ORIGINAL RESEARCH

Effect of dye concentration on the optical properties of red-BS dye-doped PVA film

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Abstract In this experimental study, the effect of dye concentration on the optical properties of red-BS dye-doped polyvinyl alcohol (PVA) thin films is investigated. Three thin film samples with different concentration of red-BS dye were prepared by spin-coating method on the glass substrate. Using transmission and reflection spectrum of films, their optical parameter such as refractive index, absorption coefficient, and dielectric function are extracted and the effect of dye impurity on theses parameters has been studied. The band gap energy of samples is calculated using Tauc method. Band gap energy of samples is decreased by increasing the concentration of dye impurity in PVA films.

Introduction

Traditionally, polymer matrix composites have been thought as insulating materials and have been used in applications like power tool handles, cable, jackets, capacitor films and electronic packaging materials. Especially the electrical and optical properties of polymers have been extensively investigated due to their applications in optical devices recently. Polymeric materials have unique properties such as low density, light weight, and high flexibility and are widely used in various industrial sectors. In recent years there has been great progress in

understanding polymer optical properties and development in their theoretical description [1–4].

Polyvinyl alcohol (PVA) is an important and interesting polymer because of its attractive physical and optical properties. Unlike most vinyl polymers, PVA is not prepared by polymerization of the corresponding monomer. The monomer vinyl alcohol is unstable with respect to acetaldehyde. PVA instead is prepared by first polymerizing vinyl acetate, and the resulting polyvinylacetate is converted to the PVA. Other precursor polymers are sometimes used, with formate, chloroacetate groups instead of acetate. The properties of the polymer depend on the amount of residual ester groups [5]. PVA is a colorless polymer, so because of its low cost and volume productivity it will be one of the key materials for using instead of glass and different coatings in optics industry. As a polymer waveguide PVA has attracted much attention. In addition it is found that it can produce a large reflective index [3]. These materials are promising candidates as nonliner optical elements [6–10].

Ultraviolet (UV) radiation initiates photo physical and photochemical processes in polymers but its influence is restricted to a thin surface layer. It is because our experiments are done on PMMA thin films. In this experimental research we have used red BS dye as an impurity in PMMA films as a powerful UV absorber. Organic compounds contained in polymer films, even in trace amounts, affect the reaction accruing during radiation. Interesting contributions concern the impact of the UV irradiation on the properties of PMMA thin films obtained by a spin-coating technique [1, 2].

In this manuscript we have investigated the effect of red-BS dye on the optical properties of PVA thin films. The manuscript is organized as follow, following the introduction in "Introduction", experimental setup is presented

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Table 1 Thickness and band gap energy of samples

Sample	S1	S2	S3
Spin coater speed (s)	2,290.2	1,307.66	942.25
Films thickness (mm)	0.03	0.025	0.019
Energy band gap (eV)	4.8	3.75	3.56

in "Experimental setup". "Results and discussion" includes results and discussion and "Conclusion" is devoted to conclusion.
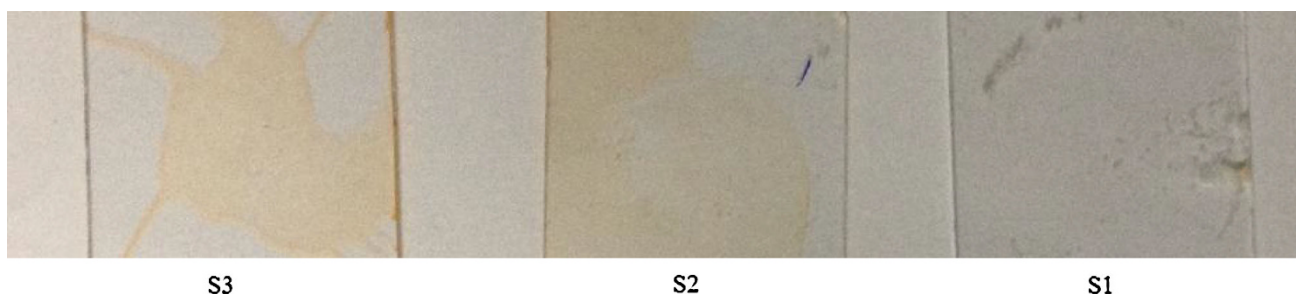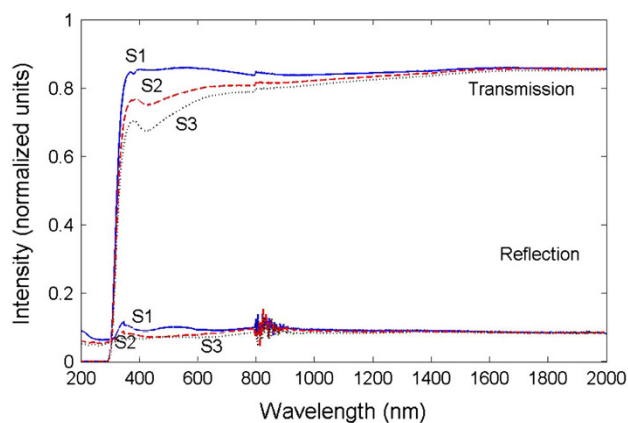
Experimental setup

