

Dielectric properties and structural conformation of melt compounded PEO-LiCF₃SO₃-MMT nanocomposite electrolytes

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Polymer nanocomposite electrolytes comprising poly(ethylene oxide) (PEO) and lithium triflate (LiCF₃SO₃) with varying concentration of montmorillonite (MMT) nano-platelets as filler were synthesized by direct melt compounded hot-press technique at PEO melting temperature. The complex dielectric function, electric modulus, alternating current electrical conductivity and complex impedance spectra in the frequency range 20 Hz-1 MHz at ambient temperature have been investigated. The *dc* conductivity shows an increase of about one order magnitude with optimum value at 2 wt% MMT. The correlation of conductivity relaxation time and the predominance of MMT intercalated structures with *dc* ionic conductivity in these solid electrolytes have been recognized, which confirm the potential use of dielectric relaxation spectroscopy for the online processing of melt compounded PNCEs materials.

Keywords: Nanocomposite electrolytes, Conductivity relaxation, Ionic conductivity, Poly(ethylene oxide), MMT clay, Lithium triflate

1 Introduction

In the last one decade, the solid-type of polymer nanocomposite electrolytes (PNCEs), which comprise a polymer complexed with alkali metal salt and inorganic nano filler have been an intense field of investigations¹⁻¹⁸. The montmorillonite (MMT) nano clay filler in polymer-salt complexes has drawn special interest in both the fundamental understanding of ion transport mechanism in nanocomposites and the enhancement in mechanical and thermal properties of the materials in view of possible applications in high-energy-density secondary batteries as a separator as well as electrolytes¹⁻¹¹.

In poly(ethylene oxide) (PEO)-alkaline metal salt composites, the salt-polymer complexes are formed due to the solvating behaviour of PEO in its melting state. The MMT as nano filler in melt PEO forms the intercalated and exfoliated structures¹⁹⁻²⁴ due to the hydrophilic nature of both the PEO and MMT. The ether oxygen atom of PEO acts as an electron donor while the metal cation as an electron acceptor. The behaviour of negative charges on MMT layers is the same as the polar group in PEO to dissolve the salt^{1,2}. Because of this, the cations form transient cross links between the PEO chain segments and the dispersed MMT layers by coordinating with the oxygen atoms on the PEO backbones and the negative charges on MMT layers in the PEO-salt-MMT nanocomposite electrolytes^{1,2,11}. In these electrolytes, the PEO

segmental dynamics and its amorphous phase govern the metal cations translational motion and also their ionic conductivity. The addition of MMT impedes the PEO crystallinity, which favours the cations conduction due to formation of greater free volume^{1,2,10,25}. The anions are usually not coordinated to the PEO chain but may form the H-bond complexes with the MMT surface hydroxyl groups.

Lithium salt based PNCEs have been investigated for their use in lithium ion rechargeable batteries^{1-4,7,8,12-14,16-18}. Among the salts, lithium triflate (LiCF₃SO₃) is very stable with low reticular energy and its anion is resistant to oxidation as well as reduction, due to which it is widely used for the synthesis of polymer electrolytes by solution-cast technique^{18,21,26,27}. As compared to the solution-cast technique, the preparation of dry solid PNCEs by melt compounded technique is more suitable for their large scale technological applications due to rapid, least expensive and dry procedure to prepare solvent free polymer electrolyte films^{10,11,17,28}. In dry solid PNCEs, the polymer host itself is used as a solid solvent along with lithium salt and inorganic nano filler and does not contain any organic liquid.

In search of new novel PNCEs materials, the detailed dielectric/electrical behaviour and ionic conduction mechanism of PEO-LiCF₃SO₃-MMT electrolytes prepared by direct melt compounded hot-press technique, have been studied in the present

paper. The concentration of the salt in these PNCEs is kept low (20:1 molar ratio of ethylene oxide units to the Li^+ cation) to explore the ion conduction in the bulk polymer matrix. Further, an attempt is made to correlate the structural properties with the dielectric parameters, and by comparing these findings with the X-ray diffraction (XRD), Fourier-transform infrared (FTIR), differential scanning calorimetry (DSC) measurements^{1,19,21}, in view of the suitability of dielectric relaxation spectroscopy for monitoring the online melt compounded processing.

