Investigations on the Electrical and Structural Properties of PVA Doped with $(NH_4)_2SO_4$

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ABSTRACT: Solid polymer electrolytes based on poly (vinyl alcohol) (PVA) complexed with ammonium sulfate $(NH_4)_2SO_4$ at different weight percent ratios were prepared using solution cast technique. The structural properties of these electrolyte films were examined by X-ray diffraction (XRD) studies. The XRD data revealed that the amorphous domains of PVA polymer matrix increased with the increase of ammonium sulfate added up to 5 wt %, after which the degree of crystallinity increases. The complexation of the salt with the polymer was confirmed by Fourier transform infrared (FTIR) spectroscopy. Electrical conductivity was measured in the temperature range of 303–373 K. The conductivity was found to obey Arrhenius formula. The dielectric permittivity ε' was studied as function of temperature and frequency, respectively.The data showed increasing in ε' values with the increase in temperature while decreased with increase in frequency for polymer electrolyte system up to 10% of ammonium sulfate added. For values of addition greater than 10%, ε' is independent of both temperature and frequency. The ac conductivity is found to obey the power relation. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 1213–1217, 2010

Key words: inorganic polymer; dielectric properties; charge transport

INTRODUCTION

Extensive investigations on solid polymer electrolytes have been in progress in recent times in view of their potential applications in solid state electrochemical cells.[1–3] The dielectric constant and dissipation factor are crucial quantities required in the design of devices and furthermore, as a function of temperature or frequency they reveal much information on the chemical or physical state of the polymer.[4] The study of relaxation behavior constitutes a powerful approach for obtaining information about the nature and types of molecular motions and the manner in which they are affected by chemical composition, molecular structure, and morphology.[5] The ac conductivity measurements are important to characterize the nature of the conduction process.[6] Polymers and polymeric composites have steadily gained growing importance in our daily life. Numerous investigations have been conducted on a variety of polymer–metal salt systems to understand the nature[7] of complexation and characterizing the obtained complexes. Poly(vinyl alcohol) (PVA) is a semicrystalline polymer and its crystalline index depends on the synthetic process and physical aging.[8] It has a carbon chain backbone with hydroxyl groups attached to methane carbons. These OH-groups can be a source of hydrogen bonding, and hence assist the formation of polymer electrolytes. PVA has gained increasing attention in the biomedical field because of its bioinertness.[9] Doping of transition metal salts into permanently polarized vinyl polymers in a multiphase system can induce pronounced changes in various properties of complexes. These complexes can be used as sensors, electrochromic displays, and solid state lasers.[10] The broad objective of this work is to develop a deep understanding of the correlation between the structure and the properties of ammonium sulfate complexed PVA polymer electrolytes, so as to allow the engineering of these compounds with the desired properties for the application in the field of electronic elements.

EXPERIMENTAL

PVA with molecular weight ~1800 was obtained from QualiKems chemical company (India). The PVA-based membranes were prepared by dissolving 1 g of PVA in distilled water, to get a 10 wt % solution. To obtain a transparent low-viscous liquid, the 10 wt % solution was left for 24 h at 50°. The x $(NH_4)_2SO_4$ addition ($x = 5, 10, 15, 20, 30$ wt %) were added to the solution. The solution was stirred for

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24 h. The transparent solution was then cast on a Petriglass dish. Then, allowed to evaporate slowly at room temperature. The final product was vacuum dried thoroughly.

The samples were examined by using Bruker X-ray analytical diffraction system, type D8 Advance. The diffraction system based with Cu tube anode of wave length $K_{\alpha 1}$= 1.5460 Å and $K_{\alpha 2}$= 1.54439 Å. The start angle (2θ) was 4° and the end angle was 60°. Infrared measurements were done by using FTIR Perkin Elmer in the range (4000–500 cm^{-1}). Samples of diameter 1 cm were taken and silver paste was deposited on both surfaces of the film to ensure good contacts in electrical measurements. Silver coated samples were sandwiched between the two similar brass electrodes of a spring-loaded sample holder. The whole assembly was placed in a furnace monitored by a temperature controller. The rate of heating was adjusted to be 2 K/min. Dielectric and electrical measurements were carried out in the temperature range 303–373 K using PM 6304 programmable automatic RCL (Fluke and Philips) meter. The measurements were carried out over a frequency range 100Hz–100 kHz.

