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Ion dynamics and dielectric relaxation behavior of PVA-PVP-NaI-SiO₂ based nano-composites polymer blend electrolytes



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ABSTRACT

In this paper we have reported the loading effect of SiO₂ nano-particles on the electrical transport properties and dielectric relaxation behavior of the PVA-PVP-NaI based nano composite polymer blend electrolytes (NCPBEs). Solution cast technique has been used for the preparation of PVA-PVP-NaI-SiO₂ based NCPBE films. AC impedance spectroscopic technique is used for the study of electrical conductivity and dielectric properties. The frequency dependence of AC conductivity with different SiO₂ concentration for all prepared NCPBEs obeys the Jonscher power law (JPL) with exponent, n \geq 1. The dielectric premittivity (e'&e''), electric modulus (M'&M'') vs. frequency plots at different concentrations and temperatures were reported. Mobility (µ), dc conductivity (σ_{dc}) and total number of charge carriers (N) were estimated and found that mobility varies with the SiO₂ concentration. Sample containing 0.6 wt% of SiO₂ shows optimum dc conductivity, $\sigma_{dc} \sim 5.07 \times 10^{-6}$ S/cm with $\mu \sim 4.60 \times 10^{-7}$ and N $\sim 6.98 \times 10^{21}$. Dielectric relaxation peaks have been observed for all samples and relaxation time (τ) is minimum for 0.6 wt%SiO₂ based NCPBE film.

1. Introduction

Nano-composite polymer blend electrolytes (NCPBEs) have generated great interest in developing new materials because of their potential application in the fabrication of electrochemical devices such as batteries, super capacitors, fuel cell etc [1,2]. The uses of solid polymer electrolytes based on alkali metal salts have certain limitations such as low ionic conductivity at room temperature, low mechanical flexibility and poor chemical stability [3-5]. Several methods have been incorporated for improving these properties such as cross-linking, polymer blending [6, 7], use of nano-fillers [8] and plasticizers [9]. In these methods, though polymer blending is cost-effective but this method has drawn much attention for improving the matrix properties due to interactions between the functional groups of polymers via hydrogen bonding and ionic interactions [6]. Poly (vinyl) alcohol (PVA) containing hydroxyl (O-H) is a semi-crystalline polymer, studied enormously because of their many important physical and chemical properties such as high dielectric constant, water solubility, good charge storage capacity and dopant dependent electrical, dielectric and optical properties [10]. Water solvable polymer, poly(vinyl) pyrrolidone (PVP) also have a special attention among the conjugated polymers because of its good environmental stability, easy processability and amorphousness which

support easy charge transportation [11-13]. The interactions between PVP-PVA were taken place via inter-chain hydrogen bonding between carbonyl group (C=O) of PVP and hydroxyl group (O-H) of PVA [14]. Addition of nano-fillers in polymer matrices has been found to be an effective method of enhancing the ionic conductivity of polymer material for higher thermal and mechanical stability which are additional requirements of solid polymer electrolytes for a wide range of electrochemical applications [15,16]. Nano-fillers provide a better ion conductive pathway by enhancing the surface area to volume ratio in the polymer matrices [17–19]. The enhancement of conductivity in the nano-composite polymer electrolytes has been described by two factors, first is the large specific surface area provided by the nano-particles (at nano scale) and second is the interactions that occur between the surface groups of the nano-particles and the polymer matrix [20-22]. The addition of nano-particles creates disorder in the polymer matrix which is directly associated with bulk ionic conductivity [23]. The nano-composite polymer films show the better electrochemical stability towards a metal anode and also enhanced cation transport number [24-26]. The ion conduction mechanism in these polymer electrolytes has not been studied so for and our interest regarding the study of ion-dynamics behavior of such systems are of the fundamental importance. A systematic study for understanding the role of nano-particles in

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modifying the electrical and dielectric properties of NCPBEs will provide an opportunity to develop new ideas in this field. In the present work we have studied the loading effect of SiO₂, nano-particles on the ac conductivity behavior, dielectric properties, mobility and total number of charge carries of PVA-PVP-NaI based NCPBE using AC impedance spectroscopic technique.

