Impedance spectroscopy and conductivity studies of CdCl₂ doped polymer electrolyte

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ABSTRACT

Polyvinyl alcohol (PVA) and Polyvinyl Pyrrolidone (PVP) based polymer electrolytes for different loading wt% of CdCl₂ were prepared by solution casting. The structural complexation was confirmed and interlayer spacing (d) was evaluated by using X-ray diffraction (XRD) study. The chemical bonding between polymer and salt was identified by using Fourier transform infrared spectroscopy (FTIR) technique. The FTIR peak at 3402.43 cm^{-1} in addition of PVP in PVA/CdCl₂ composite demonstrates the grafting between two polymers. The presence of ionic bright channels and variation in morphology for different loading wt% of CdCl₂ was confirmed by scanning electron microscope (SEM) and was also verified by Atomic force microscopy (AFM) micrographs. The analysis of impedance spectroscopy represented by semicircular pattern is driven by conduction mechanism and correlated with electrical conductivity. The enhanced AC conductivity of polymer electrolyte is directly proportional to frequency (50Hz-1MHz). The maximum value of DC conductivity 1.65×10^{-5} S/m evaluated from Arrhenius plots and attribute to high mobility of free charges at higher temperature. The evaluated results of structural, morphological and electrical properties of present composites make the present research good for electrochemical devices. Copyright © 2015 VBRI press.

Keywords: Impedance spectroscopy; AC and DC conductivity; XRD; FTIR; SEM; AFM.

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Introduction

Polymers are highly useful for several applications such as batteries, fuel cells, electrochemical display devices, photo electrochemical cells and sensors due to easy fabrication, leak proof, biodegradability and good storage capacity [1-3]. Researchers mainly focus on the preparation of polymer blend or polymer composite films. The modification of several single or multi polymer systems has been reported to achieve the compatibility for feasible applications [4, 5]. PVA and PVP polymers are being selected for present research on the basis of its on mono solvent criteria [6-8]. PVA is a semi crystalline polymer and has various interesting properties such as glossy nature, adhesive and easy film forming compactable for various applications [9]. Whereas, *PVP* draws a special attention amongst the other polymer because of its excellent wet and readily film forming property [10]. PVP presents a remarkable combination of useful properties such as toxicological safeness, transparency and gloss, chemical/biological inertness, crosslink ability and long lasting adhesion which makes it a unique polymer [11].

In the previous year's various ionic entities (CO^{2+}, Cu^{2+} and Nafion), salts (CH_3COONa), transition metal ($NiCl_2$), pizo-ceramics filler ($PbTiO_3$) was used to modify PVA/PVP polymer system for various applications [12-14]. In present study $CdCl_2$ was doped in PVA and PVA/PVP at various concentrations. $CdCl_2$ is a white crystalline compound which is a combination of cadmium and chloride. It is highly soluble in water and lightly soluble in alcohol, hence called hygroscopic solid. It is also used for different applications such as photocopying, dying and electroplating [15, 16]. The present study is focused on structural, morphological and electrical properties polymer electrolytes and was performed by using XRD, FTIR, SEM, AFM and impedance spectrum technique respectively. The conductivity of electrolyte was measured using ac impedance technique at varying range of temperature (393 – 423 K). The main objective of present study is to prepare the single and multi polymer composite and disclosed its structure, morphology, electrical performance which is feasible for electrolytes domain. The comparative study of divalent ion composed with single and multi polymer system reveals the advantages in view of high performance electrical properties.

Experimental

Materials

The $CdCl_2$ doped polymer electrolytes were prepared by solution casting method. A PVA white granule (MW 1, 25,000, laboratory research grade with degree of hydrolysis 86-89%) was procured from SD fine chem. limited, Mumbai, India. $CdCl_2$ compound (MW 228.35, make Thomas Baker, Mumbai, India) was used as a dopant in a ratio of 5, 10 and 15 wt% loading. *PVP* used as a copolymer of MW 10,000 AR grade was procured from Sigma Aldrich, India.

