increase in the amorphous phase content of the electrolyte and morphological, structural changes caused by the filler, also contributes to the observed conductivity enhancement.

Keywords: biodegradable polymer, conductivity, XRD, nanocomposite polymer electrolyte

1 Introduction

The field of polymers has a wide range of applications compared to any other class of materials available to mankind, polymer industry has grown up more rapidly than other industry in the recent past. Their application areas extend from adhesives, coatings, packaging to precursors for high-tech ceramics. More and more synthetic polymers are being added into the basket of such device materials possessing tailored properties suitable for specific applications [1]. Polymer electrolyte commonly serves as a matrix

for ionic conduction to occur and also acts as an electrode spacer or a separator. Batteries that employ a polymer electrolyte material rather than a liquid electrolyte exhibit several advantages like safety, geometrical flexibility, easy fabrication, cost effectiveness, packaging, light weight and slimness [2]. However, a large volume disposal of batteries that employ polymer electrolytes would pile up a large proportion of polymer content into the environment. Therefore, selective use of a biodegradable polymer in such applications would be expected to considerably reduce their environmental impact [3-7]. Moreover, in a battery system, polymer electrolyte plays an important role in the transfer of charges between the anode and cathode compartments. Therefore, an experimental attempt towards the possibility of utilization of a biodegradable polymer material for the development of a new family of biodegradable polymer electrolytes is certainly an important and worthwhile endeavour at this point of time to initiate the degradation of disposed batteries thereby reducing their environmental impact. In fact, poly (ϵ -caprolactone) is basically a polyester and has a carbonyl (C=O) group in its backbone so as to solvate an appropriate dopant salt when employed as the effective host to prepare new biodegradable polymer electrolytes.

In this context, the use of zinc would be expected to provide an alternative for lithium considering the fact that the sizes of Li^+ and Zn^{2+} ions are quite comparable and safety problems associated with zinc are minimal and hence the same may be handled easily. Moreover, zinc-based batteries have already been established of which well-known examples include Zn/ MnO_2 alkaline and Zn/air batteries which employ aqueous electrolytes. With the identification of suitable Zn^{2+} ion conducting polymer electrolytes having sufficient levels of ionic conductivity, new types of zinc-based primary and rechargeable battery systems could evolve in the near future thereby overcoming certain limitations of aqueous electrolytes used in such existing zinc-based devices. From the literature available to date, it is quite evident that investigations on solid polymer electrolytes related to zinc batteries are scanty [8-10]. Therefore, zinc trifluoromethanesulfonate, $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ (zinc triflate, ZnTr) has been chosen to be the dopant salt, during the course of the present work. Due to the fact that the anion size of ZnTr is large, the electrical charge on the anion is expected to be more delocalized since the lattice energy of the salt is also low [11]. As a result, the electrostatic force existing between the cation and anion within the electrolyte would be weaker and thus promote an apparently higher percentage of free ions thereby leading to an enhanced ionic conductivity.

In spite of several advantages, polymer electrolytes exhibit low ionic conductivity values as compared to liquid electrolytes and certain ceramic electrolytes. This feature may be attributed as due to the crystalline nature of the host polymer, since the ionic conduction is usually favoured by the amorphous phase of polymer. Moreover, complexation of the polymer with salt also limits the segmental mobility of the polymer which in turn confines ionic conduction. In order to reduce the crystallinity of the polymeric system, additives such as liquid plasticizers, nanofillers or both have also been incorporated in practice which would effectively disturb the local crystal field [12-15].

Accordingly, the present work was aimed at synthesizing a series of new complexes containing the chosen host polymer namely poly (ϵ -caprolactone) (PCL) and zinc triflate ($\text{Zn}(\text{CF}_3\text{SO}_3)_2$) salt.

Subsequently, the best conducting composition of this series has been considered for appropriate incorporation of additive, including iron oxide (Fe_2O_3) nanopowder.