2. Materials and experimental details

PVA having average molecular weight ~1,25,000 g/mol with purity >98% and degree of hydrolysis ~89%, PVP with average molecular weight ~44,000 g/mol with purity >99% and salt, sodium iodide (NaI) salt were procured from Merck, Germany. SiO₂ nano-particles having average particle size ~14 nm with surface area $200 \pm 25 \text{ m}^2/\text{g}$ was purchased from Sigma Aldrich. Deionized distilled water was used as a solvent for the preparation of PVA-PVP-NaI-SiO₂ based polymeric films.

The NCPBEs have been prepared using solution casting technique. In this technique the desired wt% ratio of materials [(50PVA-50PVP):30NaI]: xwt%SiO₂ with x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0 were mixed separately in solvent and the mixture was kept in oven at 50 °C for 24 h to swell, after that the solution is stirrer continuously for 5 h to obtained the viscous slurry. The viscous slurry was purred on poly propylene Petri-dishes and put into the oven at 40 °C for 10 days in order to evaporation of solvent, after that free standing films having thickness of ~50–90 µm were obtained. All the prepared films were kept in evacuated desiccators for further measurements. The prepared polymeric films were characterized using AC impedance spectroscopic technique in the frequency range 20Hz-1MHz by using high precision Wayne Kerr impedance analyzer 6500 B with bias voltage 100 mV.

3. Results and discussion

3.1. AC conductivity analysis

Frequency dependent ac conductivity formalism has been used to explore the ion dynamics behaviour of various polymer electrolytes [10, 13,27]. For polymer electrolytes it is expected that ac conductivity curves follows the Jonscher's Power law (JPL) ($\sigma_{ac} = \sigma_{dc} + Af^n$), where the exponent n is restricted to be less than one for different frequency range, A is the temperature dependent parameter, σ_{dc} is the dc/bulk conductivity and f is the frequency. The ion motion passes from free hopping (n = 0) to correlated hopping (0 < n < 1) [28] followed by caged movement of ions greater than one (n > 1), [29]. Fig. 1(A) and (B) show the ac conductivity spectra of PVA-PVP-NaI-xwt%SiO₂ (x = 0.0,

0.2, 0.4, 0.6, 0.8, 1.0) at ambient temperature (30 °C) and for PVA-PVP-NaI-0.6 wt%SiO₂ at different temperatures, respectively. It is observed that the ac conductivity spectra of NCPBEs mainly consists two regions (Fig. 1(A)). The first region is frequency independent plateau region assigned to the bulk conductivity of the sample. The bulk ionic conductivity (σ_{dc}) of the samples was obtained from extrapolation of plateau region to the Y-axis. The second region is high frequency region in which conductivity increases with frequency ($\sigma_{ac} = Af^n$). It is found that 0.6 wt%SiO2, sample consist of three regions indicating low, mid and high frequency region. In the low frequency region, conductivity decreases with increasing frequency due to polarization effect. The values of σ_{dc} , A and n for all NCPBE based polymeric films at 30 °C were obtained from fitted ac conductivity spectra and are listed in Table 1. From Table 1 it has been found that dc conductivity, σ_{dc} varies with SiO₂ concentration with n > 1 support the caged type movement of ions. Polymer blending also enhances the flexibility of polymer chains creates large free volume which facilitates the translational motion of free ions, hence an increase in the ion mobility [30]. The maximum conductivity was found to be 5.07×10^{-6} S/cm at 30 °C for PVA-PVP-30NaI-0.6 wt% SiO₂ system. Fig. 1 (B) shows the fitted ac conductivity spectra of 0.6 wt % SiO₂ based polymer blend electrolyte at different temperatures and it is found that the value of n decreases with increasing temperature (inset Fig. 1(B)). In the low frequency region conductivity decreases with frequency and there is upward shifting of plateau region with temperature due to increase in the bulk ionic conductivity.

