

Crystallinity, Morphology and Proton conductivity studies of Malonic Acid doped Poly Vinyl Alcohol Electrolytes for Electrochemical Cells

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Abstract:

Of late, conducting polymers are assuming a lot of importance. In this study, an ion conducting polymer electrolyte based on PVA complexed with Malonic acid is prepared using solution cast technique. XRD is used to examine the complexation. The results of XRD reveal that with the increase of Malonic acid concentration, the amorphous nature of PVA polymer matrix increases. FTIR spectra studies for pure and complexed polymers reveal the vibrational changes that occur due to the presence of dopant. Also, when FTIR spectrum of pure PVA is compared with the spectra of complexed polymers the presence of O-H, C-H and C-C groups is indicated. Surface photographs have been taken using SEM to study the surface morphology. The DC conductivity of the polymer samples are measured in the temperature range 303K to 373K. It is observed that the conductivity increases with the concentration of dopant as well as with temperature.

Key words: Conducting polymers, composite PVA, Malonic acid.

Introduction

Polymers find potential applications in permanent and temporary data storage devices or as a basic material for the fabrication of active & passive light guides. Ion doped organic polymers are highly efficient in holographic recording [1]. Polymers are available in solid and liquid states and it is interesting to know the methods of building polymeric structures from simple molecules. This knowledge often supports the studies in physical, chemical and biological sciences (Tomita et al 1994; DeQueirozet al 1995; Chendra and Dekker 2000).

Polymer complexes with suitable inorganic and organic acids are known as polymer electrolytes which play an important role in the development of various electrochemical devices such as fuel cells, batteries, photo electron chemical cells, electrochemical displays, smart windows etc. Very conductive mechanical properties, ease of fabrication into thin films of desirable sizes and their ability to form proper electrochemical devices are some of the important advantages of polymer electrolytes.

Very few Vinyl polymers are soluble in water and Poly Vinyl Alcohol is recognized as one among

them. By virtue of environmental sensitivity of PVA it finds extensive applications in textile wrap sizing, adhesives, paper sizing agents, ceramic binders. It is also used in cosmetics, pharmacy and electronic industry.

The aim of the present work is to study the structural and electrical properties of PVA based polymer electrolytes. These are synthesized by doping dicarboxylic acids such as Malonic acid into PVA in different proportions (weight). The study is carried out using XRD, FTIR, SEM techniques and by obtaining the dc conductivity of PVA composite polymer systems.

Preparation of polymer electrolyte films

Pure PVA (Mw 1, 40,000 from AR chemicals) complexed with Malonic acid in various compositions (90:10), (80:20), (70:30) & (60:40) by wt% ratio, are prepared using the solution caste technique. PVA & Malonic acid are dissolved in double distilled water; the solutions obtained are thoroughly stirred for 10-12 hrs to get homogenous mixture. The stirred solution is caste onto polypropylene dishes and allowed to evaporate slowly at 50°C. After one or two days solid polymer layers are formed as thin films with nearly 100 microns thickness at the bottom of dishes. These films are dried in vacuum (10^{-3} torr) to

eliminate the residual traces of water then carefully separated from the dishes and stored in evacuated desiccators.

The X-ray diffraction (XRD) patterns of the films are made with PHILIPS PW 3710 X-ray diffractometer in the range 10° - 80° . Fourier transform infrared (FTIR) spectra of these systems are recognized using JASCO FTIR- 5300 spectrometer. The measurements are taken over a wave number range of 400 - 4000cm^{-1} . The surface morphology of these polymer systems is observed using Scanning Electron Microscope (SEM). D.C. conductivity is measured using indigenously built instrument in the temperature range 300 - 373K with Keithley programmable electrometer (model No.196). Thickness of the films is measured by Mitutoyo thickness gauge (no.7301, range 0.01mm to 10mm).

Results and discussion

XRD Analysis

The X-ray diffraction patterns of pure PVA and PVA complexed with Malonic acid are as shown in fig.1. A few differences are identified between the diffraction patterns of complexed PVA films and that of pure PVA. The Fig.1 shows that the pure PVA has a characteristic peak corresponding to an orthorhombic lattice centered at 20° indicating its semi crystalline nature [2]. The peak becomes less intense as the content of Malonic acid is increased. This could be attributed to the disruption of crystalline structure of the PVA by Malonic acid.

