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Studies on Conducting Polymer Blends: Synthesis and Characterizations of PVA/PVP Doped with $CaCl_2$

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Calcium ion conducting polymer blend electrolyte films based on PVA/PVP complexed with $CaCl_2$ have been prepared by solution casting technique. The structural changes of the polymer blends have been studied by X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) spectroscopy. XRD and FT-IR studies confirmed the complex formation of polymer blends. Electrical conductivity was calculated with impedance analyzer within the frequency range 42 Hz–1 MHz and in the temperature range 303 K–340 K. The higher electrical conductivity value of 1.704×10^{-4} Scm^{-1} was observed for 50PVA:50PVP:15 wt% $CaCl_2$ concentration at room temperature. The magnitude of electrical conductivity was increased with the increase in the salt concentration as well as temperature. The electrical permittivity of the polymer films have been studied for various temperatures.

Keywords: Polymer Blend, Electrical Impedance, XRD, FT-IR, Thermal Analysis.

1. INTRODUCTION

Nowadays, various kinds of polymer nano-composites, their hybrids, and nanomaterials with nanostructures have been paid much interest regarding their advanced properties.[1–5] Conducting polymers have extensive applications in energy conversion systems such as photovoltaic cells, solar cells, bio sensors etc.[6] In the study of this, a great interest has been paid to the conducting properties of polymers. When polymers are doped with inorganic salts, they show appreciable change in their structural as well as electrical properties. For electrochemical applications, Polymer electrolytes with divalent cations are suitable. Many studies deal with the doping of metal with the polymer blends.[7–10]

In this paper, polymer blends are prepared by using polyvinyl alcohol (PVA)/Poly(vinyl pyrollidene) (PVP) because potential applications such as good charge storage capacity and dopant-dependent electrical properties. PVA is a semi-crystalline polymer, water soluble, non toxic, better film and fiber forming, biocompatible, excellent chemical resistance, good mechanical properties with varied applications.[11,12] PVP is an amorphous polymer possessing high T_g due to the presence of the rigid pyrrolidene group, which is known to form various complexes with many inorganic salts. The present study focused on the electrical conductivity of PVA/PVP blend doped with $CaCl_2$ to enhance the electrical properties. The probable interaction between the PVA-PVP polymers with dissociated salt ($CaCl_2$) has been shown below in Figure 1.

2. EXPERIMENTAL PROCEDURE

Poly(vinyl alcohol) (PVA), molecular weight, $M_w = 1$, 25,000, poly(vinyl pyrrolidone) (PVP) with molecular weight, $M_w = 90{,}000$ and Calcium Chloride ($CaCl_2$) were used as raw materials. Doubly distilled water was used throughout the experiment. To prepare the polymeric films filled with 5, 10, 15, 20, 25 and 30 wt% of $CaCl_2$, 50:50 stoichiometric quantities of PVA, PVP and $CaCl_2$ were dissolved in distilled water and then stirred until homogeneous solution was obtained. The solution was stirred continuously until the mixture became homogeneous viscous liquid. The final solution was poured into polypropylene dishes and dried in an oven at 50 °C for 6 days to ensure the removal of solvent traces. After drying, the prepared films were peeled from Petri dishes. The smooth, uniform

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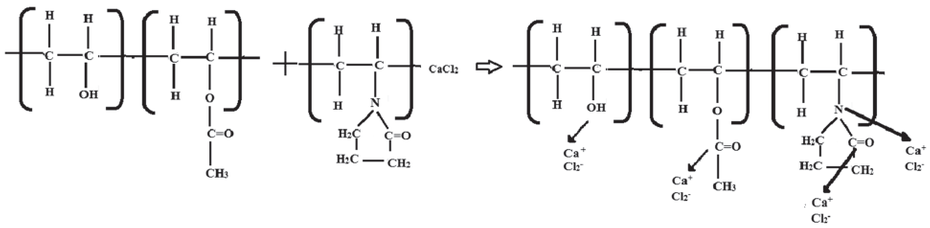

Figure 1. Possible interaction between PVA/PVP and $CaCl_2$.

and transparent films had been obtained and kept in desiccators for further studies.