3.2. Temperature dependent dc conductivity study

Fig. 2 shows the log σ_{dc} vs. 1000/T plots for different wt% SiO₂ for PVA-PVP-NaI based NCPBE samples. It shows Arrhenius type thermally activated behaviour (ion dynamics associated with thermal activation

Table 1

Values of power low exponent (*n*), A and dc conductivity (σ_{dc} (*S*/*cm*) for PVA-PVP-NaI-xwt%SiO₂ (x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0) based polymeric films at 303 K obtained from fitted ac conductivity plots.

Sample	σ _{dc} (S/cm)	n	А
X = 0.0	$5.52 \mathrm{x10}^{-8}$	1.10	$7.31 \mathrm{x10}^{-12}$
X = 0.2	1.29×10^{-7}	1.20	$9.42 \text{ x} 10^{-12}$
X = 0.4	$3.24 \text{ x} 10^{-7}$	1.10	5.07×10^{-12}
X = 0.6	5.07x10-6	1.14	$4.27 \text{x} 10^{-12}$
X = 0.8	6.32x10-8	1.17	$2.04 \text{x} 10^{-12}$
X = 1.0	2.05x10-8	1.15	$3.36 \mathrm{x10}^{-12}$

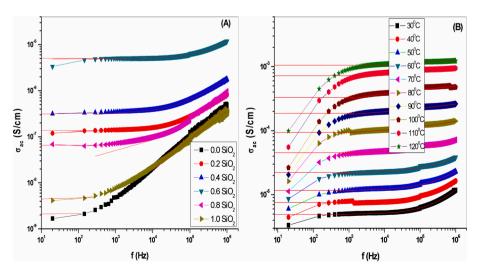


Fig. 1. Frequency dependent AC conductivity plots for (A) PVA-PVP-NaI-xwt%SiO₂ at different SiO₂ concentrations and (B) for PVA-PVP-NaI-0.6 wt%SiO₂ at different temperatures.

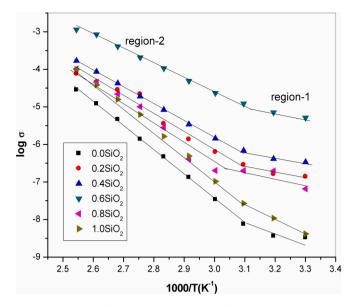


Fig. 2. Temperature dependent dc conductivity plots for PVA-PVP-NaI-xwt% SiO_2 based NCPBE films at 303 K.

energy) expressed as: $\sigma_T = \sigma_{dc} \exp\left(\frac{-E_a}{kT}\right)$ where σ_{dc} is the dc conductivity (obtained from ac conductivity spectra), Ea is the activation energy in eV, k is Boltzmann constant and T is the temperature in K. Arrhenius type behavior indicate that ion transport via hopping mechanism decoupled from polymer chain breathing. From the plots, it is evident that as the temperature increases the bulk ionic conductivity σ_{dc} increases for all the NCPBEs. From Fig. 2 it is also observed that $\log \sigma_{dc}$ vs. 1000/T plots consists of two regions one below and the other above the glass transition temperature (Tg) of PVA-PVP polymer blend [31]. It is found that the activation energy, E_{a2} is quite low above T_g in comparison to the activation energy, E_{a1} below T_g (data are listed in Table 2). Sample containing 0.6 wt% of SiO₂ shows minimum activation energy \sim 0.79 eV possibly due to interaction between functional groups of blend polymers, PVA/PVP with the electron loan pairs of oxygen SiO₂ and the cations of sodium salt, Na⁺ (Lewis acid). The Lewis acid interacts with the base of electrolytes and increases the salt dissociation by the ionic coupling and ion-filler complexation [32]. The increase in dc conductivity with temperature may be due to the increased chain flexibility which is associated with long range ion migration through coordinating sites of polymer matrix (segmental motion of polymer chains) [33]. The correlation between segmental mobility and ion transport can be explained on the basis of the free volume model [34] and hopping of charge carriers between localized states [35].

