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Comparative study of PVA based polymer Electrolytes doped with Oxalic acid and Malonic acid

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Abstract*—Of late, conducting polymers are assuming a lot of importance. In this study, proton conducting polymer electrolyte based on PVA complexed with Oxalic acid and Malonic acid is prepared using solution cast technique. XRD is used to examine the complexation of PVA polymer with Oxalic acid and Malonic acid. The results of XRD reveal that with the increase of Oxalic acid and 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 salt in the polymer. Also, the presence of O-H, C-H and C-C groups is indicated when FTIR spectrum of pure PVA is compared with the spectra of complexed polymers. The DC conductivity measurements have been taken on the polymer samples in the temperature range 303 K to 373 K. From these measurements it is observed that the conductivity is found to increase with the concentration of dopant as well as temperature. The results obtained are presented.

***Keywords*—XRD, FTIR, polymer electrolyte, conducting polymers, composite PVA, Oxalic acid,Malonic acid.**

I. 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 al1994: DeQueirozet al1995: Chandra and Dekker 2000).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.

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 conducive 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.

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 Oxalic acid and Malonic acid into PVA in different proportions (weight). The study is carried out using XRD, FTIR techniques and by obtaining the dc conductivity of PVA composite polymer systems.

II. PREPARATION OF POLYMER ELECTROLYTE FILMS

Pure PVA (Mw 1, 40,000 from AR chemicals) complexed with Oxalic acid and Malonic acid in various compositions (90:10), (80:20), (70:30) & (60:40) by wt% ratio, are prepared using the solution caste technique. PVA &Oxalic acid, PVA & Malonic acid are dissolved in double distilled water; the solutions obtained are thoroughly stirred for 10-12 hrs. to get homogeneous 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 electrolytes with nearly 100 microns thickness at the bottom of dishes. These electrolytes 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 electrolytes are made with PHILIPS PW 3710 X-ray diffractometer in the range 10^0-80^0. 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}. D.C. conductivity is measured using indigenously built instrument in the temperature range 300-373K with Keithley programmable electrometer (modelNo.196). Thickness of the films is measured by Mitutoyo thickness gauge (no.7301, range 0.01mm to 10mm).

III. METHODOLOGY AND DISCUSSION ON RESULTS

A. *XRD Analysis*

The X-ray diffraction patterns of pure PVA and PVA complexed with Oxalic acid and pure PVA and PVA complexed with Malonic acid are as shown in Fig.1a and Fig.1brespectively. A few differences are identified between the diffraction patterns of complexed PVA complexed electrolytes and that of pure PVA. Above Figs. 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 Oxalic and Malonic acid is increased. This could be attributed to the disruption of crystalline structure of the PVA by the addition of acid. The pattern pertaining to pure Oxalic/Malonic acid contains very sharp peaks. Absence of such sharp peaks corresponding to the presence of these acids in the patterns of polymer complexes indicates the dissolution of Oxalic/Malonic acid in the polymer matrices.

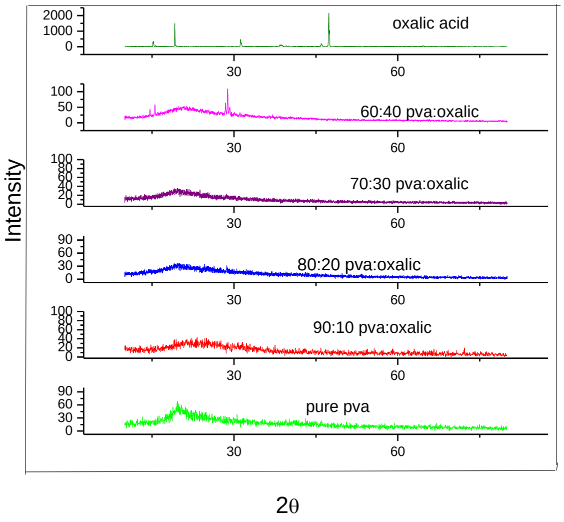

Fig. 1a XRD patterns of pure PVA and PVA complexed with Oxalic acid

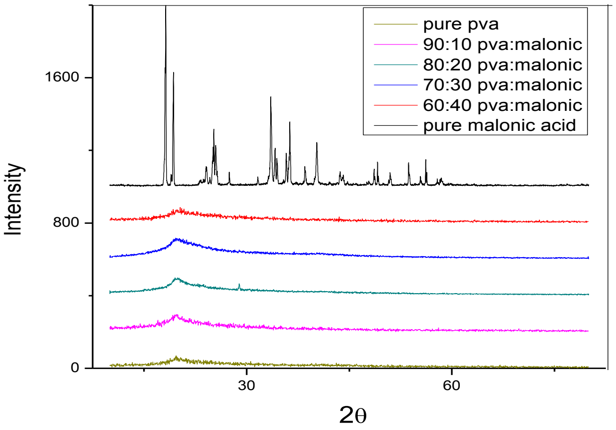

*Fig. 2*b *X-ray diffraction patterns of pure PVA and PVA complexed with Malonic acid*

As the Oxalic/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 Oxalix/Malonic acid in the polymer, suggesting the dominant presence of amorphous phase [4]. The amorphous nature results in greater ionic diffusity with high ionic conductivity which can be obtained in amorphous polymers that have flexible back bone [5].

