PVA-Coumarin Films: Materials for Optical Applications

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Abstract: Pure Poly(vinylacohol) (PVA) and PVA-coum films with different concentrations were prepared by a casting technique. Optical absorption and mechanical properties were measured. The UV–Vis absorption spectra gave the same band positions but the absorption intensity increases with increasing coumarin concentration. The dependence of the absorption coefficient on the photon energy has been determined and the energy gaps and band tails were calculated. The topography of the surface was measured by atomic force microscope (AFM). It was found that Young's modulus, the strength at the break and the band tail increase while the optical gaps for PVA-coum films decrease. RMS roughness of the surface for prepared films decreases as the coumarin concentration is increased. The obtained results illustrated that this material has promising applications in optical industries.

Keywords: Optical absorption coefficient, energy gap, mechanical properties.

1. INTRODUCTION

The addition of coumarin to a polymeric network is of considerable interest for both scientific and technological purposes [1, 2]. Poly(vinyl alcohol) (PVA) is one of the most important polymeric materials due to its high mechanical strength, easy processability, excellent thermal stability and good charge storage capacity [3-11]. The optical uses of PVA include the retardation, polarization, and filtration of light, contact lenses, and drug-delivery systems [12-17].

Coumarins are attractive molecules due to their extended spectral range, high emission quantum yields and photostability [13]. Furthermore coumarin derivatives are frequently encountered as receptors and signaling units in sensors and biosensors as well as in advanced photophysical systems [14].

Literature survey reveals that there are reports on preparation and fluorescent properties of poly(vinyl alcohol) bearing coumarin [18], or effect of coumarin concentration on the physical properties of CdO nanostructures [19]. In the present work, the absorption coefficient, the optical energy gap, band tail and mechanical properties (Young´s modulus Y, strength and strain at break ε_b) were determined and the effect of the coumarin concentration on these constants was studied.

2. MATERIALS AND METHODS

The PVA used in this work, obtained from Alfa Aesar in powder form, has average molecular weight (M.W) 10000 to 26000gm/mole. Coumarin used in this work with formula C9H602 and have been procured from ALPHACHEMIKE.INDIA.

Pure PVA film (sample a), was prepared by the casting method as follows [7]:

PVA powder was dissolved in distilled water and then maintained for 24h at room temperature to swell. The mixture was then warmed up to 60°C and stirred, using magnetic stirrer, thoroughly for 4h until the mixture was completely dissolved. The solution was poured into a flat glass plate dishes. Homogeneous film was obtained after drying in an air oven for 48h at 40°C.

PVA-coum films were prepared by adding a known quantity of PVA powder to redistilled water and kept for 24 hours to swell the granules with stirring the solution at 60°C for complete dissolution. Coumarin was dissolved in redistilled water and added to the polymeric solution with continuous stirring for 9h. Then the solution was poured onto a clean glass plate dishes and dried for 24 hours at 40°C. The films were divided into five groups a, b1, b2, b3 and b4 corresponding to the concentration of coumarin 0, 30, 70, 110 and 150ppm.

The optical absorption measurements for the prepared samples were measured by using the JASSCOV-570 spectrophotometer in the wavelength range from190 to 900nm.

The topography studies were performed by atomic force microscopy (AFM), using a Thermo Microscope Autoprobe CP Research AP-2001 in contact mode (for sample size 5μm x 5μm). The resulting data were transformed into a 3D image.

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The stress–strain measurements were performed using a mechanical test machine (AMETEK) in which a force gauge (Hunter spring AccuforceII 0.01N resolution) is attached. The readings were automatically recorded through a microprocessor as a function of time. A locally made device with motor with microswitch system was attached to the test machine to control the strain rate. The strain rate throughout the experiment was 0.04cm/s. The samples used in mechanical measurements were strips of dimensions (20 x 2 x 0.21mm) of films a, b1, b2, b3 and b4.

