

AC conductivity and relaxation behavior in ion conducting polymer nanocomposite

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Abstract We report the ac conductivity and relaxation behavior analysis for a heterogeneous polymer–clay nanocomposite (PNC) having composition (polyacrylonitrile)_gLiCF₃SO₃+*x* wt.% dodecylamine modified montmorillonite. Charge transport behavior in an ionically conducting PNC has been analyzed systematically and correlated with the macroscopic parameters like polymer glass transition temperature and available free mobile charge carriers. Intercalation of cation coordinated polymer into the nanometric clay channels has been confirmed by high-resolution transmission electron microscopy. The electrical properties of the intercalated PNC films have been studied using complex impedance/admittance spectroscopy. Excellent correlation of relaxation behavior with polymer glass transition temperature (T_g) confirmed the objectives of the work. An analysis of dielectric relaxation indicates that PNC films are lossy when compared with polymer–salt film. This result is a direct outcome of faster ion dynamics leading to strong electrode polarization effect due to the accumulation of charge carriers at the interface.

Keywords Polymer nanocomposites · Dielectric permittivity · Ion dynamics · Glass transition temperature

Introduction

Ionically conducting polymer nanocomposites (PNCs) are expected to play an important major role in new generation of solid-state energy storage/conversion devices such as high energy density solid polymer batteries, fuel cells, supercapacitors, etc. [1–5]. Such devices are expected to have an enhanced performance with added advantage of design flexibility, mouldability of shape, and size with added possibility of miniaturization as per the present demand in consumer electronics [6, 7]. Although ion conducting polymers appear to be attractive, they have inherent drawbacks of low ambient electrical conductivity, concentration polarization, and poor stability (mechanical/electrochemical/thermal) properties. A number of approaches such as plasticization, copolymerization, composite formation, etc. have been proposed to overcome the difficulties associated with the conventional solid polymer electrolytes. However, most of the efforts in this direction have not yet been able to provide any significant solution to the problems of concentration polarization and enhancement of ambient conduction properties with acceptable stability for device applications. Nanocomposite formation via intercalation of polymer–salt (PS) complex into nanometric clay channels is presently considered as one of the feasible approach to achieve high end requirements like minimization (if not elimination) of concentration polarization effects, conductivity enhancement, improvement in stability (thermal/mechanical/electrochemical) properties, and single ion conduction [8–10]. The ionic conduction in a composite phase depends to a large extent on dissociation of charge carriers

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(ions) of the salt into free mobile charges (i.e., free cations/anions) [11–14] such that the interaction between them is minimum in the course of their mobility.

The process of ion dissociation that releases mobile charge carriers for conduction is controlled by the dielectric properties of the filler (ceramic adducts/clay) in a composite phase. Hence, dielectric parameters of the components in a composite phase and their dependence on extrinsic variables (temperature, frequency, filler concentration, etc.) may be expected to affect and control ionic conduction in general and dynamics of the charge transport in a heterogeneous composite phase in particular [15–17].

The present paper aims to analyze the role of dielectric properties of the PNC films on ion dynamics in a composite phase. A comprehensive analysis of the dielectric parameters (like dielectric storage component (ϵ') dielectric loss component (ϵ'')) as a function of frequency at polymer glass transition temperature (T_g) has been described and compared with that at room temperature. Conductivity spectrum has been analyzed and correlated with polymer glass transition temperature to understand the ion dynamics.

Experimental procedure

Materials preparation

Polymer electrolyte films were prepared by a standard solution cast technique: polyacrylonitrile (PAN) as the polymer host (Aldrich mol.wt. $\sim 1.5 \times 10^5$) having the crystallinity (30%) [18] and salt (LiCF_3SO_3) with bulky anion (Aldrich) as conducting species. An appropriate stoichiometric ratio of the host polymer (polyacrylonitrile) was dissolved in *N,N*-dimethylformamide (Merck), and the solution was stirred for 18 h. Subsequently, calculated amount of the salt (LiCF_3SO_3) with an optimized N/Li ratio ~ 8 was added and stirred for 15 h to facilitate homogeneous mixing and complexation. N/Li ratio refers to the number of available electron-rich site in the host polymer backbone permitting coordination of lithium cation. It is always preferred that the number of N site per lithium cation should be large to permit migration of Li^+ ion from one available site of the host polymer to another. An optimized ratio for N/Li is 8 [19]. The resulting final PS complex solution was added with different weight ratio x (relative to polymer host) of dodecylamine modified montmorillonite (DMMT) clay with concentration varying over a limited range expressed as $0 \leq x \leq 20$. The composite solution was then stirred for another 12 h and casted in a polypropylene dishes and glass slides. Finally, dimensionally flexible free standing polymeric films were obtained after drying under inert atmosphere. The obtained films have thickness of order of ~ 1 mm for the electrical measurement.