2 Experimental Details

The PEO of molecular weight 600000 g/mol, LiCF_3SO_3 and hydrophilic MMT (Nanoclay, PGV, a product of Nanacor®), were purchased from Sigma-Aldrich, USA. The MMT has 145 meq/100g cation exchange capacity (CEC), 150-200 aspect ratio (length to width), 2.6 g/cc specific gravity and 9-10 pH value (5% dispersion).

For the preparation of seven different MMT concentration PNCEs films, firstly, 2.55 g PEO and 0.45 g LiCF_3SO_3 were taken for the 20:1 molar ratio of $\text{EO}:\text{Li}^+$ for each sample. After that, the respective amounts of MMT; 0.00, 0.0255, 0.051, 0.0765, 0.1275, 0.255 and 0.51 g with respect to the weight of PEO for the 0, 1, 2, 3, 5, 10 and 20 wt% (w/w) MMT concentration were taken and mechanically mixed with the amounts of PEO and LiCF_3SO_3 for each sample using an agate mortar and pestle. The direct melt compounding of each composition was performed at the PEO melt temperature ($\sim 70^\circ\text{C}$) in 60 mm diameter stainless steel die with 1 mm spacer using hot polymer press film making unit under 3 tons pressure. The resulting free standing solid-type PNCEs films of thickness ~ 1 mm have the general formula $(\text{PEO})_{20}\text{-LiCF}_3\text{SO}_3\text{-}x$ wt% MMT, where MMT concentration x varies from 0 to 20 wt% with respect to the PEO weight.

Agilent 4284A precision LCR meter and Agilent 16451B solid dielectric test fixture having a four terminals nickel-plated cobalt electrodes of diameter 38 mm were used for the dielectric spectroscopic measurements of the samples in the frequency range 20 Hz-1 MHz at ambient temperature ($\sim 27^\circ\text{C}$). The details of the evaluation of intensive quantities, namely complex dielectric function $\epsilon^*(\omega)=\epsilon'-j\epsilon''$, alternating current (ac) electrical conductivity $\sigma^*(\omega)=\sigma'+j\sigma''$ and electric modulus $M^*(\omega)=M'+jM''$ and the extensive quantity i.e., complex impedance $Z^*(\omega)=Z'-jZ''$ of the PNCEs films are described by us elsewhere^{11,22,23}.

3 Results and Discussion

Figure 1 shows that the real part of complex dielectric function (permittivity), ϵ' of the $(\text{PEO})_{20}\text{-LiCF}_3\text{SO}_3\text{-}x$ wt% MMT films decreases non-linearly with the increase of frequency. The gradual decrease in ϵ' values at high frequencies confirms the contribution of PEO molecular polarization and ionic conduction processes to the dielectric dispersion, whereas the large increase in ϵ' and dielectric loss, ϵ'' with decrease of frequency below 10 kHz is owing to the electrode polarization (EP) process and the dc ionic conductivity effect. The small increase in the ϵ'' values near the end of high frequency side of the spectra for some of the samples indicates the presence of another relaxation process above 1 MHz.

Dielectric studies of the polymer-clay nanocomposites (PCNs) established that the comparative variation in the ϵ' values with the change in MMT concentration in the polymer matrix have direct evidence of the predominance of MMT

