

Synthesis and Characterization of PVP: PVC: NH_4NO_3

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ABSTRACT

Polymer blending is one of the most important methods used to obtain new polymeric materials and it is a useful technique for designing electrolyte materials with required modifications in the properties such as electrical, thermal and mechanical. PVP-PVC blend membrane doped with different molar weight percentage of Ammonium nitrate has been prepared by solution casting technique using DMF as solvent. XRD, FTIR, DSC and AC impedance studies have been made for the above membrane. XRD studies revealed that amorphous nature of PVP has been increased in 70%PVP: 30%PVC. It is also observed that the amorphous nature of 70%PVP: 30%PVC is further increased on addition of different concentration of NH_4NO_3 . A complex formation of PVP: PVC, PVP: PVC: NH_4NO_3 have been confirmed by FTIR studies. Proton conductivity for above film has been measured using impedance spectroscopy. Undoped blend polymer 70%PVP: 30%PVC showed an ionic conductivity of $8.46 \times 10^{-8} \text{Scm}^{-1}$. The conductivity of the blend film increases as concentration of NH_4NO_3 increases. The maximum proton conductivity $3.42 \times 10^{-4} \text{Scm}^{-1}$ has been observed for 70%PVP: 30%PVC: 0.3 Molar weights (Mwt) of NH_4NO_3 . Dielectric and modulus behaviours have been studied for the above membrane.

Keywords: PVP, Proton conducting, DMF, conductivity analysis, Electrolyte, Relaxation frequency.

INTRODUCTION

Proton transport in solids involved more attention because of its potential use in energy devices such as fuel cell, batteries and chemical sensors. Several fast protonic conductors, organic or inorganic, crystalline and amorphous have been prepared during the past three decades^{1,2,3,4}. Many methods are available to increase conductivity, such as cross-linking two

polymers, adding plasticizers to polymer electrolytes, adding inorganic inert fillers, and blending two polymers⁵. The polyvinyl pyrrolidone (PVP) and polyvinyl chloride (PVC) were selected for the present work. From the polymers, PVP is a vinyl polymer having planar and highly polar side groups due to the peptide bond in the lactam ring⁶. It is an amorphous polymer and having high glass transition temperature (T_g) because of the presence of the rigid pyrrolidone group, which is strong at drawing polar group and is known to form various complexes with other polymers. PVC can act as a mechanical stiffener in the electrolyte due to its miscibility with the plasticizer. A literature survey reveals that conductivity study on PVP/PVC blend with ammonium salts is scarce.

The objective of this study is to prepare 70%PVP:30%PVC with different weight percentage (wt%) of NH₄NO₃ and characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC) and AC impedance spectroscopy.

Experimental technique

Films of pure PVP with PVC in the molar ratio 90:10, 80:20, 70:30, 60:40 have been prepared by solution cast technique using DMF as the solvent. The conductivity has been studied for the above films. From above compositions, 70:30 ratios have better conductivity compared to other ratios. Hence 70%PVP: 30%PVC have been chosen for the present study.

Films of pure PVP, 70%PVP: 30%PVC and films of 70%PVP: 30%PVC with Ammonium Nitrate in the molar ratios 0.1, 0.2, 0.3 have been prepared by solution cast technique using DMF as a solvent. The film of 70%PVP: 30%PVC: 0.4Mwt% and 0.5Mwt% is not able to be removed from the polypropylene dishes. The solutions of PVP, PVC and with ammonium nitrate were stirred well 10 to 12 hours to obtain a homogeneous solution and then cast on to polypropylene dishes and evaporated slowly at room temperature.