3. CHARACTERIZATION

The X-ray diffraction pattern of the composite blend polymer electrolytes was recorded using Cu-Kα (λ = 1.5406 Å), Bruker made X-ray diffractometer. FT-IR measurement was made with a Shimadzu-IR Affinity-1 spectrometer instrument in the wave number range of 400-4,000 cm^{-1}. DSC of the prepared films was studied using Perkin Elmer 4000 system. The samples were put in an Al pan and heated in the temperature range between 50 °C–300 °C at the rate of 10 °C/min. The impedance was measured for the polymer films in the temperature range of 303–343 K over a frequency range of 42 Hz–1 MHz using a computer-controlled HIOKI 3532 LCR meter.

4. RESULTS AND DISCUSSION

4.1. XRD Analysis

The structural characteristics of pure 50PVA/50PVP blends with different wt% of $CaCl_2$ were evaluated using X-ray diffraction studies and were shown in Figure 2. There is no separate peaks were observed for pure PVP, a broad hump was observed at $2\theta = 11°–18°$, which can be related with the amorphous nature of pure PVP.[13] The relative intensity of the broad peak decreases by increasing the concentration of $CaCl_2$. There is no such peak corresponding to $CaCl_2$ in the spectrum specify the absolute dissolution of $CaCl_2$ in the polymer blend up to the concentration of 25 wt% of $CaCl_2$. Besides, a feeble peak, which corresponds to the (211) $CaCl_2$ plane, was observed at 32° for the inclusion of 30 wt% of $CaCl_2$. The amorphous nature results in high ionic conductivity of the polymer blend electrolyte.

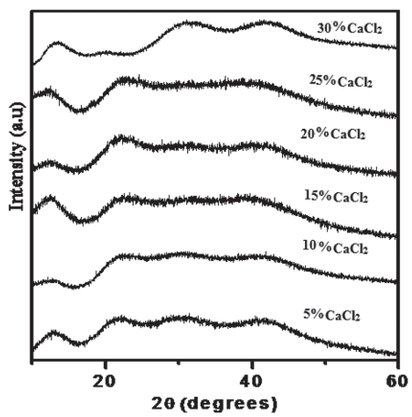

Figure 2. XRD plots of 50PVA/50PVP doped with different wt% of $CaCl_2$.

4.2. FT-IR Spectroscopy

FT-IR spectroscopy is also essential technique for the analysis of bond formation in the polymer structure, since it presents in sequence about the complexation and interactions between the various constituents in the polymer materials. The IR spectra of 50PVA:50PVP blend with different wt% of $CaCl_2$ are shown in Figure 3. The vibration band around 1645 cm^{-1} relates to the C═O stretching of PVP[14] and there is no shift for various compositions of $CaCl_2$ with the Polymer blend electrolyte. C–H asymmetric stretching of CH_2 showed an transmission band at 2934 cm^{-1} decrease in its intensity and disappears, and for 30 wt%. In all the compositions, the bands at 1266 cm^{-1} and 1423 cm^{-1} can be predictable as C–N stretching and C–H bending vibration of PVP.[15]

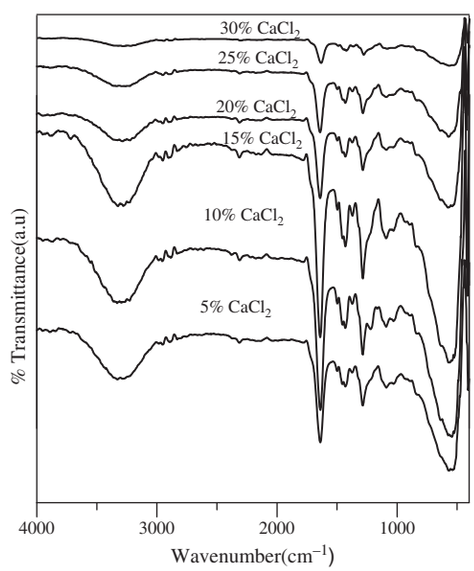

Figure 3. FT-IR spectrum of 50PVA/50PVP doped with different wt% of $CaCl_2$.

