

Studies of Dielectric Relaxation and AC Conductivity Behavior of Plasticized Polymer Nanocomposite Electrolytes

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The frequency dependent dielectric and conductivity behavior of a plasticized polymer nanocomposite electrolytes (PPNCEs) based on poly(ethylene oxide) + NaClO₄ with dodecyl amine modified montmorillonite (DMMT) as the filler and poly(ethylene glycol) as the plasticizer have been studied. The formation of nanocomposites and changes in the structural and microstructural properties of the materials were investigated by x-ray diffraction (XRD) and optical microscopy techniques. Studies of dielectric properties at lower frequencies show that the relaxation contribution is superimposed by electrode polarization effect. The appearance of peak for each concentration in the loss tangent suggests the presence of relaxing dipoles in the polymer nanocomposite electrolyte (PNCE) films. On addition of plasticizer, the peak shifts towards higher frequency side suggesting the speed up the relaxation time. The variation of ac conductivity with frequency obeys Jonscher power law except a small deviation in the low frequency region due to electrode polarization effect. The dc conductivity increases with increase in plasticizer concentration. Analysis of frequency dependence of dielectric and modulus formalism suggests that the ionic and polymer segmental motions are strongly coupled.

Keywords: Polymer nanocomposite electrolytes, X-ray diffraction, Dielectric properties, Universal power law, Dielectric loss spectra

1. INTRODUCTION

Solid Polymer electrolytes (SPEs) formed by dissolving salt in a macromolecule, typically polyether such as poly(ethylene oxide) (PEO) or poly(propylene oxide) (PPO), have received much attention over the last three decades for practical applications such as batteries, fuel cells, supercapacitors, hybrid power sources, display devices, sensors etc [1-3]. As it is well known, solid polymer electrolytes (SPEs) have several advantages over the liquid counterpart such as desirable shape mouldability, free from leakage, mechanical strength and flexibility of design, thereby permitting miniaturization. Unfortunately, SPEs have the inherent problem of low ionic conductivity at

ambient temperature that acts as a barrier to their utility when compared with the existing conventional liquid/hybrid electrolytes. The ionic conductivity of SPEs are strongly affected by various factors such as (i) crystallinity of the material, (ii) simultaneous cation and anion motions and (iii) the ion-pair formation (anion complex-cation interaction) [4, 5]. These factors reduce the cationic conductivity, and therefore this act as a barrier for potential applications. To overcome these problems, the realization of single ion conduction is fascinating alternative. Recently, an innovative approach was made to use layered silicate clay (such as montmorillonite, hecrite, laponite etc.) based nanocomposite to obtain the mobility of ions in polymeric matrix in a controlled way resulting in single ion conducting polymer nanocomposite electrolytes (PNCEs) [6]. The clay layered silicate nanocomposite could directly affect mobility of cation while reducing the mobility of anion to a negligible limit due to the intercalation of cations into the layered silicate where bulky anion cannot enter into that. This idea has attracted researchers to work on PNCEs to suppress dual ionic motions and ion-pair formation [4, 6]. Some times, it is necessary for organic modification of the clay layers, which makes the hydrophilic surface of montmorillonite (DMMT) as a hydrophobic. The hydrophobic organic modifier facilitates the intercalation of hydrophobic polymer into MMT by reducing the surface energy [7]. The another important approach in increasing the ionic conductivity of polymer electrolytes is plasticizing the polymer electrolyte with small organic molecules such as ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), PEG, etc. which have high dielectric constant and low vapour pressure [8, 9]. These plasticizers helps in improving the electrical conductivity of polymer electrolytes by (i) increasing the amorphous content of polymer electrolytes; (ii) dissociating ion aggregates present in polymer electrolytes; (iii) by lowering the glass transition temperature, T_g .

Again, despite of years of study, the mechanism(s) of ion conduction in SPEs is still not well understood. Hence, it becomes important to understand the ion transport mechanism along with polymer segmental relaxation processes in polymer electrolyte. Therefore, the study of dielectric relaxation phenomena is a powerful tool for (i) understanding of the ion transport behavior and (ii) obtaining the information of ionic and molecular interaction in solid polymer electrolytes [1, 10]. The ion transport property depends on many factors like degree of salt dissociation and its concentration, dielectric constant of host polymer, degree of ion aggregation, and mobility of polymer chains [1]. Further, the ion association in a heterogeneous system is directly related to the presence of dipoles due to solvent dipole/ion pairs. So the dielectric properties of ionically conducting polymer electrolyte provide valuable information even though these materials have high ionic conductivity [11-13]. The dielectric relaxation and frequency dependent conductivity are both sensitive to the motion of charged species and dipoles of polymers.