3.3. Tangent loss $(tan\delta)$ and relaxation time (τ) analysis

Loss tangent (tan δ) is the ratio of loss factor (ε'') to dielectric constant (ε') and can be expressed as $tan\delta = \frac{\varepsilon''}{\varepsilon}$. The ε' is related with the storage of charge carriers near the electrode-electrolyte interface and ε'' estimate the energy losses in movement of charge carriers in the presence of

Table 2

Activation energies for PVA-PVP-NaI-xwt%SiO2 based NCPBE films.

PVA-PVP-NaI-xwt%SiO ₂	E _{a1} (eV)	E _{a2} (eV)
x = 0.0	1.30	0.62
x = 0.2	0.98	0.33
x = 0.4	0.91	0.28
x = 0.6	0.79	0.30
x = 0.8	1.05	0.37
x = 1.0	1.31	0.77

electric field. The real (ϵ') and imaginary part (ϵ'') of dielectric permittivity can be expressed as:

$$\varepsilon' = \frac{z''}{(z'^2 + z''^2)\omega C_0} \text{ and } \varepsilon'' = \frac{z'}{(z'^2 + z''^2)\omega C_0}$$

where z' and z'' are the real and imaginary part of impedance, $C_0(=\frac{\varepsilon_0}{L}a)$ is capacitance of free space, ε_0 is the permittivity of free space, *l* is the thickness of the polymeric film and *a* is the area of the blocking electrode and $\omega = 2\pi f, f$ is the frequency. The relaxation time, τ is described as, $\tau =$ $\frac{1}{2\pi f_r}$ (i.e. maximum power transfer taken place) where f_r is the dielectric relaxation peak frequency. Fig. 3(A) shows that the variation of $tan\delta$ with frequency, for NCPBEs at different wt% of SiO₂. It is observed that $tan\delta$ peaks were shifted towards the higher frequency region with the addition of SiO₂ nano-particles and it is optimum for 0.6 wt% SiO₂ sample due to fast segmental motion of polymer chains of NCPBEs [36] and $tan\delta$ decreases in high frequency region. The peaks observed in $tan\delta$ vs. frequency plots reveal the matching of the relaxation frequency of polymer chains/dipole orientation with the frequency of applied external electric field. Fig. 3 (B) shows the variation of relaxation time, τ with SiO₂ concentration in prepared NCPBEs. It has been observed that the relaxation time, τ is minimum for 0.6 wt% SiO₂ sample shown in Fig. 3(B).

3.4. Complex dielectric permittivity study

Study of complex dielectric permittivity (ε^*) is an important tool for understanding the electrode polarization effect and energy dissipation in terms of dielectric constant (ε) and dielectric loss (ε), respectively of ion conducting materials. It is given by the equation:

$$\varepsilon^* = \varepsilon_{\infty} + \frac{\varepsilon_1}{1 + i\omega\tau}$$

Where $\varepsilon_1 = \varepsilon_o - \varepsilon_\infty$, ε_o is the dielectric constant at low frequency, ε_∞ is the dielectric constant at very high frequency ($\omega \to \infty$), $t^2 = -1$ and τ is the relaxation time. Real and imaginary parts of the dielectric permittivity are expressed as:

$$\varepsilon' = \varepsilon_{\infty} + \frac{\varepsilon_1}{1 + \omega^2 \tau^2}$$
 And $\varepsilon'' = \frac{\varepsilon_1 \omega \tau}{1 + \omega^2 \tau^2}$