2 Experimental

2.1. Materials and methods

During the present work PCL with $M_n = 80$ kDa, $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ with $M_w = 363.53$ g/mol, nanopowders such as Fe_2O_3 procured from Sigma-Aldrich, USA. ZnTr , Fe_2O_3 nanopowders were dried at 100°C for an hour prior to use, while PCL was used as received. Appropriate quantities of Fe_2O_3 nanopowder in 1, 3, 5, 7 and 10 wt % were incorporated into the optimized polymer– salt composition i.e., 75 : 25 wt % of PCL : ZnTr complex by solution casting method. The (75 PCL: 25 $\text{Zn}(\text{CF}_3\text{SO}_3)_2$) + a Fe_2O_3 (where a = 1, 3, 5, 7 and 10 wt%), designated as F1, F3, F5, F7, F10. Mixtures containing PCL, ZnTr , nanopowder in the common solvent tetrahydrofuran (THF) were stirred continuously for several hours at room temperature in order to obtain a homogenous viscous solution which was then solvent cast onto a glass petri dish and maintained at 50°C in order to allow THF to evaporate and then vacuum dried at 50°C for 15 h. These films were further dried slowly at room temperature inside a desiccator for 2 days so as to remove any traces of the solvent. Self-standing translucent films thus obtained were stored in a dry desiccator for further measurements.

2.2 Characterization Techniques

2.2.1 X-ray diffraction (XRD) studies:- Room temperature (298 K) X-ray diffraction (XRD) analysis was performed on all the thin film solid polymer electrolyte specimens using a Bruker D8 Advance X-ray Diffractometer with $\text{CuK}\alpha$ ($\lambda = 1.541\text{\AA}$) radiation source operated at 40 kV and 30 mA with the scanning angle over the range $10\text{--}80^\circ$ (2θ) at the scanning rate of $0.05^\circ/\text{min}$.

2.2.2 Electrical conductivity studies:- In the present study, complex impedance measurements were carried out on thin films of all the freshly-prepared polymer electrolyte samples using a computer-controlled Hewlett-Packard Model HP4284A Precision LCR Meter at room temperature in the frequency range 20 Hz – 1 MHz and the impedance data were analyzed by means of Boukamp equivalent circuit program software available internally during each measurement.

2.2.3 Differential scanning calorimetric (DSC) studies:- Differential scanning calorimetric (DSC) technique was used to understand the thermal characteristics of synthesized polymer electrolyte samples with the aid of a DSC 200 F3 Maia model thermal analyzer (NETZSCH-make) under nitrogen atmosphere, where samples of various compositions taken in the form of thin films were examined at a heating rate of $10^\circ\text{C}/\text{min}$.

2.2.4 Scanning electron microscopic (SEM) studies:- The surface morphological studies have been carried out on best conducting samples from each system by means of Hitachi-S 3400N Model scanning electron microscope (SEM) at different magnifications with an applied accelerating voltage of 15 kV.