Sample preparation

The synthesis of polymer electrolyte was initiated by dissolving PVA and $CdCl_2$ in distilled water and obtained homogeneous solution by stirring (500 rpm) at 60^oC for 1 h. Then the mixed solution was poured in the petri dish kept at room temperature (40^oC) for 12 h. The PVA/$CdCl_2$ composite films of 20μm thickness were peeled off. Thereafter equal amount *of PVP* a copolymer was mixed in PVA/$CdCl_2$ mixture and stir (500 rpm) at 60^oC for 1 h. Then the solution poured in the petri dish at room temperature (40^oC) for 12 h. The PVA/PVP/$CdCl_2$ composite films were peeled off and used for further characterization. The schematic representation of $CdCl_2$ doped single and multi polymer composite films is shown in **Fig. 1**.

Structural characterization

The X-ray diffraction of polymer composite films were carried out by using Cu Kα radiation of wavelength λ = 1.54060 Å produced by Bruker AXS D8 focus advance X-ray diffraction meter (Rigaku, Japan, Tokyo) with 'Ni-filtered'. The scans were taken in the 2θ range from 10°-80° with a scanning speed and step size of 1°/mm and 0.01^o respectively. The chemical structure of PVA/$CdCl_2$ and PVA/PVP/$CdCl_2$ composite films was characterized by FTIR spectroscopy (make Shimadzu-IR Affinity-1 spectrometer) in the wave number range of 500 - 4000 cm^{-1} operated in a transmittance mode.

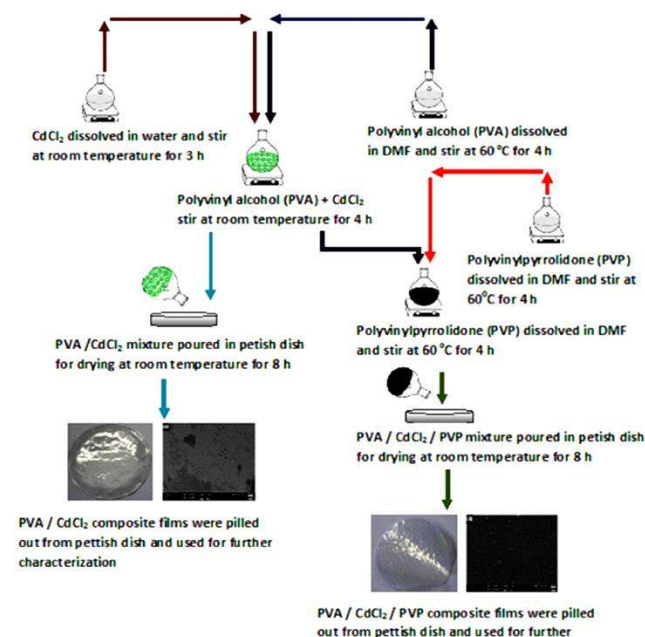**Fig. 1.** Protocol for $CdCl_2$ doped single and multi polymer composite films.

Morphological characterization

Morphological analysis of $CdCl_2$ doped single and multi polymer composite films were carried out by using Ultra high resolution, Zeiss electron microscope (SEM). The images were obtained with an acceleration voltage of 20 kV. AFM micrographs were obtained by NanoSurf EasyScan2 AFM instrument (Switzerland) operating in the air at 25^oC. The PicoView 1.10 software version was used for simultaneous recording of the topographical images of the samples.

Electrical characterization

The electrical properties were characterized by demonstrating impedance spectrum and conductivity of composite films. The electrical parameters of CdCl$_2$ doped PVA and PVA/PVP composite films (size 50 µm) were evaluated under varying range of temperature (40°C to 150°C) and frequency (50 Hz to 1 MHz) using a PSM-1735 impedance analyzer.

Table 1. XRD data analysis of (a) 95:5, (b) 90:10, (c) 85:15 of PVA/CdCl$_2$ and (d) 47.5:47.5:5, (e) 45:45:10 and (f) 42.5:42.5:15 of PVA/PVP/CdC l$_2$.