The wide band observed from the spectra in the region 3640–3000 cm^{-1} of pure PVA spectra is pertaining to the intermolecular hydrogen bonded O–H stretching in pure PVA.[16] The C–H stretching frequency of PVA is observed at 2848 cm^{-1} decrease in its intensity by the addition of $CaCl_2$ with the polymer blend. Figure 3 shows the mainly significant characterizing IR transmission band of pure PVA detected at 1428, 1078 which are ascribed as CH_2 bending, C–O stretching, respectively and decrease in its intensity by the addition of $CaCl_2$.[17,18] C–Cl stretching frequency increased by adding $CaCl_2$ and lies in the frequency range 551–581 cm^{-1}.

4.3. DSC Studies

The glass transition of different wt% of $CaCl_2$ doped PVA/PVP blend of was obtained by differential scanning calorimetry as shown in Figure 4. The samples were scanned from initial temperature (30 °C) at a rate of 10 °C/min. The exothermic peak around 130–140 °C related to the glass transition temperature (T_g) of the polymer electrolytes for all the samples. An endothermic peak was observed around 250–300 °C related to the melting point of the polymer electrolytes. The variation in the glass transition temperature, T_g of the blend with the addition of $CaCl_2$ is shown in the Figure 4. The lower values of T_g is related with the high amorphous nature of the polymer electrolyte. In the amorphous phase, there exists an improvement in the segmental motion the polymeric chain due to the flexibility of the polymer.[19]

For 30 wt% of $CaCl_2$, there exists two glass transition temperatures which indicates the crystalline nature which may corresponding to distribution of PVA and indicates the immiscibility of $CaCl_2$ with the polymer blend. At higher concentration, appeared broadness of peak is attributed to the formation of high level short range order of $CaCl_2$. The higher conductivity of the polymer blend electrolyte relates with the hydrogen bonding between PVA, PVP and $CaCl_2$.

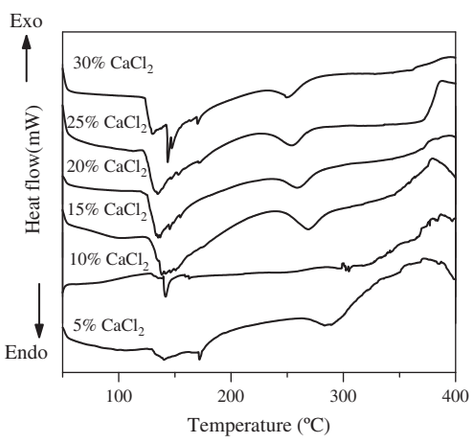

Figure 4. DSC thermograms of 50PVA/50PVP doped with different wt% of $CaCl_2$.

4.4. Electrical Conductivity Studies

The complex impedance plot of $CaCl_2$ mixed PVA/PVP at the room temperature for different wt% is given in Figures 5(a–f). This plots obtained for 5, 10 and 30 wt% of $CaCl_2$ blended with polymer showed one semicircle, which is an indication of the parallel combination of resistance and capacitance. There exist two semicircles for the compositions of 15, 20 and 25 wt% of $CaCl_2$ blended with polymer, which indicates the series of two parallel combinations of resistance and capacitance. The two semicircles obtained for the above combinations are due to the increase in the molecular packing in the PVA Chain. In XRD also, there is a starting of one hump for the concentration of 15, 20, 25 wt% of $CaCl_2$.

The intercept on the real axis at the lower frequency end of the semicircle in cole–cole plot predicts the bulk resistance of the polymer electrolyte. By measured bulk resistance from Figure 5, the electrical conductivity of $CaCl_2$ mixed polymer blend electrolytes is calculated using the method $\sigma = l/R_b A$, where 'l' the thickness of the film, 'A' the area of the film and R_b the bulk resistance of the material.