Literature survey reveals that, the dielectric studies on ionically conducting solids although important and valuable from scientific point of view, has not been studied extensively due to the limitations and complexity in data analysis. Fontanell et.al. [13] has reported low frequency dielectric properties of a few pure polymers [PEO, PPO] and their complexes with a number of salts. Mellander et.al. [11] has studied the correlation of electrical and dielectric properties of polypropylene glycol-lithium triflate (PPG-LiCF₃SO₃) complex. Elisasson et. al. [14], Singh et. al. [15] and Arof et. al.[16] Natesan et. al. [17, 18] has also reported dielectric properties of ionically conducting solid polymeric films recently. Though there has been a considerable amount of work performed on synthesis and

characterization of PNCEs (polymer-layered silicate nanocomposite electrolytes) by various research groups [4-7], not much work has been reported on dielectric and electrical properties of PNCEs as yet.

In view of the above, the present paper aims to report structural, microstructural, dielectric and electrical conductivity analysis of an ionically conducting plasticised polymer nanocomposite electrolytes (PPNCEs) system: PEO₂₅-NaClO₄+ 5 wt % DMMT + x wt % PEG₂₀₀ with x = 0-50 %. The effect of plasticizer concentration (PEG₂₀₀) on frequency dependent dielectric properties and conductivity has been investigated in order to gain the understanding of the ion transport behavior of PPNCEs.

2. EXPERIMENTAL PART

Freestanding thin films of plasticized polymer nanocomposite electrolytes (PPNCE) having a general formula PEO₂₅-NaClO₄+ 5 wt.% DMMT + x wt.% PEG₂₀₀ (x= 0, 5, 10, 20, 30 and 50) were prepared using a tape casting technique for different PEG concentration. The details preparation technique of ionically conducting polymer nanocomposite film has already been reported elsewhere [19, 20]. The x-ray diffraction (XRD) pattern of the PNCEs films was recorded at room temperature using an x-ray powder diffractometer (Rigaku Miniflex) with CuK_α radiation ($\lambda=1.5405\text{\AA}$) in the 2 θ (Bragg angles) range ($2^{\circ}\leq 2\theta \leq 10^{\circ}$) at a scan speed of $0.5^{\circ}\text{ minute}^{-1}$. Optical micrographs of the films were made through a polarizing microscope (Nikon Eclipse E 400 POL) equipped with a digital camera. An analysis of the dielectric properties of PPNCE films has been carried out using impedance spectroscopy on application of a small a. c. signal across the sample cell with blocking electrode (stainless steel). Complex impedance parameters (i.e., capacitance, dissipation factor, impedance, phase angles parameters) were measured with a computer-controlled impedance analyzer (HIOKI LCR Hi-Tester, Model:3532, Japan). A. C. conductivity has been evaluated from dielectric data in accordance with the relation: $\sigma_{ac} = \omega\epsilon_0\epsilon_r\tan\delta$ where $\epsilon_r = C/C_0$ is the relative permittivity, $\tan\delta =$ tangent loss factor, $C_0 =$ vacuum capacitance of the cell. The real and imaginary part of permittivity and modulus was calculated from the relation

$$\epsilon^* = \epsilon' - j\epsilon'' \text{ where } \epsilon' = \frac{-Z''}{\omega C_0(Z'^2 + Z''^2)}, \quad \epsilon'' = \frac{Z'}{\omega C_0(Z'^2 + Z''^2)},$$

and

$$M^* = M' + j M'' = \frac{1}{\epsilon^*} = j\omega\epsilon_0 Z^*.$$

3. RESULTS AND DISCUSSION

XRD studies have been carried out in order to monitor the formation of the nanocomposites. Fig. 1 shows the XRD patterns of Na⁺ MMT (as received MMT), DMMT (dodecylamine modified MMT) and PEO₂₅-NaClO₄+5 wt % DMMT+x wt% PEG for different value of x at room temperature in the region of 3-10^o. The peaks were assigned to the 001 basal reflection of DMMT. It is observed

that Na^+ -MMT exhibits (001) reflection peak at an angle ($2\theta=7.27^\circ$) corresponding to the interlayer spacing (d_{001}) 12.15 Å. Upon modification with dodecyl amine, the peak shifts toward the lower angle side corresponding to interlayer spacing of 15.68Å indicating the successful intercalation of alkyl ammonium ion into the gallery of MMT. When DMMT is added to polymer salt complex, there is an increase in the d_{001} (i. e., the peak position of (001) plane shift towards the lower angle side) indicates an increase in the gallery height of DMMT. This suggests the successful intercalation of polymer-salt complex into the gallery, which confirms the formation of nanocomposites [21]. Again on addition of plasticizer, the (001) peak position shifts towards the lower angle side up to 20% PEG concentration and further increase in plasticizer concentration it shifts towards the higher angle side. For different plasticizer concentrations, the corresponding interlayer spacing (d_{001}) ~ 17.50 Å as compared to the interlayer spacing (d_{001}) 12.15 Å of Na^+ -MMT. These patterns, therefore, suggest the formation of nanocomposite, where polymer-salt complex have been intercalated between the nanometric gallery of the montmorillonite. On addition of PEG, the peak position shifts towards the lower angle side is possibly due to the incorporation of the small plasticizer molecule in the interplaner spacing of the matrix of the polymer and DMMT.

