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DBS investigation on films of cobalt chloride doped PVA-PVP blend

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Abstract. Films of Cobalt Chloride (CoCl_2) doped polyvinylalcohol (PVA)-polyvinylpyrrolidone (PVP) blend (doped from 0.5 wt% up to 28 wt%) were prepared by solution casting, and characterized by XRD, DSC, UV-Visible Spectrometry TGA, FTIR and electrical measurements. In this paper, the results of Doppler Broadening Spectroscopy (DBS) in CoCl_2 doped PVA-PVP blend is discussed. An increase in crystallinity of PVA-PVP blend, is observed, on doping it with CoCl_2 . The DBS results are complemented by XRD and DSC scans.

1. Introduction

Polyvinylalcohol (PVA) is a polymeric material which has gained interest of researchers due to its potential applications, the scope for easy modification and formation of miscible blends with many other polymers. PVA doped with different redox agents have been studied, and these doped polymeric materials show significant modification of micro-structural, optical and electrical properties [1-5]. The doping of a miscible blend of PVA with polyvinylpyrrolidone (PVP) involves inter-molecular and intra-molecular hydrogen bonds [6]. Cobalt chloride (CoCl_2) has a potential to significantly modify the dielectric and optical properties of a material [7]. The modifications in the electronic band-structure caused by incorporation of cobalt chloride (CoCl_2) as dopant in polyvinylalcohol – polyvinylpyrrolidone (PVA-PVP) blend has been studied by analyzing the experimental optical spectra and electrical behaviour of the material [8]. The information provided by thermal analysis and X-ray diffraction (XRD) scans yield complementary data, which helps in understanding the micro-structural nature of semi-crystalline polymeric materials, especially the changes caused by doping [9].

Doppler Broadening Spectroscopy (DBS) or Doppler Broadening of Annihilation Radiation (DBAR) is one of the efficient techniques of Positron Annihilation Spectroscopy (PAS), giving information about the electron momentum distribution in materials [10]. The DBS spectrum can be analysed using line-shape parameters, namely S- parameter and W- parameter. The S-parameter is a measure of positrons annihilating with low momentum electrons from the molecules in amorphous (disordered) regions of the polymeric material. The W-parameter is a measure of positrons annihilating with high momentum electrons from the crystalline (ordered) regions of the polymeric material. Hence, an increase in the degree of crystallinity and width of crystalline domains is expected to be reflected in a decrease in S- parameter, and an increase in the W- parameter.



2. Experimental

The films of PVA-PVP- CoCl_2 blend were prepared by solution casting method. Films having different concentrations (doping levels from 1 wt% up to 28 wt%) of CoCl_2 were prepared. The method of preparation of these films is discussed elsewhere [8]. A Hitachi U 3310 UV-Visible spectrometer was used in the wavelength range 200-1000 nm for obtaining the Optical absorption (UV-Visible) spectra. The Urbach energy which is the width of band tails in the forbidden gap, is found to decrease significantly with increase in doping level of cobalt chloride in PVA-PVP blend films. It is 0.9 eV at 1 wt% doping level, 0.1 eV at 4.3 wt% doping level and becomes negligible at 28 wt% doping level, suggesting an increase in degree of structural order in CoCl_2 doped PVA-PVP blend, when concentration of CoCl_2 is increased. 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, using two-probe method (SES, Roorkee). The powder XRD spectra were recorded using Rigaku X-ray Spectrometer, with Cu K_α x-rays of wavelength 1.5406 angstrom.

An 8 micro-curie sodium-22 source, deposited on a thin kapton foil, was used as source of positrons. This source was sandwiched on either side by CoCl_2 doped PVA-PVP films (stacked to 1 mm thickness, on either side). This assembly was kept at a distance of 10 cm from the window of the detector. A high resolution HPGe detector was used to record the energy spectrum of annihilation gamma rays from the sample. The energy resolution was measured to be 1.4 keV at 662 keV photo-peak of Cesium-137 source.

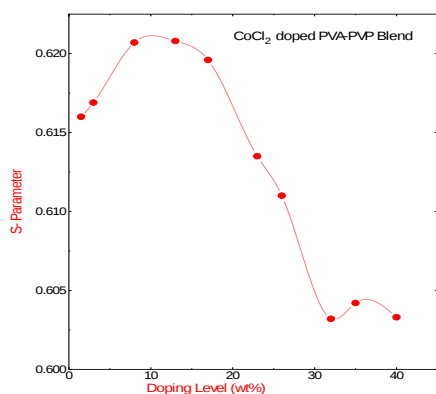


Figure 1. The variation of S- parameter w.r.t doping level of CoCl_2 in PVA-PVP blend.

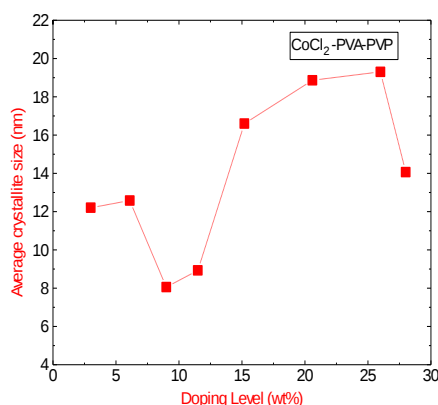


Figure 2. The variation of average crystallite size with doping level, for CoCl_2 doped PVA-PVP blend.