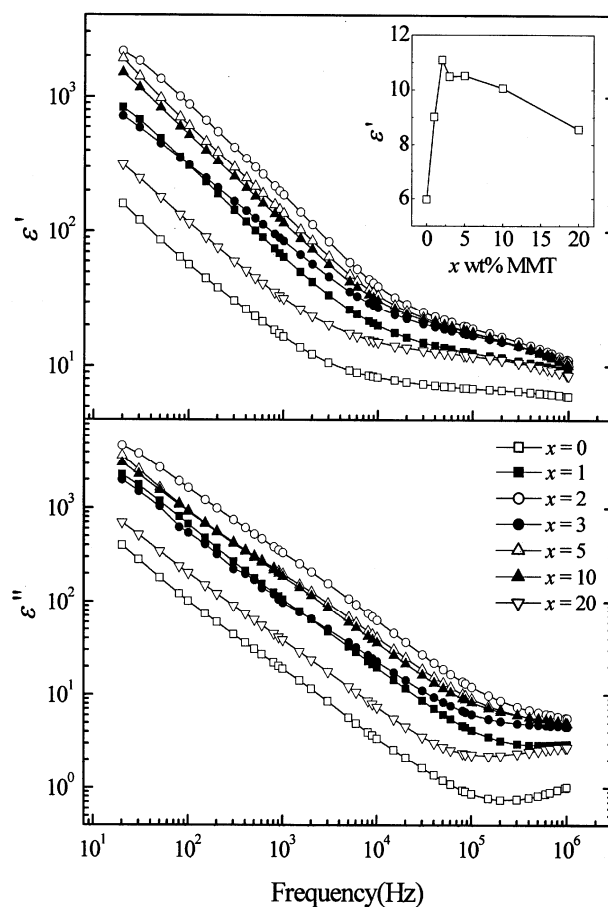


Fig. 1 — Frequency dependent complex dielectric function real part ϵ' and loss ϵ'' of melt compounded $(\text{PEO})_{20}\text{-LiCF}_3\text{SO}_3\text{-}x$ wt% MMT nanocomposite electrolytes. Inset shows the variation of 1 MHz ϵ' values with x wt% MMT

intercalated/exfoliated structures^{22-24,29,30}. In melt PEO matrix, MMT forms the hybrid structures (intercalated and exfoliated) due to their hydrophilic behaviour^{19,21}. The predominance of intercalated or exfoliated MMT, respectively, governs the increase or decrease of the ϵ' values as compared to that of the pristine polymer matrix^{22-24,29,30}. The inset of Fig. 1 shows that the ϵ' values at 1 MHz of the (PEO)₂₀-LiCF₃SO₃- x wt% MMT films of 1-20 wt% MMT filler are higher as compared to that of the without MMT electrolyte film, which confirms the formation of predominance of intercalated MMT structures. This finding is in agreement with the XRD, DSC and FTIR results on the structures of melt compounded PEO-MMT nanocomposites^{19,21}.

Frequency dependent real part of ac conductivity, σ' of (PEO)₂₀-LiCF₃SO₃- x wt% MMT films are shown in Fig. 2. It is found that the σ' values of the MMT filled PNCEs are higher than that of the without MMT, which also confirm the predominance of intercalated MMT structures in polymer-lithium salt electrolyte; because the intercalated MMT increases the ion conduction paths and hence, the ionic conductivity. All the σ' spectra have two linear slopes in the low and high frequency regions, which are mainly due to the semi crystalline behaviour of PEO. The low frequency straight line fit of the σ' data were used for the evaluation of dc ionic conductivity, σ_{dc} of these materials.

In ionically conducting electrolyte materials, the ionic conduction relaxation process is described by using an electric modulus^{11,31} $M^*(\omega)$ representation; the inverse of complex dielectric function $\epsilon^*(\omega)$. With

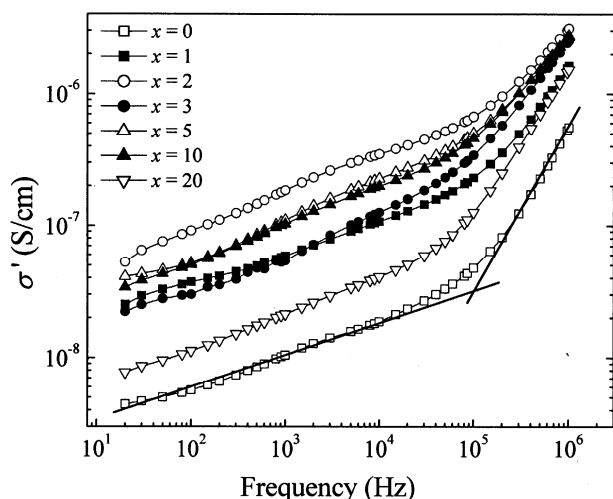


Fig. 2 — Frequency dependent real part of ac conductivity σ' of melt compounded (PEO)₂₀-LiCF₃SO₃- x wt% MMT nanocomposite electrolytes at ambient temperature