Material characterization

High-resolution transmission electron microscopy has been done using JEOL-JEM (model 2100, Japan), operating at 200 kV. Complex impedance/admittance spectrum (CIS) measurements on the composite films were carried out using a computer interfaced impedance analyzer (HIOKI LCR Hi-Tester, model 3522-50, Japan) in the frequency range of 10 mHz to 100 kHz. The PNC samples were placed in a symmetrical cell configuration of the type; SS/PNC/SS (SS stands for stainless steel blocking electrodes). An ac input signal of ~ 60 mV peak to peak was applied across the cell to carry out complex impedance measurements. Fraction of free anion has been estimated from Fourier transformed infrared spectrum data in the mid-IR region ($4,000$ to 400 cm^{-1}) using Thermo Nicolet spectrophotometer (model: NEXUS –870). The glass transition temperature has been characterized using the DSC instruments (Perkin Elmer model: Sapphire) in an argon atmosphere with a heating rate of 10 $^\circ\text{C min}^{-1}$.

Results and discussion

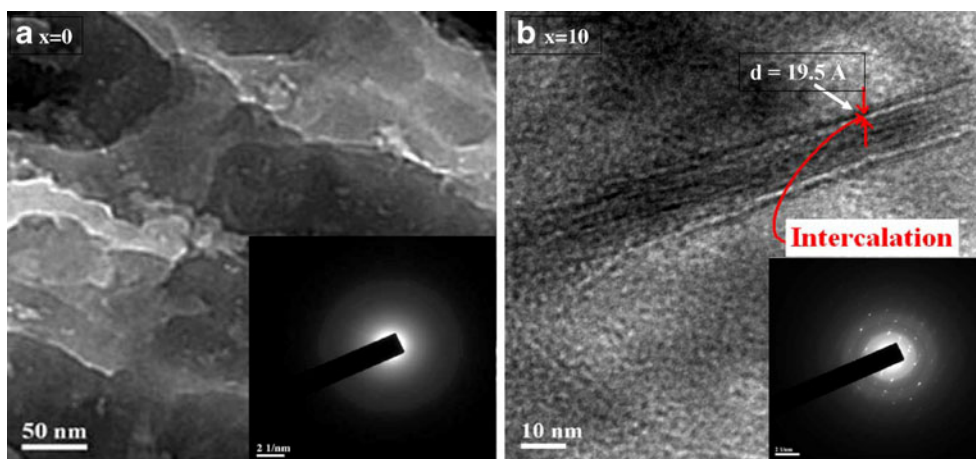
Microstructural (TEM) analysis

Transmission electron microscopy (TEM) analysis has been performed to observe the surface property and morphological features of the PNC films. Figure 1a, b depicts representative TEM micrographs of PNC ($x=10$ wt.% organoclay concentration and PS complex) film. The selected area electron diffraction (SAED) pattern is shown in the inset of corresponding microstructural micrograph. The TEM picture provides a clear visual confirmation of polymer intercalation into the clay channels indicated by well-defined stacks representing clay channels as marked in the image (basal spacing 19.5 Å; Fig. 1b). At higher clay loading, a number of intercalated tactoids are observed to be dispersed into the polymer salt complex matrix [8, 20]. The SAED pattern further supports that the crystalline nature of the PNC films has improved on nanocomposite formation and the effect appears to be stronger on addition of (10 wt.%) organoclay concentration in the PS complex film (Fig. 1b). These observation from TEM analysis agree well with the XRD results reported elsewhere [21].

Electrical property analysis

The representative CIS pattern of PS film comprises of a high-frequency semicircular arc followed by a predominant spike in low-frequency region (Fig. 2). The high-frequency semicircular arc in the CIS pattern has been attributed to bulk sample contribution whereas spike at low frequency

Fig. 1 Representative TEM (image and inset SAED pattern) picture of PNC films for **a** $x=0$ wt.% and **b** $x=10$ wt.% organomodified clay concentration



can be related to the space charge accumulation at the electrode–electrolyte interface, i.e., electrode polarization effect. A preliminary inspection of CIS spectrum suggests that bulk contribution may have been relatively masked by strong electrode polarization effect. The latter may be an outcome of faster ion dynamics. In order to confirm this hypothesis, we have used admittance formalism to analyze the sample electrical response. It is discussed below.

Admittance analysis

Figure 3a, b shows the complex admittance spectrum of PNC films compared with clay free PS complex film at room temperature and 80 °C. The admittance spectrum pattern comprises of semicircular arc. This is attributed to the electrode polarization contribution due to accumulation of charges in the interfacial region of the material–electrode contact. The intercept of semicircle on real axis gives an estimate of bulk conductance (G) of the sample. The nature

of the depressed semicircle in the material sample is a testimony of the multiphase character comprising of microstructure having both crystalline and amorphous and an intermingling of the two phases in the PS complex matrix as well as in PNC matrix. It has been observed that all PNC films have relatively larger conductance value when compared with clay free PS complex film. The pattern of the admittance spectrum of all PNC samples is almost identical at 80 °C when compared with room temperature with an essential difference in their conductance value. The conductance at 80 °C is higher in all samples when compared with room temperature. This increase in conductance may be due to the flexibility of polymer chains at and above its glass transition temperature (T_g). The dc conductivity has been estimated using the relation $\sigma_{dc} = G \times (\frac{l}{A})$, where G is the conductance, l sample thickness, and A is the area of electrode.