Sample	θ	Sin θ	d (Å)
a	9.475	0.1646	4.678
b	9.402	0.1633	4.715
c	9.402	0.1633	4.715
	9.615	0.1670	4.610
d	14.619	0.2523	3.051
	20.394	0.3484	2.210
e	9.681	0.1681	4.570
f	9.480	0.1647	4.670
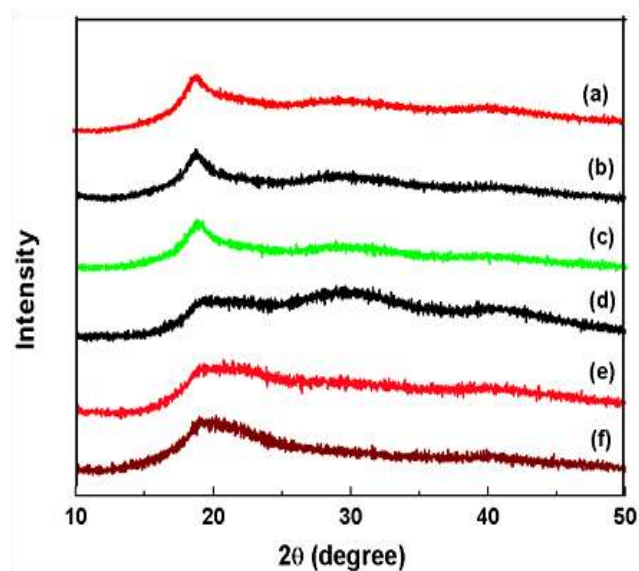
Fig. 2. XRD spectra for (a) 95:5, (b) 90:10, (c) 85:15 of PVA/CdCl$_2$, (d) 47.5:47.5:5, (e) 45:45:10 and (f) 42.5:42.5:15 of PVA/PVP/CdC l$_2$.

Results and discussion

XRD analysis

Analysis of XRD patterns for CdCl$_2$ doped single and multi polymer composites are obtained from **Fig. 2**. The major peaks for single polymer system is obtained at 2θ = 18.93° and slightly vary after adding various concentration of CdCl$_2$ as shown in **Fig 2** (**a-c**). The peak is assigned to the interlayer spacing (d) in addition of CdCl$_2$ in single polymer system. The interlayer spacing is directly proportional to the concentration of CdCl$_2$ in single polymer system as shown in **Table 1**. This result indicates the increase in degree of crystallinity. The increase in crystallinity with respect to loading wt% of CdCl$_2$ could be due to intercalation between salt and polymer. Whereas in addition of PVP in PVA/CdCl$_2$ system, there are certain other broad peaks are obtained at 2θ = 19.2° as shown in **Fig. 2** (**d-f**). The interlayer spacing increases with respect

to loading wt% of PVP in multi polymer system and tabulated in **Table 1**. The broad peaks obtained for multi polymer systems are described the amorphous nature of CdCl$_2$ doped multi polymer composites. Hence, increase in amorphous nature also provides the good conductivity results for polymer electrolytes. Hence the XRD analysis reveals the change in amorphous to crystalline phase of CdCl$_2$ doped single and multi polymer composites. Therefore the good conductivity results are obtained for multi polymer composite in comparison to single polymer composites.

Table 2. Comparative FTIR peaks assignment of PVA/CdCl$_2$ composite films.

PVA/CdCl$_2$ peaks (c.m^{-1})	Peak assignment
1714.72 - 1689.52	OH bending(absorbed water)
1421.54	C=C stretching
1251.80	COOH, acrylic acid
1226.73	C-O stretching
1138.00	C-O-C stretching

Table 3. Comparative FTIR peaks assignment of PVA/PVP/CdCl$_2$ composite films.

PVA/PVP/CdCl$_2$ peaks (c.m^{-1})	Assignment
3402.43 – 3277.06	Intermolecular OH stretching
1732.08	C-O, poly(acrylic acid)
1678.07	C=O stretching
1629.85-1620.21	OH bending
1494.83-1463.97	C=C stretching, poly(4-vinyl pyridine)

FTIR analysis

FTIR is an effective and essential characterization that determines the chemical compositions, chemical interaction and it also follows the variation in functional group during reaction [17]. In this study PVA and PVP polymers are used, where PVA contains hydroxyl group and PVP contains the carbonyl group. Therefore, the miscibility between PVA and PVP was confirmed by FTIR. The FTIR spectrum of CdCl$_2$ doped PVA and PVA/PVP polymer composites are shown in **Fig. 3** which demonstrates the shift in peak position as well as the change in shape and intensity. The comparative peak assignment is highlighted in **Table 2**. The intermolecular -OH bending (absorbed water) (1714.72-1689.52 c.m^{-1}), C=C stretching (1421.54 c.m^{-1}), COOH, acrylic acid (1251.80 c.m^{-1}), C-O stretching (1226 c.m^{-1}), C-O-C stretching (1138 c.m^{-1}) was observed as a function of wave numbers. Similarly, **Fig. 3(d-e)** represents the FTIR spectrum of PVA/PVP polymer composites for 5, 10 and15 wt % loading of CdCl$_2$. The shift in FTIR peaks for multi polymer composite is tabulated in **Table 3**. The intermolecular OH stretching (3402.43-3277.06 c.m^{-1}), C-O poly (acrylic acid) (1732.08 c.m^{-1}), C=O stretching (1678.07 c.m^{-1}), OH bending