4.5. Conductance Spectra Analysis

The distinctive plots between $\log \omega$ and $\log \sigma$ of the polymer blend electrolyte 50PVA:50PVP:$X$$CaCl_2$ ($X = 5$ wt%, 10 wt%, 15 wt%, 20 wt%, 25 wt% and 30 wt%) at room temperature and 50PVA:50PVP:15 wt% $CaCl_2$ polymer blend electrolyte at different temperatures have been shown in Figures 6 and 7, respectively. The plots have three defined regions. The low frequency dispersion region (I region) is the corresponding to the overcrowding of ions between the electrode and the electrolyte. The region II lies in the mid frequency known as the plateau region corresponding to the bulk conductivity. The region III is known as the high frequency dispersion region.

4.6. Temperature Dependent Ionic Conductivity

The activation energies were measured from plots between $\log \sigma$ versus $1000/T$ (Fig. 8) using the Arrhenius relation.

$$\sigma = \sigma_0 \exp(-Ea/kT)$$

where σ is a constant, Ea is the activation energy, K is the Boltzmann constant and T is absolute temperature.

Activation energies for $CaCl_2$ doped Polymer blends were calculated from Arrhenius plots (Fig. 8) drawn between the Conductivity versus Temperature ($\log \sigma$ vs. $1000/T$) and were presented in Table I. From Figure 8, it is confirmed that there is a gradual increase in conductivity with temperature, indicating the completely amorphous structure of polymer electrolyte.[20] The flexibility of the chain increased in the amorphous phase.[21,22] With the increase in temperature, the vibrational energy is produced surrounding its own volume of a segment is adequate to

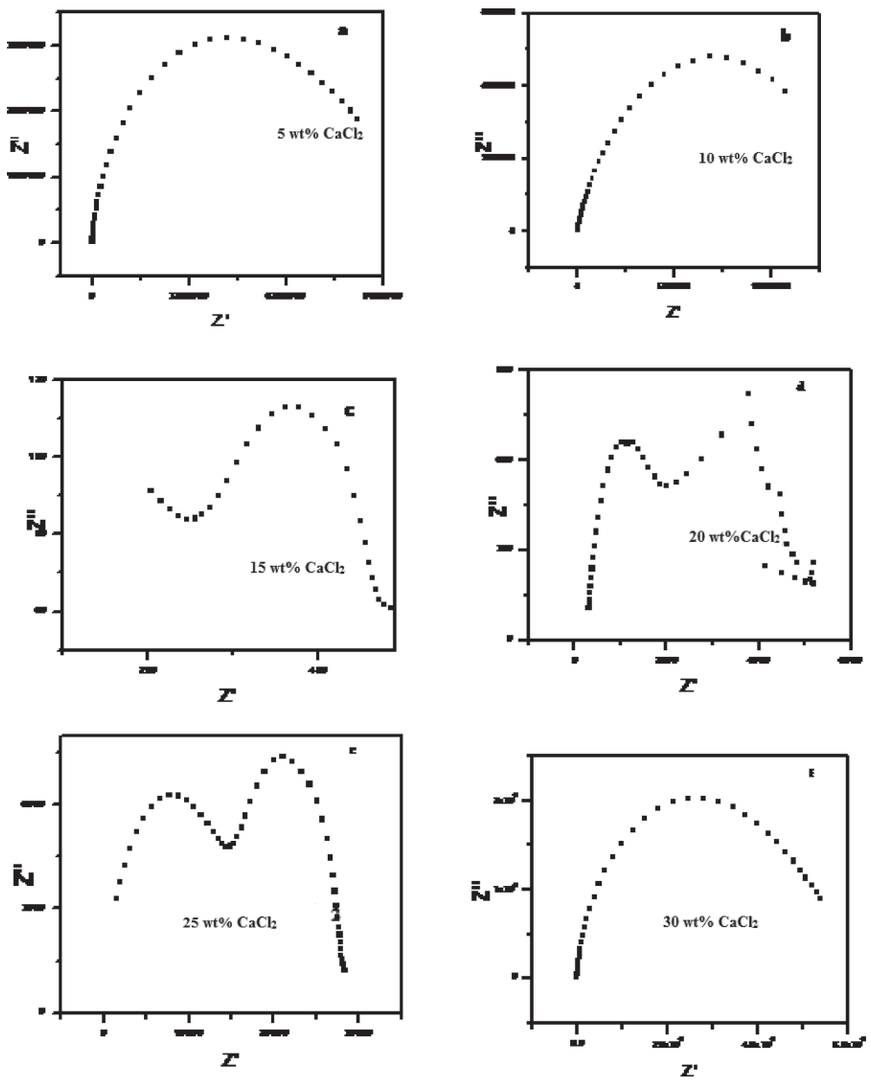

Figure 5. (a–f) Cole–cole plots of 50PVA/50PVP doped with different wt% of $CaCl_2$.