this representation a relaxation peak is obtained in the frequency spectra of the imaginary part of M^* ; no peak occurs in the corresponding plot for ϵ^* . Fig. 3 shows that the real part of electric modulus, M' of the (PEO)₂₀-LiCF₃SO₃- x wt% MMT electrolytes increases with the increase of frequency, whereas the ionic conductivity relaxation peaks in the loss part of electric modulus M'' spectra were observed in the high frequency region. The ionic conductivity relaxation frequency, f_σ corresponding to change in ions from dc to ac transport is determined from the intersection of M' and M'' spectra as depicted in the inset of Fig. 3 as representative plot for PNCE film of 1 wt% MMT. The most probable ionic conduction relaxation time, τ_σ of these materials was determined by the relation^{11,31-33} $\tau_\sigma = (2\pi f_\sigma)^{-1}$.

Figure 4 shows the complex impedance plane plots (Z'' versus Z') for the (PEO)₂₀-LiCF₃SO₃- x wt% MMT films. The frequency values of the data points in these plots increase from right to left on the arcs. The inset

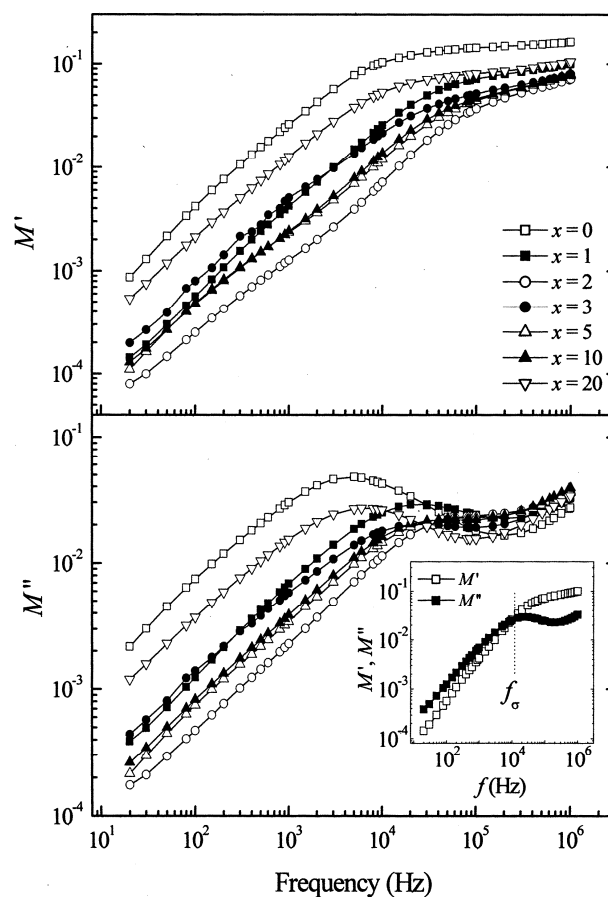


Fig. 3 — Frequency dependent complex electric modulus real part M' and loss M'' of melt compounded (PEO)₂₀-LiCF₃SO₃- x wt% MMT nanocomposite electrolytes. Inset shows the intersection of M' and M'' spectra at f_σ for 1 wt% MMT

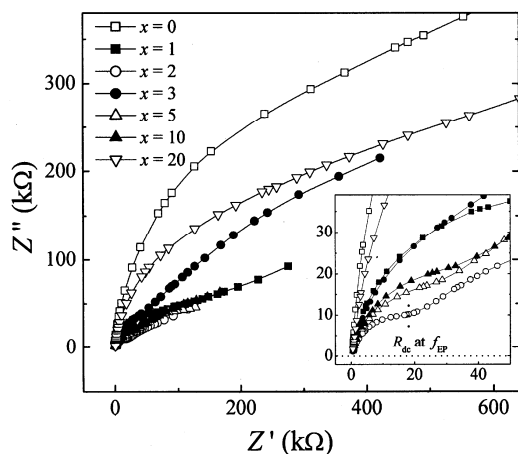


Fig. 4 — Z'' versus Z' plots of melt compounded $(\text{PEO})_{20}\text{-LiCF}_3\text{SO}_3\text{-}x$ wt% MMT nanocomposite electrolytes. Inset shows the enlarged view of the plots at high frequencies