(1629.85-1620.21 $c.m^{-1}$), C=C stretching, poly (4-vinyl pyridine) (1494.83-1463.97 $c.m^{-1}$) was determined for $CdCl_2$ doped polymer electrolyte. The major peaks (3402.43 - 3277.06 $c.m^{-1}$) was obtained in addition of PVP in $PVA/CdCl_2$ polymer system can be due to –OH stretching between two polymers. This result confirms the intercalation between polymers and $CdCl_2$.
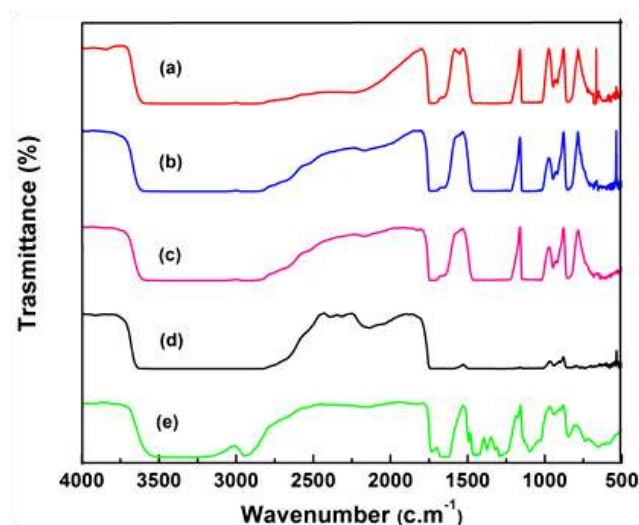

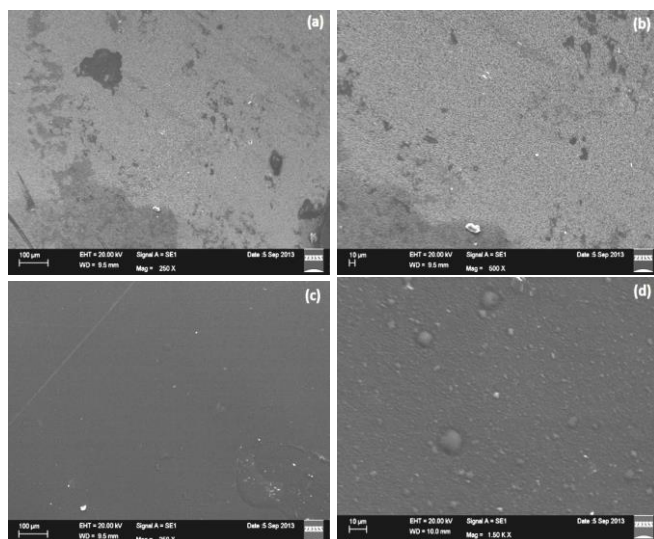**Fig. 3.** FTIR spectra (a) 95:5, (b) 90:10, (c) 85:15 of $PVA/CdCl_2$, (d) 45:45:10 and (e) 42.5:42.5:15 of PVA/PVP/CdC l_2.

Fig. 4. SEM micrographs of (a) $PVA/PVP/CdCl_2$: 95:5, (b) $PVA/CdCl_2$:: 90:10,(c)$PVA/PVP/CdCl_2$::47.5:47.5:5 and (d) $VA/PVP/CdCl_2$::45:45:10.

SEM morphology

The morphological characterization of modified polymer system is obtained by using SEM micrographs. The surface micrographs of the $PVA/CdCl_2$ and $PVA/PVP/CdCl_2$ polymer electrolytes are shown in **Fig. 4**. The uniform distribution of small bright spots on the backscattered images for 5 wt% loading of $CdCl_2$ is shown in **Fig. 4** (**a**). The bright spots present on surface are may be because of the presence of ionic entity $CdCl_2$. **Fig. 4(b)** represents the uniform smooth surface for 10 wt% loading of $CdCl_2$. The varying concentrations of CdCl2 in polymer electrolyte can also the reason for smooth surface morphology. The morphologies of multi polymer system for different loading

