

International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN : 0974-4290
Vol.6, No.3, pp 1852-1854, May-June 2014

ICMCT-2014 [10th – 12th March 2014]
International Conference on Materials and Characterization Techniques

Microstructural studies on Cobalt chloride doped PVA -PVP blend

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Abstract- Solution cast films of PVA (polyvinylalcohol) and PVP (polyvinylpyrrolidone) blend, doped with cobalt chloride (CoCl₂) in the concentration range (doping level) from 1 wt% up to 28 wt% were characterized, and the data collected was analyzed to yield information about the microstructure of these films. XRD, DTA-TGA, ATR-FTIR, UV-Vis and DC electrical measurements were performed. Although un-doped PVA-PVP blend (equal composition of PVA and PVP by weight) is amorphous, the CoCl₂ doped films showed a semi-crystalline nature, the average crystallite size increasing from 7.5 nm at 9 wt% doping level up to 19 nm at 26 wt% doping level. The FTIR and DTA-TGA spectra are used to complement the information about microstructure of these samples provided by XRD, and also correlated with electrical and optical analysis, the latter revealing a higher degree of structural order in CoCl₂ doped PVA-PVP blend films, on increased incorporation of cobalt chloride.

Keywords- Cobalt chloride, PVA, PVP, Blend, Doping, Microstructure.

1. Introduction and Experimental:

Polyvinylalcohol (PVA) is a semi-crystalline polymer, with varied applications [1]. A semi-crystalline polymeric material has regions of structural order and disorder called crystallites and amorphous regions respectively, separated by regions of inter-mediate order [2]. On the other hand, Polyvinylpyrrolidone (PVP) is an amorphous polymer, which forms a miscible blend with PVA. The miscible blend of PVA and PVP has medical use as a hydrogel [3]. The PVA-PVP blend doped with different chemicals has been studied [4, 5]. The doping of polymeric materials with CoCl₂ has a potential application as a humidity sensor [6]. The method of preparation of CoCl₂ doped PVA-PVP blend films is described elsewhere [7]. The powder XRD spectra were recorded using Rigaku X-ray Spectrometer with Cu K-alpha x-rays. The samples prepared were semi-crystalline in nature, with an average crystallite size of a few nanometers.

2. Results and Discussion:

Cobalt Chloride (CoCl₂) is a dopant which modifies the electrical, optical and structural properties of polymeric materials, including blends [7-10]. The investigation by our group on the Urbach energy (E_u), by

analysing the optical spectra of thick films of CoCl_2 doped PVA-PVP blend [7] revealed a significant decrease in its value, on increasing the CoCl_2 concentration in the PVA-PVP blend, which suggests a higher degree of structural order in the sample, caused by CoCl_2 doping. On doping PVA-PVP blend with different concentrations of CoCl_2 , extra peaks are observed in the UV-Visible spectra at lower activation energies 2.3 eV, 3.0 eV and 1.7 eV, when compared to the absorption edge. These additional peaks indicate the formation of allowed energy bands within the forbidden gap, due to doping. This is accompanied by a decrease in DC electrical resistivity of the doped samples. The Arrhenius relation for variation of electrical conductivity with temperature revealed a decrease in activation energy from 4 eV to 3.1 eV, on increasing the concentration of CoCl_2 in PVA-PVP blend. The increase in crystallinity of PVA-PVP blend on increasing the CoCl_2 concentration is confirmed by the XRD scans, from which the average crystallite size determined shows a significant increase, with increase in dopant concentration in the polymeric blend (Figure 1). This corresponds to improvement in structural order in the amorphous region, and regions of inter-mediate order, and the inter-planar spacing (d-spacing) in the crystallites does not change (d spacing = 8.5 angstroms).

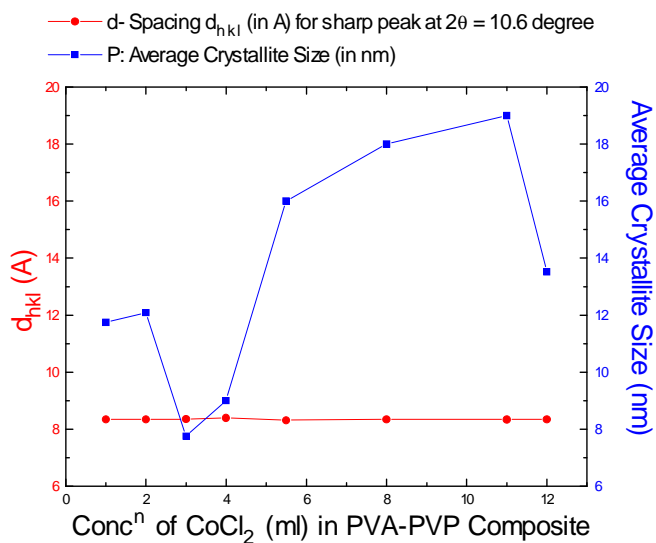


Figure 1. The d-spacing and average crystallite size for different doping levels (in ml) of cobalt chloride in PVA-PVP. See equation (1) for conversion to doping level in weight percentage.

The doping level (DL; concentration of CoCl_2 in the PVA-PVP blend) in weight percentage (wt%) can be calculated from the volume (V_{st}) of 1M standard solution (in ml) added to the blend of PVA and PVP (two gram each), using equation (1).

$$DL \text{ (wt\%)} = (V_{st} \times 0.13) / [4 + (V_{st} \times 0.13)] \quad (1)$$

The DTA/TGA scans show weight loss at three different temperature regions of the CoCl_2 doped PVA-PVP blend sample. The weight loss of 20% at 100-120 degree Celsius is due to removal of water content sorbed by the sample. The weight loss of 15 % at 220-250 degree Celsius is accompanied in the DTA scan by a melting endotherm due to melting of some of the crystallites in the sample. The weight loss of 25% at 380-450 degree Celsius is associated with degradation of the sample. The FTIR spectra of the CoCl_2 doped PVA-PVP blend films reveals absorptions at 3440 cm^{-1} due to $-\text{OH}$ stretching vibration of PVA, 1924 cm^{-1} and 2860 cm^{-1} due to CH - asymmetric and symmetric stretching respectively, 1744 cm^{-1} due to acetate groups associated with un-hydrolysed portions of polyvinylacetate in PVA, 1637 cm^{-1} due to stretching vibration of carbonyl group of PVP, 1260 cm^{-1} due to C-N stretch, 1452 cm^{-1} due to CH_2 wagging and 1405 cm^{-1} due to CH bending. Most of these vibrations in CoCl_2 doped PVA-PVP blend are at wave-numbers significantly shifted than when compared to un-doped PVA-PVP blend, indicating interaction of PVA and PVP molecules with the cobalt ion. The significant shoulder at 1160 cm^{-1} is an indicator of increased crystallinity of these samples.

The funding for this work is in terms of a Major Research Project from the University Grants Commission (UGC), Government of India; Sanction Number F.38-103/2009(SR) dated 19th December 2009. RVP acknowledges financial assistance in terms of a Project Fellowship from the UGC, Government of India.

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