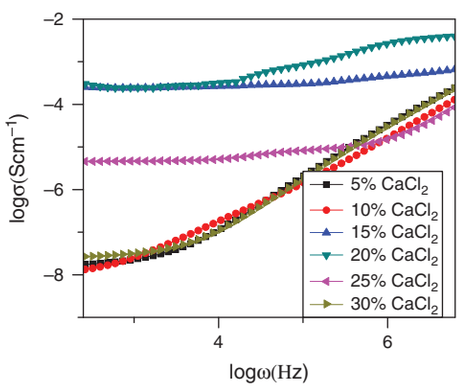

Figure 6. Conductance spectra of 50PVA/50PVP doped with different wt% of $CaCl_2$.

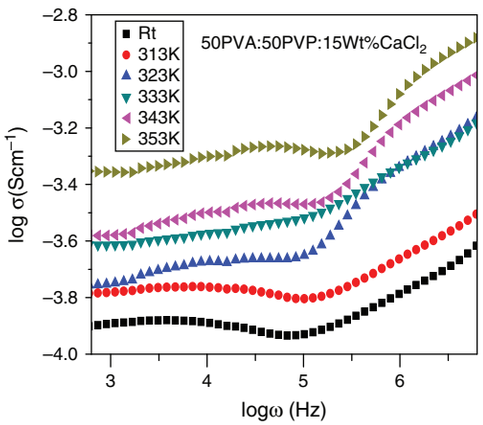

Figure 7. Conductance spectra of 50PVA/50PVP doped with 15 wt% of $CaCl_2$ at different temperatures.

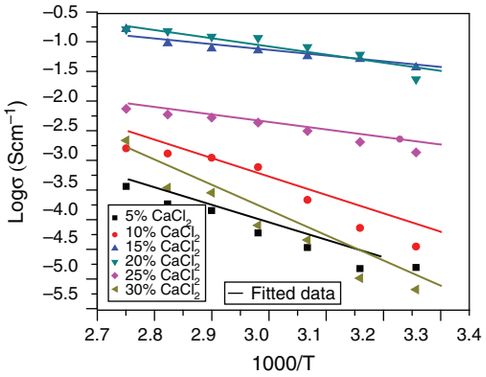

Figure 8. Temperature dependence of ionic conductivity PVA/PVP/$CaCl_2$ polymer blend electrolytes with different compositions.

push against the hydrostatic pressure imposed by its neighboring atoms. The free volume around the polymer chain increases and thereby the mobility of ions and conductivity increases. It was observed that (PVA + PVP + 15 wt%) had highest conductivity and lowest activation energy when compared to the other samples.

4.7. Concentration-Dependent Conductivity

From the Figure 9(a), it is shown that up to 15 wt%, the ionic conductivity increases and then decreases at higher salt concentrations. The Figure 9(b) presents the variation of conductivity with glass transition temperature. The increase in the conductivity is mainly due to mobility of the charge carriers. The $CaCl_2$ salt is evenly distributed in the materials, which is showed in the XRD results. The decrease in conductivity at higher salt concentrations is due to the formation of ion multiples. For 15 wt% salt-doped system, the highest conductivity is reliable with the lowest T_g of DSC results.

Table I. Conductivity, T_g, and activation energy of the 50PVA/50PVP blend with different weight percentages of $CaCl_2$.