3. Results and discussion

It is noted that the computed S- parameter and W -parameter reflect changes in the degree of crystallinity and average crystallite size of CoCl_2 doped PVA-PVP blend samples. The Variation of S-parameter of DBAR spectrum of CoCl_2 doped PVA-PVP blend w.r.t doping level is shown in Fig. 1. The variation of W-parameter with doping level is complementary to that of the S- parameter. Fig. 2 shows the variation of average crystallite size (determined from XRD scans) with doping level. There

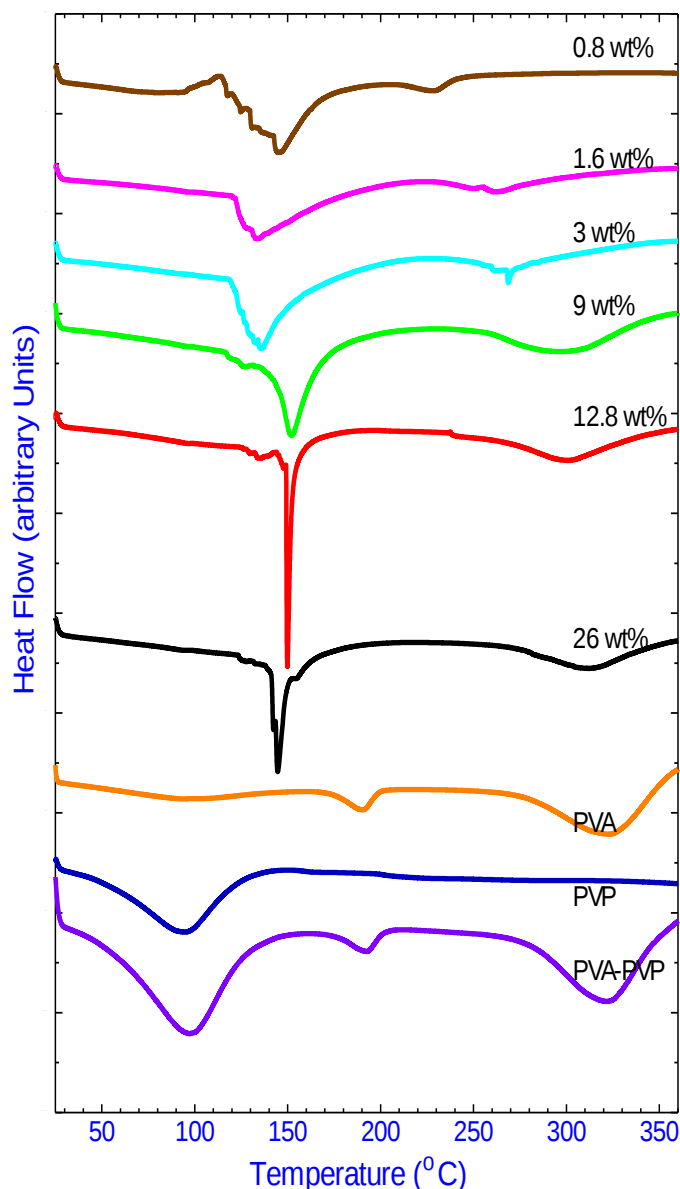


Figure 3. DSC curves of PVA, PVP, PVA-PVP blend, and different dopant levels (in wt%) of CoCl₂ in PVA-PVP blend.

indicator), in the FTIR scans of all CoCl₂ doped PVA-PVP blend samples. In addition, from DSC scans, it is observed that the temperature of onset of melting increases, and the melting endotherm becomes sharper on increased dopant concentration, indicating formation of larger crystalline domains.

4. Conclusion

Significant structural changes are caused by incorporation of cobalt chloride (CoCl₂) as dopant in polyvinylalcohol –polyvinylpyrrolidone (PVA-PVP) blend. The XRD and DSC scans reveal an increase in average crystallite size and the degree of crystallinity of the blend. The line-shape parameters of DBS complement this observation.

is complementary evidence from XRD for increase in average size of crystallites. The CoCl₂ doped PVA-PVP blend films were semi-crystalline in nature. The variation of average crystallite size versus doping level is shown in Fig. 2. The average crystallite size increased from 7.8 nm at 9 wt% up to 19 nm at 26 wt%, indicating an increase in structural order caused by doping PVA-PVP blend with CoCl₂. This is supported by the variation of S-parameter with doping level, shown in Fig. 1 and also the decrease in Urbach energy derived from the UV-Visible spectra (described in the experimental section). Note that the S-parameter, on low levels of doping, first increases and then saturates, dropping significantly on further increase in doping concentration. The S-parameter, being a measure of annihilation of positrons (or positrons bound in Ps) with low momentum electrons, shows an increase if there is an increase in amorphous nature of the sample. An increase in crystallite size will result in a drop in the S-parameter.

The DSC curves of PVA, PVP and PVA-PVP blend in Fig. 3, confirms the formation of miscible blend, with a single glass transition temperature. On doping with CoCl₂, at low dopant concentrations, a number of just resolved endotherms are observed at lower melting temperatures, indicating the formation of crystalline lamellae of different thicknesses.

As the doping concentration increases, the area under the melting endotherm increases, indicating an increase in the degree of crystallinity. This is in agreement with the XRD and DBS results.

This is supported by the presence of an absorption band at 1142cm⁻¹ (crystallinity

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