3. RESULTS AND DISCUSSIONS

3.1 Optical Characterization

Figure **1** shows the absorption spectra of the samples (a-d) in the wavelength range 190-800nm. The spectrum of the sample (a) contains three absorption bands at 200, 275 and 325nm. The three absorption bands identify carbonyl groups of the type $-(CH=CH)_n-C=O-$ where n = 1, 2 and 3, which arises from the presence of acetaldehyde in vinyl acetate monomer during polymerization [19]. There is observable increase in absorption intensity of the absorption bands with increasing coumarin concentration. This is may be due to form a cluster from PVA around coumarin molecules.

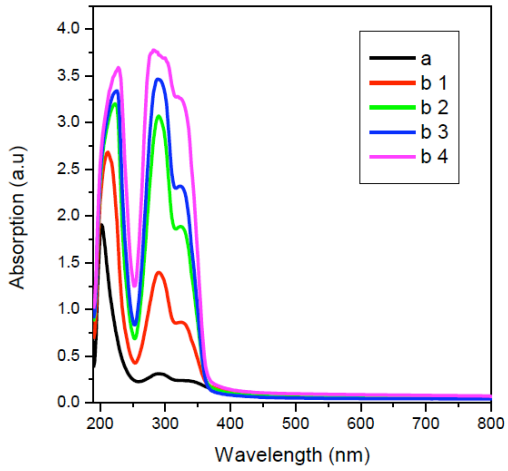


Figure 1: The absorption spectra of the samples (a and b1-b4).

The optical absorption coefficient (α) of PVA films is very important because it provides information on the electronic band structure, the band tail and energy gap E_g and it can expressed by:

$$\alpha = 2.303\frac{A}{d}$$

where: (A) absorbance, (d) material thickness (cm).

Figure **2** shows the dependence of the optical absorption coefficient (α) on the photon energy for samples (a, b1-b4). The inset figure **2** showed increase the optical absorption coefficient (α) with increase in coumarin concentration which may be attributed to electronic transitions from the bonding molecular orbit to nonbonding molecular orbit [9].

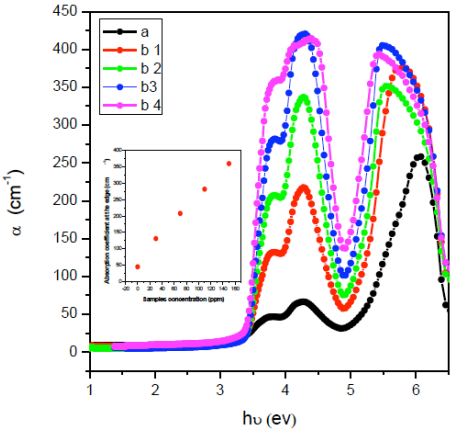


Figure 2: Absorption coefficient versus wavelength for the samples (a, b1-b4).

The absorption edge in many disorder materials follow two apporaches, one of them given by Mott and Davis [20] and the other by Urbach [21]. Mott and Davis suggested that the expression for direct transition can be written as:

$$\alpha(\omega) = \beta\frac{(\hbar\omega - E_{op})^n}{\hbar\omega}$$

where α is the absorption coefficient, β is a constant, E_{op} is the band gap and n is an index determined by the nature of the electronic transition during the absorption process. The most satisfactory results were obtained by plotting the quantity $(\alpha\hbar\omega)^{1/2}$ as a function

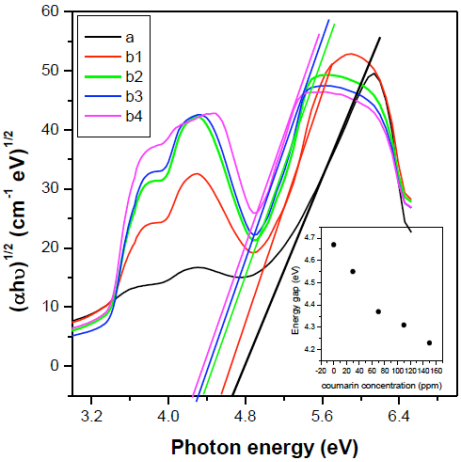


Figure 3: The dependence of $(\alpha hv)^{1/2}$ on photon energy (hv) for the samples (a, b1-b5).

of photon energy, as shown in Figure **3**. The values of E_{op} can obtained by extrapolating the linear parts of the curves to $(\alpha\hbar\omega)^{1/2}$ = 0 and the inset of Figure **3** showed decrease the optical energy gap with increase in coumarin concentration. This decrease may be attributed to the formation of defects in the polymeric matrix. These defects produce the localized states in the optical band gap.

