

## Studies on dielectric properties of a conducting polymer nanocomposite system

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Received 11 December 2006; accepted 28 February 2008

Dielectric analysis of ion conducting solid polymer nanocomposite has been investigated as a function of temperature and frequency. Effect of clay concentration in changing the dielectric relaxation behaviour of polymer salt complex film is clearly visible, observed in terms of changes in polymer chain relaxation and dipolar contribution due to ion pairs. An enhancement in relative permittivity by 2 orders of magnitude has been recorded at room temperature in nanocomposite films controlled predominantly by clay concentration. Almost similar behaviour has been observed after crystalline to amorphous phase transition temperature at  $T \geq 70^\circ\text{C}$  for both polymer salt complex and nanocomposite films irrespective of clay concentration. A lowering of relaxation time, attributed to relaxing dipoles, with clay concentration suggests faster ion dynamics in nanocomposite films.

**Keywords:** Nanocomposite, dielectric spectroscopy, tangent loss, dipole-segmental relaxation

Ionicly conducting polymer-clay nanocomposites (PNCs) constitute a very important class of organic-inorganic nanostructured material which has immense application potential in energy storage/conversion devices. The presence of salt (cations/anions) in a heterogeneous medium comprising of a semi-crystalline polymer matrix and inorganic clay such as crystalline montmorillonite imparts a situation where the dipoles are inherently created and remain trapped in the multi-phase microstructure of the composite. The dipoles arising due to spatial distribution of cations or anions are relaxing in nature and control both the dielectric and conduction properties of such a nanocomposite system. However, a realistic picture of the dielectric properties of such a system is obtained only after eliminating the contribution of conduction part to the dielectric permittivity in accordance with relation:

$$\epsilon''_{corr} = \epsilon_d = \frac{z'}{\omega c_o (z'^2 + z''^2)} - \frac{\sigma_{dc}}{\omega \epsilon_o} \quad \dots (1)$$

In order to present an unambiguous picture of the dielectric behaviour of such a system, a careful analysis and evaluation of the two major dielectric parameters namely dielectric constant (representing polarisation) and tangent of dielectric loss angle (representing relaxation phenomena) is desirable. Though frequency variation of dielectric parameter at

fixed temperature is equivalent to the temperature variation study of the same parameters at fixed frequency<sup>1</sup>, an analysis of the dielectric parameters as a function of both frequency and temperature in the present system carries much significance in view of its conducting nature and presence of structural phase transition (around crystalline melting point,  $T_m$ ).

However, such an analysis in polymer composites has not been studied extensively due to limitations and complexities involved in data analysis. Fontanell *et al.*<sup>2</sup> has reported low frequency dielectric properties of some pure polymer (PEO, PPO) and their complexes with a number of salts. Mellander *et al.*<sup>3</sup> has studied the correlation of electrical and dielectric properties of polypropylene glycol-lithium triflate (PPG-LiCF<sub>3</sub>SO<sub>3</sub>) complex. Singh *et al.*<sup>4</sup> has reported in detail about the relaxation phenomena in such polymeric conducting systems.

The present paper reports the effect of an organo-modified clay concentration on the dielectric relaxation properties of polymer nanocomposite based on PEO<sub>8</sub>LiClO<sub>4</sub> + xwt.% MMT clay (modified Na-mont-morillonite) observed as a function of temperature and frequency.

### Experimental Procedure

Solid composite polymer electrolyte (SPE) films were prepared by solution cast technique using AR grade precursor materials. Polyethylene oxide, PEO (M/s Aldrich, M.W.  $\sim 6 \times 10^5$ ), LiClO<sub>4</sub> (M/s Fluka) as the salt for complexation and organically modified

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Na-montmorillonite (MMT) as clay for intercalation. The details of the sample preparation procedure are reported elsewhere. The free standing polymer-clay nanocomposites so obtained can be expressed as:  $(\text{PEO})_{25}\text{LiClO}_4 + x \text{ \% wt. MMT}$  ( $x: 0 - 25$ ).

The dielectric properties of the composite films were measured using a computer interfaced impedance analyzer (HIOKI LCR Hi-Tester Model 3532, Japan) in the frequency range of 100 Hz to 1 MHz. The samples were placed in a cell configuration of SS | PNC | SS (SS stands for stain less steel blocking electrodes and PNC for polymer nano-clay composite electrolyte) with an ac input signal of 20 mV applied across the cell.