Thus the value of $\omega \tau$ changes from 0 to ∞ and hence the dielectric constant varies from ε_o to ε_{∞} , i.e. decreases due to blockage of ion migration or ion diffusion [37, 38]. Fig. 4 (A-B) show the variation of ε' and ε'' with frequency at different concentration of silica nano-particles for PVA-PVP-NaI-SiO₂ based NCPBEs and Fig. 4 (C-D) at different temperatures for PVA-PVP-NaI-0.6 wt% SiO2, respectively. It has been observed that in Fig. 4 the values of ε' and ε'' are high in low frequency region because of space charge polarization near the electrode electrolyte interface [39,40]. With increasing the concentration of silica nano-particles in PVA-PVP-NaI polymer matrix there is an increase of localization of charge carriers near the electrode electrolyte interfaces hence an increase in ε' and ε'' values, respectively. Dielectric loss ($\varepsilon'')$ spectra for 0.6 wt% SiO2 based NCPBE consists single relaxation peak associated with the dielectric relaxation of polymer blend. At the higher frequency, changing of applied field direction has been rapid periodic reversal that create a negative environment for dipole alignment, so that ion diffusion stop in the direction of field and hence ε' and ε'' both decreases with increasing frequency for all PVA-PVP-NaI-SiO₂ based NCPBEs [41].

3.5. Variation of ε' and ε'' with temperature and SiO₂ concentration

The variation of ε' and ε'' with temperature at different frequencies for PVA-PVP-NaI-0.6 wt%SiO₂ and the variation of ε' and ε'' with silica nano-particles (SiO₂) at different frequencies are shown in Fig. 5(A-B)

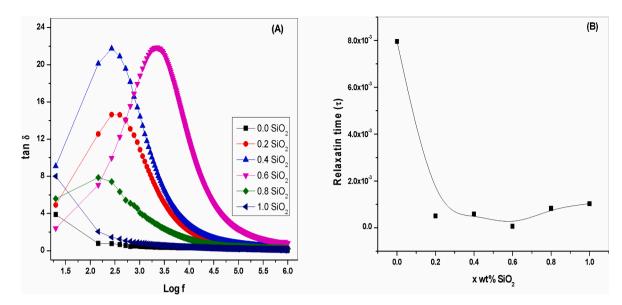


Fig. 3. (A) Loss tangent (tanδ) vs. frequency (f) plots of PVA-PVP-NaI-xwt%SiO₂ and (B) Variation of relaxation time, τ with SiO₂ content for NCPBE films at 303 K.

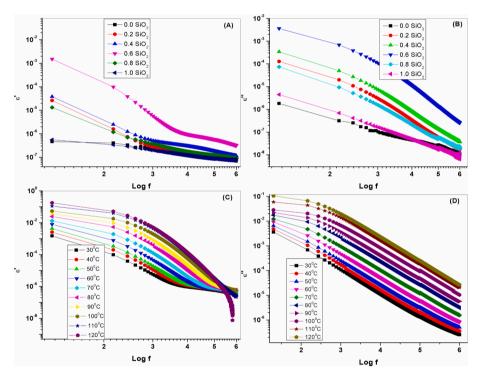


Fig. 4. Variation of dielectric permittivity, (A) real part (ε') and (B) imaginary part (ε'') with frequency for PVA-PVP-NaI-xwt%SiO₂ based films at 303 K, (C) real part (ε') and (D) imaginary part (ε'') with frequency for PVA-PVP-NaI-0.6 wt%SiO₂ based film at different temperatures.

and Fig. 5 (C-D), respectively. It is observed that in Fig. 5 (A) the values of ε' increases with temperature exponentially and decreases with frequency. The values of ε'' for 0.6 wt%SiO₂ containing sample increases exponentially with temperature as well as frequency (Fig. 5 (B)). This is because of re-orientation of dipoles (functional groups of PVA and PVP) attached with the chains of polymer/polymer blend [42]. The values of ε' and ε'' are optimum near 0.6 wt%SiO₂ nano-particles loading in the PVA-PVA-NaI based sample and their values decreases with frequency (Fig. 5 (C-D)). With the loading of SiO₂ in PVA-PVP-NaI based films, the ε' is optimum for 0.6 wt% containing sample, because of weak interactions between loan pair of electrons of oxygen of SiO₂ with the functional groups of PVA-PVP polymer blend. The high values of permittivity indicates the enhancement in ionic conductivity expressed

as $\sigma_{dc} = Nq\mu$ where N, q and μ are the total number of charge carrier density, electric charge and mobility, respectively.

