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Synthesis and physical properties of Al^{3+} doped PVA polymer electrolyte films

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Abstract

Polymer electrolyte films of PVA with Al(NO$_3$)$_3$ as the dopant at different concentrations were prepared using solution casting technique. Optical absorption studies exhibited that the values of optical absorption coefficient, direct and indirect optical band gaps are found to decrease with increase in Al(NO$_3$)$_3$ concentration which indicates the charge transfer in complexes between the polymer and the dopant. Dielectric and electrical modulus studies of the samples were performed in the frequency range of 100 Hz to 1 MHz at different temperatures.

Keywords: *Polymer electrolyte, thick films, optical properties, dielectric properties and electric modulus.*

1. Introduction

Water soluble polymers are important in industry. Polyvinyl alcohol (PVA) is the most interesting polymer because of its high dielectric strength and thermal stability, good charge storage capacity, and dopant-dependent electrical and optical properties [1, 2]. At room temperature, PVA is a semi-crystalline polymer with both amorphous and crystalline phases. It also has a carbon chain backbone with hydroxyl groups attached to the carbons of methane. These -OH groups can act as a source of hydrogen bonding and thus aid in the formation of polymer blends. PVA is a potential material with optical, electrical, and thermal properties that depend on the dopant. Incorporating metal salts or rare-earth salts into polar organic polymers can result in significant changes in polymer properties. According to some studies, the optical and thermal properties of PVA can be controlled through doping for various applications [3,4].

Rare-earth complexes are good candidates for light emitting diodes, optical fibres, laser materials, and optical signal amplification. Furthermore, rare-earth salts have a significant impact on polymer structure, optical, and thermal properties [5]. PVA with a high refractive index is available. PVA with a high refractive index is very useful in optics and photonics because it can reduce reflection losses and interfaces, increasing light output. Al^{3+} is one of the most reactive rare earth metal ions, with numerous applications in a variety of fields [6].

PVA has been doped with various rare-earth ions such as Ho^{3+}, Er^{3+}, Sm^{3+}, Eu^{3+}, and La^{3+} [7-9], but there has been little research on PVA doped with Al^{3+}. This article describes an investigation into the effect of aluminium concentration on the optical and dielectric properties of PVA films in order to improve these properties. To make it more applicable, it has been developed a polymeric film with controllable optical, dielectric and electric modulus parameters in this paper.

2. Experimental details

Polyvinyl alcohol (PVA) and anhydrous aluminium chloride (AlCl$_3$) were purchased from HiMedia Laboratories Pvt. Ltd, India and used as received. Solution casting was used to create PVA and PVA : Al^{3+} films. A known amount of PVA was dissolved in double distilled water and then gently heated in a water bath to prevent polymer thermal decomposition. The hot solution was stirred until the polymer was completely dissolved and the solution became clear and viscous. This is known as PVA stock solution. In addition, different amounts of AlCl$_3$ were dissolved in doubly distilled water to achieve the desired concentrations (0, 10 and 20 mol%), and then mixed together in PVA stock solution while stirring thoroughly with a magnetic stirrer. PVA and PVA:Al(NO$_3$)$_3$ solutions were filtered to remove air bubbles trapped in the solution by stirring and then set aside for the required time to achieve the desired viscosity. A known quantity of the obtained solution was poured onto a levelled clean glass plate and allowed to dry for few hours at 70°C. The films were peeled from the glass plate and stored in vacuum desiccators. Then the films have been characterized for studying the optical, dielectric and electric modulus properties. The room temperature optical absorption spectra were studied using the Perkin-Elmer LAMBDA 35 UV–VIS–NIR spectrometer over the wavelength range of 200–800 nm. The dielectric and electric modulus measurements were performed using N4L Phase Sensitive Multimeter interfaced with Impedance Analyzer with a cell with stainless steel electrodes in the temperature range of 303-423 K over a frequency range of 100 Hz–1 MHz