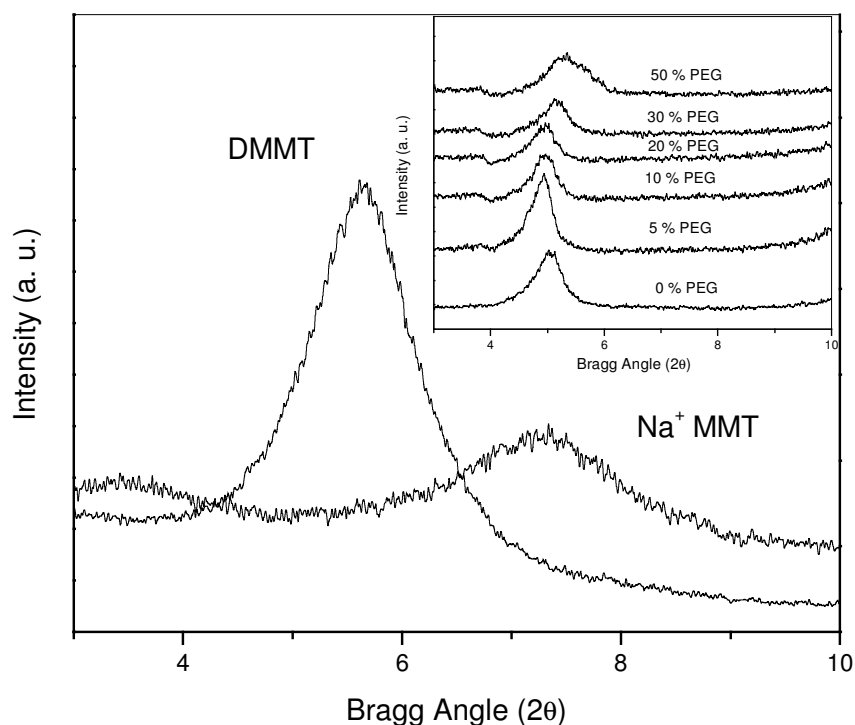


Figure 1. Comparison of XRD patterns of Na^+ MMT (as received MMT), DMMT (dodecylamine modified MMT) and $(\text{PEO})_{25}\text{-NaClO}_4 + 5 \text{ wt } \% \text{ DMMT} + x \text{ wt } \% \text{ PEG}_{200}$, with different concentration of PEG (x).

Fig. 2 shows optical micrographs of $\text{PEO}_{25}\text{-NaClO}_4 + 5 \text{ wt } \% \text{ DMMT} + x \text{ wt } \% \text{ PEG}$ for different value of x. The micrograph of PNCE (x=0%) provides the presence of spherulites that shows

characteristic lamellar microstructure. The boundary between the spherulites shows the existence of amorphous phase. The spherulite shows the surface roughness that may be related to the crystalline fraction of the material. On addition of plasticizer, it is observed that there is a decrease in the surface roughening and crystalline texture gradually on increasing concentration of plasticizer. Ultimately results into the appearance of smooth texture of the surface. These changes may be attributed to the effect of plasticization resulting in the reduction of crystallinity of host polymer (i.e., polyethylene oxide) and subsequent enhancement in the overall amorphous fraction in the materials.