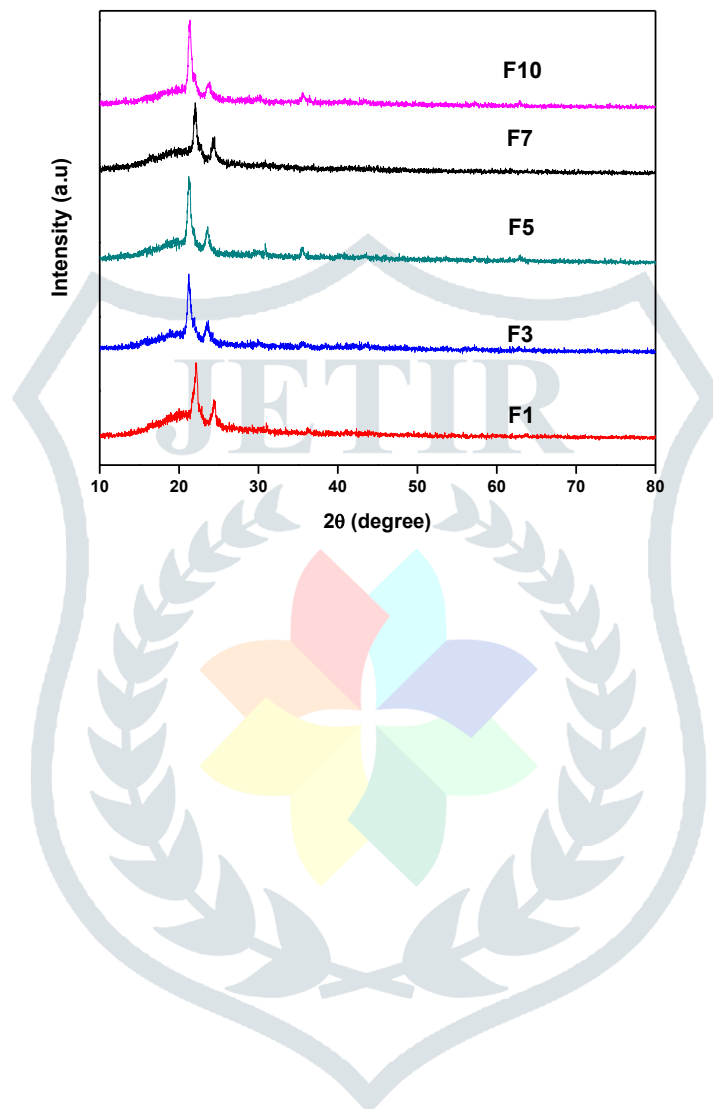
3. Results and Discussions

3.1 X-ray diffraction results

Relevant XRD patterns obtained for PCL-Zn (CF₃SO₃)₂-a wt% Fe₂O₃ (where a = 1, 3, 5, 7 and 10 respectively) nanocomposite polymer electrolyte system are depicted in Figure 1 designated as F1, F3, F5, F7 and F10. The XRD patterns obtained for the nanocomposite polymer electrolyte films containing various wt% of Fe₂O₃ nanoparticles also exhibit some crystalline peaks at $2\theta = 21.4, 22$ and 23.7° . The peak at $2\theta = 21.4$ and 22° may correspond to the typical reflection plane (110) and (111) indicating that the film is semicrystalline comprising both crystalline and amorphous phases [16,17]. Upon addition of nanofiller, it is seen that those diffraction peaks corresponding to the crystalline phases further decrease in intensity due to the probable transformation of crystalline and amorphous phases owing to the occurrence of an interaction between filler, salt and polymer. The fact that no peaks corresponding to the nanofiller are present in the XRD pattern suggests the feasibility of a complete amalgamation of the host polymer, salt and nanofiller without any phase separation [18].



Fig. 1 XRD patterns of four different samples in the PCL-Zn (CF₃SO₃)₂- Fe₂O₃ nanocomposite polymer electrolyte system at room temperature (25 °C)



This indicates that the complexation has taken place between polymer, salt and nanofiller. In addition to that, the intensity of the peak decreases as the concentration of nanoparticles is increased and this aspect implies the disordered nature of the film increases as a function of concentration of Fe₂O₃ nanoparticles. Furthermore, the intensity of all the peaks greatly reduced for the PCL - 7 wt% Fe₂O₃ nanocomposite

polymer electrolyte system thus indicating the amorphous nature of the film. As the amorphous nature increases the ionic mobility is expected to increase as supported by the present conductivity results too. It is also observed that in the case of those samples having a = 10 wt% Fe₂O₃ nanoparticles in the PCL -Zn (CF₃SO₃)₂-a wt% Fe₂O₃ nanocomposite polymer electrolyte system, the intensity of the polymer peak gradually increases.

3.2 Electrical conductivity results

Figure 2 shows the observed impedance plots of optimized composition of PCL–ZnTr polymer electrolyte containing different weight percentages of Fe₂O₃ nanofiller. With an increase of nanofiller concentration, R_b tends to decrease up to 7 wt% of Fe₂O₃ which indicates the increase in the ionic conductivity. The observed increase in conductivity corresponding to the increase of filler concentration may be attributed to the increase in the number of free ions available for conduction and to an increase in the amorphous phase occurring as a result of polymer–filler–salt interaction [19]. Maximum conductivity obtained was found to be $2.7 \times 10^{-5} \text{ S cm}^{-1}$.

