

Structural, vibrational, thermal, and electrical properties of PVA/PVP biodegradable polymer

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Abstract

The A biodegradable solid polymer blend electrolyte was prepared by using polyvinyl alcohol (PVA) and polyvinylpyrrolidone (PVP) polymers with different molecular weight percentages (wt.%) of ammonium acetate, and its structural and electrical properties were evaluated. The polymer blend electrolyte is prepared using solution casting technique, with water as a solvent. Xray diffraction shows that the incorporation of ammonium acetate into the polymeric matrix causes decrease in the crystallinity degree of the samples. The ionic conductivity of the prepared polymer electrolyte was found by impedance analysis. A maximum conductivity of $8.12 \times 10^{-5} \text{ Scm}^{-1}$ was observed for the composition of 50 PVA/50 PVP/30 wt.% ..

Keywords: PVA/PVP blend . XRD . FTIR , SEM.

1. Introduction

Proton transport in solids has attracted much attention because of its potential use in clean energy devices such as fuel cell, batteries, and chemical sensors. The numbers of fast protonic conductors, organic or inorganic, crystalline and amorphous, have been prepared during the past three decades [1, 2, 3, 4]. Understanding the mechanism of ion transport and enhancing the conductivity of solid polymer electrolytes are of critical importance. Many approaches are available to increase conductivity, such as cross-linking two polymers, adding plasticizers to polymer electrolytes, adding inorganic inert fillers, and blending two polymers [5]. Polymer blends are physical mixtures of structurally different polymers that interact through secondary forces and that are miscible at the molecular level. The most common interactions present in blends are hydrogen bonding and ionic and dipole interactions. The significant advantages of polymer blends are that the properties of the final product can be tailored to the application requirements, which cannot be achieved by one polymer alone. However, the film properties

depend upon the miscibility of the blend [6]. The polyvinyl alcohol (PVA) and polyvinyl pyrrolidone (PVP) polymers were selected for the present work.

Among the polymers, PVA has excellent physical properties such as mechanical strength, electrochemical stability, non-toxicity, good film-forming capability, and biocompatibility. It contains hydroxyl group attached to methane carbons. These hydroxyl groups can be a source of hydrogen bonding. PVP is a vinyl polymer possessing planar and highly polar side groups due to the peptide bond in the lactam ring [7]. It is an amorphous polymer and possesses high glass transition temperature (Tg) 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. Therefore, a hydrogen-bonding interaction may take place between these two polymers [8, 9]. Hydrogel blends are stable within the physiological environment because of physical cross-links consisting of intermolecular hydrogen bonds and intramolecular hydrogen bonds within PVA, which is responsible for the solubility of PVA and PVP in water [10]. A literature survey reveals that conductivity study on PVA/ PVP blend doped with ammonium salts is scarce. The main objective of the present study is to prepare 50 PVA/50 PVP with different weight percentages (wt.%) characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), SEM, and impedance to find out the best optimum composition suitable for practical electrochemical application..

2. Experimental technique

Materials used The polymer blend electrolyte was prepared by solution casting technique. PVA (molecular weight (Mw) 1,40,000; AR grade, SD fine), PVP -K30 (Mw 40,000, SLR grade, SD fine), and ammonium acetate (CH₃COONH₄, HIMEDIA) were used as the raw materials in this study. Film casting An equal quantity of PVA/PVP blend (50:50)

by weight was added to double-distilled water, stirring the solution at room temperature to complete the dissolution. The required quantity (5, 10, 20, 30 and 35 wt.%) of ammonium acetate is also dissolved in the above solution. The solution was poured onto cleaned Petri dishes and dried in room temperature. After drying, the films were peeled from the Petri dishes and kept in desiccators until use. These polymer electrolytes were characterized by different experimental techniques

3. Characterization

The X-ray diffraction pattern of the polymer electrolytes was recorded using Cu K α (λ 01.5406 Å). FTIR measurement was made with a Shimadzu-IR Affinity-1 spectrometer instrument in the wave number range of 400–4,000 cm⁻¹. Thermal stability of the electrolytes was studied using SII EXSTAR 6000 system. The samples were put in an Al pan and heated at the rate of 10 °C/min. The ionic conductivity study of the polymer electrolytes was carried out in the temperature range of 303–373 K over a frequency range of 42 Hz–1 MHz using a computer-controlled LCR meter. The complex formation between the polymer was characterized using a X-ray diffraction analysis Figure 1 shows that the XRD spectra of pure PVA, pure PVP, the 50 PVA/50 PVP blend, and the 50 PVA/ 50 PVP blend with different weight percentages . A broad peak around 20° ascribed to the pure PVA was found in Fig.1. The broad peaks between 12°–15° and 19°–24°, which can be associated with the crystalline nature of pure PVP, were observed and The PVA peak decreased in intensity with the addition of PVP The diffraction peaks of 50 PVA/50 PVP decrease in intensity has been described.