Urbach assumed that the absorption coefficient near the band edge shows exponential dependence on photon energy and obeys the following empirical relation,

$$\alpha(\omega) = \beta \exp\left(\hbar\omega / E_t\right)$$

β is a constant, E_t is the width of the band tails of the localized states in the band gap that are associated with the amorphous nature of the material. Plotting the relation between ln α and photon energy near the absorption edge produced straight lines as shown in Figure **4**. The reciprocal of the slope of line was taken

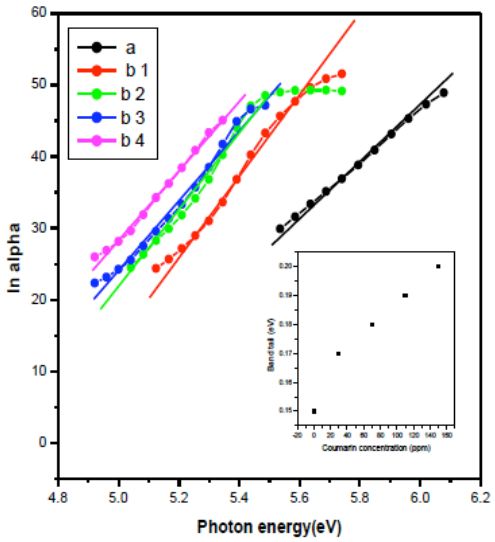
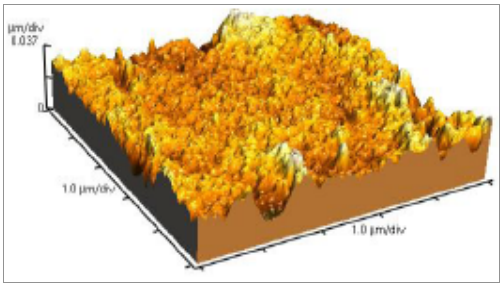
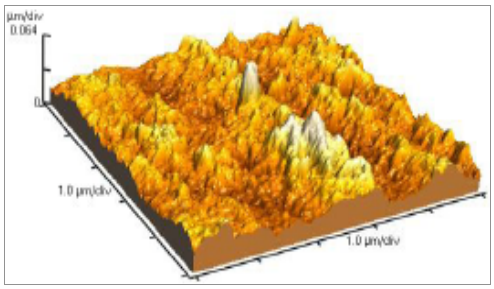


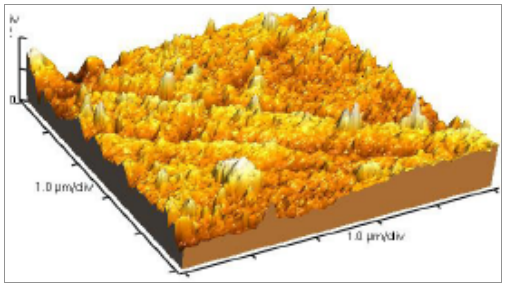
Figure 4: ln (α) versus hv for the samples (a. b1-b4).



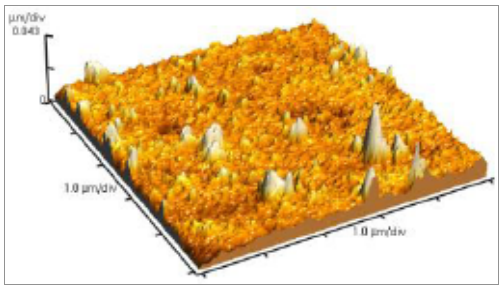
Sample a



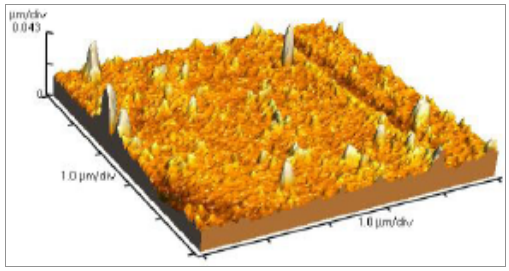
Sample b 1



Sample b 2



Sample b 3



Sample b 4

Figure 5: 3D AFM images of 5 x 5µm2 region for the samples (a. b1-b4).

as the band tail of the samples and the inset figure showed increase the band tail with increase in coumarin concentration.