## Results and Discussion

Ionically conducting PNC films have inherently present ionic groups (cations/anions). These dipoles are very sensitive to external variable such as applied electric field, temperature and frequency and responds to such changes thereby modulating overall electrical response of the sample.

### Temperature dependence of dielectric parameters

Figure 1 (a-d) depicts variation of relative permittivity of the PNC films as a function of temperature over a range of frequency. The relative permittivity ( $\epsilon_r$ ) of the polymer-salt (PS) complex appears to increase with increasing temperature, the magnitude of permittivity increase being progressively sharp and high (more than an order of magnitude) on and above crystalline melting

temperature ( $T_m = 70^\circ\text{C}$ ) of the polymer host PEO. This feature remains almost the same for PS sample irrespective of frequency range of investigation with a difference that the magnitude of permittivity ( $\epsilon_r$ ) decreases with increase in frequency as expected. The permittivity value of PS even at room temperature appears to be appreciably higher than that of polymer host permittivity ( $\epsilon_r = 5$ )<sup>5</sup>. The origin of a higher value of the  $\epsilon_r$  in PS may be traced to the presence of dipolar interaction between cations ( $\text{Li}^+$ ) coordinated to the ether oxygen ( $-\ddot{\text{O}}-$ ) of the polymer host and anion ( $\text{ClO}_4^-$ ) present in the polymer network separated by finite distance with polymer network acting as spacer in the matrix. A very sharp increase in the  $\epsilon_r$  with rise in temperature ( $T \geq T_m$ ) may be related to an increased possibility of the formation of transient dipoles due to ion-pair formation in the amorphous polymer matrix when crystalline to amorphous phase transition ( $T \geq T_m$ ) has occurred. In such a situation, polymer matrix becomes more flexible with minimum internal friction permitting faster ion transport. The fast moving ions (cations and anions) in the matrix, therefore, get an opportunity to come closure to each other more frequently than before (at  $T \leq T_m$ ). As a result, the probability of dipole (ion-pair) formation in the PS complex increases thereby enhancing the relative permittivity due to the contribution chiefly from immobilization of conducting species.

The pattern of dielectric permittivity variation undergoes a clear shift in its variation pattern as a

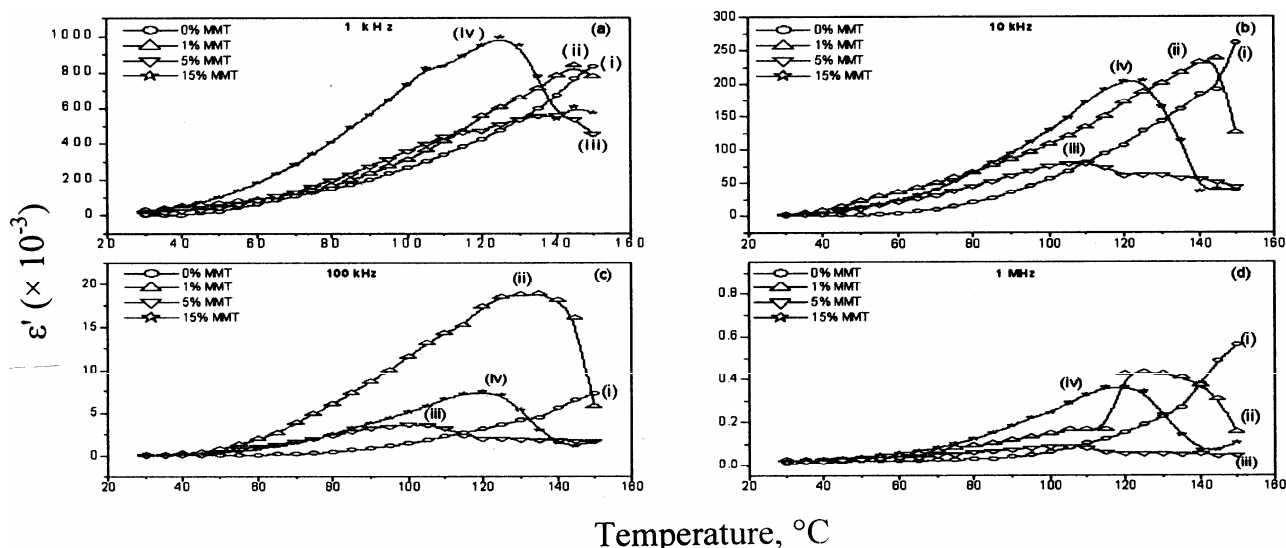


Fig. 1—Temperature variation of relative permittivity for frequencies 1 kHz, 10 kHz, 100 kHz and 1 MHz for  $\text{PEO}_8\text{LiClO}_4 + x\% \text{ MMT}$  ( $x = 0, 1, 5, 15$ ).