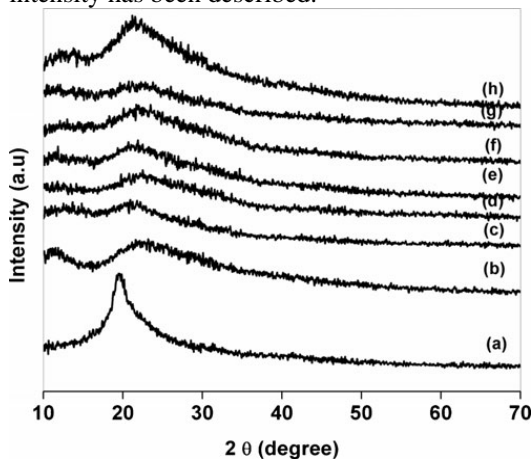


Fig1: X-Ray Diffraction Of Various Doped 50/50 PVA,PVP With Ammonium Acetate

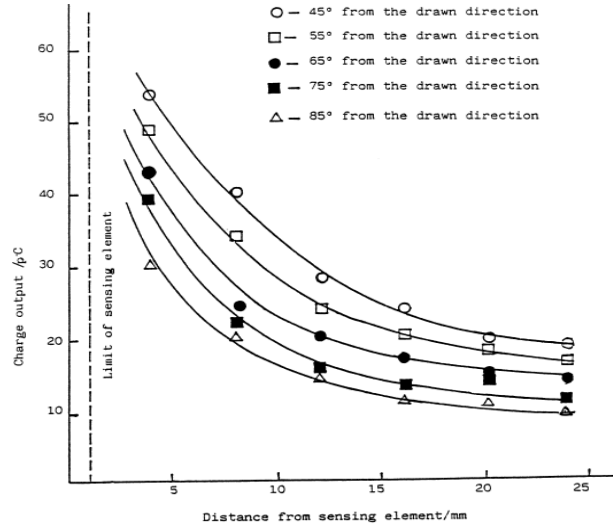
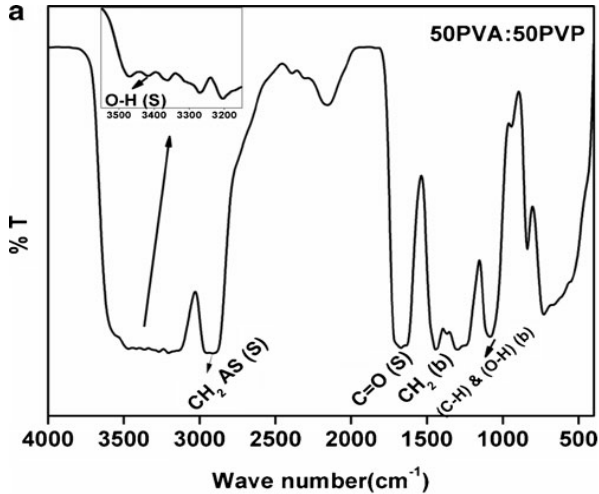


Fig 2 Dielectric study of PVA/PVP blend with ammonium acetate

This may be due to the further increase of the crystalline nature of the 50 PVA/50 PVP using electrospinning . This result can be interpreted by considering the work by Hodge et al. [11] which establishes a correlation between the intensity of the peak and the degree of crystallinity. The results observed from the XRD measurements strongly suggest that the crystallinity of PVA/PVP . polymer electrolytes were present in the XRD pattern, indicating the complete association of the the polymer matrix. Thus, the X-ray diffraction analysis clearly reveals the complex formation between the dissociated salt and the polymer matrices. The high amorphous nature was observed for the composition of 50 PVA/50 PVP/30 wt.%. The FTIR analysis Information pertaining to ion–polymer interaction and molecular structure can be obtained from FTIR studies. If there is any interaction, the vibrational modes of the molecules in that particular system will show shift in wave numbers. Polymers can interact with one another to form secondary bonding, i.e., hydrogen bonding. PVA contains the hydroxyl group and PVP contains the carbonyl group. Therefore, the miscibility between PVA and PVP can be investigated by FTIR by observing changes in the polymer blend electrolyte.

