PVP Influence on PVA crystallinity and optical band gap

Sudha Kamath M. K.[1], Harish Kumar H. G.[1], Chandramani R.[2] and Radhakrishna M. C.[3]

[1]Department of Physics, R V College of Engineering, Bangalore, Karnataka, India
[2]Department of Physics, DSCE, Bangalore, Karnataka, India
[3]Department of Physics, Bangalore University, Bangalore, Karnataka, India

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ABSTRACT

Thin films of PVA/PVP blend have been obtained by solution casting method. These films have been subjected to structural (XRD) and optical (FTIR, UV-VIS) studies. The crystallnity of PVA/PVP blends decreases with the increase in concentration of PVP. The FTIR spectra show the blending of PVA and PVP at different concentration. The UV-Vis spectroscopic analysis shows that optical band gap energy of PVA/PVP blends decreases with the increase in concentration of PVP.

Key words: Polymer, XRD, UV-vis spectroscopy, Band gap
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INTRODUCTION

Polymers have increasingly become attractive because of their wide range of applications *viz.,* photonics, biotechnology and optoelectronics. In recent years the blending of different polymers together is one of the strategic methods to improve the performance of a material which allows realization of novel polymer systems that enhance the performance of the parent polymer at low cost. It is a useful technique for designing materials with a wide variety of macroscopic properties. This method is a result of modifying the structure at the microscopic scale [1]. Poly (vinyl alcohol) (PVA) is a water-soluble polymer with high transparency and outstanding mechanical and thermal properties. PVA has been widely used in textiles, paints, building materials, electronic products, automotive, aerospace, medicine, paper making, printing, packaging, and other industries. It is often blended with other polymers to improve the properties of the bulk material. The polymers such as cellulose (and its derivatives) and poly(vinylpyrorrolidone) (PVP) are known to be miscible with PVA, presumably due to hydrogen-bonding interactions between the hydroxyl groups of PVA and appropriate interacting sites in the blend partner (carbonyl groups of PVP and secondary hydroxyl groups of cellulose)[2-5]. PVP is an amorphous polymer of high environmental stability, easy processability, and moderate thermal conductivity [2]. PVP is one of the most commonly used polymers in medicine because of its solubility in water and its extremely low cytotoxicity [5]. When PVA and PVP are mixed together, the interactions between PVA and PVP are expected to occur through interchain hydrogen bonding between the carbonyl group of PVP and the hydroxyl group of PVA. Therefore it is reasonable to expect significant changes in optical properties when two polymers are blended. In the present work a series of PVA/PVP blend films are prepared by solution casting method and the effect of concentration on the optical properties of the polymer blend system are studied.

MATERIALS AND METHODS

Poly (vinyl alcohol) (PVA) with an average molecular weight of 70000 and poly (vinyl pyrrolidone) (PVP) of average molecular weight 1,300,000 from SIGMA, Aldrich are used. Pure PVA, pure PVP and PVA/PVP blend (in the weight percent ratios 80:20, 60:40, 50:50, 40:60, 20:80) films are prepared by solution casting method by dissolving required quantity of polymers in doubly distilled water and by stirring the solution at 50 °C for complete

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dissolution. The films are obtained by pouring the solution into clean glass plates and drying in an oven at 70 °C for 4 days to ensure removal of the solvent traces.

The thickness of the prepared samples is measured using Interference technique and it is found in the range 50-150 micrometer. The X-ray diffraction spectra of the prepared samples are obtained using Philips XRD 'X'PERT Pro diffractometer using Cu K_α radiation (λ=1.5438A°), the tube operated at 30kV, the Bragg's angle (2θ) in the range 5-50°. FT-IR Spectra of the samples are obtained in the spectral range of 4000-400 cm^{-1} using FTIR spectrometer (Perkin Elmer). UV-VIS absorption spectra of the prepared films are measured in the wavelength region 190-500 nm using single beam UV-VIS Spectrophotometer (Elico).