RESULTS AND DISCUSSION

X-ray diffraction results

The obtained X-ray diffraction patterns for all samples are presented in Figure 1. It is clear that the pure PVA sample (x = 0) exhibit a single broad peak around 2θ = 20°, indicating the semicrystalline nature.[11] The X-ray intensity composition dependence is shown in Figure 2. At x = 0.05, the intensity almost unchanged. As well as the area under the hump tend to decrease; this implies to an increase on the degree of amorphousity. Hence, there is significant motion of polymer chain existing in the amorphous phase while the crystalline phase is nonconducting. This results in greater ionic diffusivity with high ionic conductivity, which can be obtained in amorphous polymers that have flexible backbone.[12–14] For $x > 5$ wt % the intensity of X-ray shows semilinear increase. This may be due to the doping inducing a short range ordering at low content, as well as at high content, there are sharp crystalline peak attributed to the change in the crystalline form.[12]

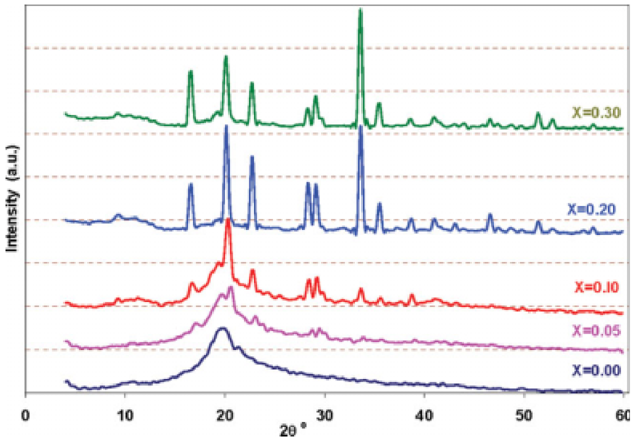

Figure 1 XRD patterns of PVA films prepared at different amount of ammonium sulfate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

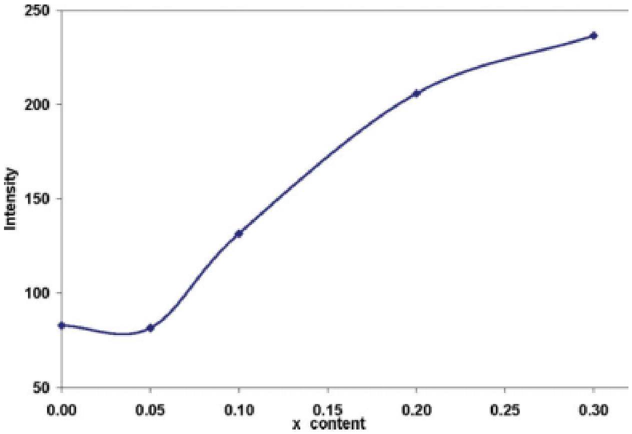

Figure 2 The XRD counts as a function of ammonium sulfate content. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

FTIR spectroscopy

The FTIR spectroscopy was used to study the structural change in the samples due to the interactions between the electrolyte atoms and the chains on the ionic conductivity of PVA films.[15] The obtained FTIR spectra in the region 4000–500 cm^{-1} for all samples are shown in Figure 3. It is clear that a very

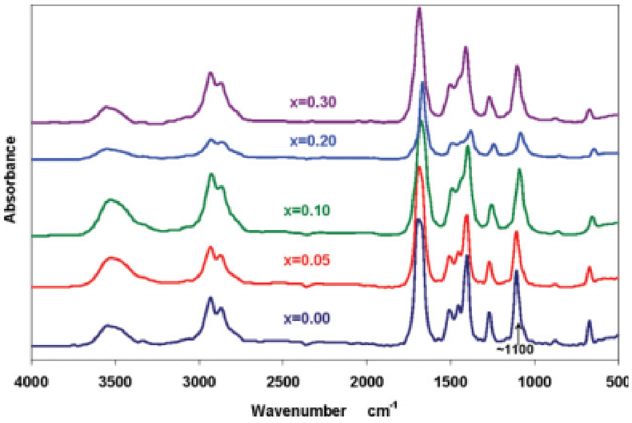

Figure 3 IR absorption spectrum for all films at different compositions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