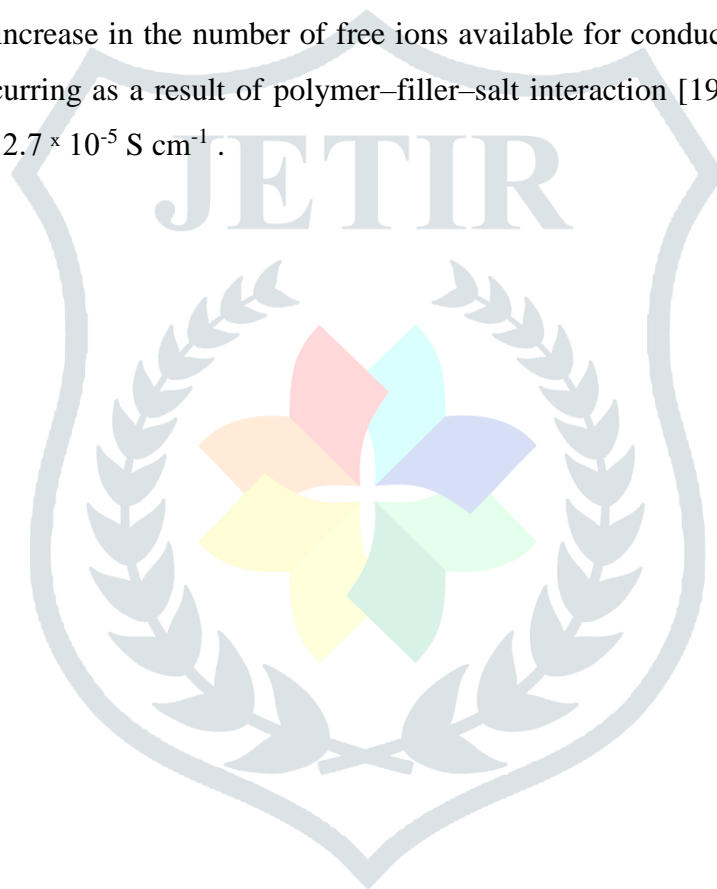
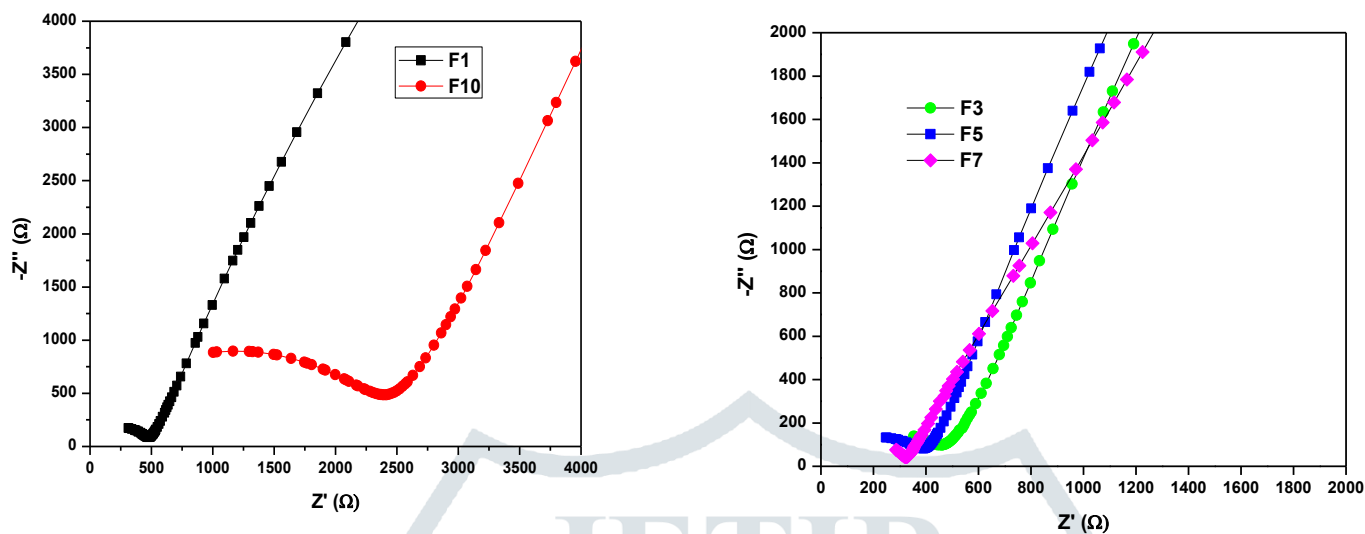


Table 1 : Calculated electrical conductivity values of all the prepared samples ofPCL-ZnTr-Fe₂O₃ nanocomposite polymer electrolyte system at 25 °C

