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Research Article

OPTICAL ANALYSIS OF PURE AND KBr DOPED POLYMER BLEND (PVP/PMMA) ELECTROLYTE THIN FILMS

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ABSTRACT

Solid polymer electrolyte films based on polymer blends of polyvinyl pyrrolidone (PVP) and poly methyl methacrylate (PMMA), with different concentration of KBr were prepared using casting technique. Optical studies were performed using Ultraviolet-visible (UV-Vis) spectroscopy. The optical properties of these films were varied by varying KBr concentration. The results show the absorption edge for electrolyte samples shifts toward a lower energy region by increasing the salt concentration, leading to the band gap reduction. The band gap energy data showed that the incorporation of KBr into the polymeric system causes charge transfer complexes in the blend polymer, which lead to increase in the electrical conductivity, by providing additional charges in the lattice.

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INTRODUCTION

The production, storage, and distribution of energy are the main concerns of society. For this purpose, ion-conducting solid polymer electrolytes play important role in various electrochemical devices like solar cells, supercapacitors, rechargeable batteries, and sensors [1-6]. Ion-conducting solid polymer electrolyte can be formed by complexation of salt in different polymer hosts like PEO, PPO, PVP, PMMA and PVA.

Among these polymers, polyvinyl pyrrolidone (PVP) deserves a special attention because of its good electrical properties, easy process ability, moderate electrical conductivity and charge transport mechanism [7]. PVP is an amorphous polymer and possesses high T_g due to the presence of the rigid pyrrolidone group which is known to form various complexes with many inorganic salts [8]. PMMA is good compatible nature with other polymers, high resistance, non-tracking characteristics, surface resistance, optical properties. Appetecchi *et al*. [9] elucidated the strong effects of PMMA on the stabilization of electrode –electrolyte interface. PMMA was

used as host in the plasticized polymer electrolytes, first reported by Iijima *et al*. [10]. Also, Bohnke [11] studied the kinetics and stability of lithium electrode in PMMA-based gel electrolytes. In view of the above, the present paper aims to optical studies of polymer blend electrolyte system based on polyvinyl pyrrolidone (PVP) and poly methyl methacrylate (PMMA) complexed with potassium bromide (KBr).

Experimental

Films of (thickness ~140 μm) pure PVP/PMMA blend and various compositions of complexed films of PVP/PMMA with KBr salt were prepared in weight percent ratios (47.5:47.5:05), (45:45:10) and (42.5:42.5:15) by solution cast technique using Dimethylformamide (DMF) as a solvent. PVP/PMMA and KBr salt were dissolved in DMF and stirred at room temperature for 10–12 h to get a homogeneous mixture. The solution was cast onto polypropylene dishes and allowed to evaporate slowly at room temperature. The final product was dried thoroughly to remove all traces of the solvent. The dried composite polymer

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films were peeled off from the polypropylene dishes and stored in a dry vacuum box.

UV-Vis absorption spectra of prepared samples were recorded in the range 200-900 nm at room temperature using JASCO UV-VIS-NIR spectrophotometer (model- V.700). From these data the optical constants such as band edge, optical band gap (both direct and indirect) were determined.

RESULTS & DISCUSSIONS

The UV absorption mainly corresponds to the electron transition from the top of the valence band to the bottom of the conduction band. The UV-vis absorption spectra of blend PVP/PMMA and PVP/PMMA/KBr solid polymer electrolyte films are recorded at room temperature in the wavelength range (200-900) nm as shown in Fig.1. From Figure, the spectrum of pure PVP/PMMA polymer blend film shows a shoulder like peak at about 228 nm which is assigned to the carbonyl group of pure polymer blend. In doped film the shoulder shift towards the higher wavelengths and the absorption coefficient increases as doping level increases. This may be due to increase in the number of carbonyl groups and strong interaction between PVP/PMMA and KBr salt [12].

