



A STUDY ON OPTICAL BAND GAP AND ASSOCIATED BAND-TAILS IN LASER DYE COUMARIN DOPED POLY (METHYL METHACRYLATE) (PMMA) FILMS

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ABSTRACT

Transparent films of pure and Laser dye Coumarin (%wt) doped Poly (Methyl Methacrylate) (PMMA), were prepared using solution cast technique. Samples were characterized using optical absorption spectroscopy (UV-Vis) and absorption spectra were recorded at ambient temperature for wavelengths ranging from 190 nm to 1100 nm. Electronic transition type, optical band gap energy (E_g) and associated band tails (Urbach energy ' E_u ' and Weak absorption tail (WAT) energy ' E_w ') were estimated for the prepared samples.

KEYWORDS: PMMA, Coumarin, Optical band gap, Urbach energy, Weak Absorption Tail

Optical polymers (OP) are an important class of materials and proper understanding of their electronic properties is required for technological applications. As electronic properties are directly related with the optical properties/behaviour of the material. Some of this information can be extracted by analyzing the optical absorption spectra and the region of strong fundamental absorption (Shimakawa *et al.*, 2006, Philipp *et al.*, 1967). Poly methyl methacrylate (PMMA) is the most common polymer belonging to the methacrylic group and most widely used optical plastic. First plastic optical lenses, for ophthalmic applications, were made using PMMA (Tolley, 2005).

In the present study, PMMA is doped with laser dye coumarin and characterized using UV-Vis. absorption spectroscopy. The resulting absorption spectra's were analyzed to determine optical band energy gap (E_g) for pure and doped samples. Further, from low absorption region Urbach energy tail (E_u) and associated weak absorption tail (WAT) energy were estimated and analyzed for influence of coumarin doping on these parameters.

EXPERIMENTAL DETAILS

Material Used

PMMA used in this study was supplied as beads by Himedia, with average molecular weight 15,000 g/mol. Laser dye Coumarin is used as dopant to prepare dye doped PMMA films. AR grade Benzene was used as a common solvent for both PMMA and coumarin.

Sample Preparation

The polymer sample films were prepared using solution casting technique. Pure PMMA and coumarin dye was dissolved separately in a solvent (benzene) at room temperature. A magnetic stirrer was used to prepare a homogeneous solution. The two solutions were then mixed in different concentration and the solution was cast onto glass molds and left for almost 48 hrs to form transparent films. Sample films were then peeled off from the glass substrate, with thickness ranging from 70 – 80 microns. The doping concentrations of coumarin dye in prepared samples are 0, 0.0005, 0.001, 0.005, 0.01, 0.05, and 0.1 percent by weight (% wt.).

MEASUREMENTS

Optical Absorption Spectroscopy

We studied the optical band gap and associated band tails using optical absorption spectroscopy. The UV-Visible absorption spectra of the polymeric samples were recorded using Shimadzu's UV-1800 UV-Vis Spectrophotometer at ambient temperature, for the entire wavelength range from 190 nm – 1100 nm.

RESULTS AND DISCUSSION

Figure 1 shows the absorption spectra for pure and coumarin doped PMMA films. Very high absorption was observed for UV (quartz) region of the spectrum. Analyzing different regions of the absorption spectra for the polymeric samples proves to be a useful tool in understanding its electronic processes.

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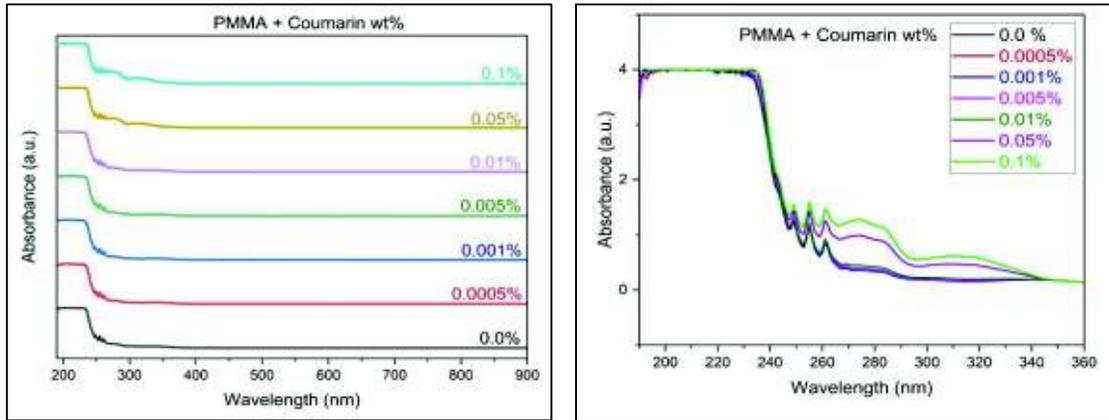