Figure 2 shows the FTIR spectrum of 50 PVA/50 PVP blend. Blending PVA with PVP to form the polymer blend and shifting peak position, shape, and intensity were observed for the polymer blend 50

PVA/50 PVP. The changes in the IR spectra of the 50 PVA/50 PVP blends are observed at 3,477, 2,955, 1,675, 1,439, 1,370, 1,088, and 940 cm^{-1} have been attributed to the O–H stretching, CH₂ asymmetric stretching, C=O (S), CH₂ (b), CH₂ twisting (out of plane), C–H and O–H bending, and syndiotacticity of the PVA.

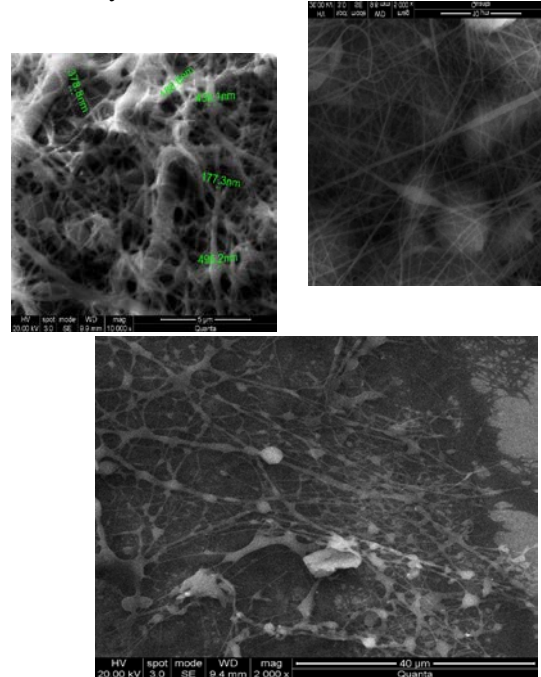


Concentration dependence of ionic conductivity
 Figure 9 shows the variation in room temperature ionic conductivity and the glass transition temperature of the 50 PVA/50 PVP with 20, 30, and 35 wt.% of polymer blend electrolyte as a function of salt concentration. It has been found that the conductivity increases with increase in ammonium acetate concentration up to 30 wt.%. This may be attributed to the increase in the number of mobile charge carriers and also to increase in the amorphous nature of the polymer electrolyte and is confirmed by XRD analysis. The high conductivity and low glass transition temperature were observed for the composition of 50 PVA/ 50 PVP/30 wt.%.

3.1 SEM

The morphology of the PVA 50 =PVP 50, PVA 75 =PVP 25, PVA=PVP 1:4 ration fibers produced were examined using SEM micrographs. Figure (a) shows the SEM images of PVA=PVP fibers. There seen elongated and straight electrospun nanofibers with relatively homogeneous diameters ranging from 170 to 370 nm. The average diameter of these nanofibers was measured as 289 nm. Figure (b) is the image of PVA=PVP with 5% chitosan. Fiber diameters range from 100 to 250 nm. Measured average diameter is 168nm for these nanofibers. Figure 7(c) is the image of PVA=PVP fibers with

diameters ranging from 100 to 500 nm. The average diameter of PVA= PVP- nanofibers measured greater than the others as 330 nm. Fiber diameter distributions could be seen from Fig. 8r. The increase in chitosan contents resulted in the curly and wavy fiber structures. This was attributed to the increase in the viscosity of the solution and the electrical



4. Conclusions

PVA/PVP blend polymer electrolytes with different weight percentages of ammonium acetate were prepared by solution casting technique using distilled water as a common solvent for the proton-conducting membrane. The amorphous nature of the 50 PVA/50 PVP blend was confirmed by XRD analysis. The complex formation between the polymer was confirmed by FTIR. From the impedance analysis, the maximum conductivity was found to be $8.12 \times 10^{-5} \text{ Scm}^{-1}$ for the composition of 50 PVA/50 PVP/30 wt.% polymer. This improved ionic conductivity is due to the enhancement of ionic mobility and number of carrier ions. The hopping rate and DC ionic conductivity were calculated from the conductance spectra. The hopping frequency was

found to be high for the high-conductivity composition. The polymer blend electrolyte's increase in conductivity with salt concentration is explained by the increase of the crystalline phase and the reduction of T_g , which reduces the energy barrier to the segmental motion.

Appendix

Appendixes, if needed, appear before the acknowledgment.

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