function of temperature on addition of organo-modified montmorillonite clay into the PS matrix. The changes occurring are clearly noticeable even at 1% clay addition observed in terms of appearance of a peak at  $\sim 140^\circ\text{C}$  to  $145^\circ\text{C}$  irrespective of the frequency range of investigation. The observed feature in the composite sample may be attributed to an improved dipolar ordering on composite formation. This temperature relaxation feature of permittivity maxima, that remains invariant with frequency, is basically the effect of clay interaction with ionically conductive polymer matrix. It seems logical in view of the dipolar characteristics of the clay comprising of central octahedral layer flanked by tetrahedral silicate layer on either side.

Further, on increasing clay concentration into PS matrix, the permittivity versus  $T$  pattern retains its peak feature for all clay concentration at all the frequencies. However, the peak position changes in both x and y scale depending on clay concentration. This result is very important suggesting an active role of clay concentration in modulating the interaction and profile of electrical charge distribution in the PS matrix. The variation in peak temperature suggests distribution of relaxation time controlled by clay concentration. This may be related to the role of clay in controlling ion dynamics in nanocomposite films.

Figure 2 shows variation of dielectric loss tangent ( $\tan\delta$ ) for the polymer nanocomposite films as a function of temperature over a range of frequencies in the present studies. The dielectric loss pattern of PS complex has a characteristic peak at  $\sim 35^\circ\text{C}$  at 1 kHz. Beyond this temperature,  $\tan\delta$  follows a

monotonically decreasing pattern achieving a saturation value at  $T \geq 60^\circ\text{C}$ . This feature of  $\tan\delta$  versus  $T$  for PS complex remains almost the same even at higher frequencies (10 kHz, 100 kHz, 1 MHz) as shown in the Fig. 2 (b-d) with a difference that the peak position shifts higher temperature side at  $45^\circ\text{C}$  and  $55^\circ\text{C}$  at 10 kHz and 100 kHz respectively. The loss peak becomes very much broad and diffused for PS complex at 1 MHz.

The observed dielectric loss ( $\tan\delta$ ) behaviour of PS complex as a function of temperature, which shows a temperature relaxation changing with frequency, is directly a manifestation of polymer chain mobility and its interaction with relaxing dipoles present in the polymer-salt matrix. Such a relaxation phenomena, conventionally termed as  $\alpha$ -relaxation, may be attributed to the dipole-polymer segment interaction effect observed normally at temperature above the polymer glass transition temperature ( $T_g$ ). The loss occurring due to such interaction depends on a number of factors, viz., the number/type of constituents in the matrix, the number of repeat units and its mobility, molecular (intra/inter) interaction and their relaxation time. A stronger interaction among the sample constituents is expected to reduce the molecular motion in the polymer matrix resulting in a shift of loss peak towards higher side of the temperature scale. This shift occurs with increasing frequency together with enhancement in the magnitude of loss factor.

The  $\tan\delta$  versus  $T$  variation pattern shows a contrasting behaviour in the composite films. Even at 1 wt.% of clay, the loss pattern shows a dispersive

