Thermal properties and electrochromic behaviour of PVA complexed electrolytes using PEG as plasticizer

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Thin films of PVA complexed with H$_3$PO$_4$ in different molar ratios using polyethylene glycol (PEG) as plasticizer are prepared by solution cast technique. Thermal study of the system of PVA-H$_3$PO$_4$-PEG indicates that glass temperature decreases as acid concentration increases in the presence of the plasticizer and hence, electrical conductivity of the complexed polymer increases. Thin films of higher conductivity are used in the fabrication of electrochromic devices. Optical absorption has been measured in transmission mode and time response of instantaneous change in optical density during colouring and bleaching sequence has been investigated by applying $-5.00$ to $+5.00$V to the WO$_3$ side with respect to ITO electrode for fixed duration. The modified device using PVA-H$_3$PO$_4$-PEG system shows maximum change in optical density (0.13 for the sample PVA- H$_3$PO$_4$) and gives higher value of contrast ratio due to high electrical conductivity. It is found that the plasticizer is effective to get shorter response time for the system of PVA- H$_3$PO$_4$-PEG in comparison to the PVA- H$_3$PO$_4$ system for which observed colouration and bleaching times are 105 and 85 s, respectively.

Keywords: Complexed electrolytes, PVA, Plasticizer, Electrical conductivity, Electrochromic display

1 Introduction
Solid polymer electrolytes have been the focus of a wide variety of fundamental and application oriented studies due to possibilities of their potential use in a various electrochemical devices$^{1-6}$. It is observed that nobium and tungsten oxide based thin films show better transmission modulation and hence are most suited for electrochromic display applications$^{7,9}$. However, the ionic conductivity of complexed system is comparatively low at room temperature applications. The conducting polymers having high ionic conductivity at ambient temperature have been developed. The ions within the amorphous region are responsible for high ionic conductivity in polymeric electrolytes along with introduction of crosslink into the amorphous phase$^{10}$. In the present paper, enhanced ionic conductivity has been reported for plasticizer polymer based complexes using PVA complexed with H$_3$PO$_4$ in different molar ratio. Thermal and electrical conductivity of complexed polymeric materials have been measured$^{11}$. The plasticizer polymer based film of suitable and desirable characteristics have been used in the fabrication of electrochromic display device and various parameters have been measured$^{12,13}$.

2 Experimental Details
2.1 Sample Preparation
Pure PVA with average degree of polymerization of 1750 supplied by Lobe Chemie India (containing 1-2 mole% of acetyl group) was kept 24 h under vacuum at 50°C before use. Films (80-250µm thick) of complexed polymer electrolyte were prepared using standard solution cast technique. The appropriate ratio of PVA and H$_3$PO$_4$ was dissolved in de-ionized triple distilled water separately. The solution was then mixed and stirred thoroughly for 4-5 h at 70°C to make it homogeneous. The different percentage of PEG was then added and stirred for 4-5 h. The mixed solution was spread over teflon moulds to evaporate the solvent slowly in air at room temperature. Finally, these polymeric films available on the moulds are dried under vacuum ($10^{-5}$ torr) to remove traces of solvent or any other volatile materials present in the sample. Polymer films, thus, obtained are rinsed with benzene/methanol and dried to remove any residual contents or traces of free acids present on the surface of the film.

3 Results and Discussion
3.1 Thermal studies
The structural characteristics and interpret various transition temperatures for complexed PVA with H$_3$PO$_4$ using PEG as plasticizer have been studied. DTA studies have been made at a heating rate of 10°C/min with alumina as reference material using LINSEIS Instrument (Type 2045). Various endothermic and exothermic peaks in different
temperature range of pure PVA, PVA+H$_3$PO$_4$ and PVA+H$_2$PO$_4$ using PEG as plasticizer have been compared. It is observed that glass transition temperature and melting temperature corresponding to the crystalline part decrease with increase of plasticizer in the PVA-H$_3$PO$_4$ complexes. Plasticizer molecules penetrate into the polymer matrix and establish polar attractive forces between it and the chain segments. These attractive forces reduce the cohesive forces between the polymer chains and increase the segmental mobility, thereby, reducing the $T_g$ value$^{18}$.

3.2 Electrical conductivity studies
The bulk electrical conductivity has been determined from the complex admittance ($B$-$G$) plots method for the PVA complexes with H$_3$PO$_4$ and PEG as plasticizer. At low temperature (below phase transition), $B$-$G$ plots show a steep rise in conductivity in high frequency range. At high temperature (after phase transition), a second dispersion region has also been found in the high frequency range. Knowing the bulk conductance ($G$) from $B$-$G$ plots; the bulk conductivity ($\sigma$) can be obtained from the relation:

$$\sigma = G \left(\frac{d}{A}\right) S \text{ cm}^{-1}$$

Where $A$ is the area of cross-section of the specimen in cm$^2$ and $d$ is the thickness in cm. The plasticized PVA complex shows higher electrical conductivity about ten times in magnitude than without using the plasticizer PEG shown in Fig.1.

On addition of plasticizer, there is an increase in electrical conductivity caused by increase in mobility of ions and polymeric bond rotations due to segmental motion of chains in the PVA complexes at higher temperature. The linear variation of $\sigma$ verses $1000/T$ plots before and after glass transition temperature suggests an arrhenous-type thermally activated process.

3.3 Electrochroic display device studies
An arrangement for the measurement of optical absorption in the transmission mode as a function of time has been made and shown in Fig.2. A halogen lamp of 600W illuminated the cell. The schematic arrangement of the electrochromic display cell assemblies along with electrical circuit for measurement can be made$^{13}$. Thin film of PEG plasticized based PVA H$_3$PO$_4$ complexed polymer electrolyte of size 1x1 cm$^2$ of uniform thickness and desirable characteristics was taken. WO$_3$ was deposited on one side of these polymer electrolytes by thermal evaporation technique ($10^5$ torr) using vacuum coating unit (Hindvac Model 12A4).

These films were sandwiched between two conducting glass plates. During colouration cycle, negative voltage is applied to the WO$_3$ side whereas bleaching cycle is obtained by reversing the polarity of the field. The redox chemical reaction associated with colouration and bleaching of WO$_3$ film can be represented as

$$\text{WO}_3 + xe^- + x\text{H}^+ \leftrightarrow \text{H}x\text{WO}_3$$

(Transparent) (Blue)

The colouration and bleaching times have been calculated from the transmitted light intensity (TLI) measurement$^{13-17}$. It is found that the plasticizer is effective to get smaller response time for the system of PVA-H$_3$PO$_4$-PEG in comparison to the PVA-H$_2$PO$_4$ system as shown in Table 1.
For further detailed investigations, other device parameters such as colouration efficiency, injected charge density and transmission modulation are needed to show the better performance of the system. It may be due to the reason that amorphous films contain pores and voids, which may promote the diffusion of ions for electrochromic processes.

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References
2 Fenton D E, Parker J M & Wright P V, Polymer, 14 (1973) 589.

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<thead>
<tr>
<th>Sample</th>
<th>Colouration time</th>
<th>Bleaching time</th>
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<tbody>
<tr>
<td>PVA+H₃PO₄</td>
<td>tₐ s</td>
<td>tₕ s</td>
</tr>
<tr>
<td>PVA+H₃PO₄+PEG 98</td>
<td>85</td>
<td>79</td>
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Table 1—Determination of colouration and bleaching times from optical transmission transient response