RESULT AND DISCUSSION

XRD Analysis

Figure 1 represents the XRD patterns for pure PVP, 70%PVP: 30%PVC doped with NH₄NO₃ having different mole ratios. It has been observed from fig (1) that the broad peaks between 12-15° and 19-24° can be combined with the nature of pure PVP^{1,6}. The relative intensity of the broad peaks decreased when adding 30% PVC and further decreased with increase of NH₄NO₃ concentration. These changes in diffraction intensities indicated that the amorphous nature of the polymer increased with an increase in NH₄NO₃ doping blend polymer². Figure 1(c-e) shows that the pure PVP and 70PVP:30PVC peaks become less intense, when the concentration of NH₄NO₃ is increased. This could be interference of PVP and PVC structure by ammonium salts (Fig. 1c). This shows a decrement in the degree of crystalline of the polymer due to the addition of ammonium nitrate and its maximum for 70PVP:30PVC:0.3 NH₄NO₃ (Fig. 1e). No peaks corresponding to NH₄NO₃ appeared in the complexes which indicate the complete suspension of the salt in the polymer matrices.

FTIR Analysis

FTIR spectroscopy is used to investigate the interaction in polymer blend, along with atoms or ions in electrolyte systems. Figure 2 shows the FTIR spectra of pure PVP, 70%PVP:30%PVC blend and blend with different concentrations of NH_4NO_3 at room temperature. The observed band around 640 cm^{-1} has been attributed to C-H bend for pure PVP, this peak is shifted to 644 cm^{-1} , 528 cm^{-1} , 648 cm^{-1} and 680 cm^{-1} for 70PVP:30PVC, 70PVP:30PVC:0.1Mwt%, 70PVP:30PVC:0.2Mwt%, 70PVP:30PVC:0.3Mwt% of NH_4NO_3 respectively. The observed band at 585 cm^{-1} has been attributed to C-Cl stretch of 70PVP:30PVC, this peak gets shifted to 575 cm^{-1} , 570 cm^{-1} for 70PVP:30PVC:0.1Mwt% and 70PVP:30PVC:0.2Mwt% respectively. This indicates the complexation between PVP, PVC and ammonium nitrate salt.

The observed band at 1641.28 cm^{-1} has been attributed C=O stretching for pure PVP. This peak is shifted to 1638.82 cm^{-1} , 1618 cm^{-1} , 1528 cm^{-1} for 70PVP:30PVC, 70PVP:30PVC:0.1Mwt%, 70PVP:30PVC:0.2Mwt% of NH_4NO_3 respectively. The above PVP and PVC bands get shifted, when the NH_4NO_3 is added in the PVP –PVC blend. FTIR assignments have been presented in table 1.

DSC analysis

The DSC curve of pure PVP, 70PVP:30PVC polymer blend with different Mwt% of ammonium nitrate is shown in the Fig.3a-e. The T_g was measured at mid-point of the each transition. Glass transition temperature for the salt free 70PVC:30PVC blend was observed at 200°C .

The T_g value of 58°C was found for the composition of 0.1Mwt% NH_4NO_3 doped 70PVP:30PVC blend. A low T_g of 54°C was found for the composition of 0.3Mwt% NH_4NO_3 doped 70PVP:30PVC blend. The T_g value of 56°C was found for the composition of 0.2 Mwt% NH_4NO_3 doped 70PVP:30PVC blend. The observed T_g shifts to lesser values with the addition of salt due to the plasticizing effect of the salt in the host polymer matrix⁷. Addition of ammonium nitrate concentration, the observed T_g values decreased drastically. This may be due to the softening of the polymer blend by the addition of salt, which is helpful for easy proton transport⁸. The low glass transition temperature causes the higher segmental motion of the polymer electrolyte. The glass transition temperatures have been tabulated in table 2.