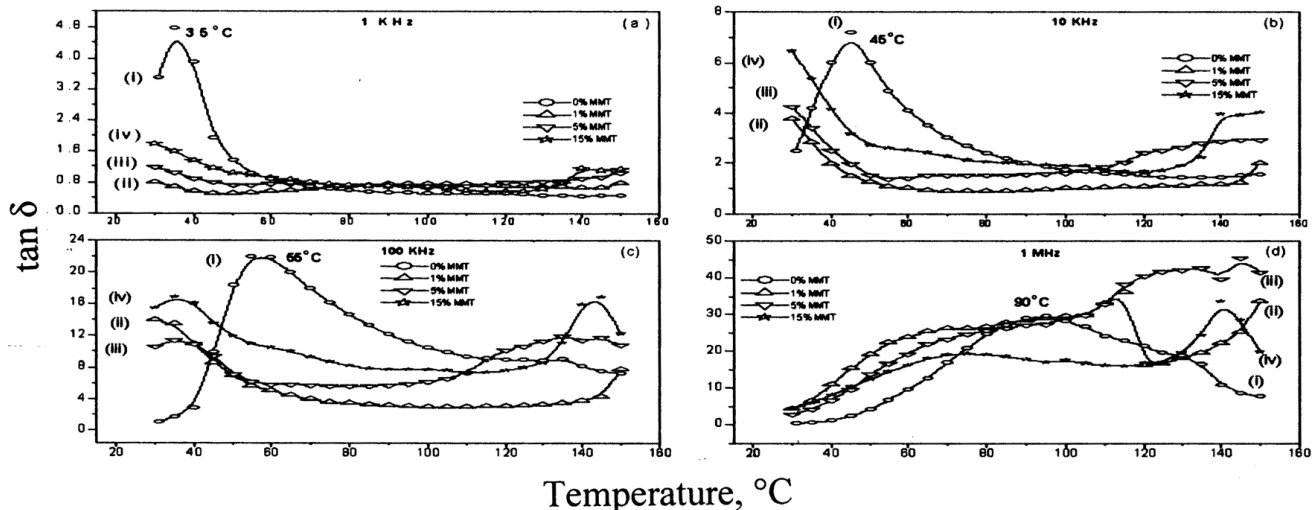


Fig. 2— $\tan\delta$ - temperature plot a fixed frequencies for different clay concentrations (0, 1, 5, 15 wt.%)

characteristic at ambient temperature and attains saturation at  $T \geq 50^\circ\text{C}$  at 1 kHz. However, the presence of relaxation characteristic to the polymer chain motion becomes noticeable also for composite films at high frequencies (say 100 kHz). The disappearance of  $\alpha$ -relaxation peak in nanocomposite films at lower frequency (towards dc limit) under ambient conditions is suggestive of an active role of clay in assisting ion transport even at low clay concentration. However, this relaxation behaviour and role of clay in modulating it can be analyzed properly in terms of variation of dielectric function with respect to frequency.

#### Study of frequency dependence of dielectric parameters

Figure 3 (a & b) shows the variation of real part of permittivity ( $\epsilon_r$ ) with frequency as isotherms at room temperature ( $30^\circ\text{C}$ ) and  $70^\circ\text{C}$  respectively for different clay concentration. The permittivity pattern for PS at room temperature shows a typical low frequency dispersion followed by high frequency saturation with a decrease by 3 orders of magnitude as we move from low frequency (100 Hz) to a saturation limit in the high frequency region. This low frequency dispersion may be due to the space charge polarization at sample-electrode interface whereas the saturation in the high frequency region may be related to the orientational polarization effects due to relaxing dipoles. Addition of clay into PS matrix causes substantial modification in its dielectric behaviour by an intermediate frequency dispersive region sandwiched in between two saturation region in the low and high frequency irrespective of clay concentration.

Such a change in frequency dependence of  $\epsilon_r$  is observed on immediate clay addition with very low clay content of 1%. A comparison of  $\epsilon_r$  value of composites with that of pure PS shows a phenomenal increment by 2 orders of magnitude. This improvement in  $\epsilon_r$  value may be attributed dipolar characteristics of clay. Clay layers itself comprise of a stacked arrangement of positive and negative charges and hence have finite dipolar contribution. Low frequency saturation, intermediate frequency dispersion and high frequency saturation may be related to  $\alpha$ -relaxation of polymer chain, clay assisted ion-migration and dipolar relaxation respectively.

The frequency dependence of  $\epsilon_r$  changes its behaviour at  $70^\circ\text{C}$  (Fig 3 (b) in comparison to room temperature pattern.  $\epsilon_r$  versus frequency plot of PS

shows a mid frequency dispersion in between two saturation regions at low and high frequency. However, no high frequency saturation region could be observed in the present range of frequency studies for composites at  $70^\circ\text{C}$ . A comparison in terms of absolute value of  $\epsilon_r$  at low frequency limit for RT and  $70^\circ\text{C}$  shows an increase by 2 orders of magnitude for PS and 1 order of magnitude for composites at  $T \geq T_m$ . Such an increase in relaxation strength at temperature above  $T_m$  is suggestive of faster ion migration at high temperature due to amorphous nature of backbone polymer matrix with a comparable value of  $\epsilon_r$  for both PS and composites in the whole frequency range.