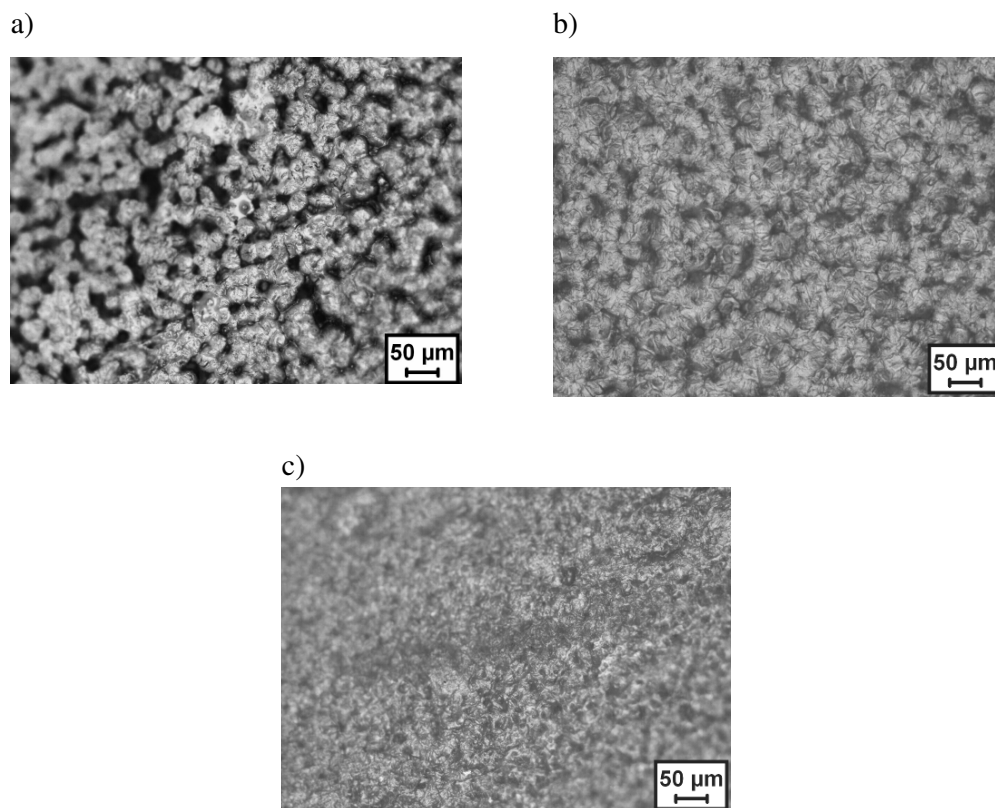


Figure 2. Optical micrographs of PPNCs thin films of $(\text{PEO})_{25}\text{-NaClO}_4 + 5\text{wt.}\% \text{ DMMT} + x \text{ wt.}\% \text{ PEG}_{200}$ with different concentration of x . (i.e., (a) $x=0$, (b) $x=10$ and (c) $x=50$).

Fig. 3 compares the variation of relative dielectric constant (ϵ_r) with frequency for different PEG concentration at room temperature. In all the cases, a strong frequency dispersion of permittivity is observed in the low frequency region followed by a nearly frequency independent behavior above 10 kHz. The decrease of ϵ_r with increase in frequency may be attributed to the electrical relaxation processes, but at the same time the material electrode polarization cannot be ignored, as the samples of our investigation are ionic conductors. The material electrode interface polarization superimposed with other relaxation processes at low frequencies. It is seen that with addition of plasticizer, ϵ_r value increases in the lower frequency and nearly same in the higher frequency region. The plasticizer addition may result in more localization of charge carriers along with mobile ions causing higher ionic

conductivity. This may be the reason for higher ϵ_r and strong low frequency dispersion on plasticization [10, 22].

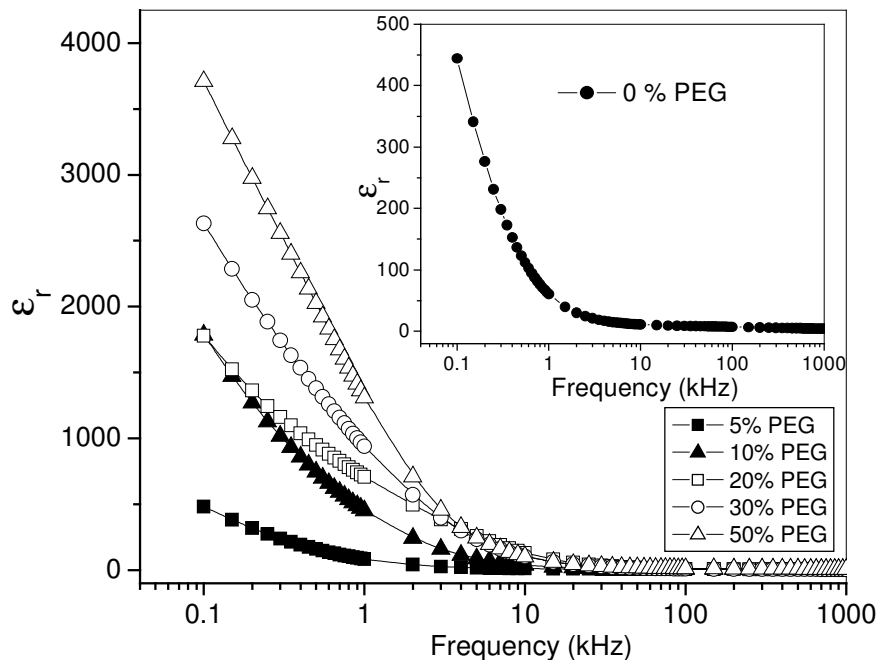


Figure 3. Variation of relative dielectric constant (ϵ_r) of PNCEs with frequency for different concentration of PEG ((PEO)₂₅-NaClO₄+5wt.% DMMT+ xwt.%PEG₂₀₀) at room temperature.