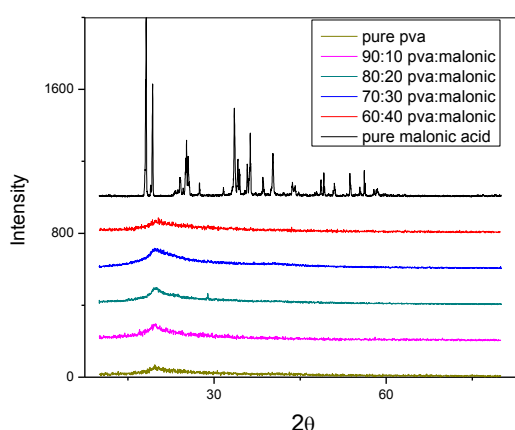


Fig.1: X-ray diffraction patterns of pure PVA and PVA complexed with Malonic acid

The pattern pertaining to pure Malonic acid contains very sharp peaks. Absence of such peaks

corresponding to Malonic acid in the patterns of polymer complexes indicates the complete dissolution of Malonic acid in the polymer matrices. As the Malonic acid content is increased in the polymer, the diffraction peaks become less intense, suggesting the decrease in the degree of crystallinity and simultaneous increase in the amorphousness of those polymer electrolyte films. The intensity of XRD pattern of PVA decreases as the amorphous nature increases [3]. No sharp peaks were observed for higher concentrations of Malonic acid in the polymer, suggesting the dominant presence of amorphous phase [4]. The amorphous nature results in greater ionic diffusivity with high ionic conductivity, which can be obtained in amorphous polymers that have flexible back bone [5].

FTIR Analysis

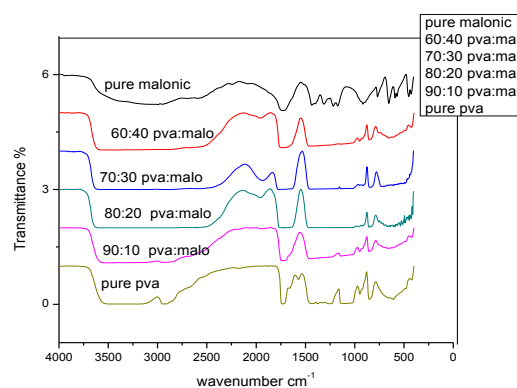


Fig.2: FTIR spectra of Malonic acid complexed PVA polymer electrolyte films.

Fig.2 shows the FTIR spectra pertaining to pure PVA, PVA complexed with different compositions of Malonic acid and pure Malonic acid. The following changes in the spectral features have been observed after comparing the spectrum of complexed PVA with that of pure PVA & Malonic acid.

The absorption band in the region 3550 - 3114cm^{-1} is due to inter molecular hydrogen bonded O-H stretching frequency of PVA which is shifted to 3592 - 3092 , 3613 - 2739 , 3624 - 2676 , 3603 - 2853cm^{-1} in the 10, 20, 30&40 % acid complexed PVA films respectively. In addition to this, the C-H bond stretching of CH_2 showed an absorption band at 2947cm^{-1} in pure PVA and is shifted to 2968cm^{-1} , 2739cm^{-1} , 2635cm^{-1} , 2624cm^{-1} respectively. The C-H bending of CH_2 in pure PVA exhibited

absorption at 1453 cm^{-1} and it is shifted to 1464, 1464, 1453&1464 cm^{-1} in the complexed films respectively.

Deformation is coupled to C-H wagging gives rise to a peak at 1438 cm^{-1} in pure PVA and it is shifted to 1468,1448,1458&1470 cm^{-1} in 10,20,30& 40% of complexed PVA with Malonic acid films respectively. In pure PVA, the C-C stretching occurs at 948 cm^{-1} and it is shifted to 937, 925, 914&925 cm^{-1} in complexed films of PVA polymer electrolyte respectively. The complexation of PVA and Malonic acid clearly indicates the changes in the FTIR spectra.

Morphological studies

SEM micrographs for pure PVA, PVA: Malonic acid (70:30) and pure Malonic acid are as shown in Fig.3. The SEM micrographs show that the Malonic acid is completely complexed with PVA polymer.