Dielectric analysis

The dielectric permittivity describes the polarizing ability of a material in the presence of an applied external electric field. The effect of polarization is to produce accumulation of bound charges in the material sample. The applied external electric field influences the orientation of electrical charges carriers in a given medium including charge migration and electric dipole reorientation. This is simply represented by electric displacement vector: $D = \epsilon E$, where ϵ is the permittivity and it depends on the strength of the applied external electric field. Since permittivity is a function of frequency so, it is complex quantity. A change in frequency therefore introduces a phase difference (δ) between D and E [22]. In order to obtain an exact relationship between the two, let us consider that an ac electric field (E) is applied across the sample cell such that the relationship of amplitude E_0 and angular frequency ω acting across the dielectric material is $E = E_0 \cos \omega t$. This, in turn, causes an effective polarization creating dipole that may be permanent/transient. If the frequency is

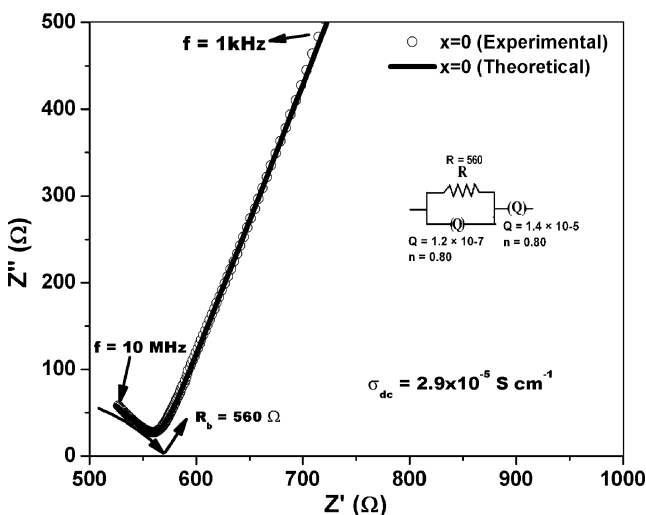
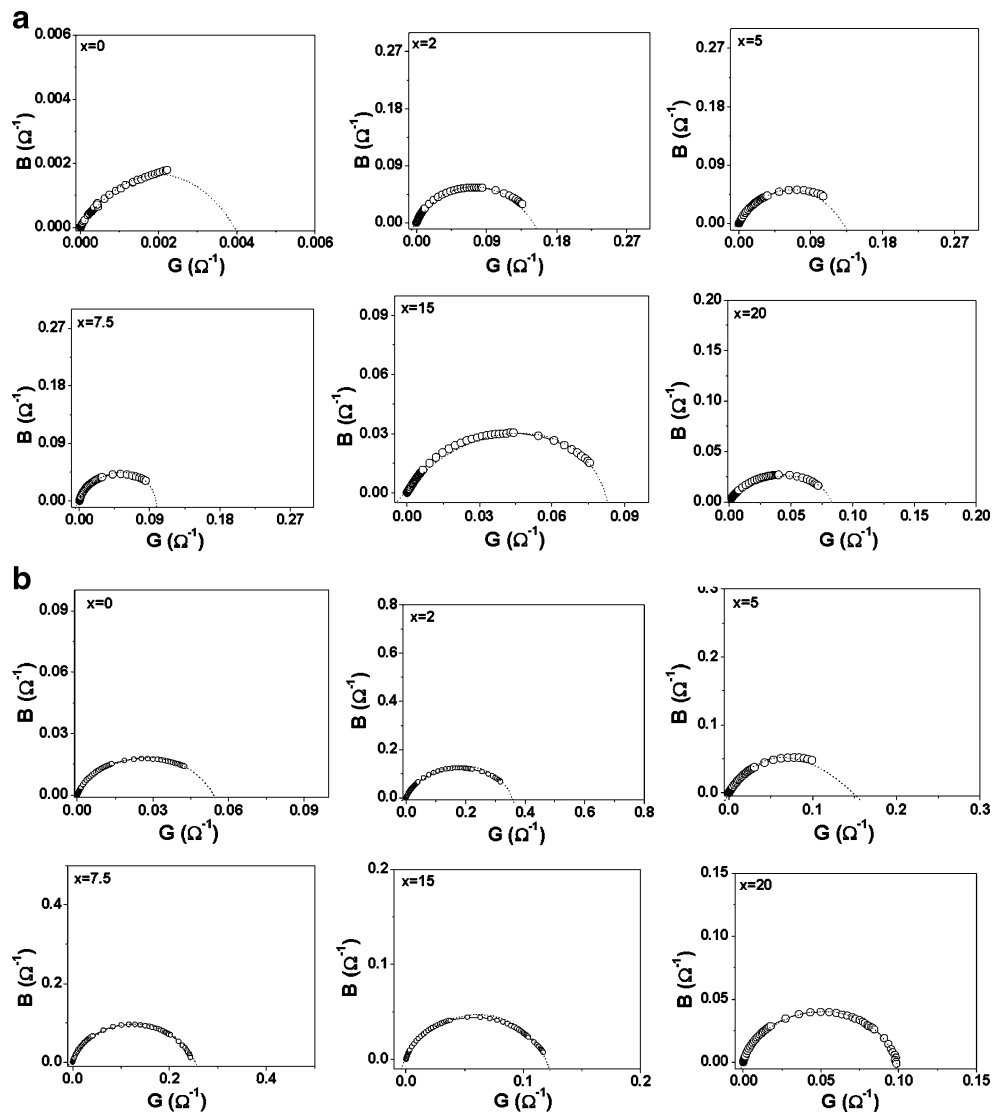