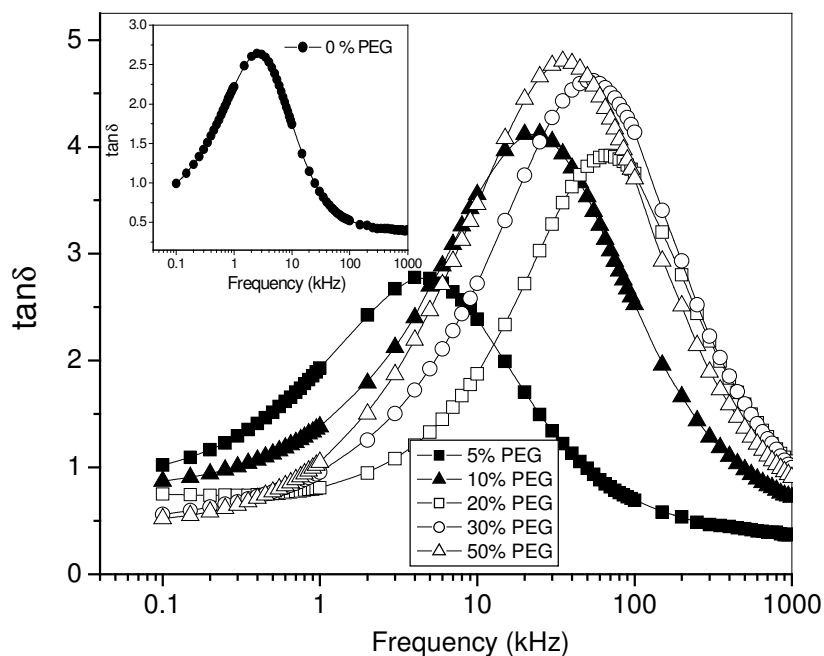


Figure 4. Variation of $\tan\delta$ of PPNCE thin films with frequency for different concentration (x) of PEG at room temperature.

Fig. 4 shows the variation of tangent loss with frequency of PPNCE films for different concentration of PEG at room temperatures. The loss spectra characterized by peak appearing at a characteristic frequency for both plasticizer free (PNCE) and plasticized (PPNCE) samples suggest the presence of relaxing dipoles in all the samples. The strength and frequency of relaxation depend on characteristic property of dipolar relaxation. The tangent loss peaks shift towards the higher frequency side on increase in plasticizer. On addition of plasticizer it is believed that there is an increase in the amorphous content in the materials. The small and mobile diluent molecule (PEG_{200}) speed up the segmental motion by increasing the available free volume. It is evidenced by the peak shifting towards higher frequency side, thereby reducing the relaxation time. The relatively fast segmental motion coupled with mobile ions enhances the transport properties on plasticization.

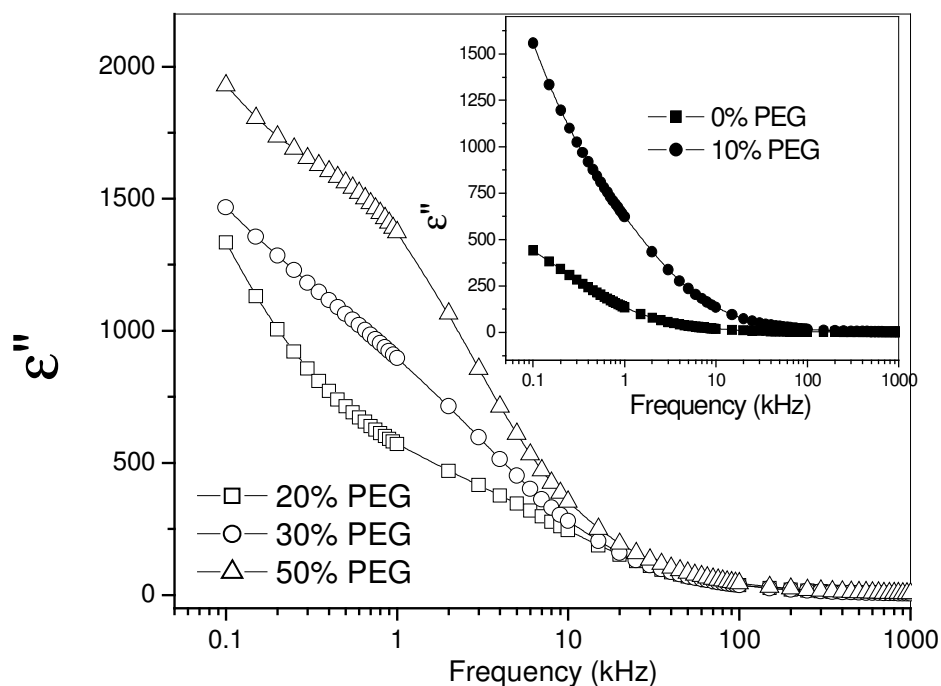


Figure 5. Variation of imaginary part of permittivity (ϵ'') with frequency for different concentration of PEG of $(\text{PEO})_{25}\text{-NaClO}_4 + 5\text{wt.}\% \text{ DMMT} + x \text{ wt.}\% \text{ PEG}_{200}$ at room temperature.