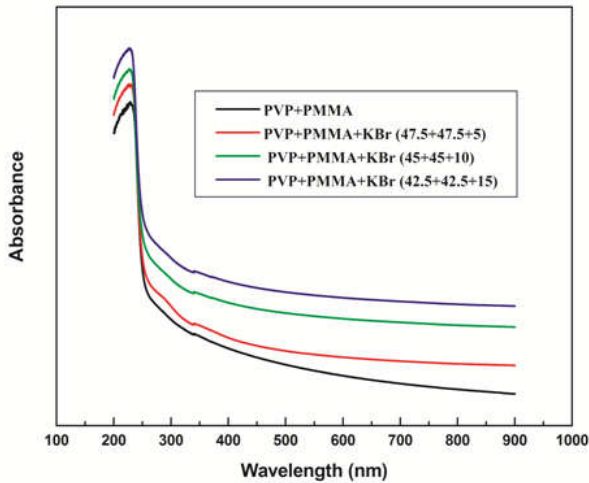


Fig 1 UV-Vis absorption spectra of pure and KBr doped PVP/PMMA polymer blend films

Optical absorption studies on PVP/PMMA and various concentrations of KBr doped PVP/PMMA films are used to determine the optical constants such as optical band gap (E_g) and the position of the fundamental band edge. The main feature of the absorption edge is an exponential increase of the absorption coefficient (α) with photon energy ($h\nu$). The absorption coefficient α can be determined from the spectra using the formula [Fig.2].

$$\alpha = \left(\frac{A}{d}\right) * 2.303 \tag{1}$$

where A is the absorbance and d is the thickness of the sample. For pure PVP/PMMA film absorption edge lies at 3.77 (eV) and for doped films the values decrease from 3.60 to 3.34eV.

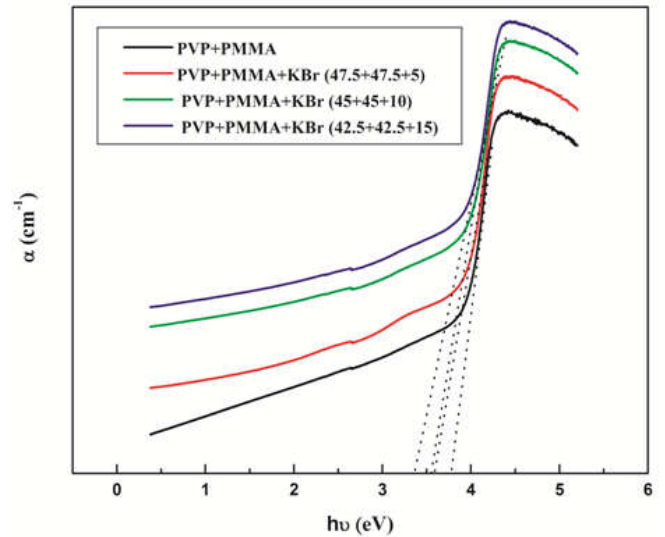


Fig 2 α vs $h\nu$ plots of pure and KBr doped PVP/PMMA polymer blend films

When a direct band gap exists, the absorption coefficient has the following dependence on the energy of the incident photon [13, 14, 15].

$$\alpha h\nu = c(h\nu - E_g)^{\frac{1}{2}} \tag{2}$$

Where E_g is the band gap, c is a constant, ν is the frequency of light and h is the Planck's constant. A graph of $(\alpha h\nu)^2$ vs $h\nu$ (photon energy) as shown in Fig. 3 observed to be linear. The intercept on the energy axis on extrapolating the linear portion of the curve to zero absorption value may be interpreted as the value of the band gap. For pure PVP/PMMA film, the direct band gap lies at 3.94eV while for doped films the values are from 3.90 to 3.83eV [Table].

