

Study of visible luminescence performance in highly transparent PMMA/PVP polyblends

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This work reports the structure and optical spectroscopic study of solution cast PMMA/PVP polyblends by using x-ray diffraction, optical and fluorescence techniques. The first diffraction halos, characteristic of the amorphous state shift towards smaller diffraction angles while the other two of the PMMA polymer starts disappearing upon blending with PVP. The optical gap is found to decrease with an increase in Urbach's energy indicating the rise in disorder upon blending. The broad luminescence band in the visible region at 350-550 nm using 300 nm excitation wavelength has been deconvoluted to two/three bands, with a red shift in their position with PVP content. The structure-property relationship with improved luminescence in visible region has been elaborated for designing efficient optical devices using PMMA/PVP polyblends.

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1. Introduction

Polymer blending is one of the most important contemporary ways for the development of new polymeric materials and it is a useful technique for designing materials due to the possibility of simultaneously exploiting the attractive features of each component for broad range of technological and scientific applications. The study of various blends i.e. fabrication of bulk hetero junction solar cells, design of optical components, etc. as well provides a substitute for the technologically important applications due to their superior properties over homo polymers and depends upon miscibility or functional group interaction of their components at molecular scale [1]. The various experimental techniques, such as thermal analysis, infrared absorption/RAMAN, fluorescence, scanning electron microscopy and electrical measurements are used to extract the structure-property relationships for understanding their behavior. Optical spectroscopy, one of the techniques widely used to explore the polyblends for their applications as active material in designing optical components, medical and industrial application [2-4]. These studies have also found significance for developing an insight into the basic process of mixing of components to form miscible/immiscible polyblends and effects thereto. On the other hand, PVP polymers are available in several viscosity grades, ranging from low to high molecular weight [5]. It has been already established the ability of PVP for complex formation with many other polymers due to electrostatic intermolecular interactions or hydrogen bonding to form highly miscible blends [6, 7]. While the PMMA polymer is highly transparent polymer with light molecular weight, high strength, excellent dimensional stability, weatherability but with highly brittle nature which limit its potential applications. The dielectric

spectroscopy reveals that the PVP forms the compatible blends with PMMA only in this family, where the methyl group being substituted with ethyl or butyl groups in this polymer [8]. Thus, the study of optical and fluorescence spectra of these blends may come out from their individual limits for the device applications as well filling the gap of knowledge for their miscibility behavior. In the present work, the effect of PVP content on the optical and luminescence studies of solution cast PMMA/PVP membranes has been studied in detail for probable luminescent device applications.

2. Experimental details

Poly (n-vinyl pyrrolidone) (PVP), poly (methyl methacrylate) (PMMA) (Sigma Aldrich, USA) and acetonitrile (Thomas Baker, INDIA) were used without any further treatment. For preparation of polyblends, the component polymers PVP and PMMA were mixed with appropriate weight percentage in 20 ml of acetonitrile and stirred for 3 h. The resulting solutions were poured into the Petridis and solvent was allowed to evaporate for 6 h and then heated at 333 K for 12 h to yield completely dried membranes for further characterizations. Samples of different weight percentages 100/0, 95/5, 90/10, 70/30 and 50/50 of PMMA/PVP polyblends were prepared using the same procedure. The thickness of these membranes was measured using the screw gauge and was found to be ~0.1 mm. The amorphous/crystalline nature of these samples was studied by using x-ray diffractometer (Model D8 FOCUS, Bruker, Germany) using Cu K_α radiation. The optical absorbance spectra were measured by using UV-Vis spectrophotometer (Lambda 35, PerkinElmer, USA) and fluorescence spectrums at 300 nm excitation from the

xenon arc lamp were measured using the spectrofluorometer (Lambda 45, Perkin Elmer, USA).

3. Results and discussion

3.1 X-Ray Diffraction

The XRD studies were used to reveal the structure and amorphous/crystalline nature of PMMA/PVP polyblends. Fig. 1 shows the diffraction patterns for all the compositions (wt%) viz. S1 (100/0), S2(95/5), S3(90/10), S4(70/30), S5(50/50) PMMA/PVP polyblends. Three characteristic diffraction halos for the amorphous state at 15.89° , 30.78° and 42.68° has been observed for the intrinsic PMMA membranes; the first diffraction halo broadens along with its position shift towards smaller diffraction angles while the other two starts disappearing with the increase in PVP content in the polyblends. In general, narrow diffraction peaks are associated with a good degree of crystallinity (i.e. full width at half maximum, $fwhm \approx 0.2$), and broader ones for their semi-crystalline/amorphous behavior ($fwhm \geq 1$) [9].