Composition	Room temperature electrical
1	1.7×10^{-5}
3	1.9×10^{-5}
5	2.3×10^{-5}
7	2.7×10^{-5}
10	3.7×10^{-6}

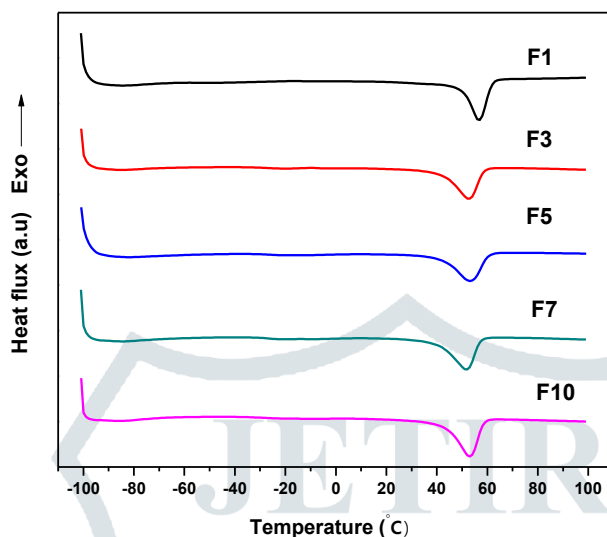
Fig. 2. Impedance plots of nanocomposite polymer electrolytes with different wt% of Fe₂O₃ Nanofiller

3.3 Differential scanning calorimetric data

Figure 3 shows the observed DSC results in the case of System I, PCL- Zn (CF₃SO₃)₂-a wt% Fe₂O₃ (where a = 1, 3, 5, 7 and 10 respectively). It is evident from Fig. 3 that DSC traces obtained in the case of System I nearly followed the same trend as in the case of optimized PCL : ZnTf. Furthermore, changes in melting peak (T_m) observed in System I shown in Fig. 3 indicated a change from crystalline phase into a disordered phase. From the area of melting temperature T_m, degree of crystallinity, can be calculated and presented in Table 2. From the above table, it is clear that the degree of crystallinity is 27.1 % for the PCL - Zn(CF₃SO₃)₂-7 wt% Fe₂O₃ nanocomposite polymer electrolyte system. The results obtained in terms of degree of crystallization show slight variation for higher concentrations of 10 wt% Fe₂O₃ nanoparticles as shown in Fig.3 representing possible reduction in the ionic conductivity of the polymer matrix. This may be due to the excess amount of nanoparticles accumulated in the conducting surface area of polymer electrolytes. Hence, it is evident from Fig. 3 that the nanofiller Fe₂O₃ appears to support in suppressing the degree of crystallization of PCL. All these observations clearly suggest that a major contribution to the conductivity enhancement is likely to arise from the structural modifications associated with the polymer host matrix and Fe₂O₃ nanoparticles. Hence, it is evident from Fig.3 and data summarized in Table 2, that the presence of nanophase Fe₂O₃ appears to considerably influence the degree of crystallization in the case of PCL. Glass transition temperature (T_g) is one of the most important parameters for determining the amorphous phase as well as flexibility of the material under investigation. Since the inclusion of Fe₂O₃ nanoparticles into several complexed polymer electrolyte systems is found to influence slightly on their glass transition temperature (T_g) [20, 21].