wt% of $CdCl_2$ are shown in **Fig. 4** (**c-d**). The multi polymer composites represents relatively smooth surface for 5 wt% loading of $CdCl_2$ than that of single polymers system as shown in **Fig. 4** (**c**). However, the rough morphology with bubble spots is obtained for increased wt% of $CdCl_2$ in multi polymer system as shown in **Fig. 4** (**d**). The morphology with rough surface for multi polymer system can be due to increased wt% of $CdCl_2$. In addition of secondary host polymer PVP in $PVA/CdCl_2$ mixture could also be the reason for the difference in morphological smoothness of single and multi polymer system. The result of SEM morphology demonstrates the miscibility state of polymer electrolytes. This can be due to proper entanglement of salt with single and multi polymers [18]. The proper miscible state of present polymer electrolyte is directly related to loading wt% of salt.
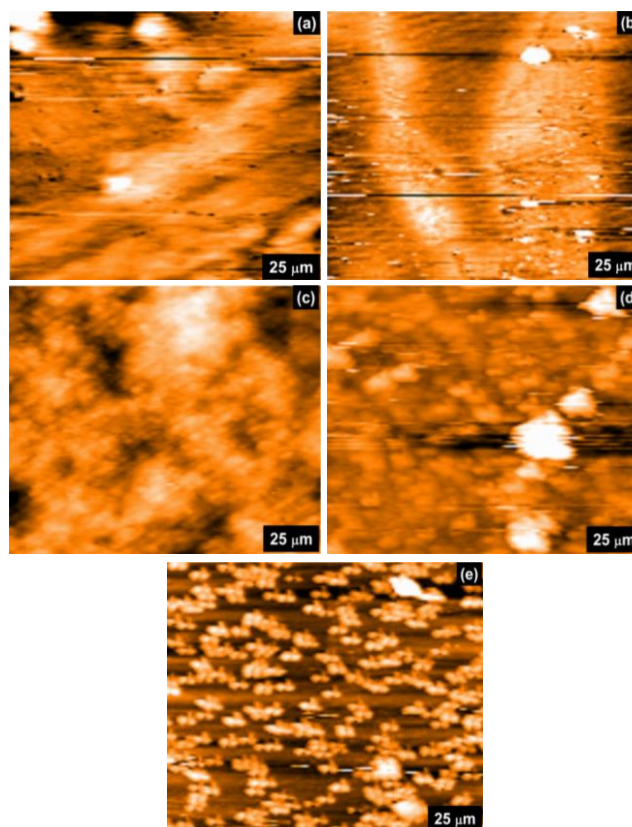

Fig. 5. AFM micrographs of (a) $PVA/CdCl_2$:: 95:5, (b) $PVA/CdCl_2$:: 90:10,(c) $PVA/PVP/CdCl_2$::47.5:47.5:5, (d) $PVA/PVP/CdCl_2$::45:45:10 and (e) $PVA/PVP/CdCl_2$:: 42.5:42.5:15.

AFM analysis

AFM is an advance surface analysis technique used for the investigation of surface morphology, nano/micro-structure of polymer composites [19]. AFM topographic images of the surface and interface of $PVA/CdCl_2$ and $PVA/PVP/CdCl_2$ composite are shown in **Fig. 5** (**a-e**). The uniform dispersion of $CdCl_2$ in PVA system is shown in **Fig. 5** (**a**). But the AFM topography for 10 wt% loading of $CdCl_2$ in single polymer system are represented by the occupied divalent cluster as shown in **Fig. 5** (**b**). The AFM micrographs of multi polymer system doped with 5 wt% of $CdCl_2$ is shown in **Fig. 5** (**c**). The smooth surface of micrographs can be due to the presence of $CdCl_2$. The