RESULTS AND DISCUSSION

3.1 X-ray diffraction analysis

The X-ray diffraction (XRD) profiles of samples are shown Fig 1. The figure shows a peak at $2\theta\sim 21°$ for pure PVA which confirms the semi crystalline nature of the polymers. It is reported in literature that pure PVP shows two peaks at $2\theta\sim10.3°$ and $19.4°$ [6]. These two peaks are observed for PVA/PVP (50:50), at $2\theta\sim 21°$ and $2\theta\sim9°$, which confirms the polymer blend formation. Further it is observed that for PVA/PVP (40:60, 20:80) blends there is a decrease in the peak intensity and an increase in the bandwidth with the increase of PVP concentration in PVA. These results indicate that the blends become more amorphous with the increase in the concentration of PVP in PVA [7].
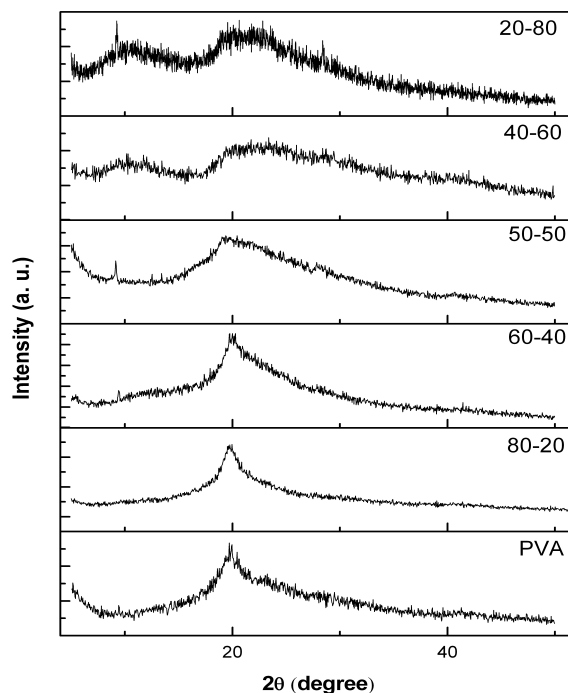

Fig 1: XRD spectra of PVA and PVA/PVP blends

3.2 Fourier Transform Infrared Analysis.

The FTIR spectra of pure PVA, pure PVP and PVA/PVP blends in the spectral range 4000-400 cm^{-1} are shown in Fig 2. In pure PVA one can see broad and intense band at ~3444 cm^{-1}, which is attributed to O-H stretching vibration of hydroxyl group. The band at ~2927cm^{-1} corresponds to asymmetric stretching vibration of CH_2. The band at about 1096 cm^{-1} corresponds to C–O stretching of acetyl groups present on the PVA backbone. The vibration band at about 1647 cm^{-1} corresponds to C=O stretching. In the spectra of pure PVP a broad peak is observed at 934 cm^{-1}, which is due to the outer face vibration oscillation of the hydroxyl group and the peaks centered at 1455cm^{-1} and 1257cm^{-1} are assigned to the inner face bending vibrations of the hydroxyl group. We have also observed a broad band at 3626cm^{-1} in the spectrum of PVP. The vibration band of C=O group appears at 1681cm^{-1} indicating some H-bonding carbonyl groups present in PVP. Also in the spectra of PVA a prominent peak is seen at 1565cm^{-1} which is also seen in 80:20 concentrations. But this peak disappears with increase in PVP concentration. The band at 2874cm^{-1} is attributed to the characteristic stretching vibrations of C-H band. The FTIR