B. *FTIR Analysis*

The FTIR spectra pertaining to pure PVA, PVA complexed with different compositions of Oxalic acid and pure Oxalic acid are shown in Fig.2a. After comparing the spectra of complexed PVA samples with those of pure PVA & pure

Oxalic acid, the following changes in the spectral features have been observed. The absorption band, in the region 3551-3114 cm^{-1}, due to inter molecular hydrogen bonded O-H stretching frequency of pure PVA, appears shifted to 3603-3090, 3613-3101, 3623-2784, 3634-2824 cm^{-1} respectively in the 10, 20, 30 & 40% acid complexed PVA electrolytes.

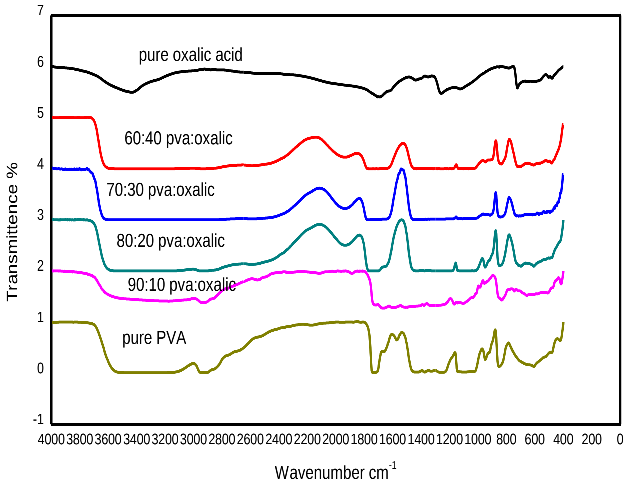

Fig.2a FTIR spectra of PVA & PVA complexed with oxalic acid polymer electrolytes.

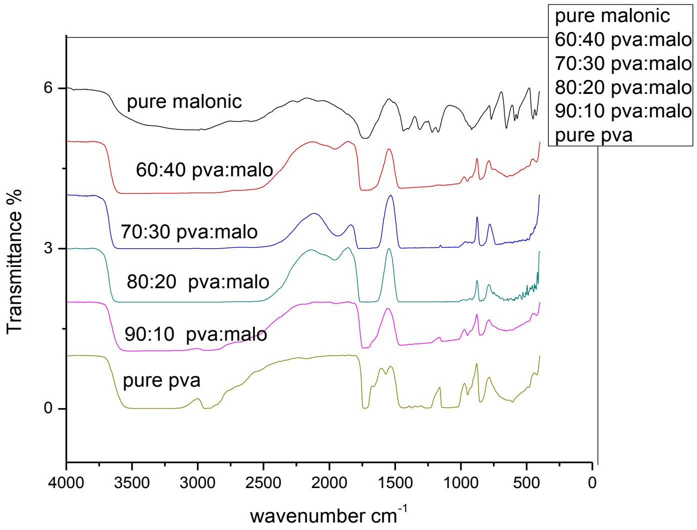

Fig.2bFTIR spectra of PVA & PVA complexed with Malonic acid polymer electrolytes

In addition to this, the C-H stretching of CH_2 showed an absorption band at 2947 cm^{-1} in pure PVA which is also shifted to 2957cm^{-1}, 2868cm^{-1}, 2743cm^{-1}, 2631 cm^{-1} respectively. The C-H bending of CH_2 in pure PVA exhibits absorption band at 1453 cm-1 again is correspondingly shifted to 1493, 1473, 1453&1443 cm^{-1} in the different complexed electrolytes. In pure PVA, the C-C stretching which occurs at 948 cm^{-1} also gets shifted to 941, 951, 930 and 920 cm^{-1} respectively in the complexed polymer electrolytes of PVA. The nature and amount of shift depend on the band of interest and the combined material properties of both PVA and Oxalic acid.

The FTIR spectra are plotted with appropriate scale so that the shifts and changes in the positions of some prominent frequencies and bands can be identified and resolved. These significant changes in the portions of the FTIR spectra clearly lead to the conclusion that the complexation of PVA with Oxalic acid has mainly caused changes in the behaviour of pure PVA.

Fig.2b. 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 3550-3114 cm^{-1} is due to inter molecular hydrogen bonded O-H stretching frequency of PVA which is shifted to 3592-3092, 3613-2739,3624-2676, 3603-2853 cm^{-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 2968 cm^{-1}, 2739 cm^{-1},2635 cm^{-1}and 2624 cm^{-1} respectively.The C-H bending of CH2 in pure PVA exhibited absorption at 1453 cm-1 and it is shifted to 1464, 1464, 1453 and 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&925cm^{-1} in complexed films of PVA polymer electrolyte respectively. The complexation of PVA and Malonic acid clearly indicates the changes in the FTIR spectra.