3. Results and discussion

3.1. Optical studies

The UV-Visible optical absorption spectra of pure and Al^{3+} doped PVA polymer electrolyte films are shown in Fig. 1(a). It is clear that the spectrum of PVA polymer electrolyte film exhibits an absorption band around 287 nm which may be attributed to π-π^* transition. It comes from unsaturated bonds (C=O and/or C=C), mainly C=O [10]. Furthermore, the optical spectra of the doped films show that the absorption band position is shifted towards the higher wavelength side and is found to be within the range from 293 to 298 nm as the concentration of aluminium nitrate increases from 10 to 20 mol%. The absorption also increases with increase in salt concentration which implies that the increase of absorbance is approximately proportional to the aluminium nitrate concentration based on the effective mass approximation. In order to determine the optical band gap of the films, the absorption coefficient (α) was determined from the following formula:

$$\alpha = 2.303\times\frac{A}{d} \tag{1}$$

where A is the absorbance and d is the film thickness. The optical energy band gap of the films was determined from the absorption spectra near the absorption edge. The absorption coefficient dependence on photon energy is expressed as:

$$(\alpha h\upsilon)^r = B(h\upsilon - E_g) \tag{2}$$

where B is a constant, $h\upsilon$ is the photon energy and E_g is the optical energy band gap, r is an exponent which can take values of 1, 2, 3, 1/2, 3/2 depending on the nature of the electronic transitions responsible for the optical absorption [11]. The best straight line can be determined from the slope of the linear part of $(\alpha h\upsilon)^2$ versus $h\upsilon$ and $(\alpha h\upsilon)^{1/2}$ versus $h\upsilon$. This suggests that the transition energy for electrons may account for direct and indirect allowed transitions. The absorption coefficient, direct and indirect optical band gaps were estimated by extrapolating the linear portion of their curves as shown in Figs. 1(b-d). It is clear from the Figs. 1(b-d) that the absorption coefficient, direct and indirect band gap values decrease with Al doping which is due to fact that the salt concentration significantly decreases the optical energy gap in the way of producing some defects in the films. These defects cause the localized states which reflects the increase in the degree of disorder in films [12].

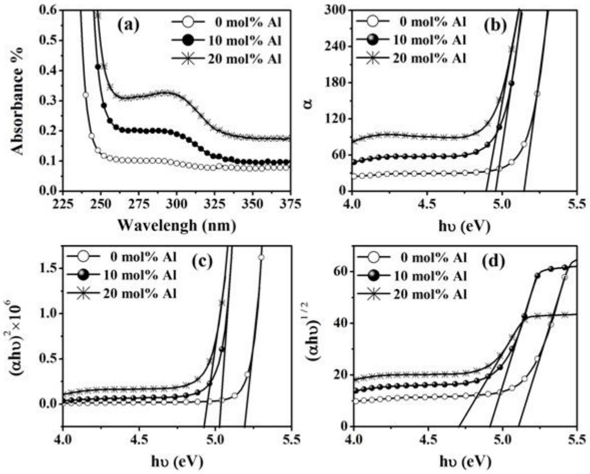

Fig. 1 *(a) Optical absorption spectra, (b) α vs $h\upsilon$ plots, (c) $(\alpha h\upsilon)^2$ vs $h\upsilon$ plots and (d) $(\alpha h\upsilon)^{1/2}$ vs $h\upsilon$ plots of pure and different concentrations of Al doped PVA polymer electrolyte films.*

3.2. Dielectric studies

Fig. 2 presents the plot of (a) real (ε') and (b) imaginary (ε'') parts of dielectric constant as a function of frequency for undoped and Al^{3+} doped PVA films. From the Figs. 2 (a and b), the highest dielectric constant could be observed at lower frequencies while they decrease with increasing frequency. This significant behavior is due to the presence of space charge polarization phenomena at the electrodes. At high frequencies, oscillating dipoles in the direction of applied electric field are lagging behind the field. This can be associated with the inability of rotation of dipoles which decreases the dielectric constant values at higher frequencies. It is also noticed that dielectric constant increases with the increase in Al dopant concentration which proves the introduction of $Al(NO_3)_3$ would increase the dielectric constant of PVA film. The maximum dielectric constant at low frequency is found for 20 mol% Al doped film. Figs. 2(c and d) show the dielectric plots of 20 mol% Al doped polymer films at different temperatures. The dielectric constants increase with increasing temperature because dipole orientation is facilitated by increasing the temperature, thus increasing the dielectric constant [11-13].