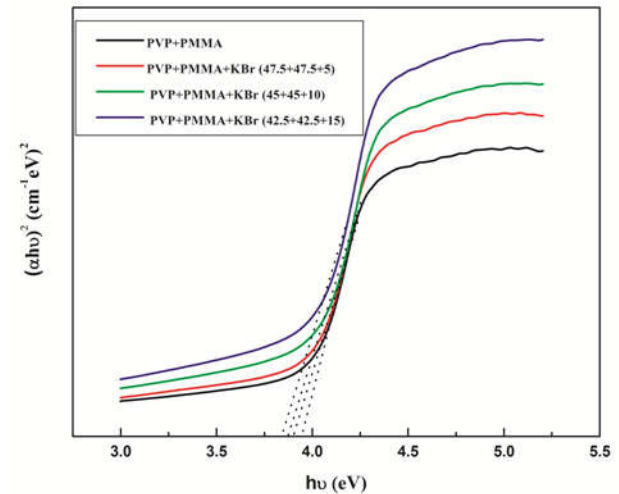


Fig 3 $(\alpha h\nu)^2$ vs $h\nu$ plots of pure and KBr doped PVP/PMMA polymer blend films

For indirect transition which requires phonon assistance, absorption coefficient has the following dependence on the photon energy [13,14, 15].

$$\alpha h\nu = A(h\nu - E_g + E_p)^2 + B(h\nu - E_g - E_p)^2 \tag{3}$$

Where E_p is the energy of phonon associated with transition and A and B are constants depending on the band structure. The indirect band gaps were obtained from the plots of $(\alpha h\nu)^{1/2}$ vs $h\nu$ as shown in Fig.4.

For pure PVP/PMMA film, the indirect band gap lies at 3.83eV, while for doped films the values vary from 3.71 to 3.55eV.

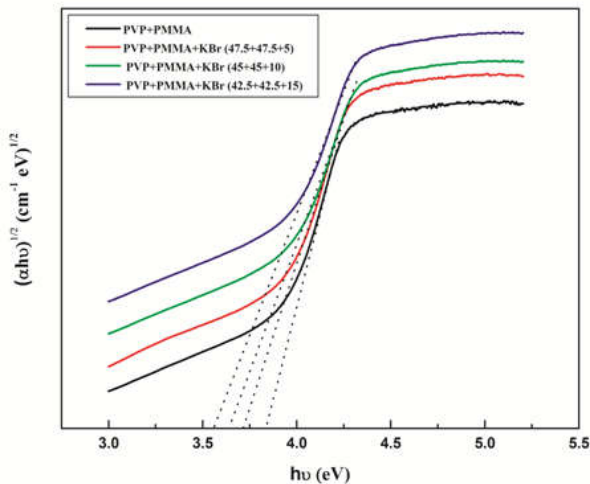


Fig 4 $(\alpha h\nu)^{1/2}$ vs $h\nu$ plots of pure and KBr doped PVP/PMMA polymer blend films

The band gap energies (direct and indirect) and absorption edge of the pure and KBr doped PVP/PMMA polymer films obtained in the present work are given in Table.

Table Absorption edge optical band gap values of pure and KBr doped PVP/PMMA films.

Concentration of PVP+PMMA+KBr (Weight %)	Absorption edge (eV)	Optical band gap energy(eV)	
		Direct	Indirect
PVP+PMMA	3.77	3.94	3.83
PVP+PMMA+KBr (47.5+47.5+5)	3.60	3.90	3.71
PVP+PMMA+KBr (45+45+10)	3.51	3.86	3.63
PVP+PMMA+KBr (42.5+42.5+15)	3.34	3.83	3.55

From Table, the values of direct band gap and indirect band gap decrease with increase in doping level. This decrease may be attributed to the formation of defects in polymeric matrix. These defects produce the localized states in the optical band gap, which overlaps with band system are responsible for decrease in band gap energy. This indicates that with increase in concentration of KBr as a dopant, PVP/PMMA film become more semiconducting in nature [16, 17].

CONCLUSIONS

The solid polymer electrolyte films PVP/PMMA/KBr were prepared by a solution casting method, and are characterized by UV-Vis spectroscopy. Optical absorption edge and optical band gap (direct and indirect) showed a decreasing trend with increased of KBr salt content, which attributed to formation of the charge transfer complexes with the blend polymer, and decrease in the degree of crystallinity in the polymer blend electrolyte.

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