Figure 1: Absorption Spectra of pure and coumarin doped PMMA sample films

OPTICAL BAND GAP ENERGY (E_g)

One of the most important physical parameter for optical plastics is the optical band energy gap E_g and is usually determined from the absorption spectrum of the material. As per the Tauc (Tauc, 1974) and Davis-Mott (Mott *et al.*, 1979) models for amorphous materials, the fundamental optical absorption can be characterized by the empirical relation given as

$$\alpha h\nu = B(h\nu - E_g)^r \text{ ---- (1)}$$

where α is the absorption coefficient, B is a proportionality constant for optical frequency range, E_g is the optical band energy gap (or Tauc gap) of the material, $h\nu$ is the incident photon energy and r is the index characterizing the electronic transition type. The parameter 'r' can take values equal to 1/2, 2, 3/2, 3 corresponding to direct allowed, indirect allowed, direct forbidden and indirect forbidden transition respectively. The optical absorption in Fig. 2 (a) shows the transition plot $\ln(\alpha h\nu)$ vs $\ln(h\nu - E_g)$ used to determine the value of index r (eq.1). The value of r is required to know the transition type and to subsequently determine the band gap energy (E_g). In present case study, the transition was found to be of direct allowed type, both for pure and coumarin dye doped PMMA. Using extrapolation method, intersection on the energy axis (x-axis) Fig. 2 (b), gives the value of the Tauc gap (E_g). Table-1 lists the estimated values of band gap for pure and coumarin doped PMMA films. Fig. 3 displays the variation in optical energy gap (E_g) of PMMA with coumarin doping percentage. The optical energy gap increases initially for low doping percentage and then starts falling off with further increase in doping percentage. This increase in band gap values for low doping concentration can be attributed to nanoparticles formation (Brus, 1984, Mehta *et al.*, 2016). Doping polymer matrix with coumarin may

result in formation of defects and associated energy states in optical band gap resulting in decrease of band gap values with increase in doping percentage. Thus decrease in band gap indicates increase in the degree of disorder in sample films (Mott *et al.*, 1979). Doping samples with coumarin dye results in some change in band gap but does not very significantly affect the optical band gap values. This small variation in optical band gap values is very likely due to small variations in doping concentration.

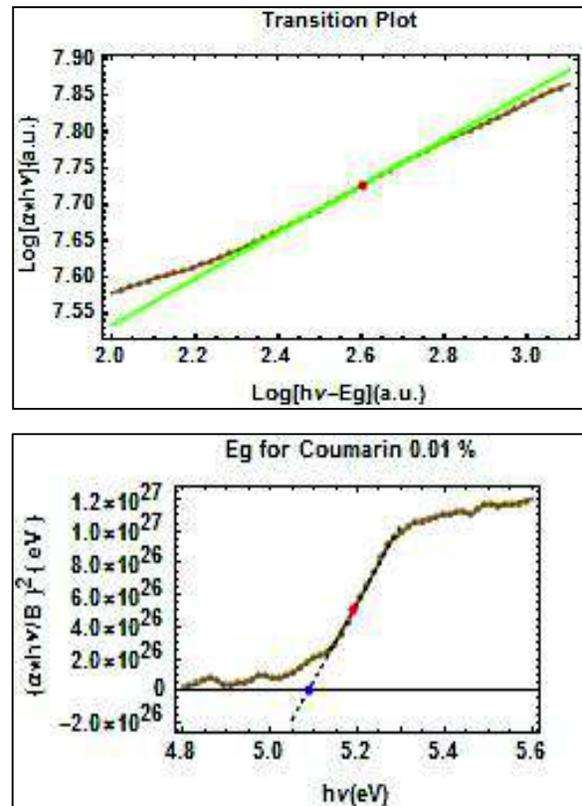


Figure 2: (a) Transition plot (b) Tauc plot of optical absorption coefficient for PMMA doped with coumarin dye (0.01 %)

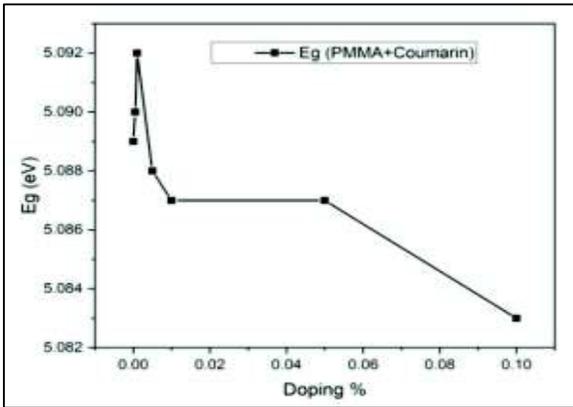


Figure 3: Optical Band Energy gap variation with doping percentage for PMMA

Band Tailing

Estimating parameters at energies before the fundamental absorption edge also proves to be an important tool in understanding the electronic energy – band structure of amorphous materials (Mott *et al.*, 1979). Tailing of bands edge is attributed to impurities and disorder in materials (Shimakawa *et al.*, 2006, Mott *et al.*, 1979). Further this can be analyzed in two parts, both exhibiting exponential behaviour.