Composition	σ from the conductance spectra (Scm^{-1})	σ from cole–cole plot (Scm^{-1})	Glass transition temperature (°C)	Activation energy (eV)
50PVA/50PVP/ 5 wt.% $CaCl_2$	5.16×10^{-8}	2.161×10^{-8}	144	0.6455
50PVA/50PVP/ 10 wt.% $CaCl_2$	2.74×10^{-6}	24.744×10^{-6}	141	0.6137
50PVA/50PVP/ 15 wt.% $CaCl_2$	1.704×10^{-4}	1.736×10^{-4}	133	0.2004
50PVA/50PVP/ 20 wt.% $CaCl_2$	3.01×10^{-5}	3.114×10^{-5}	135	0.2645
50PVA/50PVP/ 25 wt.% $CaCl_2$	4.50×10^{-6}	1.56×10^{-6}	138	0.2871
50PVA/50PVP/ 30 wt.% $CaCl_2$	2.19×10^{-8}	8.742×10^{-8}	145	0.8861

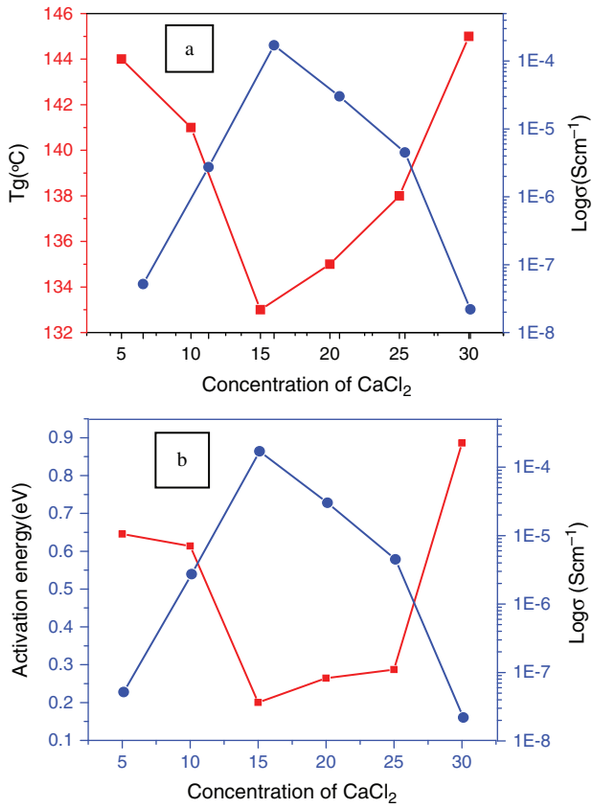

Figure 9. (a) Variation of conductivity and glass transition temperature as a function of different weight percentages of $CaCl_2$ concentration. (b) Variation of conductivity and activation energy as a function of different weight percentages of $CaCl_2$ concentration.

4.8. Dielectric Studies

Dielectric permittivity analysis is used to estimate the storage of charge by polymeric material. Dielectric study is performed to confirm the enhancement of ionic conductivity due to the increment in mobility. The dielectric permittivity of polymer electrolyte is determined by means of following equation.

$$\varepsilon^* = \varepsilon' - j\varepsilon''$$

where ε' and ε'' denotes the dielectric constant and dielectric loss of the system. Figure 10(a) shows the frequency dependence of dielectric constant ε' at various temperatures and Figure 10(b) shows the frequency dependence of dielectric loss ε'' at various temperatures for PVA/PVP/$CaCl_2$ polymer blend electrolytes.

It is well known from the figure that ε' value increases sharply at lower frequencies region. The increase in ε' at lower frequencies is due to improvement of charge carrier density in the space charge accumulation region which is also known as non Debye type of behavior.[23–25] The value of ε' decreases at higher frequencies, due to the high periodic replacement of the applied electric field at the electrolyte-electrode interface. There is no excess ion transmission in the direction of the electric field.