3.6. Electric modulus studies

Ion transport mechanism of prepared NCPBEs was further explored by using electric modulus formalism [43]. The complex electric modulus (M^*) is the inverse of the complex dielectric permittivity (ε^*) and can be expressed as:

$$M^{*}(\omega) = \frac{1}{\varepsilon^{*}(\omega)} = M'jM^{''} = \frac{\varepsilon^{'}}{\varepsilon^{'2} + \varepsilon^{''2}} + j\frac{\varepsilon^{''}}{\varepsilon^{'2} + \varepsilon^{''2}}$$

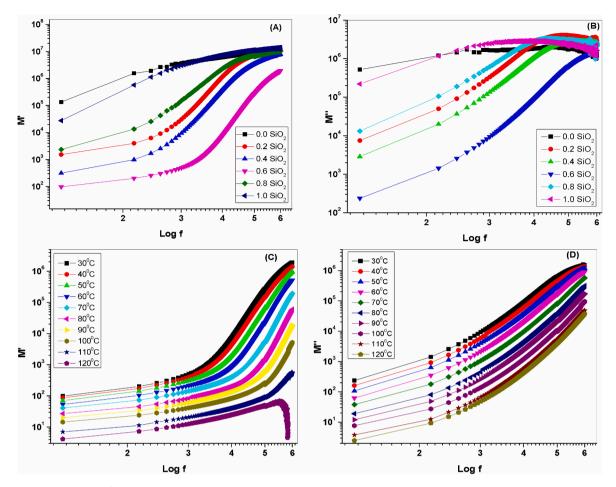


Fig. 5. Variation of (A) real part (ε'), (B) imaginary part (ε'') of dielectric permittivity with temperature at different frequencies for PVA-PVP-NaI-0.6 wt% SiO₂ based film (C) real part (ε'), (D) imaginary part (ε'') of dielectric permittivity with SiO₂ concentration at different frequencies for PVA-PVP-NaI-xwt%SiO₂ based polymer electrolyte films.

where *M*′ and *M*″ are the real and imaginary parts of the complex electric modulus $M^*(\omega)$ in terms of ε' and ε'' . The frequency dependence of M'and M" spectra at different wt% of SiO₂ for PVA-PVP-NaI-SiO₂ based NCPBEs is shown in Fig. 6(A-B). Similarly, frequency dependent variation of M' and M'' at different temperatures for highest conducting NCPBEs i.e. 0.6 wt% of SiO₂ are shown in Fig. 6(C-D). It is observed that the electric modulus in low frequency region is approaching to zero due to negligible contribution of electrode polarization. The value of M' and M'' as a function of frequency at ambient temperature for NCPBEs dispersed with different wt% of SiO₂, suggests that large capacitance is associated with the electrodes and confirms the non-Debye behavior. At high frequencies the value of M' and M'' increases with increasing frequency. It is also observed that with increasing the temperature the value of M' and M'' decreases due to increase in mobility of charge carriers with temperature. The value of M' and M'' shows some relaxation peak which shifts towards higher frequency with increasing temperature because of faster ionic motion, leading to decrease in relaxation time. Thus the charge carriers are thermally activated. From Fig. 6 (A-B) it is also observed that M' and M'' vs. frequency spectra are much broader than what is expected for the ideal Debye type and show the asymmetricity and skewed towards the high frequency. Such a broad nature of peak is an indication of the non-Debye type relaxation.