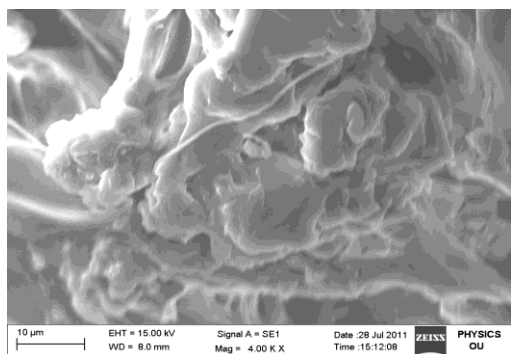


Fig.3 (a) SEM micrograph of Pure PVA

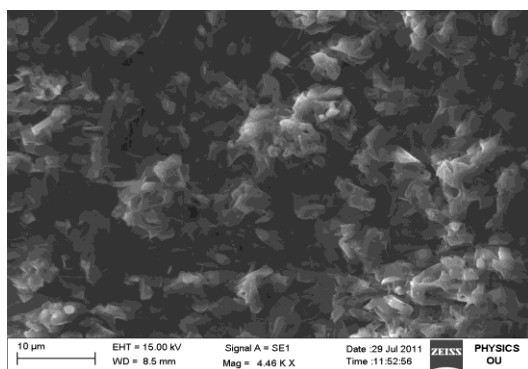


Fig.3(b) SEM micrograph of PVA : Malonic acid (70:30) complexed electrolyte film

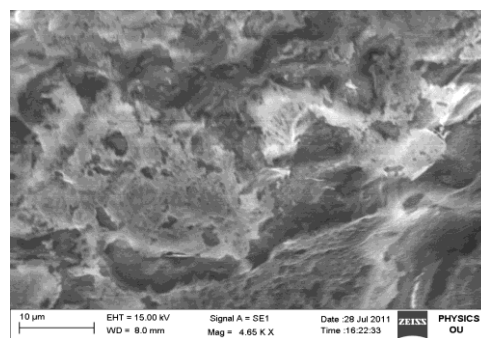


Fig.3(c) SEM micrograph of Pure Malonic acid.

Electrical properties

Conductivity of polymer electrolytes depends on the actual concentration of conducting species and their mobility.

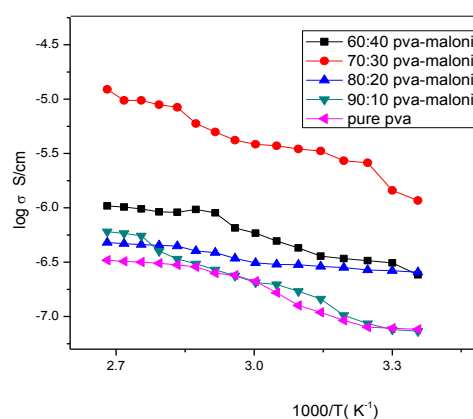


Fig.4: Electrical conductivity as a function of temperature and compositions of PVA-Malonic acid.

The conductivity (σ) varies with temperature (T) according to the equation

$$\sigma = \sigma_0 \exp(E_a/kT)$$

Where σ_0 is pre exponential factor, E_a is activation energy, k is Boltzmann constant and T is absolute temperature.

The conductivity was found to increase with the increase in temperature in pure PVA as well as all the compositions of polymer electrolytes. The conductivity versus temperature follows Arrhenius behavior throughout.

Table 1: Conductivity of PVA and PVA: Malonic acid electrolyte films.

	Conductivity at 303K (S/Cm)	Conductivity at 373K (S/Cm)
Pure PVA	7.62×10^{-8}	3.3×10^{-7}
90:10 PVA-Malonic	7.33×10^{-8}	3.73×10^{-7}
80:20 PVA-Malonic	2.56×10^{-7}	4.796×10^{-7}
70:30 PVA-Malonic	1.17×10^{-6}	1.23×10^{-5}
60:40 PVA-Malonic	2.42×10^{-7}	1.04×10^{-6}

The conductivity values do not show any abrupt jump with temperature, which indicates that, these electrolytes exhibit amorphous nature [6]. This type of behavior is observed in a number of PVA based electrolyte systems [7, 8]. Fig. 4 shows the variation of electrical conductivity as a function of temperature for pure PVA and for different compositions of Malonic acid doped polymer electrolytes in the temperature range 303K-373K. These are also shown in the table1. Quite interestingly, it is observed that the conductivity values are highest for 70:30 PVA: Malonic acid electrolyte film.

The increase in conductivity with temperature is due to decrease in viscosity and increase in chain flexibility and mobility [9]. The conductivity-temperature data obey Arrhenius relationship, the nature of cation transport is quite similar to that in ionic crystals, where ions jump into neighboring vacant sites and increases the ionic conductivity [10]. The increase in conductivity may be due to the transition from semi crystalline phase to amorphous phase. Due to this phase change conductivity shows an increasing trend with temperature and this can be interpreted as hopping mechanism between coordinating sites, local structure and segmental motion of the polymer [11]. As the amorphous region increases, the polymer chain acquires faster internal modes in which bond rotations produce segmental motion. This in turn favors hopping inter-chain and intra-chain movements and thus increases in the conductivity of the polymer.

Conclusions

The complexation of PVA polymer with Malonic acid is confirmed with XRD and FTIR studies. The surface morphology of pure PVA and PVA+ Malonic acid polymer electrolytes at different weight percentages is studied using SEM. The increase in the concentration of Malonic acid resulted in increase in conductivity which is attributed to decrease in the degree of crystallinity and increase in the amorphousness. The proton (ionic) conductivity also increases with increase in dopant concentration and with temperature. The results conclusively prompt the possibility of fabricating an electrochemical cell using the PVA+Malonic polymer electrolyte systems.

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