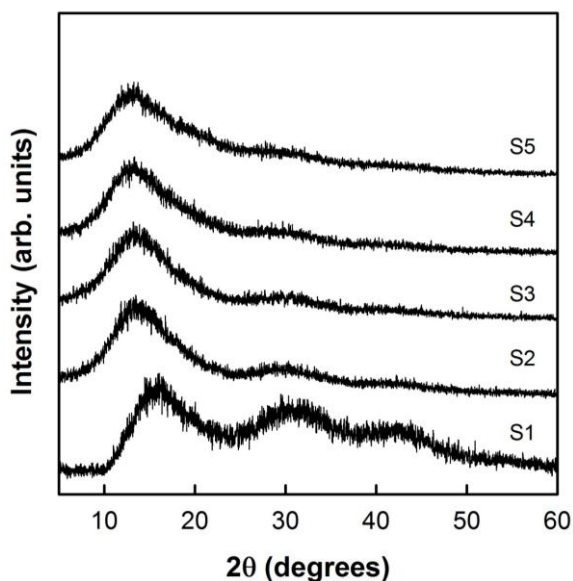


Fig. 1. XRD patterns for different composition S1 (100/0), S2 (95/5), S3 (90/10), S4 (70/30) and S5 (50/50) of PMMA/PVP polyblends.

Therefore, the broadening of the diffraction bands reveals the enhancement in the amorphous or semi-crystalline nature of PMMA/PVP membranes upon blending. Thus, the change in the position and broadening of diffraction bands confirming the intermolecular interactions or complexation of the constituent polymers upon blending. Also, the miscibility leads to the formation of homogeneous blends, while the immiscibility results to form heterogeneities or phase separation at the micro/nano scales.

The miscibility is defined as the ability to be mixed at molecular level or to form complexes with the interaction between their functional moieties to produce new systems with improved properties. The different spectroscopic techniques such as FTIR spectroscopy, XRD, SEM, NMR and DSC are used to elaborate the characteristic interaction between different polymers. However, the change in the shape and position of the diffraction halos indicates the change in structural ordering at molecular level for homogeneous PMMA/PVP blends in the studied compositions.

3.2 Optical and Fluorescence Spectroscopy

The study of optical absorption spectra is one of the most productive tools for understanding and developing the band structure of both crystalline and amorphous materials. Fig. 2 (a) shows the absorption spectra of PMMA/PVP polyblends in 200 and 1100 nm spectral region. It has been observed that the increase in PVP content decreases the transmission for otherwise nearly transparent pure PMMA membranes. The linear absorption coefficient ' α ' can be directly determined from the optical absorbance according to relation: $\alpha = x/d$, where ' x ' is absorbance and ' d ' is the thickness of membranes. Fig. 2(b) shows the variation of absorption coefficient (α) with incident photon energy ($h\nu$) for PMMA/PVP polyblends. The calculated values of optical gap are summarized in Table 1 and found a linear decrease in its value obeys the rule of mixing for an increase in PVP content for these polyblends.

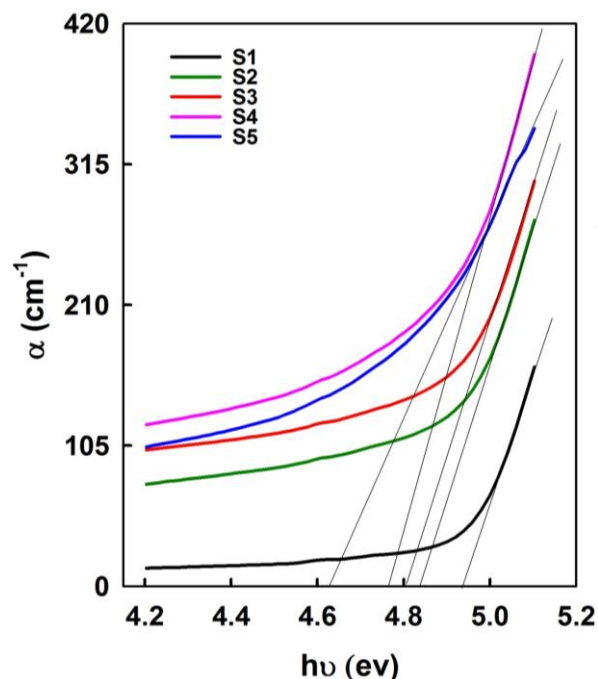


Fig. 2. Variation of optical absorption coefficient with photon energy for PMMA/PVP membranes.

Table 1. Summarization of various optical parameters such as optical gap (E_g), Urbach's energy (E_U) and centers of deconvoluted luminescence band for PMMA/PVP polyblends.