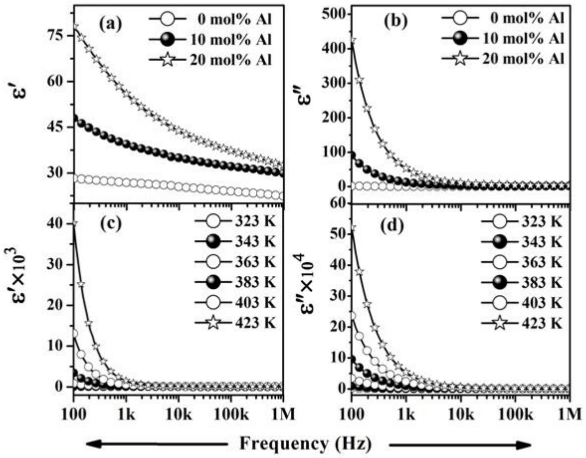

Fig. 4 *Dielectric plots (a) ε' and (b) ε'' of pure and Al doped PVA polymer electrolyte films at room temperature. (c) ε' and (d) ε'' plots of 20 mol% Al doped PVA polymer electrolyte film at different temperatures.*

3.3. Electric modulus analysis

The electric modulus plots of three films are displayed in Fig. 3. It can be seen from the Figs. 3(a and b) that the values of M′ and M″ at low frequency side decreased with increase of salt concentration which confirms the two factors: (1) the removal of electrode polarization and (2) the conductivity relaxation time ($\tau_m=1/\omega_m$ where ω_{max} is angular frequency maximum) is small for Al doped films. Temperature dependent electrical modulus spectra as function of frequency for the pure and Al^{3+} doped PVA films are shown in Figs. 3(c and d). The values of M′ and M″ were found to be low and finally it reaches to zero value which confirms the removal of electrode polarization [14]. The decrease in the value of electrical modulus with increasing temperature results the increase in the mobility of charge carriers in PVA film with Al^{3+} doping. As seen in Fig. 3(d), M″ shows an asymmetric peak centered at the dispersion region of M′ which indicates the conductivity relaxation peak for the distribution of relaxation times of the free charges and the broadening of the peaks suggests a non-Debye type of relaxation in the film. The shift in the peak position towards higher frequency side could be observed as the temperature is increased. This might be related to thermally activated relaxation process, and charge carrier hopping takes place. The frequency region on the pre-peak decides the range whereas the mobility of charge carriers are on long distances while region to the post-peak is where the confinement of carriers in potential wells, being mobile on short distances which are consistent with conductivity studies as mentioned above [12-14]. The frequency maximum (f_{max}), which corresponds to the M″$_{max}$, gives the relaxation time (τ_c) from the condition, $\omega_{max}\tau_c=1$.

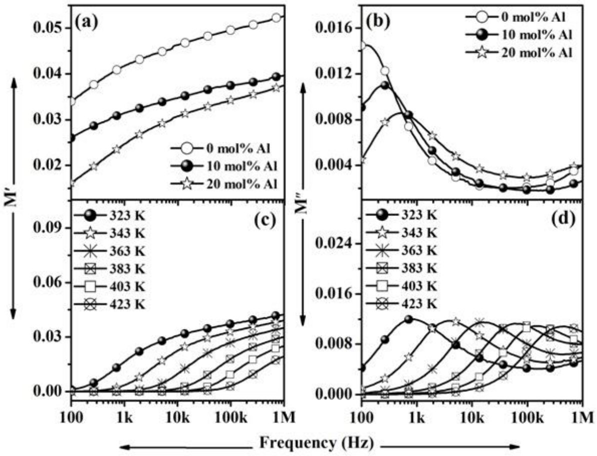

Fig. 9. *Modulus spectra (a) M′ and (b) M″ of pure and Al doped PVA polymer electrolyte films. (c) M′ and (d) M″ plots of 20 mol% Al doped PVA polymer electrolyte film at different temperatures.*

4. Conclusion

Al doped PVA polymer electrolyte films have been synthesized using solution casting technique. Optical absorption spectra exhibited that the values of absorption edge, direct and indirect band gaps are decreased with increase in salt concentration. This result indicates the formation of charge transfer complexes between polymer and Al(NO$_3$)$_3$ dopant. The plots of dielectric constant showed an increase in the dielectric constant at low frequency with Al concentration which is attributed to the presence of space charge polarization phenomena at the electrodes. The electric modulus plots of Al doped PVA polymer electrolyte films have confirmed the non-Debye type of relaxation in the films.

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