increased wt% of CdCl$_2$ in multi polymer system is represented by brighter nodules as shown in **Fig. 5** (**d**). The ionic centers (brighter in nature) are identified at X25μm resolution for higher wt% of CdCl$_2$ in multi polymer system as shown in **Fig. 5** (**e**). The AFM investigation was carried out to know the presence of ionic filler as shiny bright channels in multi polymer system with AFM which was not observed in SEM images.
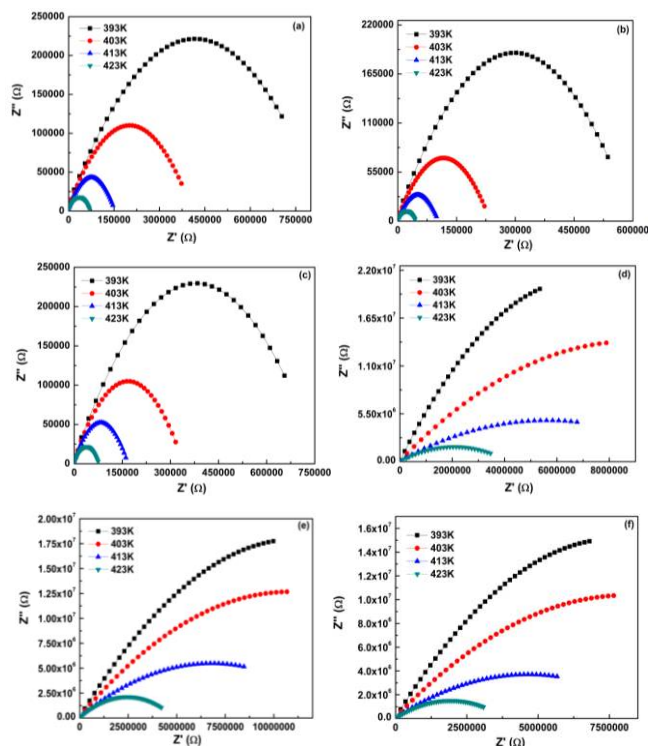

Fig. 6. Cole-Cole plot for (**a**) 95:5, (**b**) 90:10, (**c**) 85:15 of PVA/CdCl$_2$ and (**d**) 47.5:47.5:5, (**e**) 45:45:10, (**f**) 42.5:42.5:15 of PVA/PVP/CdCl$_2$ at different temperature.

Impedance analysis

The ac impedance method and electrical behavior of samples was studied over a wide range of temperature. This study enables us to separates the real and imaginary components of the complex impedance [**20, 21**]. The representation of impedance data is based on the plot of the imaginary component Z$^{''}$ versus real component Z$^{'}$. This impedance spectroscopy technique enables the real and imaginary components and hence provides the structure-property relationship of the sample. The real and complex impedance is evaluated by Nyquist plot (Cole-Cole plot) by using following formalism:

Complex Impedance:

$$Z^*(\omega) = (Z' - jZ'')$$ (1)

Where, $Z' = |Z|cos\theta$ and $Z'' = |Z|sin\theta$

The impedance spectrum (Z$^{''}$ versus Z$'$) for PVA/PVP/CdCl$_2$ at varying range of temperature is shown in **Fig. 6** (**a-f**). The complex plane of CdCl$_2$ doped polymer electrolyte represented by semicircles demonstrates the grain effect, grain boundary effect and grain electrode

effect. **Fig. 6** (**a-c**) represents the impedance spectrum for different loading wt% of CdCl$_2$ in single polymer system. The particular semicircular pattern was obtained for single polymer system because slope of the line decreases with respect to temperature and bends towards Z$'$ axis. But for PVA/PVP/CdCl$_2$ the exact semicircular pattern was not obtained as shown in **Fig. 6** (**d-f**), which represents the low DC conductivity of the prepared composites. This may be due to ionic conduction which is dominant at lower temperature. Therefore the impedance spectrum navigates the conduction mechanism.
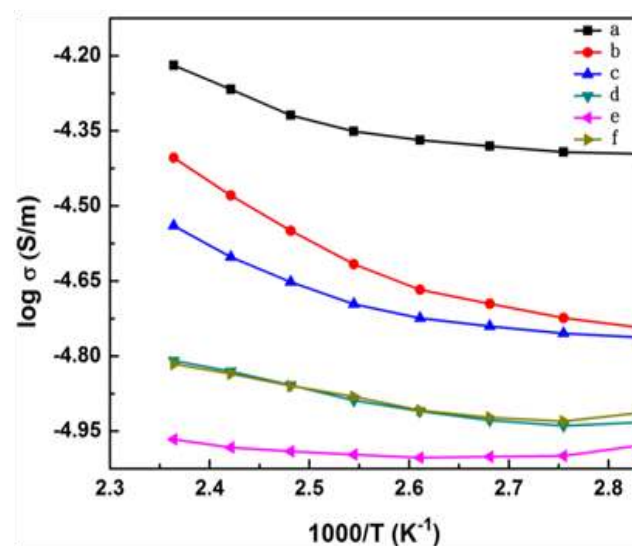

Fig. 7. Variation in DC conductivity with respect to temperature for (**a**) 95:5, (**b**) 90:10, (**c**) 85:15 of PVA/CdCl$_2$ and (**d**) 47.5:47.5:5, (**e**) 45:45:10, (**f**) 42.5:42.5:15 of PVA/PVP/CdCl$_2$.