Fig. 2 Representative pattern of complex impedance spectrum of polymer–salt complex sample at room temperature

Fig. 3 Complex admittance spectrum PNC films **a** at room temperature and **b** at 80 °C



high enough, the orientation of any dipoles which are present will inevitably lag behind the applied external electric field. It can be expressed mathematically as a phase lag δ in the electric displacement:

$$D = D_0 \cos(\omega t - \delta)$$

$$D = D_0 \cos \omega t \cos \delta + D_0 \sin \omega t \sin \delta$$

$$D = D_1 \cos \omega t + D_2 \sin \omega t$$

where $D_1 = D_0 \cos \delta$, $D_2 = D_0 \sin \delta$ are the electric displacement in real and imaginary part, respectively.

It enables us to define two distinct permittivities as:

$$\epsilon'(\omega) = \frac{D_1}{\epsilon_0 E_0} = \frac{D_0 \cos \delta}{\epsilon_0 E_0} \rightarrow \text{represents real part of the permittivity}$$

$$\epsilon''(\omega) = \frac{D_2}{\epsilon_0 E_0} = \frac{D_0 \sin \delta}{\epsilon_0 E_0} \rightarrow \text{represents imaginary part of the permittivity}$$

These components are related to the complex permittivity (ϵ^*) as

$$\epsilon^*(\omega) = \epsilon'(\omega) - j\epsilon''(\omega) = \frac{D_0}{\epsilon_0 E_0} (\cos \delta - j \sin \delta) \tag{1}$$

Here, ϵ' is related to the stored energy within the medium

and ϵ'' is related to the dissipation (dielectric energy loss) of energy within the medium. Both the parameters depend strongly on frequency and nature of electrical response from sample. The latter depends on interaction among the charge carries. We have systematically analyzed this interaction in the present studies. It is described below.

Figure 4a, b shows the representative variation of dielectric permittivity (ϵ') with frequency for PNC samples at room temperature (30 °C) and 80 °C (i.e., polymer glass transition temperature (T_g)). The pattern of real part of dielectric permittivity (ϵ') variation indicates two distinct regions of changes (marked as regions I and II in the Fig. 4a, b) irrespective of temperature in all PNC samples. The region I exhibits weak frequency dependence (low dispersive region) followed by region II where frequency dependence of ϵ' becomes stronger and well marked (high dispersive region) in the high-frequency region irrespective of organomodified clay concentration and temperature. The high value of dielectric permittivity observed in the low-

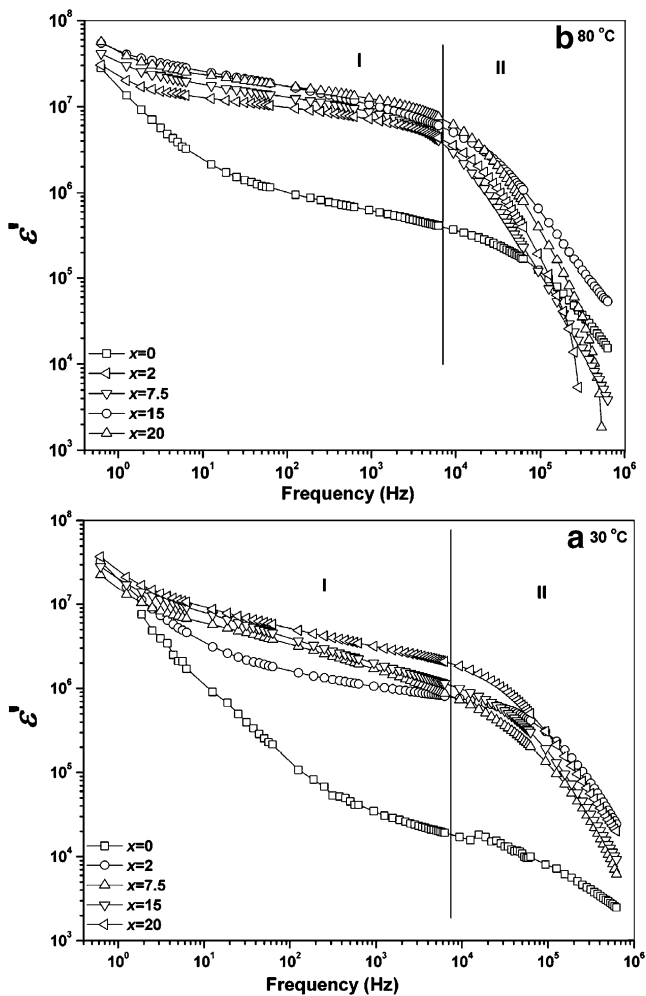


Fig. 4 Frequency dependence of dielectric permittivity ϵ' . **a** at room temperature and **b** at 80 °C

frequency region (region I) may be attributed to the accumulation of space charge [23] near the electrode–electrolyte interface due to polarization effect. The overall effect causes immobilization of charge carriers at low frequency by which the value of dielectric permittivity became so high. ϵ' decreases on increase of frequency due to high periodic reversal of the field at the interface. With increasing frequency, a consequent reduction of charge carriers occurs that contributes in lowering the dielectric constant in the electrode polarization region. In region II, the lowering of real part of permittivity may be due to weakening of the strength of ion–ion interaction in the transient dipoles (lithium to electron-rich site of the polymer), i.e., in the dc conduction. The dispersive behavior in region II may also be related to the cumulative effect of the weakening of dipolar interaction and space charge barrier across the material sample. The overall effect would be migration of charge carrier due to long-

range ion transport. The observation seems logical and consistent with the frequency dependence of electrical conductivity.