PMMA/PVP (wt.%)	E_g (eV)	E_U (eV)	Luminescence peaks (nm)		
			1	2	3
100/00	4.93	0.61	405	442	-----
95/05	4.84	1.15	392	431	-----
90/10	4.80	1.28	402	455	501
70/30	4.77	1.31	434	479	520
50/50	4.62	1.48	419	466	511

The exponential dependence of absorption coefficient on energy in both crystalline and amorphous semiconductors might arise from the random fluctuations of the internal field associated with structure disorder that occurs in many amorphous solids [10]. Therefore, the density of electronic transitions between localized states in the band edge tails, which is assumed to fall off exponentially with energy. For many amorphous materials, the electronic transitions at the band edge fall off exponential with energy and found to obey an empirical relation [11-14]: $\alpha = \alpha_0 \exp(h\nu/E_U)$, where E_U is the Urbach's energy characteristic of disordered state of the system and α_0 is a constant. Fig. 3 shows the variation of $\ln \alpha$ versus photon energy ($h\nu$) for different PMMA/PVP membranes. The straight line fit suggests that the absorption follows the quadratic relation for interband transition and obey the Urbach's rule [12]. The values of band tail E_U were calculated from the reciprocal of the slopes and are tabulated in table 1. It has been observed that its value increases with the increase in PVP content in the polyblends. Since, the formation of polymer blends may induce tail states by perturbing the band edge via a deformation potential, Coulomb interaction, and Fluctuations of internal fields [14]. Thus, the characteristic change in the optical properties could be related to the blend formation accompanied with the disorder induced tail state formation due to the intermolecular interaction of the component polymers [7, 15].

Fig. 3 (a) shows the normalized fluorescence spectra at 300 nm excitation energy for all the samples. It has also been observed that the addition of PVP results in the improvement in the luminescent intensity by three times at the luminescence peak, which exhibits a linear shift with composition except for the S2 sample. The small shift of luminescence band towards smaller wavelengths may be due to homogenous blend formation while higher content favors the development of other phases too in the PMMA/PVP network. The Gaussian fit for the deconvoluted broad luminescence band is shown in the Fig.

3(b) and the peak fit values for different samples are summarized in Table 1. Two luminescence peaks at 405 and 442 nm has been observed for the pure PMMA polymer films. The anomalous trend for the variation of the first and third peak upon blending while the blue shift in the position of second peak for 5 wt.% of PVP content and thereafter, the peak maxima shifts towards longer wavelength side upon blending has been observed. The tailoring of the peak maxima in the visible region will be important for the designing of energy efficient and low cost illumination sources.

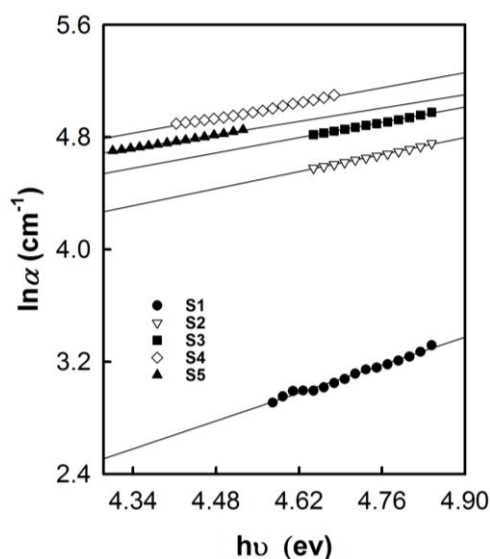


Fig. 3. Plot of $\ln \alpha$ versus photon energy ($h\nu$) for PMMA/PVP membrane samples.

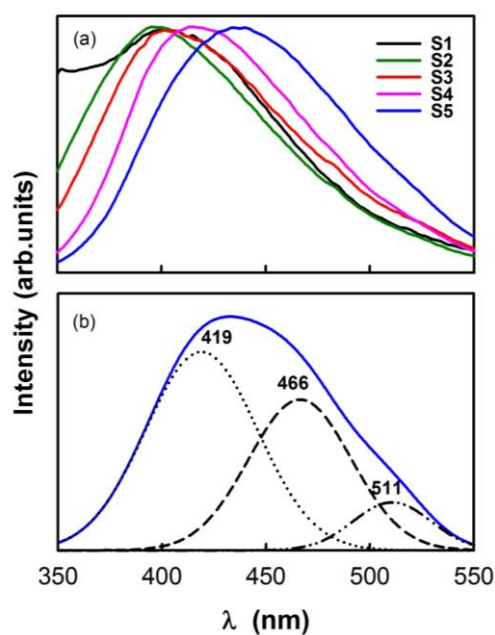


Fig. 4. (a) Emission spectra at 300 nm excitation for different compositions of PMMA/PVP polyblends and (b) Deconvoluted Gaussian fitting for emission band for 50/50 (PMMA/PVP) polyblends.

4. Conclusion

We have studied the effect of PVP blending on the structural and optical properties of solution cast PMMA/PVP polyblends using x-ray diffraction, optical and fluorescence spectroscopy. The XRD studies reveal the change or modifications in the local structure. The red shift in the optical absorption edge and an increase in the Urbach's energy along with the decrease in transmittance have been observed upon blending. The shift in position of broad fluorescence band for longer wavelength side while the increase in the number of Gaussian fit bands upon blending at 300 nm excitation has been observed. The intermolecular interaction and change in the local structure of the polyblends has been used to discuss the behavior of PMMA/PVP polyblends.

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