of Fig. 4 shows that these plots have partial semicircular type behaviour in high frequency region, which is corresponding to bulk material properties. The gradual increase in Z'' values with the decrease of frequency in the low frequency region confirms the formation of electric double layers (EDLs) capacitances by the free charges that build up at the interface between the dielectric material and the metallic electrode surfaces, which is a very common behaviour of the electrolyte materials^{4,5,11,17,26,34-36}.

Figure 5 shows the variation of τ_c and σ_{dc} against x wt% MMT of the $(\text{PEO})_{20}\text{-LiCF}_3\text{SO}_3\text{-}x$ wt% MMT films. At ambient temperature, the σ_{dc} value of pure PEO film^{11,37,38} is nearly 10^{-10} S cm^{-1} , which increases by about one order of magnitude with the addition of LiCF_3SO_3 at the mole ratio 20:1 of the EO to that of the Li^+ (Fig. 5, at $x = 0$ wt%). This increase of σ_{dc} confirms the dissociation of LiCF_3SO_3 ions in the melt PEO matrix during melt compounding process.

The σ_{dc} values of $(\text{PEO})_{20}\text{-LiCF}_3\text{SO}_3\text{-}x$ wt% MMT films for $x=1$ to 10 wt% MMT filler were further enhanced by about one order of magnitude as compared to that of the without MMT film, with the maximum at 2 wt% MMT (Fig. 5). The large increase in σ_{dc} values with the small amount of MMT filler may be due to increase in the salt dissociation concentration, the minimization of ion-pairing effect, the increase of nanometric channels for cation mobility, the increase of PEO amorphous phase, and also the enhance in PEO chain segmental dynamics. Regarding the dynamics of polymer on one hand, a close contact of polymer segments to a rigid inorganic MMT structure through ion-dipolar interactions increases hindrance and may slow down their local

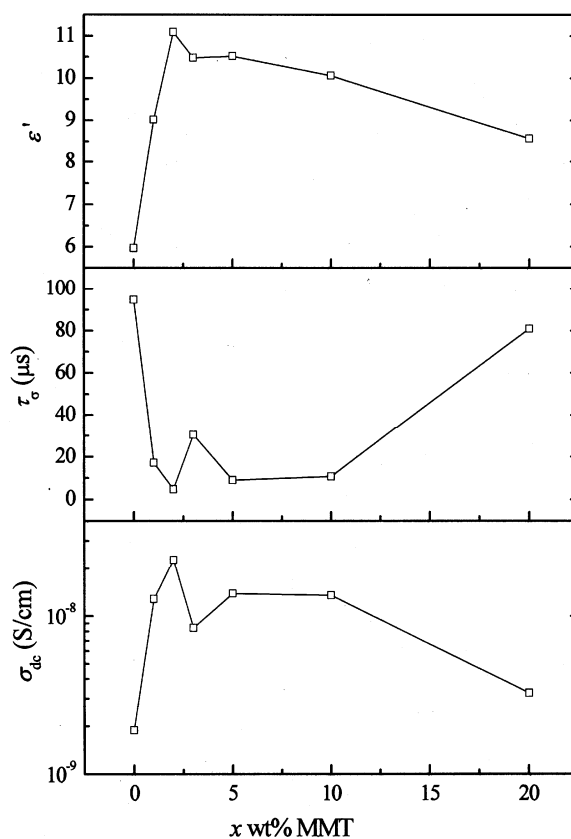


Fig. 5 — x wt% MMT concentration dependent 1 MHz ϵ' values, the ionic conduction relaxation time τ_c and dc ionic conductivity σ_{dc} of melt compounded $(\text{PEO})_{20}\text{-LiCF}_3\text{SO}_3\text{-}x$ wt% MMT nanocomposite electrolytes at ambient temperature