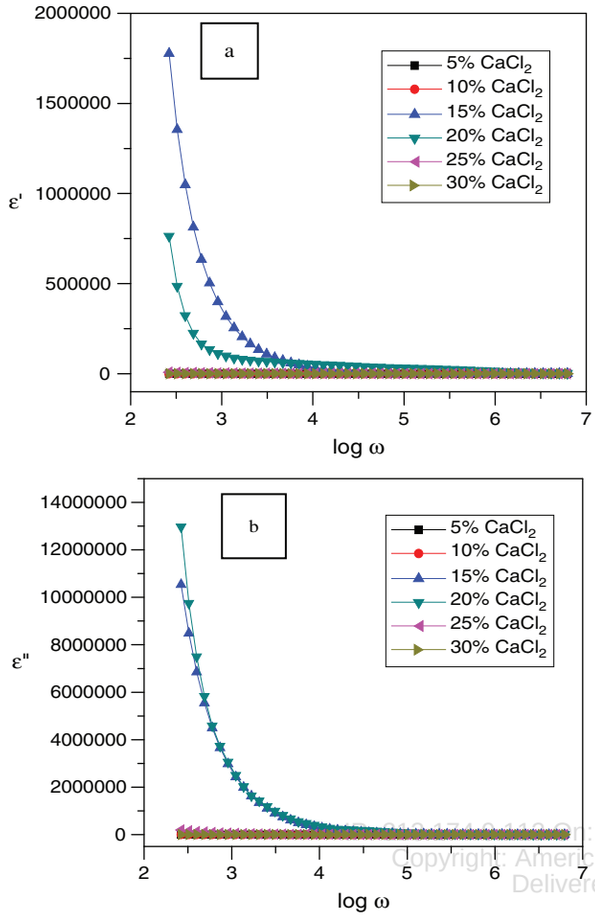

Figure 10. (a) Dielectric constant ε' versus $\log \omega$ for PVA/PVP/$CaCl_2$ polymer blend electrolytes with different compositions. (b) Dielectric loss ε'' versus $\log \omega$for PVA/PVP/$CaCl_2$ polymer blend electrolytes with different compositions.

4.9. Modulus Analysis

Figures 11 and 12 show that the frequency dependence real and imaginary part of the modulus for 50PVA:50PVP: 15 wt% $CaCl_2$ polymer blend electrolyte at different temperatures. Electric modulus M^* defined in terms of the reciprocal of the complex relative permittivity ε^*, i.e.,

$$M^* = 1/\varepsilon^* = M' + iM''$$

The real and imaginary parts of the dielectric modulus is given by

$$M' = \varepsilon'/\varepsilon'^2 + \varepsilon''^2$$

$$M'' = \varepsilon''/\varepsilon'^2 + \varepsilon''^2$$

The real and imaginary parts of the modulus come close to zero at low frequencies, representing the negligible contribution of electrode polarization. The extended tail at lower frequencies is appeared due to the connection of large capacitance with the electrode. The height of the peak (M'') decreases with the increase in temperature symptomatic of a majority of relaxation mechanisms.

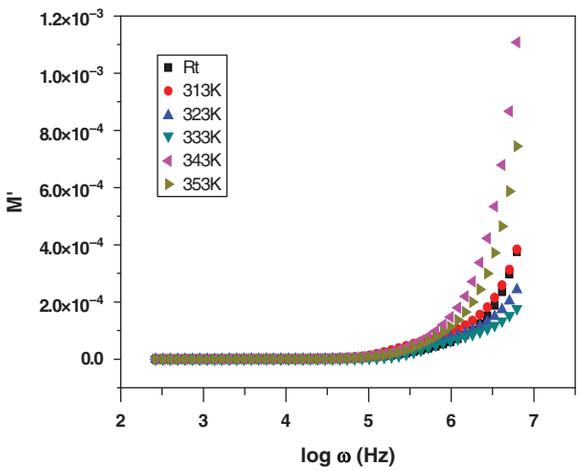

Figure 11. Variation of real part $M'(\omega)$ for 50PVA:50PVP:15 wt% $CaCl_2$ polymer blend electrolyte at different temperatures.

4.10. Transference Number Measurement

Transference number tells about the contribution of ions and electrons for the overall transport across the cell. DC polarization techniques are used to find the ionic (t_{ion}) and electronic (t_{ele}) transport number for PVA:PVP:$CaCl_2$ polymer blends electrolyte systems and shown in Table II. In this technique, the variation of the dc current with time by applying fixed dc voltage across the sample using stainless steel blocking electrodes. The result of dc polarization measurement on 50PVA:50PVP:$X$$CaCl_2$ ($X = 5$, 10, 15, 20, 25, 30 wt%) polymer electrolytes is shown in the Figure 13.