Figs 5 and 6 show the variation of imaginary part of dielectric permittivity (ϵ'') with frequency for different value of x at room temperature and 70°C (above melting temperature of crystalline PEO). At room temperature, ϵ'' decreases with increasing frequency. The higher value of dielectric loss (ϵ'') at low frequency is due to the free charge motion within the materials. On addition of plasticizer ϵ'' increases in the lower frequency region reflect the enhancement of mobility of charge carrier. At 70°C , ϵ'' first decreases with rise in frequency in low frequency region followed by a peak in the loss spectra. The loss peak is shifting towards the higher frequency side on addition of plasticizer. The appearance of peak is attributed to the relaxation phenomena of polymer (motion of salt free chain segment). Similar types of observations have been reported in literature [10, 23].

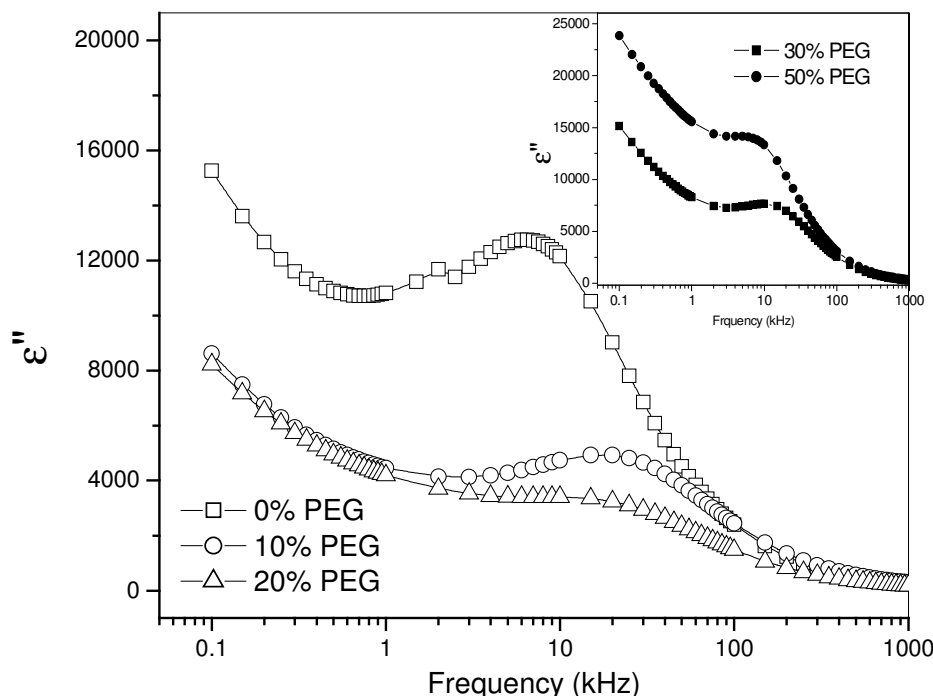


Figure 6. Variation of imaginary part of permittivity (ϵ'') of PPNCs with frequency for different concentration of PEG at 70°C .

It is generally believed that dielectric data is characterized by superposition of two processes: a conductivity contribution that produces an increase of both real part ϵ' and the imaginary part ϵ'' of the dielectric function on decreasing frequency and a relaxation process exhibiting a maximum in ϵ'' that shifts higher frequency side with increase in temperature. The measured dielectric loss (ϵ'') spectrum contains contribution from two sources: dipolar orientation and diffusion of charge carrier. When interfacial polarization occurs it can be written [24] as

$$\epsilon''_{\text{meas}}(\omega, T) = \epsilon''_{\text{pol}}(\omega, T) + \epsilon''_{\text{inter}}(\omega, T) + \epsilon''_{\text{dc}}(\omega, T)$$

with $\epsilon''_{\text{dc}}(\omega, T) = \epsilon''_{\text{dc}}(T) / (\epsilon''_0 \omega^{1-k})$ where $k = 0 \leq k \leq 1$

when the losses is due to Ohmic electrical conduction where ϵ''_{dc} dominates and then

$$\epsilon''_{\text{meas}}(\omega, T) = \sigma_{\text{dc}}(\omega, T) / (\epsilon''_0 \omega^{1-k})$$

Addition of plasticizer resulted in overall increase of ϵ' and ϵ'' due to both dipolar and free charge contributions. So the increase of the molecular mobility is reflected both by increase of free charge mobility and the shift of the peak towards the higher frequency side with simultaneous increase of its magnitude (Fig. 6). The over all result is enhancement of conductivity on addition of plasticizer.