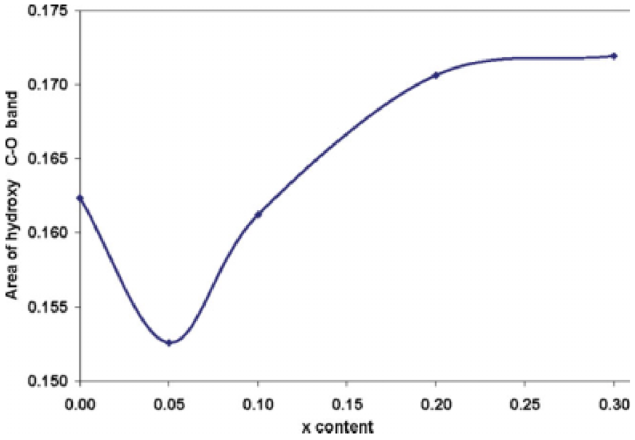

Figure 4 Composition dependence of the relative area under the hydroxy C—O bands (locate at ~1100 cm^{-1}) of PVA films. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

broad and strong band centered at ~3500 cm^{-1} which is concerned with the interaction of different OH groups vibrations. As well as two strong peaks at 2920 and 2860 cm^{-1} are the characteristic bands of asymmetric and symmetric C—H stretching, respectively.[16] In the region 2000–500 $cm^{-1,}$ the band around ~1680 cm^{-1} may be attributed to the glycosidic link in PVA blend, and the other bands which locate less than 1500 cm^{-1} assignment to PVA polymer formation.[14–17] In all samples around ~1100 cm^{-1} the important absorption band was attributed to the hydroxy C—O stretching.[18] The $(NH_4)_2SO_4$ addition dos not induce any new bands, but the intensity of this band become weaken at 5 wt %, and then with more addition of $(NH_4)_2SO_4$ its shows semilinear increase. The relative area under this bands, are illustrated in Figure 4. The spectra indicated that the hydroxyl groups of PVA were interacted with the $(NH_4)_2SO_4$. Hence, this band was also a measure of the degree of crystallinity of PVA,[18] this result clearly consistent with the XRD results.

The dc conductivity

The variation of logarithmic dc conductivity of $(PVA{:}(NH_4)_2SO_4)$ polymer electrolytes as a function of temperature for different compositions of $(NH_4)_2SO_4$ was shown in Figure 5. From the plots, it is clear that the conductivity is found to increase with the increase in temperature for pure PVA as well as in all the compositions of $(PVA{:}(NH_4)_2SO_4)$ polymer electrolyte films. The plots follow Arrhenius behavior through two regions and different activation energies. Similar behavior was observed in number of other polymer electrolyte systems.[19–21]

The dc electrical conductivity obeys the well-known Arrhenius formula given by:

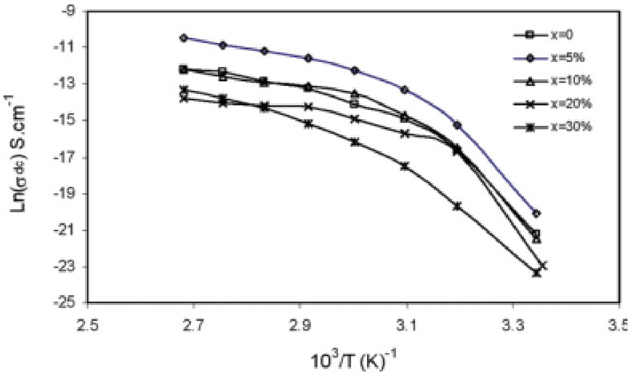

Figure 5 Temperature dependence of dc conductivity for all composition. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

$$\sigma_{dc} = \sigma_0 \exp\left(\frac{-E_a}{k_B T}\right) \tag{1}$$

where σ_0 is the pre-exponential factor, E_a the activation energy, k_B the Boltzmann constant and T is the absolute temperature. The increase in the conductivity with temperature may be attributed to the transitions from crystalline/semicrystalline phase to amorphous phase. The increase in conductivity with temperature is interpreted in terms of hopping mechanism between coordination sites, local structural relaxation and segmental motion of polymer.[22]

The activation energies calculated for both regions are given in Table I. Figure 6 shows the variation of conductivity with the amount of ammonium sulfate. It can be seen that the conductivity increases with the amount of ammonium sulfate added up to 5 wt % after which the conductivity decreases. This can be explained on the basis that the polymer films are known to be a mixture of amorphous and crystalline region. As the amorphous region increase, however, the polymer chain acquires faster internal modes in which bond rotations produce segmental motion. This, in turn, favors the hopping interchain and intrachain ion movements, and the

TABLE I
The Values of Activation Energies (E_a) and dc Conductivity of Ammonium Sulfate Doped PVA Polymer Electrolytes Films

Ammonium sulfate concentration gm %	First region eV	Second region eV	dc conductivity at room temperature S cm^{-1}
0	2.21	0.59	$6.07E^{-10}$
5%	2.39	0.47	$1.92E^{-09}$
10%	2.39	0.33	$4.79E^{-10}$
20%	2.59	0.25	$1.1E^{-10}$
30%	2.03	0.67	$7.2E^{-11}$