Fig. 3 DSC thermograms obtained for all the samples of the PCL-ZnTr-Fe₂O₃

nanocomposite polymer electrolyte system

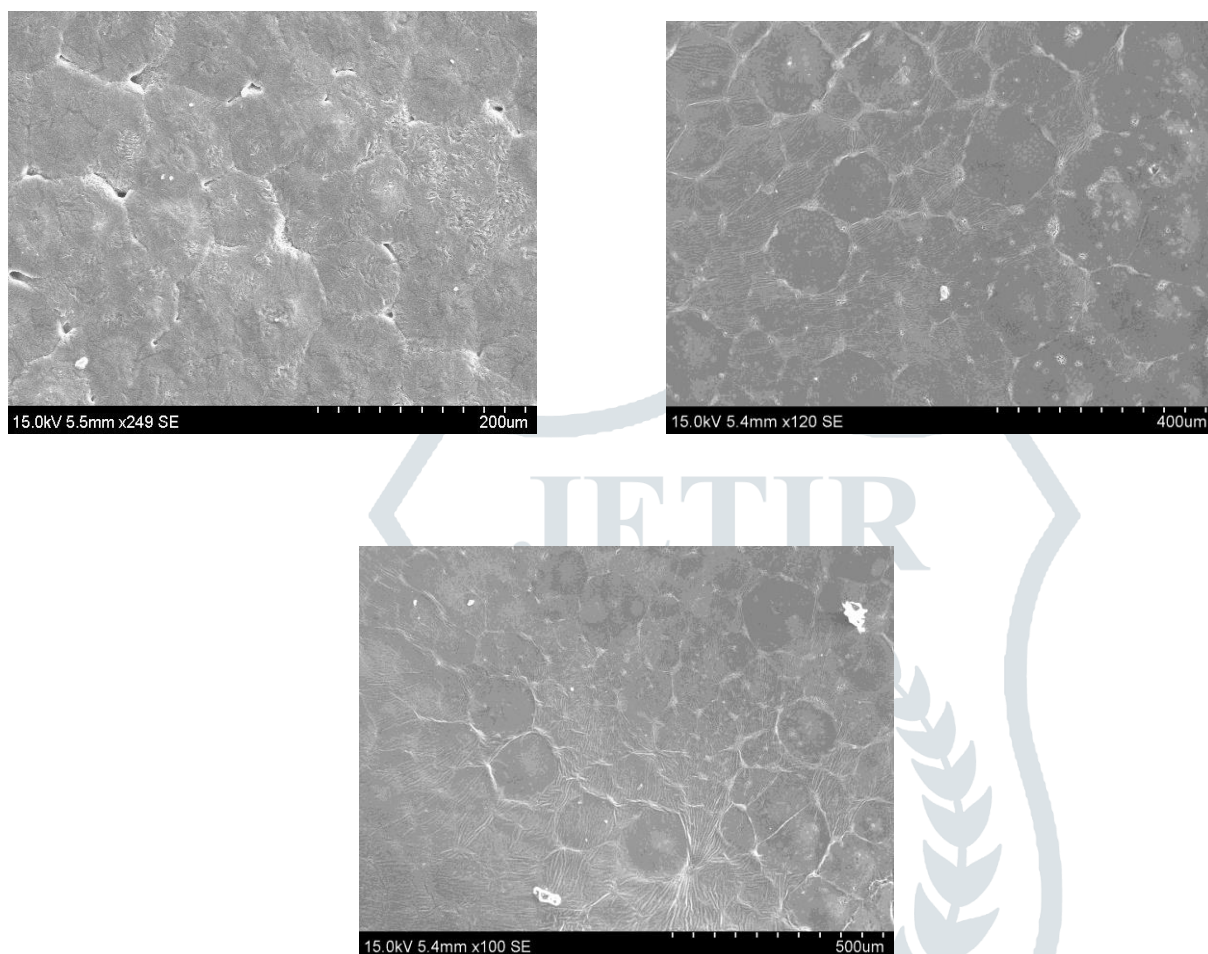
**TABLE 2**

Sample code	T _g (°C)	T _m (°C)	χ _c (%)
F1	-54.7	56.7	30.4
F3	-55.3	52.7	29.6
F5	-59.1	53.2	27.3
F7	-61.4	51.7	27.1
F10	-58.5	53.1	28.3

3.4 Scanning electron microscopic (SEM) data

Figure 4 shows the respective SEM micrographs and surface morphology of nanocomposite polymer electrolyte system PCL-ZnTr- Fe₂O₃. It is evident that the spherulite size decreases along with an increase in the number of spherulites upon incorporation of the Fe₂O₃ nanofiller. The surface Fe groups of the Fe₂O₃ nanofiller may act as nucleation centres for crystallization of PCL polymer chains from the solution. The fact that there are no aggregates of salt or filler on the surface of the nanocomposite polymer electrolyte with 7 wt% nanofiller also confirms the result obtained from XRD analysis.

Fig. 4 SEM micrographs of PCL-ZnTr nanocomposite polymer electrolyte system containing (a) 1 wt% (b) 5 wt% and (c) 7 wt% of Fe_2O_3 .