Temperature dependence conductivity analysis

An electrical property of polymer composite films depends on the concentration of dopant [**6, 22**]. The DC conductivity of the polymer electrolyte samples is examined by using the equation:

$$\sigma_{dc} = l/R_b A$$ (2)

Where, σ_{dc} is the conductivity, l is the thickness of the sample, A is the area of the sample and R$_b$ is the bulk resistance. The bulk resistance of sample was obtained from impedance spectroscopy. The DC conductivity of PVA/CdCl$_2$ and PVA/PVP/CdCl$_2$ composite films was evaluated by using impedance spectrum. The variation in DC conductivity as a function of temperature is shown in **Fig. 7**. The highest DC conductivity (1.67x10^{-5} S/m) was evaluated for 10 wt% loading of CdCl$_2$ in single polymer system at 150°C is shown in **Fig. 7**. The decrease in conductivity with respect to temperature is shown in **Fig. 7**. The rate of flow of electrons is hampered due to polymer chain density and the mobility charge carrier's increases in the composite film. The increased value of conductivity can also be explained by the fact that polymer chains in composite are fully rearranged by heating and also allows a high flowing rate of electrons. **Fig. 7** (**d-f**) represents that in addition of PVP in PVA/CdCl$_2$ the DC conductivity decreases with temperature. This may be due to strong

intercalation between both PVA and PVP polymer which does not get disturbed by heating and it offers mobility of charge carriers only at lower temperature. Hence, this investigation demonstrates that the PVA/CdCl2 polymer electrolyte represents the conducting behavior at high temperature and PVA/PVP/CdCl2 polymer electrolyte behaves as conductor at lower temperature.
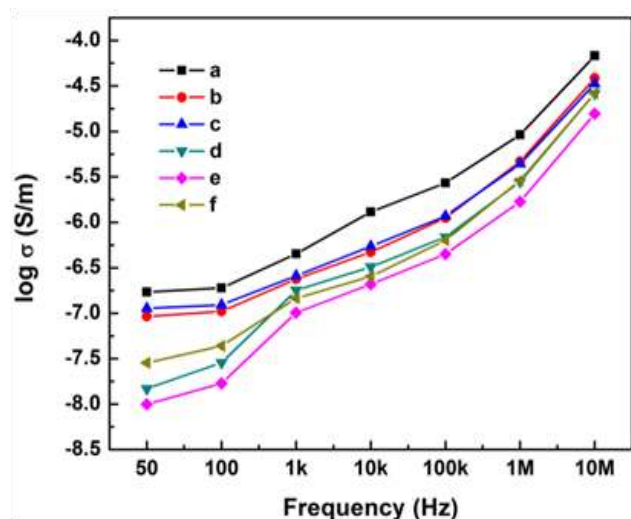