Red-BS dye-doped PVA films were synthesized by solving red BS dye in PVA solution. The PVA powder was provided by Merck Co., Germany. An aqueous solution of PVA contains 2 g PVA, dissolved in 40 ml water was prepared. This mixture was stirred for about 150 min using magnetic stirrer at 55 °C temperature. Red BS dye samples were added into mixtures and again stirred for 30 min at the same temperature. Amounts of red BS dye solution were 0 g, 1 and 2 cc for samples 1–3, respectively. Samples 1–3 are labeled as S1–S3, respectively. Then a drop of 2 ml of each sample was poured on a glass plate which was placed in a spin coater. To prepare thin red BS dye-doped films of different thicknesses at room temperature, the speeds of spin coater were different which are presented in Table 1. PVA is a colorless polymer but the colors of the films which contain red BS dye are reddish depending on the concentration of dye. Samples are introduced in Table 1 and the thin films on the glass substrate are shown in Fig. 1.

Varian Carry 500 UV–Vis–NIR spectrometer was used to obtain the transmission and reflection spectrum of samples in this range.

Results and discussion

The picture of pure PVA and PVA doped with red BS dye thin films are presented in Fig. 1. PVA is colorless polymer and with adding red BS dye its color is changed to red.

Fig. 2 Transmission and reflection of samples

The variation of transmittance (T) and reflectance (R) as a function of wavelength for sample 1–3 were recorded at room temperature and are showed in Fig. 2. One can observe that with increasing the amount of dye in samples their transmission, especially in the range of visible light is decreased. The transmittance spectrum of the samples exhibits a shoulder like-band between 300 and 315 nm, which is due band gap of PVA. This figure clearly indicates that after adding red BS dye in PVA polymer (S2 and S3), in the visible region a valley at 420 nm has been created, that its intensity continuously increasing with increasing concentration of the dopant. As observed, it can be concluded that light is not dispersed and this indicates that the thin films are homogenous and optical flat. It is quite clear that at a larger wavelength (>950 nm), the samples becomes transparent and no light is scattered or absorbed, i.e., there is a non-absorbing region ($T + R = 1$). The inequality $T + R < 1$ at a shorter wavelength (<950 nm) implies the existence of absorption, i.e., an absorbing region. The value of reflectance is decrease in wavelength $\lambda < 900$, with increasing concentration of red BS dye doped in polymer but in IR region, almost unchanged.

The optical absorption coefficients of samples are evaluated from the transmittance data using;

Fig. 1 The photo of red BS dye-doped PVA thin film on glass substrate

Fig. 3 The optical absorption coefficient of samples
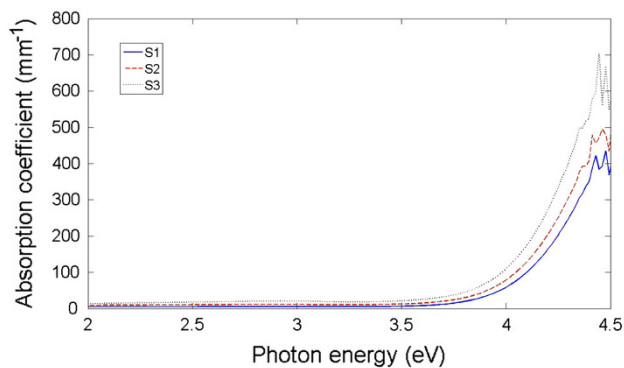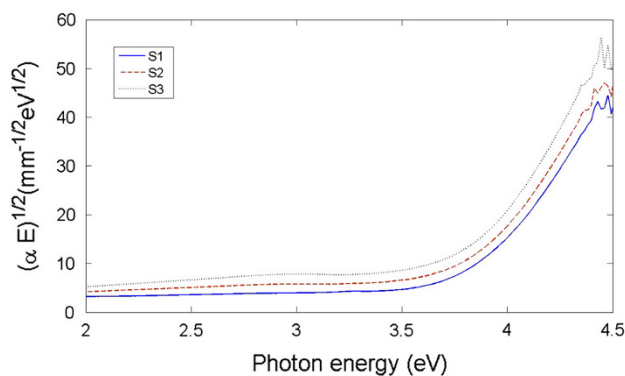