Further, it has been observed (Fig. 4a, b) that dielectric permittivity (ϵ') increases by two orders of magnitude in PNC films when compared with PS complex sample. This change is systematic and consistent with increasing organo-modified montmorillonite clay concentration. This type of nature has been observed both at room temperature as well as at (polymer glass transition temperature) 80 °C. However, the enhancement is clearly visible in the later case. This may be related to the flexibility of the host polymer backbone. Electrical conduction properties and dynamics of charge transport in the PNC films under ambient condition have also been investigated in terms of dielectric relaxation spectrum and conductivity spectrum. The experimental results are described in the Fig. 5a, b at room temperature, and near polymer glass transition temperature (T_g), respectively, indicates the variation of the imaginary part of dielectric permittivity (total dielectric loss) vs. frequency. It exhibits a marked change in the PNC films when compared with that of the PS film. The origin of the imaginary component of the dielectric permittivity (dielectric loss) in a system lies in the contribution of energy absorbed by the dipoles (relaxing, ionic, permanent, etc.) present in the material system. However, in an ionic conductor, bulk conductivity of the polymer electrolyte also plays an important role. In the case of polymer electrolytes, the loss due to the dipolar contribution is normally suppressed by the polarization of charge conducting species present in the material system because of its high ionic conductivity. Therefore, dc conductivity correction is a must in order to estimate actual dipolar contribution in the relaxation process. The corrected dielectric permittivity ($\epsilon''_{corrected}$) [24] obtained after subtracting the dc conductivity contribution ($\frac{\sigma_{dc}}{\omega\epsilon_0}$) from the observed (ϵ''_{total}) dielectric permittivity is expressed as:

$$\epsilon''_{corr} = \epsilon''_d = \frac{Z'}{\omega C_0(Z'^2 + Z''^2)} - \frac{\sigma_{dc}}{\omega\epsilon_0} \tag{2}$$

This equation provides true picture of the presence/absence of dipolar relaxation in a system and is useful for analysis. The variation of imaginary part of corrected dielectric permittivity ($\epsilon''_{corrected}$) vs. frequency at room temperature and near polymer glass transition temperature (T_g) is shown in Fig. 6a, b. A comparison indicates that the $\epsilon''_{(corrected)}$ peak has a lower value than ϵ''_{total} . The presence of relaxation peak, though broad, is clearly visible. Further, the broadening of relaxation peaks appears to be a function of clay concentration. This may be attributed to relative difference in energy

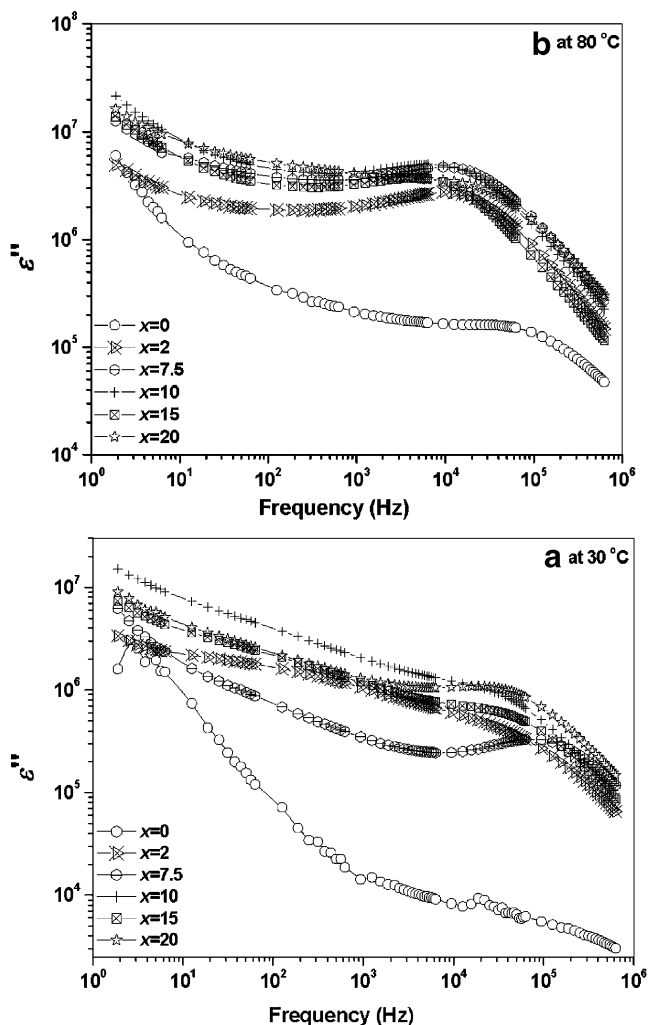


Fig. 5 The frequency dependence of total dielectric loss ($\epsilon''_{\text{total}}$) **a** at room temperature and **b** at 80 °C

absorbed by the relaxing dipoles (ion aggregates), permanent dipoles present in the PNC matrix at a particular clay concentration [25, 26].