The transference numbers are calculated by using the current versus time plot.

$$t_{ion} = (I_i - I_f)/I_i$$

$$t_{ele} = I_f/I_i$$

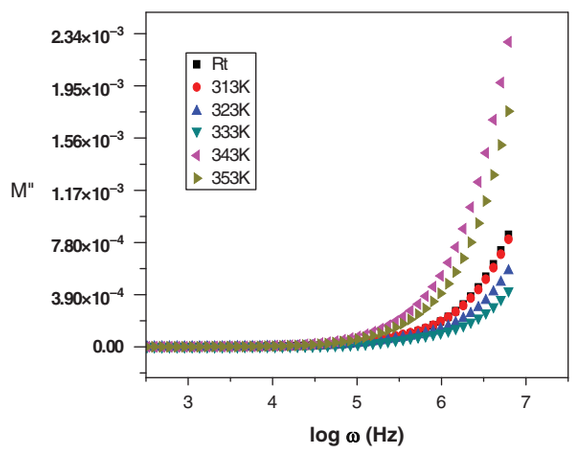

Figure 12. Variation of real part $M''(\omega)$ for 50PVA:50PVP:15 wt% $CaCl_2$ polymer blend electrolyte at different temperatures.

Table II. Variation of composition versus transference number.

Composition	Transference number
50PVA:50PVP:5 wt% $CaCl_2$	0.98
50PVA:50PVP:10 wt% $CaCl_2$	0.99
50PVA:50PVP:15 wt% $CaCl_2$	0.95
50PVA:50PVP:20 wt% $CaCl_2$	0.99
50PVA:50PVP:25 wt% $CaCl_2$	0.93
50PVA:50PVP:30 wt% $CaCl_2$	0.99

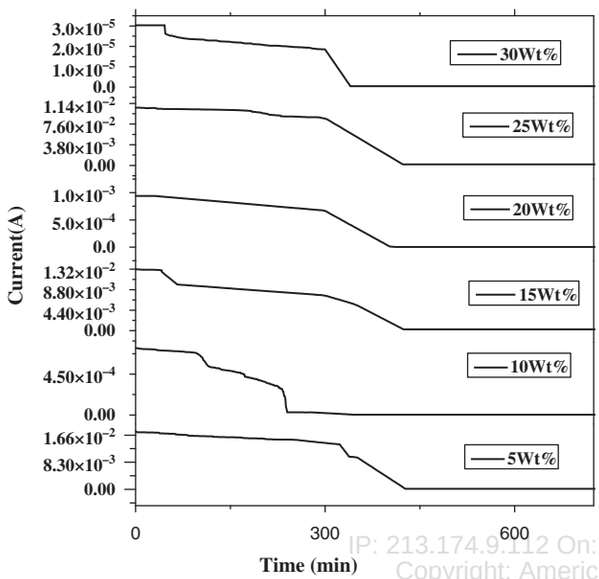

Figure 13. Current versus time plots for PVA/PVP/$X$$CaCl_2$ polymer electrolytes.

I_f is the final current and I_i is the initial current. For all the prepared electrolytes, the ionic transference number is in the range of 0.9. By this, it is confirmed that the charge transport is mainly due ions.

5. CONCLUSIONS

The $CaCl_2$ doped polymer electrolytes based on PVA:PVP were prepared using solution cast technique. The XRD pattern of the prepared polymer electrolytes reveals the increase in the amorphous nature with the addition of the salt. The complexation of the salt was confirmed from FT-IR analysis. The composition of PVA:PVP:15 wt% $CaCl_2$ showed the highest ionic conductivity (1.736×10^{-4} S cm^{-1}) and low activation energy (0.25 eV). From the thermal analysis, it is confirmed that PVA:PVP:15 wt% $CaCl_2$ polymer electrolytes have a low glass transition temperature. The ionic conductivity increases with the increase in the concentration as well as temperature. The decrease in dielectric constant with frequency is an indication of polar nature of the material. The ionic transference number measurement indicates the major contribution of charge transport is mainly due to ions.

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