spectra of PVA/PVP blends show the prominent peaks of both PVA and PVP indicating the blending of PVP with PVA.
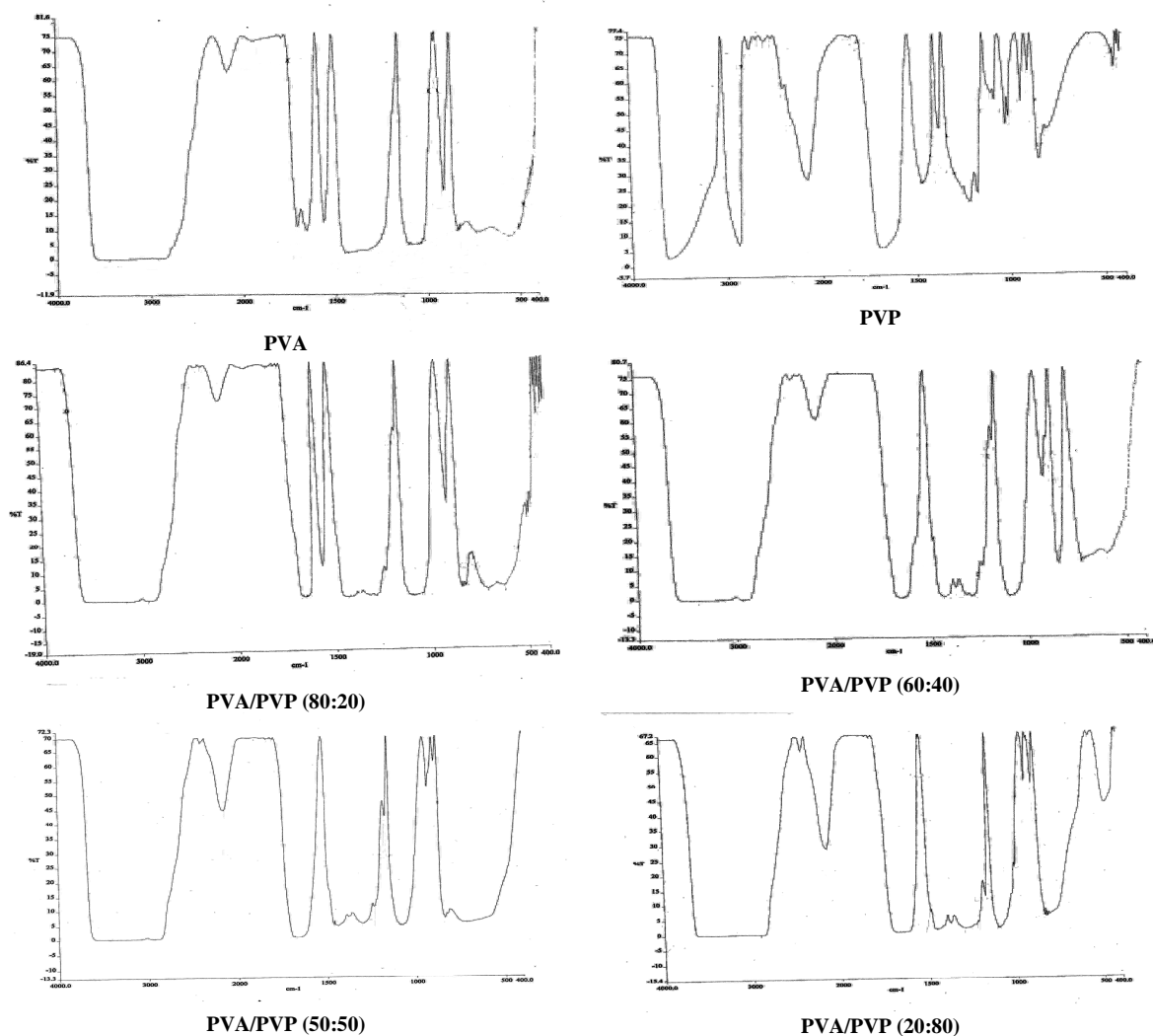

Fig 2: FTIR spectra of pure PVA, PVP and PVA/PVP blends

3.3 Ultraviolet-visible spectroscopic analysis

The UV-VIS absorption spectra of pure PVA, pure PVP and PVA/PVP blends are given in Fig 3. It can be seen that pure PVA shows absorption peak at ~ 191 nm and pure PVP absorption peak in the range 200-240nm. This absorption peak may be assigned to the localized $\pi \rightarrow \pi^{*}$ transition. Further one can notice that the absorption edge of the polymer blends is shifting towards longer wavelength region with increase in concentration of PVP in PVA. These shifts indicate the complexation between the PVP and PVA. It can be attributed to the change in crystallinity of polymer blends as confirmed by the XRD studies.