The diffused relaxation peak for dielectric loss component (ϵ''_{corr}) with a very high magnitude of the order of $\sim 10^7$ provides a clear indication of dipolar contribution due to ion pairs that behaves as transient dipoles in the PNC matrix. Further, the magnitude of these components keeps on increasing with increasing organoclay concentration. It is believed that an increase in dielectric loss component of a system occurs due to mobility of conducting species. The higher the mobility of conducting species, the higher is the dielectric loss component. It is clearly evidenced in Table 1. In view of this hypothesis and corroborative experimental results, it seems logical to say that ion mobility (ion dynamics) in the PNC films is improved when compared with PS film. The changes observed in the dielectric results and correlation with conductivity as mentioned in Table 1 necessitate a detailed description of the latter. It is described in the next section.

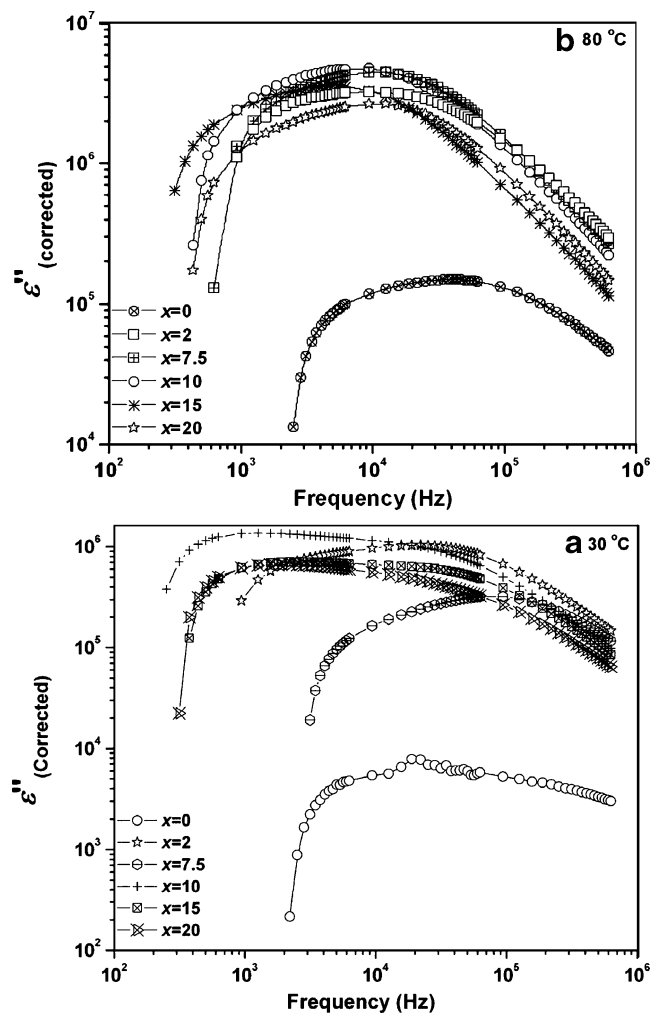


Fig. 6 The frequency dependence of corrected dielectric loss ($\epsilon''_{\text{corrected}}$) **a** at room temperature and **b** at 80 °C

AC conductivity analysis

The variation of ac conductivity vs. frequency at room temperature and at polymer glass transition temperature (80 °C) is shown in Fig. 7a, b. The ac conductivity of the PNC films is obtained from dielectric loss using the relation:

$$\sigma_{\text{ac}} = \epsilon_0 \omega \epsilon'' = \epsilon_0 \omega \epsilon' \tan \delta \quad (3)$$

where ϵ_0 is the dielectric permittivity in free space and ω is the angular frequency. The conductivity spectrum exhibits typical features of low-frequency dispersion with a high-frequency saturation unlike previous report on similar analysis [27]. This observation is indicative of complex ion transport process possibly due to the combined effect of space charge polarization (electrode polarization at the electrode electrolyte interface) at low frequency followed by long-range ion migration at high frequency. The experimental results on conductivity spectrum in the

Table 1 The calculated value of permittivity (real and imaginary) electrical conductivity (ac and dc) at room temperature and at polymer glass transition temperature (80 °C) of polymer nanocomposite films based on (PAN)₈LiCF₃SO₃+x wt.% DMMT