Figures 4a and 4b show the variation of tangent loss as a function of frequency before  $30^\circ\text{C}$  and after crystalline melting ( $70^\circ\text{C}$ ) temperature limits. The room temperature loss peak as a function of frequency for both PS and composites are broad enough suggesting presence of strong dipolar interactions with wide distribution of relaxation times. It represents, in fact, a situation of the polymer chain connectivity where no dipoles (ion-pair) can move independently. Such a relaxation process depends on factors such as fraction of free ions, ion-pairs, clay concentration and temperature. The relaxation frequency therefore can be taken as a probe of the local flexibility of the polymer chains. The estimated relaxation time and its variation with clay concentration shown in Fig. 4a (inset) suggests that clay interaction with PS matrix reduces relaxation time of the ionic species thereby assisting ion-transport even at room temperature. As temperature increases to a limit approaching polymer  $T_m$  a shift in

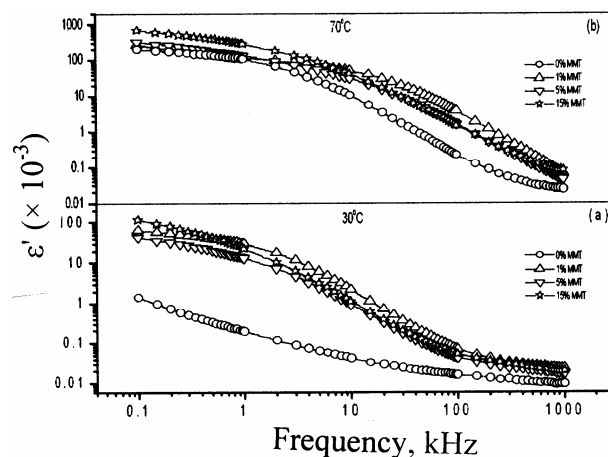


Fig. 3—Frequency response of permittivity as isotherms for polymer-salt complex and clay composites of different clay concentrations.

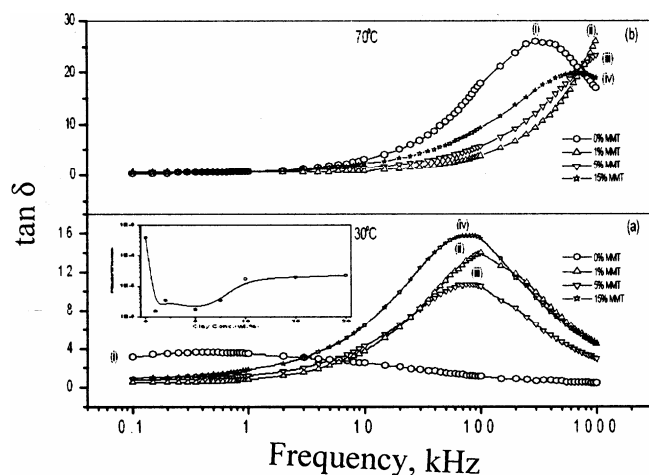


Fig. 4—Frequency response of tangent loss isotherms for polymer salt complex and for composites with various clay concentrations. The inset shows the variation of relaxation time with clay concentration

relaxation peak towards high frequency side has occurred (Fig. 4b). This may be related to a decrease in the strength of relaxation process caused by enhanced flexibility of the polymer segment. This in turn assists ion transport due to the coupling ion pair relaxation with the conduction process caused by lowering of polymer viscosity.

## Conclusions

In this study, dielectric behaviour of ionically conducting PNC films has been investigated. Nanocomposite formation with organo-modified clay appears to have changed the rate of ion transport observed in terms of lowering in relaxation time attributed to relaxing dipoles formed due to ion pairing in polymer matrix. Dielectric analysis appears to provide an insight into ion dynamics in such a material system.

## Acknowledgement

Authors acknowledge financial support received from Council of Scientific and Industrial Research (CSIR, New Delhi) vide sanction no. 03(1007)/04/EMR-II, Dated: 16.04.2004.

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