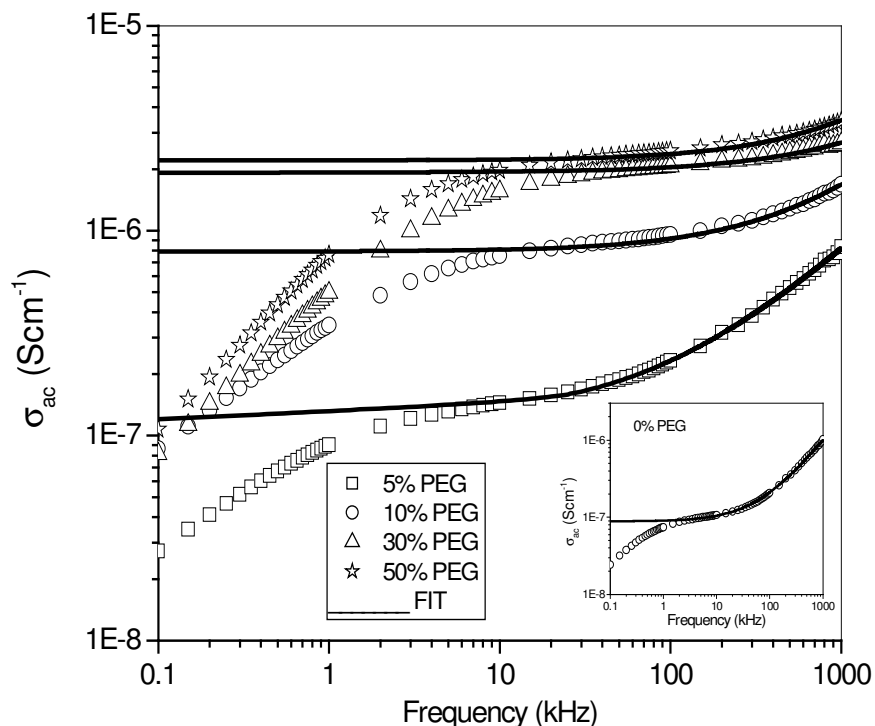
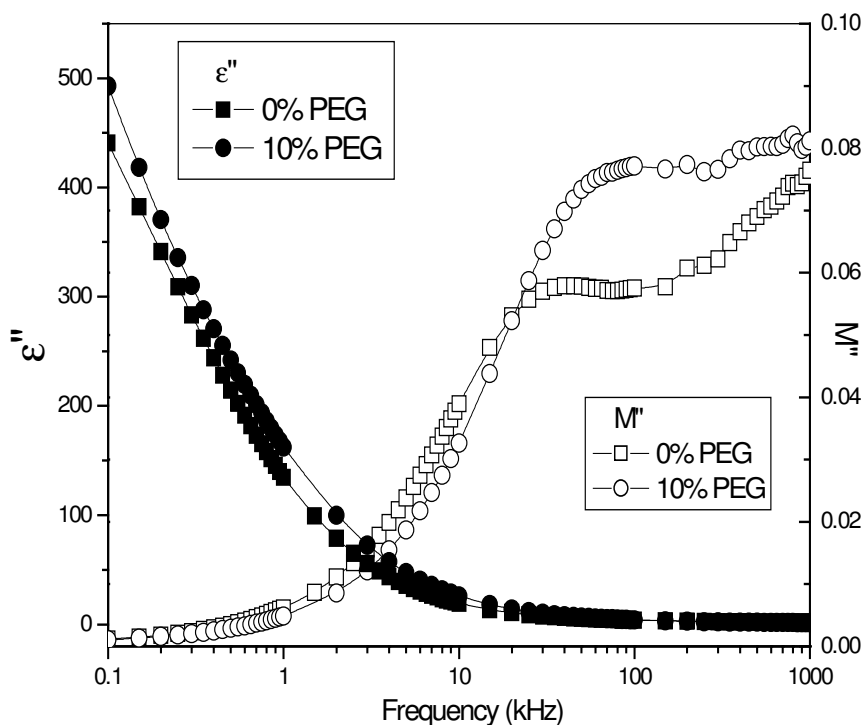


Figure 7. Variation of a. c. conductivity with frequency $(\text{PEO})_{25}\text{-NaClO}_4+5 \text{ wt.}\% \text{ DMMT}+ x \text{ wt.}\% \text{ PEG}$. The continuous solid line denotes the fit of experimental data to the power law.