x wt.%	At 30 °C and at frequency 10 kHz				At 80 °C and at frequency 10 kHz			
	ϵ' ($\times 10^5$)	ϵ'' ($\times 10^5$)	σ_{ac} (S cm ⁻¹)	σ_{dc} (S cm ⁻¹)	ϵ' ($\times 10^5$)	ϵ'' ($\times 10^5$)	σ_{ac} (S cm ⁻¹)	σ_{dc} (S cm ⁻¹)
0	0.16	1.62	2.9×10^{-5}	2.4×10^{-4}	3.42	0.08	1.3×10^{-6}	3.8×10^{-3}
1	1.14	3.55	4.4×10^{-5}	1.2×10^{-3}	9.67	0.15	1.9×10^{-6}	4.9×10^{-3}
2	7.21	3.45	7.5×10^{-4}	8.4×10^{-3}	43.25	1.08	2.4×10^{-4}	2.5×10^{-3}
5	1.15	6.57	1.6×10^{-4}	6.7×10^{-3}	6.87	3.31	8.1×10^{-5}	1.4×10^{-2}
7.5	6.31	4.65	8.3×10^{-4}	6.8×10^{-3}	50.57	2.52	2.5×10^{-4}	1.9×10^{-2}
10	7.32	4.73	1.4×10^{-3}	5.9×10^{-3}	42.72	1.16	1.4×10^{-4}	1.5×10^{-2}
15	8.89	3.12	1.3×10^{-4}	4.7×10^{-3}	21.88	7.01	1.4×10^{-4}	6.7×10^{-3}
20	16.44	2.24	1.3×10^{-3}	3.7×10^{-3}	29.09	5.63	2.9×10^{-5}	6.7×10^{-3}

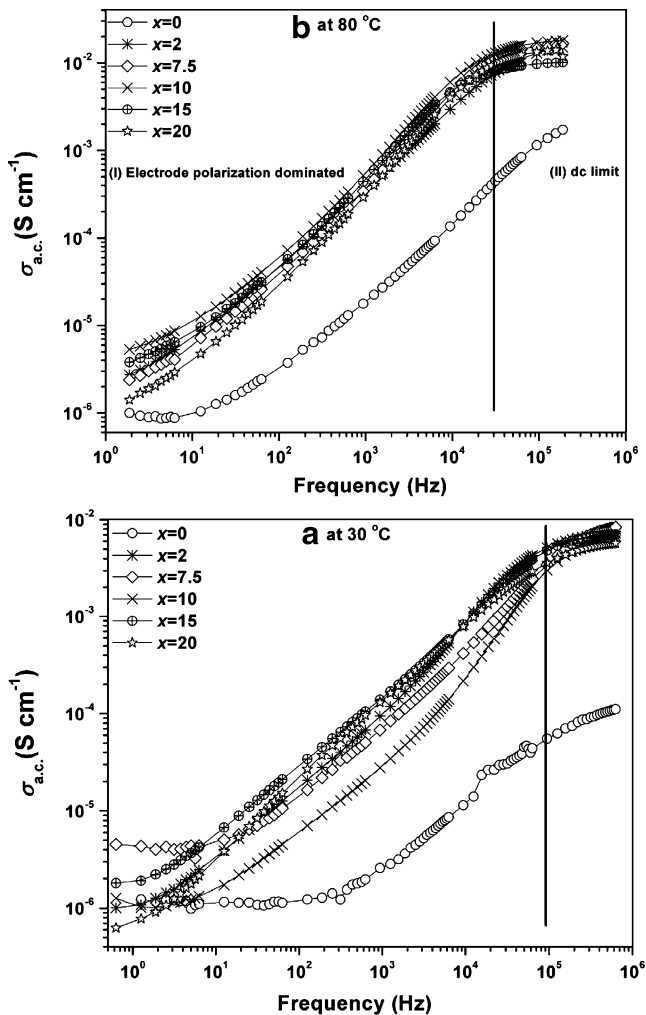


Fig. 7 AC conductivity spectrum of polymer nanocomposite films based on (PAN)₈LiCF₃SO₃+x wt.% DMMT **a** at room temperature and **b** at 80 °C

present studies suggest a predominant contribution of electrode polarization effect up to a frequency range of 10⁵ Hz at room temperature. This frequency limit shifts slightly toward the lower side of the spectrum at 80 °C. The electrode polarization contribution in conductivity is clearly marked by strong dispersive effect which is typical to a fast ion conductor. At the saturation limit of electrode polarization effect, a steady state is achieved where a change in the mechanism of ion migration occurs. This threshold frequency, where such a transition in the charge transport occurs, marks the dc limit or long-range migration. It is believed, in general, that ac conductivity in polymeric conductors may occur via two types of phenomenon: long-range conduction and preferred site hopping conduction through the polymer hetero sites. The former effect suggests that long-range conduction occurs due to the migration of free cations and anions in polymer nanocomposites. On the other hand, hopping process takes place at higher frequencies such that the mean charge carrier displacement gets reduced resulting in strong frequency dependence of conductivity. In PNCs, clay concentration also plays an active role in long-range ordering.