chain motion. On the other hand, dimensional restrictions in the nanometer range may have an effect on the cooperativity of motional process possibly leading to enhanced polymer mobility. Chen and Chang¹ studied the solution cast $\text{PEO-LiCF}_3\text{SO}_3\text{-MMT}$ nanocomposites with the concentration variation of both the LiCF_3SO_3 and MMT by using alternating current impedance, the DSC, FTIR and XRD measurements. The FTIR spectra revealed that the existence of MMT is able to dissolve the lithium salt easier and thus increases the fraction of free ions. Further, they observed the maximum ionic conductivity of these electrolytes for 3 wt% MMT at which σ_{dc} increases by about one order of magnitude as compared to that of the without MMT electrolyte. Our results of melt compounded PNCES are in good agreement with that of the solution cast PNCES films¹.

The comparatively small enhance of σ_{dc} at 20 wt% MMT of these electrolytes can be attributed to the fact that excess MMT content may clutch the lithium cation tightly, and thus restricts the mobility of the

cations. The optimum ionic conductivity for melt compounded PNCEs is found at 2 wt% MMT, which may be owing to the formation of dynamic equilibrium of the various attractive forces between the MMT layers, the ethylene oxide groups and lithium cations in the composite. DSC measurements on solution cast PNCEs confirmed the formation of the transient cross-linked structures of PEO and layered MMT coordinated with Li^+ cations, which act as crystallization retarders due to the steric hindrance and leads to lower PEO crystallinity which results in the increase of ionic conductivity¹. Further, the XRD study of the solution cast PEO- LiCF_3SO_3 -MMT revealed the predominance of intercalated PEO chains within the MMT galleries¹. The increase of ϵ' values at 1 MHz of the MMT loaded melt compounded PNCEs as compared to without MMT (Fig. 5), also favours the predominance of intercalated MMT structures, which enhances the nanometric channels for cations mobility and hence, the ionic conductivity of these nanocomposite electrolytes.

Figure 5 shows a good resemblance of σ_{dc} with the τ_σ values i.e., the σ_{dc} value increases when τ_σ decreases and vice-versa over the 0-20 wt% MMT concentration; confirms the ionic conductivity and conductivity relaxation time have strong correlation in these melt compounded electrolyte materials. Similar behaviour was also observed for the PNCEs materials investigated by the dielectric relaxation spectroscopy^{9,11}. This correlation reveals that the PEO segmental motion and cation mobility are strongly coupled process in the MMT filled PNCEs materials. The decrease of τ_σ value confirms the increase of cation coordinated PEO segmental motion, which is owing to the increase of intercalated MMT structures in the PEO matrix and hence, the enhancement of ionic conductivity. Such intercalated MMT structures increase the conduction paths for the cations translational motion. The small amount of MMT as a filler in the PEO matrix significantly improves the mechanical and thermal strength of the PEO-MMT nanocomposite materials^{10,25}. Considering this fact alongwith the σ_{dc} values, it is inferred that the PNCE film of $(\text{PEO})_{20}\text{-LiCF}_3\text{SO}_3\text{-2 wt\% MMT}$ prepared by direct melt compounded technique can be used as solid-type ion conductor of improved mechanical and thermal strength.

4 Conclusions

The real parts of dielectric function and ionic conduction relaxation process have strong correlation with the structures and ion conduction mechanism in

melt compounded $(\text{PEO})_{20}\text{-LiCF}_3\text{SO}_3\text{-}x$ wt% MMT films. The conduction relaxation time and ionic conductivity correlation inferred the coupled motion of cations coordinated PEO segments in the nanocomposite electrolytes. The *dc* ionic conductivity increases by about one order of magnitude with the MMT filler in the PNCEs and has optimum value at 2 wt% MMT. These dielectric properties indicate good resemblance with the structures of the PNCEs explored from various spectroscopic and morphological techniques, which establish the suitability of dielectric relaxation spectroscopy as a novel tool for the online processing, structural monitoring, also off-line ion conduction and structural characterization of the PNCEs materials synthesized by direct melt compounded technique.

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