Fig. 7 shows the variation of σ_{ac} with frequency for different concentration of PEG at room temperature for $(\text{PEO})_{25}\text{-NaClO}_4+5 \text{ wt.}\% \text{ DMMT}+ x \text{ wt.}\% \text{ PEG}$. The ac conductivity patterns show a frequency independent plateau in the low frequency region and exhibits dispersion at higher frequencies. This behavior obeys the universal power law [25, 26], $\sigma(\omega) = \sigma_0 + A\omega^n$, (the solid line is the fit to the expression) where σ_0 is the dc conductivity (frequency independent plateau in the low frequency region), A is the pre-exponential factor and n is the fractional exponent between 0 and 1. On plasticization the conductivity spectrum remains similar as that of the PNCEs (unplasticized), except dispersion in the low frequency region, where the deviation from σ_{dc} (plateau region) is more prominent. The deviation from σ_{dc} (plateau region) value in the conductivity spectrum (in the low frequency region) is due to the electrode polarization effect. The values of σ_0 , A and n were obtained by fitting the $\sigma(\omega)$ to $\sigma(\omega) = \sigma_0 + A\omega^n$ is tabulated in Table1. Generally, for ionic conductors, power law exponents (n) can be between 1 and 0.5 indicating the ideal long-range pathways and diffusion limited hopping (tortuous pathway) respectively [27]. The value of exponent of the higher frequency slopes (Table-1) shows that the long-range drift of ions may be one of the sources of ion conduction. From the Table-1, it is clear that the dc conductivity (σ_0) increases with increase in plasticizer concentration. The overall behavior of σ_{ac} follows the universal dynamic response [25], which has widely been observed in disordered materials like ionically conducting glasses, [28] conducting polymers, and also doped crystalline solids [29, 30] and is generally believed to be reflected in the mechanism of charge transport behavior of charge carriers.

Table 1. Comparison of parameters obtained from fit the experimental data to $\sigma(\omega) = \sigma_0 + A\omega^n$ of (PEO)₂₅-NaClO₄+5 wt.% DMMT+ x wt.% PEG for different PEG concentration at room temperature.

PEG conc.	σ_0 (Scm ⁻¹)	A	n
0%	8.9×10^{-8}	5.13×10^{-12}	0.875
5%	1.19×10^{-7}	1.18×10^{-11}	0.796
10%	7.9×10^{-7}	6.57×10^{-12}	0.855
30 %	1.99×10^{-6}	1.12×10^{-11}	0.806
50%	2.2×10^{-6}	7.01×10^{-12}	0.87

**Figure 8.** Variation of imaginary part of dielectric permittivity and modulus of PPNCs ((PEO)₂₅-NaClO₄+5wt.% DMMT + xwt.%PEG₂₀₀ for x=0% and 10%) as a function of frequency at room temperature.

A comparison of the experimental data in the M^* and ϵ^* formalism is useful to distinguish long-range conduction process from the localized dielectric relaxation. To visualize this, we have plotted the imaginary part of complex dielectric permittivity (ϵ'') and modulus (M'') as a function of frequency for some selected PNCEs as representatives [Fig. 8]. Dielectric relaxation is a result of the reorientation process of dipoles in the polymer chains, which show a peak in ϵ'' spectra. For electrolyte (with higher ion concentration), the movement of ions from one site to another will perturb the electric potential of the surroundings. Motion of the other ions in this region will be affected by perturb potential. Such a cooperative motion of ions will lead to non-exponential decay, or a conduction processes with distribution of relaxation time [31]. It has been observed that [Figure 8] in the

imaginary part of modulus spectra, a relaxation peak is observed for the conductivity processes, whereas no peak is observed in the dielectric spectra. This suggests that ionic motion and polymer segmental motion are strongly coupled manifesting as a single peak in the M'' spectra with no corresponding feature in dielectric spectra [32]. So the conduction in polymer electrolytes takes place through charge migration of ions between coordinated sites of the polymer along with the segmental relaxation of polymer. An enhanced ionic conduction is a natural consequence of plasticization.

4. CONCLUSIONS

The effect of plasticizer (PEG₂₀₀) on dielectric and electrical properties of plasticized polymer nanocomposite electrolytes have been studied. At low frequency, the variation of relative dielectric constant with frequency shows the presence of material electrode interface polarization processes. The loss tangent peaks appearing at a characteristic frequency suggest the presence of relaxing dipoles in all the samples. On addition of plasticizer, the peak shifts towards higher frequency side suggesting the speed up the relaxation time. The frequency dependence of ac conductivity follows the universal power law with a small deviation in the low frequency region due to the electrode polarization effect. The conductivity increases with increase in plasticizer concentration. Analysis of electrical modulus and dielectric permittivity functions suggest that ionic and polymer segmental motions are strongly coupled.

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