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Basavarajeshwari M. Baraker, Preeti B. Hammannavar, and Blaise Lobo

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Optical, Electrical, Thermal Properties Of Cadmium Chloride Doped PVA – PVP Blend

Basavarajeshwari M Baraker, Preeti B Hammannavar and Blaise Lobo*

Department of Physics, Karnatak Science College, Karnatak University, Dharwad-580001, India
**E-mail: blaise.lobo@gmail.com*

Abstract. Films of polyvinylalcohol (PVA) – polyvinylpyrrolidone (PVP) blend doped with Cadmium Chloride ($CdCl_2$) in the doping range 1 wt% to 40 wt% were prepared by solution casting technique. These films were characterized using optical/UV-Vis- NIR spectroscopy, Differential Scanning Calorimetry (DSC) and DC electrical measurements. The UV-Visible spectra were quantitatively analyzed to yield the optical parameters. The UV-Visible Spectra show intermediate absorption bands (before the final absorption edge) due to formation of energy bands in the forbidden gap of PVA-PVP. There is a prominent absorption band at 2.9 eV, from 0.5 wt% up to 1.8 wt% doping level (DL) caused by the dopant ($CdCl_2$). The DC electrical studies showed an increase in activation energy from 2.8 eV at 0.5 wt% DL up to 3.5 eV at 4.4 wt% DL, reaching a low of 2.4 eV at 11.2 wt% DL. DSC scans show evidence of formation of chain fragments, at doping levels beyond 8 wt%.

Keywords: Cadmium Chloride, Doping, PVA- PVP Blend, DSC, Optical Analysis.
PACS: 36.10.Dr, 78.70.Bj, 61.25.hk, 78.40.-q, 61.43.-j, 71.60.+z

INTRODUCTION

Polyvinylalcohol (PVA) is a versatile, poly-hydroxyl polymeric material, which has gained the interest of researchers due to its many potential applications, the scope for easy modification and formation of useful miscible blends with many other polymers. PVA doped with different red-ox agents [1-5] like iodine, ferric chloride, barium chloride and other salts have been studied, and these doped polymeric materials show significant modification in their micro-structural, optical and electrical properties, (when compared to pure PVA films). The analysis of optical and electrical properties of a doped polymeric blend enables the determination of properties concerning electronic band-structure of the material.

PVA forms a miscible blend with polyvinylpyrrolidone (PVP), which is a hygroscopic polymer, often used as a capping agent for nano-particles [6]. The opto-electronic and micro-structural properties of PVA-PVP blend films doped with different red-ox agents (dopants) have been experimentally investigated by many researchers [7-8]. In this paper, we have discussed the preparation and characterization of PVA - PVP blend films, doped with different concentrations of $CdCl_2$ (with dopant concentration in PVA-PVP blend ranging from 0.5 wt% up to 40 wt%). A survey of literature reveals that PVA-PVP blend doped with $CdCl_2$ has not been studied earlier, but PVA-$CdCl_2$ electrolyte has been studied by some authors [9-11]. These studies indicate that the degree of crystallinity of PVA decreases and its conductivity increases with increase in $CdCl_2$ doping level (DL) in PVA [9]. It has been suggested, from FTIR studies, that Cd^{2+} has the ability to induce polymer chain scission [10]. Differential Scanning Calorimetry (DSC) scans can reveal formation of chain fragments. The optical band gap of PVA-$CdCl_2$ electrolyte is reported to reduce with increase in concentration of $CdCl_2$ [11].

SAMPLE PREPARATION

A standard solution of cadmium chloride mono-hydrate ($CdCl_2.H_2O$) was prepared in distilled water. Different volumes of this standard solution were added to aqueous solutions of PVA-PVP (equal proportion by weight) prepared earlier, in different beakers. The doped solutions of the PVA-PVP aqueous blend were then dried in glass petri-dishes, using an air cooled, temperature controlled oven maintained at 40°C. The films, after drying, were carefully peeled from the glass substrate, labeled and stored. These films were characterized by optical (UV-Visible and Near IR), electrical and thermal (DSC) measurements.

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ANALYSIS OF OPTICAL SPECTRA

Hitachi U 3310 UV-Visible spectrometer was used in the wavelength range 200-1000 nm, for obtaining the Optical absorption (UV-Visible) spectra. The spectra were recorded at room temperature and analyzed to extract optical parameters like activation energy and optical band gap. It was observed that the absorption coefficient is a function of photon energy, and obeys Mott-Davis model [12]. According to this model, one can obtain the optical band gap E_g of materials by applying equation (1).

$$\alpha(\nu)\, h\nu = B(h\nu - E_g)^m \qquad (1)$$

In equation (1), B is the disorder parameter, and E_g is the optical energy band gap. The value of m is 1/2, 3/2, 2 and 1/3 for direct allowed transition, direct forbidden transition, indirect allowed transition and indirect forbidden transition, respectively. The nature of optical transitions were found to be of indirect allowed type (best fit), although the fit of the absorption edge data for direct allowed transitions was also satisfactory.