C. *Electrical properties*

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

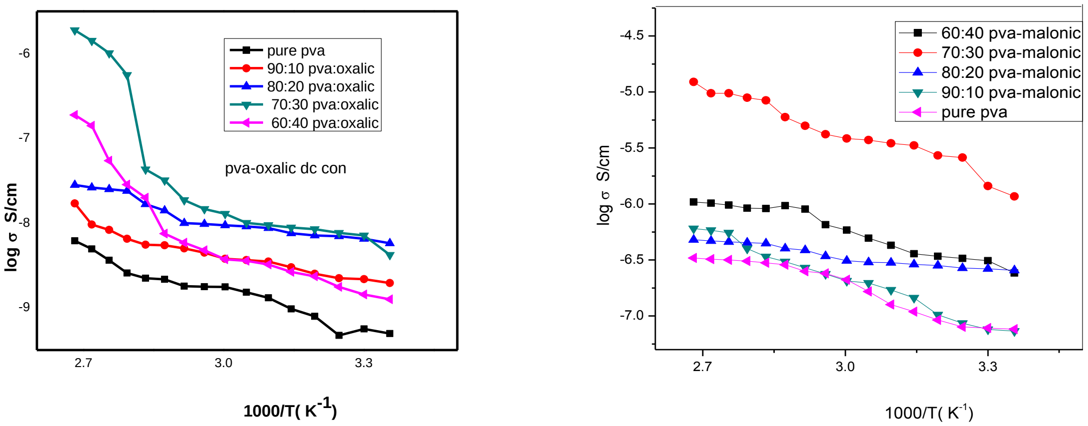

Fig.3 Electrical conductivity as a function of temperature and compositions of PVA-Oxalic acid and PVA- Malonic acid.

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. 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. 3 shows the variation of electrical conductivity as a function of temperature for pure PVA and for different compositions of Oxalic acid/Malonic acid doped polymer electrolytes in the temperature range 303K-373K. These are also shown in the table-1a & table -1b. Quite interestingly, it is observed that the conductivity values are highest for 70:30 PVA: Oxalic acid &70:30PVA: Malonic acid electrolytes.

TABLE I
CONDUCTIVITY OF PVA AND PVA: OXALICACID ELECTROLYTE FILMS.

Polymer electrolyte	**Conductivity S/cm at 303K**	**Conductivity S/cm at 373K**
PVA	5.62×10^{-10}	6.15×10^{-9}
PVA: Oxalic acid (90:10)	2.17×10^{-9}	1.70×10^{-8}
PVA: Oxalic acid (80:20)	6.50×10^{-9}	2.81×10^{-8}
PVA: Oxalic acid (70:30)	7.14×10^{-9}	1.89×10^{-6}
PVA: Oxalic acid (60:40)	1.43×10^{-9}	1.89×10^{-7}

TABLE III
CONDUCTIVITY OF PVA AND PVA: MALONIC ACID ELECTROLYTE FILMS.

Polymer electrolyte	**Conductivity S/cm at 303K**	**Conductivity S/cm at 373K**
PVA	$5.62\text{x}10^{-10}$	$6.15\ \text{x}10^{-9}$
PVA: Malonic acid 90:10)	$7.33\text{x}10^{-8}$	$3.73\text{x}10^{-7}$
PVA: Malonic acid (80:20)	$2.56\text{x}10^{-7}$	$4.796\text{x}10^{-7}$
PVA: Malonicacid (70:30)	$1.17\text{x}10^{-6}$	$1.23\text{x}10^{-5}$
PVA: Malonic acid (60:40)	$2.42\text{x}10^{-7}$	$1.04\text{x}10^{-6}$

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.

IV. CONCLUSIONS

The complexation of PVA polymer with Oxalic acid and with Malonic acid is confirmed with XRD and FTIR studies. The conductivity of pure PVA is about $7.62\text{x}10^{-8}$&$3.3\text{x}10^{-7}$ S/Cm at room temperature & at 100^0C respectively and these values increase to $7.14\text{x}10^{-9}$ &$1.89\text{x}10^{-6}$ S/Cm when PVA complexed with Oxalic acid (70:30). This particular sample of PVA complexed with Oxalic acid (70:30) has provided the maximum conductivity compared to other samples.

Similarly, the conductivity values of pure PVA at room temperature & at 100^0C and increase to $1.17\text{x}10^{-6}$&$1.23\text{x}10^{-5}$ S/Cm when PVA complexed with Malonic acid (70:30). This particular sample of PVA complexed with Malonic acid (70:30) has provided the maximum conductivity compared to other samples.

Among the two types of PVA complexed polymer electrolytes, due to relatively high conductivity, PVA complexed with Malonic acid (70:30) electrolyte could be a promising electrolyte for applications in electrochemical cells.

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