3.5 CONCLUSION

XRD studies shows that NCPE system contains amorphous phase which corresponds to highly conducting composition. From DSC studies it is evident that there is a change from crystalline to amorphous phase indicated by the changes observed in the melting peaks which contributes to high conductivity of NCPE system. SEM shows spherulite size decreases along with an increase in the number of spherulites upon incorporation of the Fe_2O_3 nanofiller. Impedance studies shows that increase in conductivity corresponding to the increase of filler concentration. Hence from the above discussions it is concluded that the conductivity increase in the highly conducting composition of NCPE is due to the phase change from crystalline to amorphous phase due to increase in concentration of nanofiller.

4 References

- [1] J-S. Lee, S.T. Kim, R. Cao, N-S. Choi, M. Liu, K.T. Lee, J. Cho, *Adv. Energy Mater.* **1** (2011) 34–50.
- [2] R. C. Agrawal, G. P. Pandey, *J. Phys. D: Appl. Phys.* **41** (2008) 1–18.
- [3] C.P. Fonseca, D.S. Rosa, F. Gaboardi, S. Neves, *J. Power Sources* **155** (2006) 381-384.
- [4] H.J. Woo, S.R. Majid, A.K. Arof, *Solid State Ionics* **199-200** (2011) 14-20.
- [5] C.P. Fonseca, S. Neves, *J. Power Sources* **159** (2006) 712–716.
- [6] C.P. Fonseca, F. Cavalcante Jr., F.A. Amaral, C.A.Z. Souza, S. Neves, *Int. J. Electrochem. Sci.* **2** (2007) 52 – 63.
- [7] B.C. Ng, H.Y. Wong, K.W. Chew, Z. Osman, *Int. J. Electrochem. Sci.* **6** (2011) 4355 – 4364.
- [8] G.G. Kumar, S. Sampath, *Solid State Ionics* **176** (2005) 773-780.
- [9] G.G. Kumar, S. Sampath, *Solid State Ionics* **160** (2003) 289-300.
- [10] G.G. Kumar, S. Sampath, *Polymer* **45** (2004) 2889-2895.
- [11] M. S. Su'ait, A. Ahmad, H. Hamzah, M.Y.A. Rahman, *Electrochim. Acta* **57** (2011) 123-131.
- [12] S. Jung, D.W. Kim, S.D. Lee, M. Cheong, D.Q. Nguyen, B.W. Cho, H.S. Kim, *Bull. Korean Chem. Soc.* **30** (2009) 2355-2361.
- [13] B. S. Lalia, K. Yamada, M. S. Hundal, J-S.Park, G-G.Park, W-Y.Lee, C-S. Kim, S. S. Sekhon, *Appl. Phys. A* **96** (2009) 661-670.
- [14] Y. Zhang, Y. Zhao, D. Gosselink, P. Chen, *Ionic* DOI: 10.1007/s11581-014-1176-2.
- [15] Y. Zhang, Y. Zhao, Z. Bakenov, D. Gosselink, P. Chen, *J. Solid State Electrochem.* **18** (2014) 1111–1116.
- [16] Mark J. E.: Polymer data handbook. Oxford University Press, New York (1999).
- [17] K. Sownthari*, S. A. Suthanthiraraj *eXPRESS Polymer Letters Vol.7, No.6 (2013) 495–504*
- [18] Sundaram NTK, Vasudevan T, Subramania A (2007) *J Phys Chem Solids* 68:264–2710
- [19] M. A. S. A. Samir, F. Alloin, W. Gorecki, J-Y. Sanchez, A. Dufresne, *J. Phys. Chem. B* **108** (2004) 10845–10852.
- [20] P. S. Anantha, K. Hariharan, *Solid State Ionics* **176** (2005) 155.
- [21] C. Capiglia, J. Yang, N. Imanishi, A. Hirano, Y. Takeda, O. Yamamoto, *Solid State Ionics* **154** (2002) 7.

Table 3: Cationic transference number (t_{zn^+}) data for the PCL-ZnTr- Fe_2O_3 nanocomposite

polymer electrolyte system at 25 °C

Composition a (wt.%)	Zinc ionic transference number (t_{zn^+})
1	0.40
3	0.47
5	0.51
7	0.57
10	0.49