The activation energy for optical transitions E_A can be calculated from the rising edge of absorption bands in the UV-Visible spectrum, as illustrated in figure 1. If λ_A is the x-intercept of the straight line fit of the rising edge optical data, in the plot of absorbance versus wavelength, the activation energy E_A (in eV) is calculated from λ_A (in nm), using equation 2.

$$E_A = \frac{1240.8}{\lambda_A} \qquad (2)$$

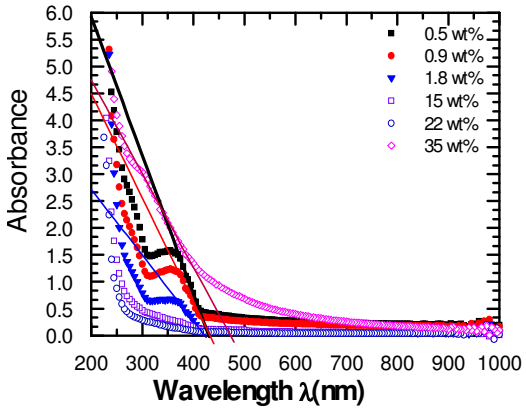

Figure 1. The optical Spectra of $CdCl_2$ doped PVA-PVP blend, showing the intermediate absorption bands

It is seen from the optical spectra that there are absorption peaks of intermediate photon energies, before the higher photon energy absorption edge. The samples of $CdCl_2$ doped PVA-PVP blend shows an intermediate absorption band at 2.9 eV (from 0.5 wt% to 1.8 wt%), reducing to 2.8 eV (at 8 wt%) and 2.6 eV (at 35 wt% to 40 wt%). This corresponds to the energy levels introduced into the forbidden gap by the doping process. These absorption peaks in the optical spectra are due to polaron and bi-polaron bands. Hence, they lead to a decrease in the activation energy obtained by the DC electrical measurement. At the high energy absorption edge, the activation energy for optical transitions increased from 3.8 eV at 0.9 wt% doping level (DL) to 4.7 eV at 5.4 wt% DL, where it remains unchanged up to 9.3 wt% DL, and drops significantly at higher levels of doping due to widening of intermediate bands created in the polymeric blend by the dopant.

ELECTRICAL PROPERTIES

An arrangement for temperature variation (PID Controlled oven/ furnace) of polymer samples has been used with a temperature controller accurate to one degree Celsius, for the study of temperature variation of electrical conductivity (σ) using two-probe method. There is an exponential drop in electrical resistivity of the sample with increase in absolute temperature *(T)*, which can be explained with the help of the Arrhenius relation (equation (3)). In equation (3), k_B is the Boltzmann constant (1.38×10^{-23} J K^{-1}).

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{2k_B T}\right) \qquad (3)$$

The factor 2 in equation (3) is to account for both electrons in conduction band and holes in valence band as the mobile charge carriers responsible for electrical conduction. The results are presented in table (1). The DC electrical studies showed an increase in activation energy from 2.8 eV at 0.5 wt% DL up to 3.5 eV at 4.4 wt% DL, beyond which it is found to decrease.

TABLE 1. Activation energy of $CdCl_2$ doped PVA-PVP blend, from DC electrical measurements.

Dopant Level DL (wt%)	Activation Energy E_a (eV)
0.5	2.8
0.9	2.8
1.8	2.7
2.2	3.2
3.3	3.5
4.4	3.5
5.4	3.4
6.4	3.0
8.4	3.0
10.3	2.4
15.5	2.4
25.6	2.8

THERMAL ANALYSIS

The thermal properties of the prepared films were characterized using Differential Scanning Calorimetry (DSC), for which TA instruments DSC Q20 V24.10 Build 122 was used. The sample was heated from temperature 25°C up to 400°C, at heating rate 10°C/minute.

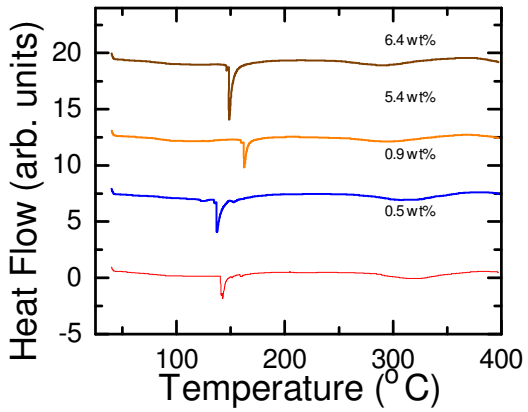

Figure 2. DSC curves of lightly and moderately doped ($CdCl_2$) PVA-PVP blend

The DSC curves (see figure 2) show sharp endotherms between 123°C and 160°C, at low and moderate $CdCl_2$ doping levels (between 0.5 wt% and 6.3 wt%). However, a broad endotherm is observed between 60°C and 200°C, for doping levels beyond 8.4 wt%, indicating enhanced formation of polymer chain fragments at high dopant concentrations.

CONCLUSION

The $CdCl_2$ doped PVA-PVP blend films were prepared in the doping range from 0.5 wt% up to 40 wt%, and their optical, electrical and thermal properties were investigated. The analysis of optical and electrical experimental data reveals the formation of allowed energy bands within the forbidden gap of PVA-PVP, on doping with $CdCl_2$. DSC scans show evidence for chain scission at doping levels beyond 8 wt%. Activation energy was determined from DC electrical measurements and analysis of the optical spectra.

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