The study of optical absorption gives information about the band structure of the polymer. In the high absorption region the absorption coefficient (α) as a function of photon energy (hν) can be expressed as [8, 9]

$$\alpha(\nu)h\nu = B(h\nu - E_g)^r$$

Where $(h\nu)$ is the incident photon energy, E_g, the optical band gap energy, B is a constant and *r* is an exponent which can take values ½, 3/2 2 & 3 depending on the nature of the electronic transition responsible for the optical absorption. The best fit value of *r* can be determined from the slope of the linear part of $(\alpha h\nu)^{1/r}$ versus $h\nu$. We obtained a best straight line fit to our spectral data for r = 2, which indicates that which indicates that an indirect transition is allowed near the fundamental band edge.[10] We estimated the values of the band gap energy from the extrapolation of the straight line part of the plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ to the zero photon energy as shown in

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Figure 3 and the estimated values of the E_g are given in Table 1. It can be observed from the table that the E_g of the polymer blends decreases with the increase in the concentration of PVP in PVA. This may be explained by invoking the occurrence of local cross linking within the amorphous phase of the polymer, in such a way to increase the degree of ordering in these parts [11].
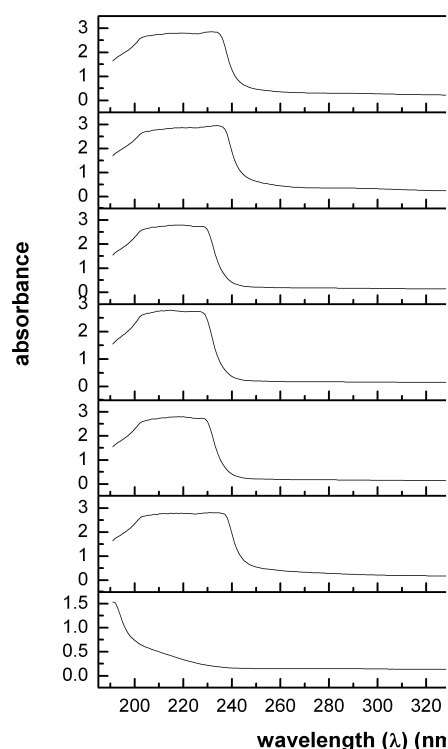
Fig 3: UV-Vis absorption spectra of (a) PVA (b) PVP (c) PVA/PVP (80/20) (d) PVA/PVP (60/40) (e) PVA/PVP (50/50) (f) PVA/PVP (40/60) (g) PVA/PVP (20/80)
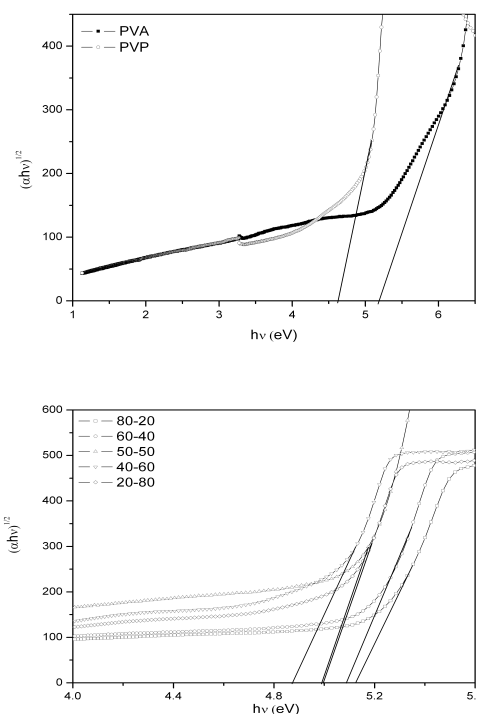
Fig 4: Plot of $(\alpha h\upsilon)^{1/2}$ versus $h\upsilon$ for   (a) pure PVA and PVP (b) PVA/PVP blends

Table 1: Measured values of optical energy gap (E_g) for pure PVA, pure PVP and PVA/PVP blends

Samples	PVA	PVP	PVA/PVP (80/20)	PVA/PVP (60/40)	PVA/PVP (50/50)	PVA/PVP (40/60)	PVA/PVP (20/80)
Optical band gap energy (E_g) [eV]	5.17	4.61	5.12	5.08	5.00	4.98	4.87

CONCLUSION

The crystallinity of PVA/PVP blends decreases with the increase of PVP concentration. The FTIR spectra show the blending of PVA and PVP at different concentrations. PVA (50)/ PVP (50) is more stable and suitable sample for investigation with respect to the brittleness of the samples of different concentration. Amorphosity of this composition provides a favorable environment for ion diffusion. The UV-Vis spectroscopic analysis justifies the tailoring of the optical band gap energy of PVA/PVP blends with increase of PVP concentration.

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