Urbach Energy (E_u)

The absorption coefficient (α) exhibits exponential dependence on photon energy, near the band edge for the amorphous materials, giving rise to Urbach's tail and is expressed as (Urbach, 1953):

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_u}\right) \text{ ---- (2)}$$

where α_0 is a constant. This region is known as Urbach region, where E_u is the width of the band tails of the localized electronic states. Band tailing and electronic states localization is the manifestation of absence of long-range order in amorphous materials. Appearance of

exponential tail (Urbach's tail) in the low energy region is common and considered as a universal characteristic for most of the amorphous (disordered) materials. Urbach energy value is helpful in evaluating and indicates the degree of disorder in the material. From table -1 it is clear that there is increase in E_u with increase in doping concentration. Doping promoted an increase in disorder in the polymer matrix.

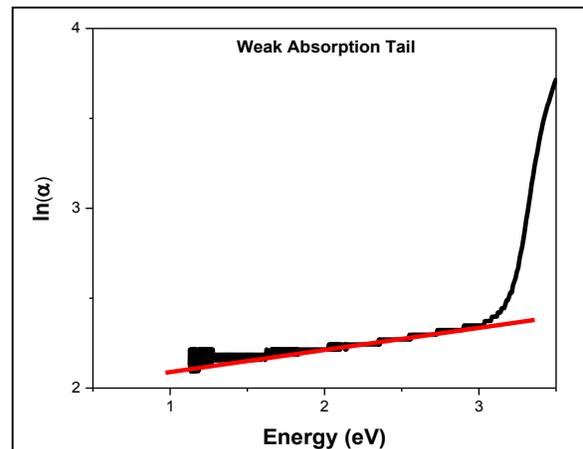
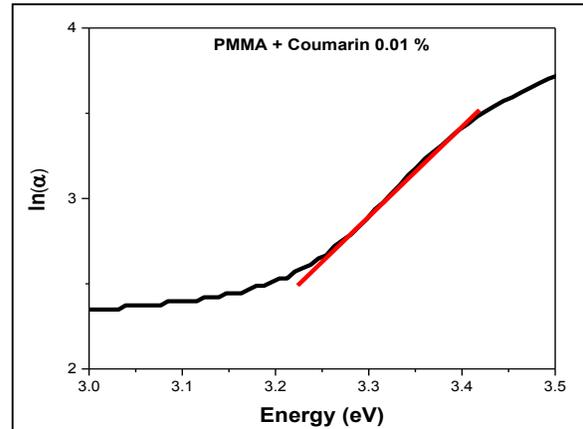


Figure 4: Variation of absorption coefficient with photon energy (a) Urbach region (b) Weak absorption (Residual Absorption) Tail region

Table 1: The values of direct band gap (E_g), Urbach energy (E_u) and Weak Absorption Tail energy (E_w) for pure and coumarin doped PMMA films

Doping (wt %)	E_g (eV)	E_u (eV)	E_w (eV)
0.0	5.089	0.181	9.7
0.0005	5.09	0.194	8.62
0.001	5.092	0.194	9.4
0.005	5.088	0.187	8.33
0.01	5.087	0.196	9.7
0.05	5.087	0.196	9.0
0.1	5.083	0.197	10.0

Residual Absorption (E_w)

For very low absorption region another tail is observed following exponential behavior and is expressed as (Mott *et al.*, 1979, Wood *et al.*, 1972)

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_w}\right) \quad \text{with } E_w > E_U \quad \text{----- (3)}$$

This is referred as weak absorption tail (WAT) or residual absorption, exhibiting a small slope. Being a structure-sensitive property (Wood *et al.*, 1972), absorption in this region is dependent on the sample preparation technique, thermal history and on purity of the sample. It has been proved experimentally (Wood *et al.*, 1972) that this weak absorption tail is not due to a light scattering artifact and instead there is actual light absorption. This may be associated with the localized states in the band gap. Estimated values of weak absorption tail energy (E_w) for sample films is listed in Table-1. It can be seen that the estimated values of residual absorption region (E_w) is too high (compare to E_a). This discrepancy in E_w may be because absorption in this region is too small and the technique employed (UV-Vis spectroscopy) is not sensitive enough to measure the residual absorption region. So physics of the problem has to be worked out differently, if we have to estimate E_w using UV-Vis absorption data.

CONCLUSION

The UV-Vis. spectra of the sample films were analyzed using Mott-Davis and Tauc model. Transition was found to be of direct allowed for both pure and doped samples. Doping samples with coumarin dye results in some change in band gap but not significantly affect the optical band gap values. These small variations in optical band gap values are due to small variations in doping concentration.

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