Discussion

An excellent correlation between polymer glass transition temperature (*T_g*), dc conductivity (σ_{dc}), and fraction of free mobile charge carriers has been observed. The role of clay concentration has a profound role in it as noted in Fig. 8. It shows a relative decrease in the value of glass transition temperature (*T_g*) on addition of organomodified montmorillonite clay in PS complex matrix. This effect is attributed to the clay induced flexibility in the PNC. It is generally believed that the glass transition temperature (*T_g*) of the host polymer is directly related to the flexibility of the

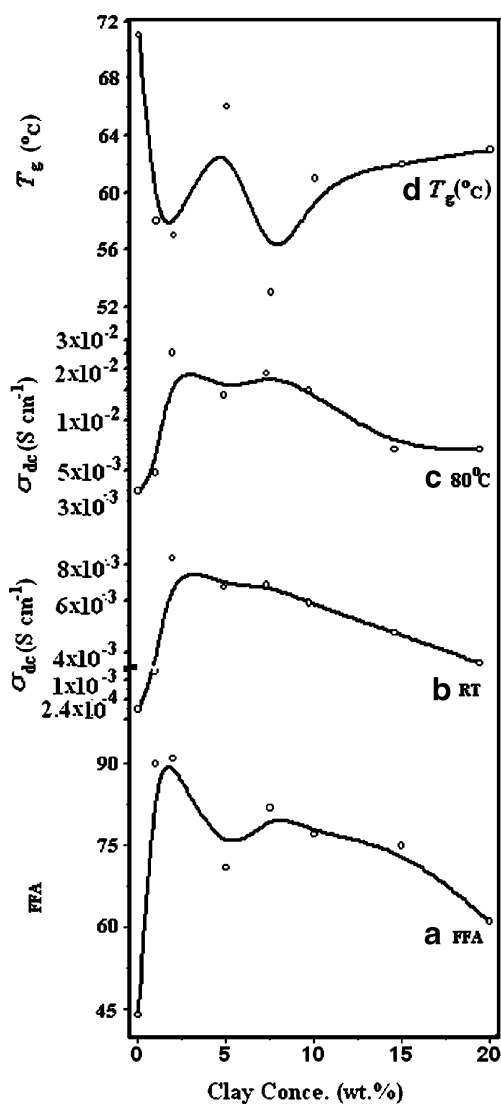


Fig. 8 Correlation of σ_{dc} , T_g , and FFA with varying organoclay concentration

polymeric segments in its amorphous phase. So, a lowering in T_g in a host polymer causes loosening of the bonds in polymer backbone. It results in a consequential enhancement in the flexibility of polymeric chains. The overall traces its origin to a possible delinking of the polymeric chains due to evidenced interaction of clay with the polymer backbone in the host matrix. On the other hand, an increase in the concentration of clay causes a relative lowering in the flexibility of the polymeric chains and subsequent enhancement in T_g possibly due to bridging/cross linking effect of the clay particles with two nearby polymeric segments. Such an effect is now well understood and reported in literature exclusively for a number of systems: PEO-LiClO₄+MMT clay [28], PEO-LiClO₄+n-CeO₂/n-YSZ [29], PMMA-LiClO₄+MMT clay [30], and PEO-NaClO₄+Na₂SiO₃/SnO₂ [31].

It has been observed that the ionic conductivity as well as fraction of free anion increases at the same specific clay concentration where lowering in T_g occurs. The two effects exhibit strong correlation. In fact, dc conductivity in heterogeneous PNC depends on a number of factors including (a) available site (heteroatom/electron-rich site) in the host polymer matrix (N/Li ratio), (b) lowering in polymer glass transition temperature that, in turn, permits greater mobility of polymer segments (chains), (c) larger anion size, (d) nature of interaction among composite components and its impact on the release of free charge carriers, and (e) phase composition of the host polymer (i.e., crystallinity/amorphous contents), etc. Clearly, crystallinity of the host polymer is one of the factors that may affect conductivity. In the present case, the host polymer (PAN) itself is predominantly amorphous (70%). So, a marginal improvement in crystallinity of the host polymer on clay addition should not be considered as the major factor. The factors mentioned above also produce positive impact for conductivity enhancement. So, on increase of clay concentration, the ionic conductivity increases which is already observed in the ac conductivity analysis. An increase in the free anion fraction in the PNC films confirm enhanced ion dynamics due to an effective interaction among composite components [32].

Further, a comparative analysis of dielectric spectrum suggests that addition of clay in the PNC matrix has the effect of increasing relaxation time by at least 1 order of magnitude from 10 μ s in the PS to 100 μ s in PNC film. Additionally, the diffuseness of relaxation peaks increased manifold (Fig. 6) together with increase in the fraction of loss in the PNC in sharp contrast to that of the PS. This increase in dielectric loss with increasing in clay concentration has been found to agree well with the change in the flexibility of host polymer backbone as revealed by variation of polymer glass transition temperature with clay in the PNC films. The overall effects of both these changes are directly related to enhanced mobility of the charge carriers in the PNC matrix due to lowering of the electrical resistance. The intensity of this effect further increase under thermally activated condition with rise in temperature. The representative figure at 80 °C is shown in Fig. 6b.

Summary

Frequency dependence of dielectric results suggests presence of relaxation contributed by dipoles (ion pairs, ion aggregates as well as polar groups of the polymer backbone). However, the role of conducting species cannot be ignored. Conductivity spectrum suggests clay concentration dependent ion dynamics in the PNC films with hopping type mechanism of charge transport. The hopping

mechanism in PNC is in sharp contrast to the long-range ion migration in clay free polymer–salt complex film. Ion transport in PNC films may be attributed to the combined effect of ion–ion interaction and the dynamics of the polymer chain motion in composite phase, where concentration of the organomodified montmorillonite clay plays a decisive role. It is concluded that, in heterogeneous PNC system, ion dynamics is controlled by a number of factors that include both physical and structural parameters.

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