Fig. 8. Frequency dependence of AC conductivity of PVA/CdCl2 and PVA/PVP/CdCl2 with respect to Frequency at different concentration (**a**) 95:5, (**b**) 90:10, (**c**) 85:15 of PVA/CdCl2 and (**d**) 47.5:47.5:5, (**e**) 45:45:10, (**f**) 42.5:42.5:15 of PVA/PVP/CdCl2.
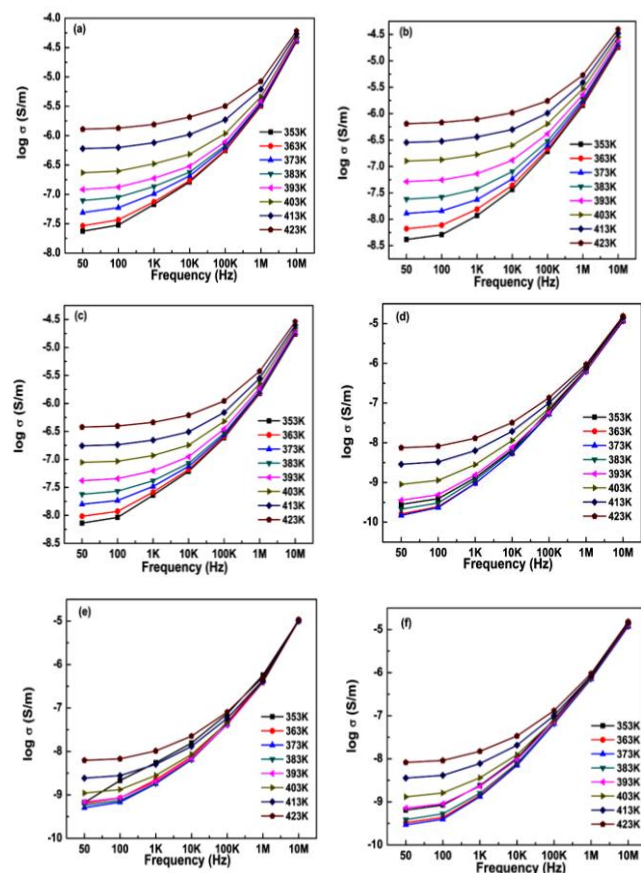
Fig. 9. Frequency dependence of AC conductivity at different temperature for (a) 95:5, (b) 90:10 (c) 85:15 of PVA/CdCl2 and (d) 47.5:47.5:5, (e) 45:45:10, (f) 42.5:42.5:15 of PVA/PVP/CdCl2.

Frequency dependence AC conductivity analysis

The increase in conductivity with respect to frequency and temperature is a common respond for polymeric and semiconductor samples [23]. The values of AC conductivity are approximately same as the DC conductivity at lower temperature it is because of tremendous increase in mobility of charge carriers in the composite films. The frequency dependant conductivity σ_{ac} for different loading wt% of CdCl2 in single and multi polymer composite is shown in **Fig. 8**. The AC conductivity of polymers is strongly dependant on the structural disorder of samples and doping procedure [24-26]. The highest conductivity for CdCl2 doped single polymer composite was obtained at higher frequency as shown in **Fig. 8** (**a-c**). This can be due to small polaron hopping in the present samples [27, 28]. The conductivity of CdCl2 doped single polymer composites increases with respect to applied frequency which is due to hopping of charges [29, 30]. In addition of PVP in PVA/CdCl2 polymer composite, the conductivity increases as a function of frequency as shown in **Fig. 8** (**d-f**).

In present study the AC conductivity of CdCl2 doped single and multi polymer system was also evaluated with varying function of temperature and frequency. The AC conductivity of CdCl2 doped PVA and a PVA/PVP polymer composite is shown in **Fig. 9** (**a-f**).

The evaluated value of AC conductivity represents a regular change with respect to frequency. The drastic variation in AC conductivity value of CdCl2 doped single polymer system was observed as a function of temperature. However, the highest conductivity was obtained at lower temperatures in addition of PVP with single polymer system. The conductivity value decreases in addition of PVP with single polymer system with respect to temperature can be due to reduction in hopping [31, 32]. The conductivity is more sensitive at higher temperature regime for CdCl2 doped single polymer composite film and at lower temperature regime for multi polymer composites. The conductivity at lower temperature can be due to bipolar hopping mechanism whereas the conductivity at higher temperature is because of thermally activated single polaron hopping [33-35]. Therefore the CdCl2 doped single and multi polymer composites represents better conductivity response for temperature as well as for frequency.

Conclusion

The multi polymer PVA and PVA/PVP based polymer composite with different loading wt% of CdCl2 were synthesized by solution casting method. The structural characterization and chemical composition of polymer electrolytes were investigated on the basis of XRD and FTIR spectrum respectively. The phase separation and roughness of composite films was determined by AFM in presence of CdCl2 in single and multi polymer system. SEM morphology represents the presence of ionic entity and also revealed the proper entanglement between salt and polymers. The maximum value of DC conductivity 1.65×10^{-5} S/m was obtained for 10 wt% loading of CdCl2 at 150°C. The ac impedance spectra implies for investigating different electrical parameters of polymer electrolyte. The

increased value of DC conductivity as a function of temperature is driven by free movement of mobility charge carriers. The DC and AC conductivity are almost same at lower temperature because of rapid increment of the mobility charge carriers in composite. Hence the present study demonstrates that the change in conductivity value depends on concentration of salt as well as on different polymeric system. Therefore the result obtained from various characterizations performed for present polymer electrolytes suggest it for the development of different electrochemical applications.

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