CONDUCTIVITY STUDIES

As a general trend, in many studies for the dependence of salt concentration on the ionic conductivity in solid polymer electrolytes at low salt concentration, the conductivity increases due to build-up of charge carriers. And at high salt concentrations, the conductivity decreases due to build-up of charge carriers offset by the retarding effect of ion cloud. In these studies, the conductivity increases with increase in ammonium salt concentration. The Figure 4 shows the frequency dependent of the conductivity for all composition of PVP: PVC: NH_4NO_3 polymer electrolyte at room temperature. The pure PVP exhibit higher conductivity

than 70%PVP: 30%PVC blend electrolytes. This observed decrease in conductivity by the addition of PVC is due to the increase in crystalline nature PVC⁹. A maximum conductivity $3.42 \times 10^{-4} \text{ Scm}^{-1}$ is observed for the composition of 70PVP: 30PVC: 0.3Mwt% NH_4NO_3 . The high ionic conductivity in an electrolyte is attributed to increased ionic mobility and increased ionic charge carrier concentration.

The Figure 4 shows two different regions. The first region observed at low frequencies corresponds to the frequency independent conductivity. This conductivity value has been assigned to the bulk conductivity of the sample. In the high frequency region, the conductivity increases with frequency¹⁰. The ionic conductivity for other composition is given in table 3.

Dielectric analysis

Figure 5 & 6 show the plots of dielectric constant ϵ' and dielectric loss ϵ'' against log frequency. From figure 5, pure PVP at high frequency, the dielectric constant is not zero but when PVC is added to pure PVP, the dielectric constant becomes zero. On adding ammonium nitrate in the ratio 0.1Mwt%, 0.2Mwt% and 0.3Mwt% to 70%PVP: 30%PVC, the dielectric constant increases with decreasing frequency.

Energy dissipation and contribution of charge or a dipole from the ionic transport and from the polarization is measured directly by dielectric loss⁷. From the figure 6, the dielectric loss values are very high at low frequency on increasing molar weight percentage of ammonium nitrate to 70%PVP: 30%PVC.

From the graph, it is clear that the values ϵ' and ϵ'' decreases with increasing frequency and reaches a constant value at higher frequencies. The values ϵ' and ϵ'' are high at lower frequencies, but as the frequency of the field is increased the values begin decrease which could be due to the dipoles not being able to follow the field variation at higher frequencies and also due to polarization effect. The low dispersion region attributed to the charge accumulation at the electrode-electrolyte interface. At higher frequencies the periodic reversal of the electric field occurs so fast that there is no excess ion diffusion in the direction of the field¹⁰. The values ϵ' and ϵ'' are increases with increasing salt concentration.

Concentration – Dependent Conductivity

At room temperature, ionic conductivity of 70PVP; 30PVC with different molar weight percentage of the NH_4NO_3 polymer electrolyte is shown in Figure 7. It clearly confirms that conductivity increases with increasing salt concentration can be related to the increase in the number of mobile charges in the polymer electrolyte shown in Table. The pure PVP shows higher conductivity than blend with PVC. 70PVP:30PVC composition exhibit low conductivity is due to increase in crystalline nature of PVC. A maximum conductivity $3.42 \times 10^{-4} \text{ Scm}^{-1}$ was found for the composition of 70%PVP: 30%PVC: 0.3Mwt% of NH_4NO_3 .