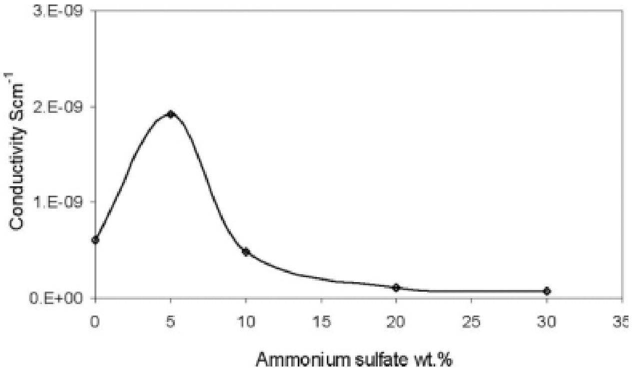

Figure 6 Variation of conductivity with amount of ammonium sulfate added.

conductivity of the polymer thus becomes high.[23] These results are fairly agree with that obtained from XRD analysis.

Dielectric and ac conductivity studies

The variation of dielectric permittivity ε′ and dielectric loss ε″ with frequency is shown in Figures 7 and 8, respectively. These figures clearly display that both ε′ and ε″ decreases abruptly with increase in frequency below 10 kHz approximately. This may be attributed to interfacial effects such as space charge polarization etc. From Figure 7, it can be seen that the dielectric permittivity decreases with the increase of frequency at ammonium sulfate added up to 10 wt %. For values of addition greater than 10 wt %, the ε′ is independent of frequency. Generally, this is because, for polar materials, the initial value of the dielectric permittivity is high, but as the frequency of the field is increased the values of dielectric permittivity begin to drop which could be due to the incapability of dipoles to follow the field variation at higher frequencies and also due to the polarization effects.[24]

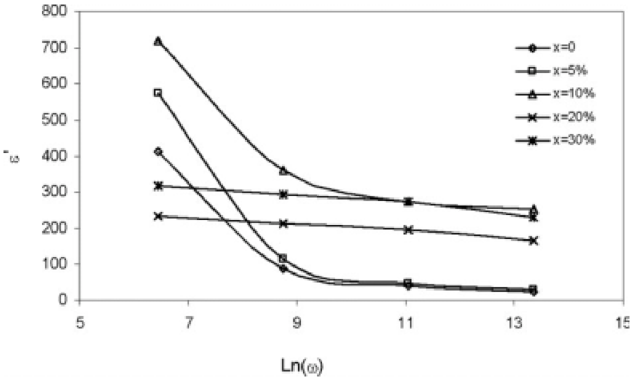

Figure 7 Variation of dielectric permittivity ε′ with frequency for all compositions at $T = 353$ K.

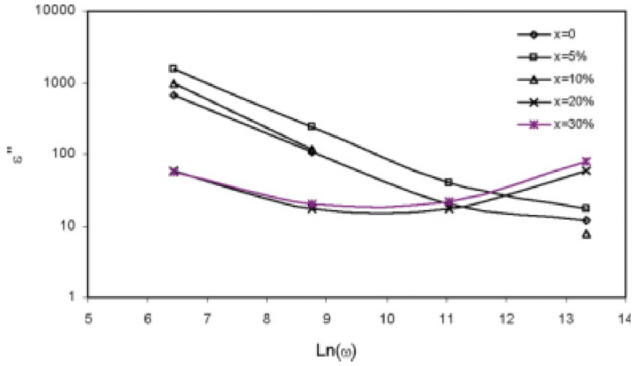

Figure 8 Variation of dielectric loss ε″ with frequency for all compositions at $T = 353$ K. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The temperature dependence of both ε′ and ε″ at 1 kHz for all samples are shown in Figures 9 and 10, respectively. From Figure 9 it is evident that dielectric permittivity increases with the increase of temperature for PVA:$(NH_4)_2SO_4$ polymer electrolyte system up to 10 wt % ammonium sulfate added. The variation of ε′ with temperature is different for nonpolar and polar polymers. In general for nonpolar polymers ε′ is independent of temperature. But in the case of polar polymers the ε′ increases with the increase of temperature.[24] This behavior is typical of polar dielectric in which the orientation of dipoles is facilitated with the rising temperature and thereby the permittivity is increased. Also, it can be noticed that the dielectric permittivity is independent of temperature at relatively high concentration of $(NH_4)_2SO_4$ (up to 10 wt %). This behavior is typical of ammonium sulfate in which ammonium ions start free rotations at 440 K with activation energy $E_a = 0.35$ eV.[25–27] The same trend was observed for dielectric loss ε″.