3.7. Variation of σ_{dc} (Scm⁻¹), N (m⁻³) and μ (m²V⁻¹s⁻¹) with silica nano-particles

The ion diffusivity (D), μ and N can be obtained by analyzing the dielectric and ac conductivity spectra. D can be estimated by using the

relation: $D = \frac{2\pi f_{max}l^2}{32(tan\delta_{max})^3}$ where $tan\delta_{max}$ is the maximum value of $tan\delta$, f_{max} is the frequency at which $tan\delta$ is maximum and l is the thickness of film [44]. By knowing the value of D (obtained from Fig. 3(A)) and σ_{dc} (obtained from fitted ac conductivity spectra) N could be calculated using the Einstein equation: $N = \frac{\sigma_{dc}kT}{Dq^2}$ where k is the Boltzmann's constant, T is the absolute temperature and q is the elementary charge. The μ can also be calculated from the relation: $\mu = \frac{\sigma_{dc}}{qN}$. The value of ion diffusivity varies from 5.99×10^{-8} to 3.68×10^{-7} . The value of total number of charge carriers varies from 2.18×10^{21} to 1.84×10^{17} . The mobility is varied from 2.29×10^{-6} to 1.41×10^{-5} with the increasing concentration of SiO₂. The value of N (~6.98 $\times 10^{-21}$ m⁻³) and μ (~4.60 $\times 10^{-7}$ m²V⁻¹s⁻¹) is optimum for PVA-PVP-NaI-0.6 wt%SiO₂ based NCPBE film.

4. Conclusions

The AC conductivity spectra of NCPBEs with SiO₂ concentrations and temperatures follow the Jonscher power law (JPL) with n > 1(caged type charge carriers hopping takes place). The maximum dc conductivity at room temperature has been found to be ~ 5.07×10^{-6} S/cm for 0.6 wt%SiO₂ containing NCPBE film with lowest activation energy ~0.79 eV. Mobility (µ) and total number of charge carriers (N) were estimated for all samples and it is found that mobility varies with the concentration of SiO₂. Sample containing 0.6 wt% SiO₂ shows optimum mobility, optimum total number of charge carriers with highest relaxation frequency (f_{max}). Dielectric loss (ϵ'') spectra for 0.6 wt%SiO₂ based NCPBE consists single relaxation peak associated with the dielectric

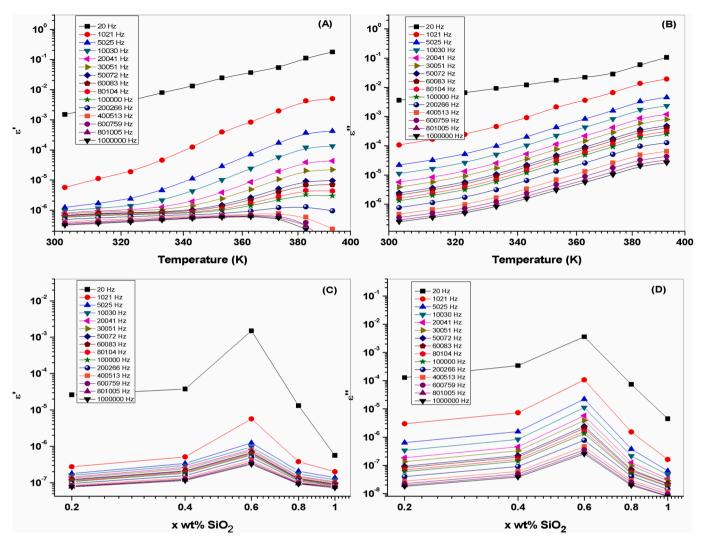


Fig. 6. Variation of (A) real part (M'), (B) imaginary part (M'') of electric modulus with frequency for PVA-PVP-NaI-xwt%SiO₂ (x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0) based films at 303 K, (C) real part (M') and (D) imaginary part (M'') of electric modulus with frequency for PVA-PVP-NaI-0.6 wt% SiO₂ based film at different temperatures.

relaxation of polymer blend. The dielectric permittivity and electric modulus studies shows the non–Debye relaxation behavior.

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P. Singh et al.

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Physica B: Physics of Condensed Matter 578 (2020) 411850

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