ORDER OF FIGURES AND TABLES

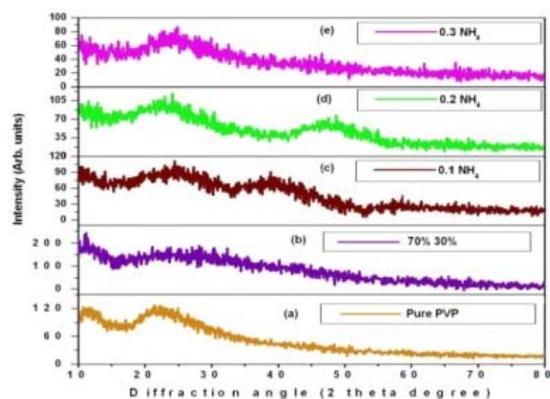


Figure1. XRD patterns of pure PVP & PVP: PVC doped with NH₄NO₃

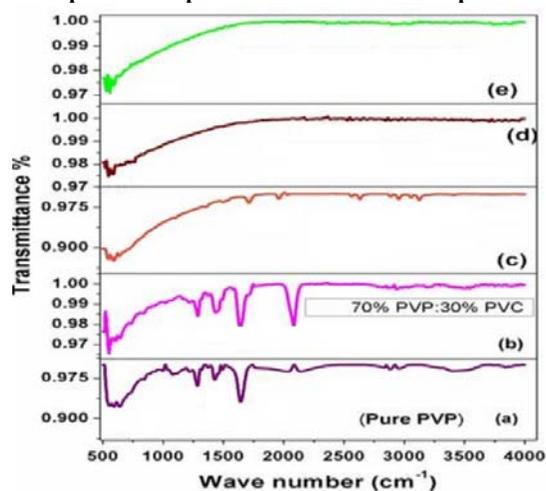


Figure 2. FTIR Spectrums for pure PVP & PVP: PVC doped with NH₄NO₃

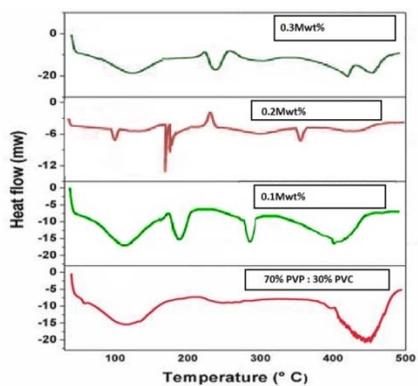


Figure3. DSC thermo grams for PVP: PVC doped with NH₄NO₃

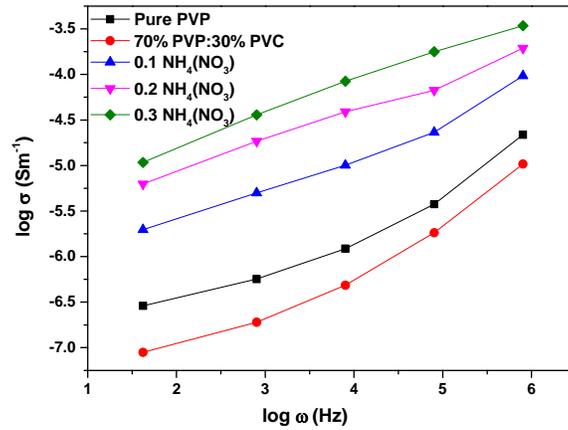


Figure 4. Conductance spectra of pure PVP & PVP: PVC doped with NH_4NO_3

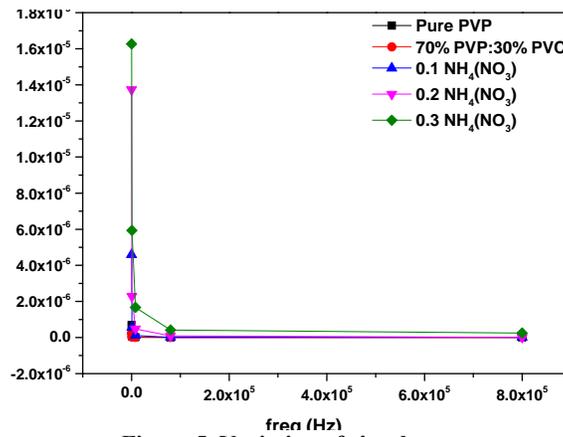


Figure 5. Variation of ϵ' vs $\log \omega$.

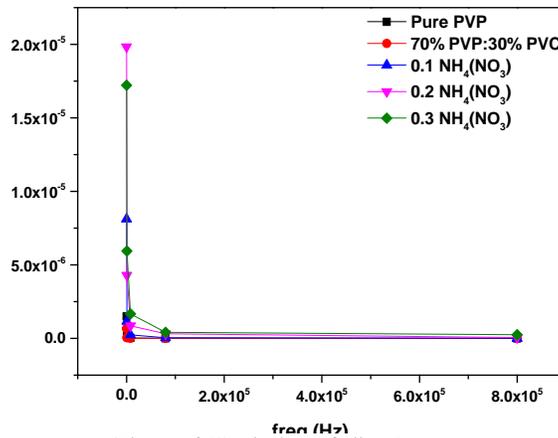


Figure 6. Variation of ϵ'' vs $\log \omega$.