The values of ac conductivity $\sigma_{ac}(\omega)$ for all compositions are found to obey the general relation;

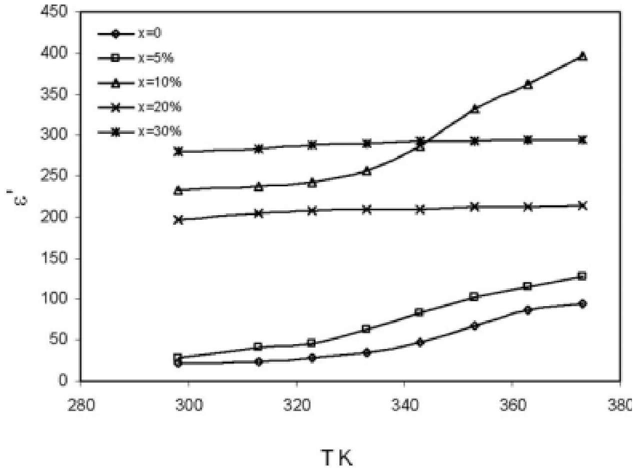

Figure 9 Variation of dielectric permittivity with temperature for all compositions at 1 kHz.

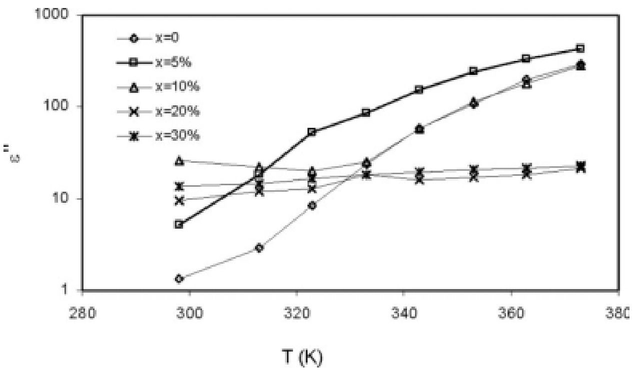

Figure 10 Variation of dielectric loss with temperature for all compositions at 1 kHz.

$$\sigma_{ac}(\omega) = A\omega^s \tag{2}$$

where A is the pre-exponential factor and s is the fractional exponent. Eq. (2) is valid for several low mobility polymers and even crystalline materials.[28] The variation of the ac conductivity with frequency at 253 K for all compositions is shown in Figure 11. The exponent s estimated from the slops of Figure 11 using fitting technique. It can be noticed that s varies between 0.2 and 1.5.

CONCLUSIONS

XRD patterns of the $(PVA:(NH_4)_2SO_4)$ electrolytes revealed that maximum amorphous domains at 5 wt % of $(NH_4)_2SO_4$ doped PVA polymer electrolyte. FTIR spectral studies confirmed optimum complexation of the salt with the polymer at x =5 wt %. Incorporation of 5 wt % of ammonium sulfate as a salt doping increases the amorphous phase of the complex and enhances the conductivity approximately one order. These results show that 5 wt % $(PVA:(NH_4)_2SO_4)$ sample is a potential candidate for electrochemical devices under modification. Further extensive investigations are required, however, to raise the performance of ionic conductivity for 5 wt % $(NH_4)_2SO_4$ doped PVA polymer electrolyte to practical levels.

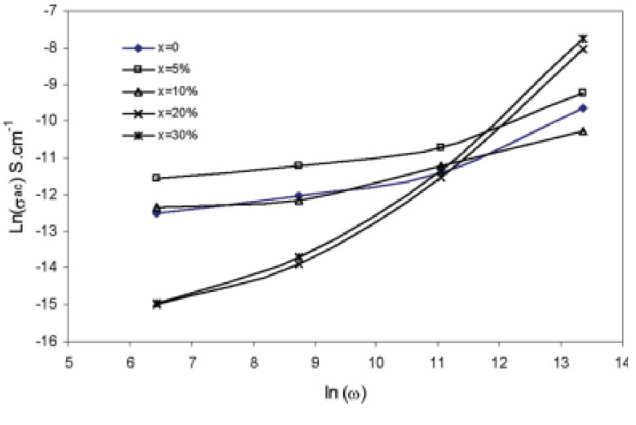

Figure 11 The frequency dependence of the ac conductivity for PVA doped with different concentrations of ammonium sulfate at T = 253 K. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

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