3.2. Atomic Force Microscopy (AFM)

The surface morphology of the prepared samples were studied using atomic force microscopy (AFM). Figure **5** shows 3D AFM images covering an area of 5μm × 5μm of samples (a, b1-b4) respectively. The various parameters like variation of Average roughness, RMS roughness and mean height of the samples are calculated from AFM data (Table **1**). Average roughness, RMS roughness of samples (b1-b4) decrease with increasing the coumarin concentration.

3.3 Mechanical Properties

Figure **6** shows the stress–strain behaviors, Table **2** summarizes the mechanical properties Young´s modulus Y, strength σ and strain at break ε_b for the samples (a, b1-b4).

The stress- strain curves for the prepared samples include two regions. The first region corresponding to elastic strain obeying Hook´s law. As the slope of this region is systematically increasing with increasing the coumarin concentration while the second one corresponding to plastic strain. Table **2** reveals a tendency for an increase in Young's modulus Strength at break with increasing coumarin concentration.

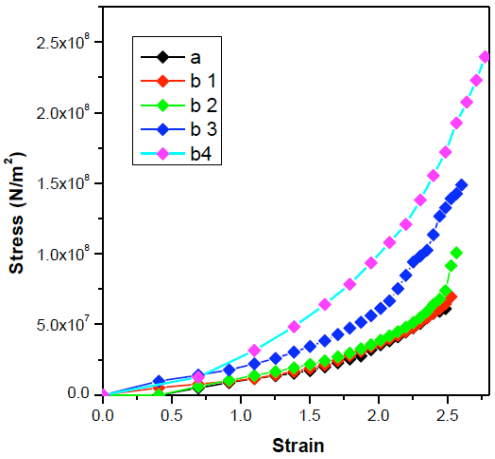


Figure 6: Stress-strain behavior for the samples (a. b1-b4).

It may be seen in Figures **3-6** and Table **2** that the band tail, Young's modulus and the strength at the break for the prepared samples to increase as the coumarin concentration is increased. This could be, explained as follows:

Pure PVA is partially crystalline and consists of crystalline layers or lamellas of folded chains joined together by tie molecules, which form amorphous regions between the lamellas [13]. Increasing of coumarin concentration will lead to an increasing degree of disorder. The increasing degree of disorder causes the band tail, Young's modulus and the strength at the break to increase, which according to the electronic structure of amorphous materials [14] will lead to a decrease of the estimated optical gap.

Table 1: Variation of RMS Roughness, Average Roughness and Mean Height of Samples (a, b1-b4)

Sample	Rms Roughess (Rq) (nm)	Ave Roughess (Ra) (nm)	Mean Ht (nm)
a	6.983	5.114	49.09
b1	15.830	12.150	45.24
b2	6.293	4.795	31.69
b3	5.424	3.319	18.92
b4	5.151	3.051	31.04

Table 2: The Mechanical Properties of the Samples (a, b1-b4)

Samples	Young's Modulus Y(N/m^2) x10^7	Strength at Break (σ) (N/m^2) x10^7	Strain at the Break ε_b
a	0.5	6.1	2.52
b1	1.2	7.1	2.54
b2	1.4	10.0	2.57
b3	1.9	15.0	2.60
b4	2.7	24.0	2.80

4. CONCLUSION

The detailed study of PVA-coum samples has shown that the optical absorption coefficient increases while the optical band gaps decrease. This decrease may be attributed to the formation of defects in the polymeric matrix. The stress- strain curves for the prepared samples include two regions. The first region corresponding to elastic strain obeying Hook's law, while the second one corresponding to plastic strain. Young's modulus and Strength at break increase with increasing coumarin concentration. Average roughness, RMS roughness of the prepared samples decrease with increasing the coumarin concentration.

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