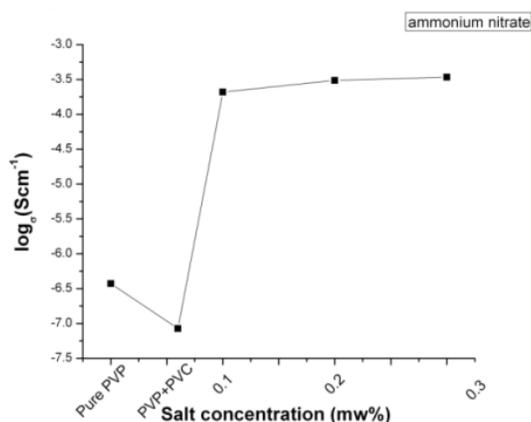


Figure. 7 Conductivity and concentration of ammonium nitrate at room temperature.

Table1: Peak position and their assignment for PVP-PVC blend NH_4NO_3

S.No	Wave number cm^{-1} Pure PVP	0%PVP:30PVC	70%PVP:30PVC:Mwt% of $\text{CH}_3\text{COONH}_4$			Assignments
			0.1	0.2	0.3	
1	640	543	528	648	680	C-H bend
2		585	580	575		C-Cl Stretch
3	1641.28	1638.82	1618	15287	-	C=O Stretching

Table 2: the glass transition temperature for PVP & PVP: PVC doped with NH_4NO_3

Composition	Glass Transition Temperature(T_g) $^{\circ}\text{C}$
Pure PVP	160 $^{\circ}\text{C}$
70PVP:30PVC	200 $^{\circ}\text{C}$
70PVP:30PVC:0.1	58 $^{\circ}\text{C}$
70PVP:30PVC:0.2	56 $^{\circ}\text{C}$
70PVP:30PVC:0.3	54 $^{\circ}\text{C}$

Table 3: Conductivity values of the polymer complexes at room temperature.

S. No	Polymer complexes	Ionic Conductivity (σ)
1.	Pure PVP	$3.7245 \times 10^{-7} \text{ Scm}^{-1}$
2.	70%PVP:30%PVC	$8.46752 \times 10^{-8} \text{ Scm}^{-1}$
3.	70%PVP:30%PVC:0.1Mwt% NH_4NO_3	$2.082 \times 10^{-4} \text{ Scm}^{-1}$
4.	70%PVP:30%PVC:0.2Mwt% NH_4NO_3	$3.08 \times 10^{-4} \text{ Scm}^{-1}$
5.	70%PVP:30%PVC:0.3Mwt% NH_4NO_3	$3.42 \times 10^{-4} \text{ Scm}^{-1}$

CONCLUSION

The 70%PVP: 30%PVC blend polymer electrolyte was prepared by a solution casting technique. The maximum ionic conductivity of $3.42 \times 10^{-4} \text{ Scm}^{-1}$ is observed when the polymer

blend electrolyte is complexes with 0.3Mwt% of ammonium nitrate at room temperature. The amorphous nature of polymer electrolyte has been confirmed by XRD studies. A complex formation of PVP: PVC: NH_4NO_3 has been confirmed by FTIR studies. The thermal transition of the polymer electrolyte has been studied by DSC. The dielectric studies have been made by all the composition. From the concentration dependent conductivity studies, the conductivity decreases with the addition of PVC and increases with salt concentration have been observed. The polymer electrolyte 70%PVP: 30%PVC: 0.3Mwt% NH_4NO_3 possess high amorphous nature, more free ion concentration and low glass transition temperature.

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