Fig. 4 The optical energy gap of samples

$$\alpha = \frac{1}{d} \ln \left[\frac{(1-R)^2}{2T} + \sqrt{\frac{(1-R)^4}{4T^2} + R^2} \right] \quad (1)$$

where T and R are the transmittance and reflection, respectively, α is the absorption coefficient, and d is the thickness of the samples. The absorption coefficients of the samples for different photon energies are shown in Fig. 3. As can be seen, with increasing concentration of dopant, the absorption coefficient of the samples in the UV region ($E > 3.5$ eV), has increased because of presence red BS dye in PVA hybrid matrix. The position of the absorption edge was determined by extrapolating the linear portions of α vs. $h\nu$ curves to zero absorption value. It is clear from the Fig. 2 that the band edge showed a decrease with increasing concentration of dopant in PVA polymer. The absorption edge shifts towards lower energies side, indicating the decrease in the optical band gap for the doped, thin films. Thus, shift of the absorption edge in the UV region, due to changes in the electron–hole in the conduction and valence bands.

The optical energy gap E_g is another important quantity that characterizes semiconductors and dielectric materials since it has a paramount importance in the design and modeling of such materials. It is worth to mention that the fundamental gap: "HOMO-LOMO gap", E_g, is the minimum energy formation of a separated, uncorrelated free electron and hole, and associated with the transport of single particles in the solid. The optical energy gap of samples was deduced from the intercept of the extrapolated linear part of the plot of $(\alpha E)^{1/2}$ vs. the photon energy E with abscissa (see Fig. 4). This followed from the method of Tauc et al. [11] where:

$$\alpha E = B(E - E_g)^m \quad (2)$$

In this equation α is the absorption coefficient, E is the photon energy, and B is a factor depends on the transition probability and can be assumed to be constant within the optical frequency range, and the index m is related to the distribution of the density of states. The index m has discrete values like 1/2, 3/2, 2, more depending on whether the transition is direct or indirect and allowed or forbidden. In the direct and allowed cases, the index $m = 1/2$ whereas for the direct but forbidden cases it is 3/2. But for the indirect and allowed cases $m = 2$ and for the forbidden cases it is 3 or more. Taking $m = 2$ corresponds to indirect allowed transitions in samples, the band gap energies of thin films were calculated, which are shown in Table 1.

As can be seen, the energy gap of pure PVA sample (S1) is equal to 3.86 eV, with increasing the concentration of the red BS dye in PVA polymer, is reduced. Thus the doped, thin films show a blue shift behavior (see Fig. 4); it can be concluded that the presence of dopant and its interaction results in the creation of new molecular dipoles, which could be results of point defects created within the band gap. Nitrogen and oxygen has a high electronegativity. Due to the presence of nitrogen in the red BS dye structure and the possibility to establish covalent bonds with hydrogen and carbon in the PVA structure, the thin films are highly capable of being polarized. It can be explained by the fact that with larger amount of red BS dye in PVA polymer we have more molecules dipoles in deposited thin films, in other words deposited thin films is closer to semiconductors, with low magnitude of band gap energy.

Determination of the optical constants n and k, is one of the most challenging tasks when studying the optical properties of materials since this involves complex equations and a great deal of computing. The refractive index is one of the fundamental properties of a material, because it is closely related to the electronic polarizability of ions and the local field inside the material. A number of methods and different approaches exist to determine the optical constants of materials. The complex refractive index is:

$$n = \left(\frac{1+R}{1-R} \right) + \sqrt{\frac{4R}{(1-R)^2} - k^2} \quad (3)$$
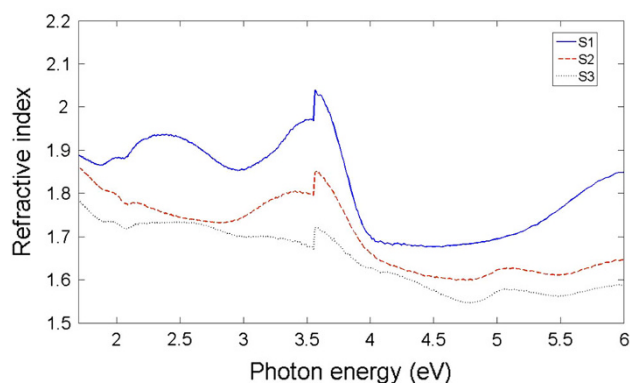
Fig. 5 Refractive index of samples
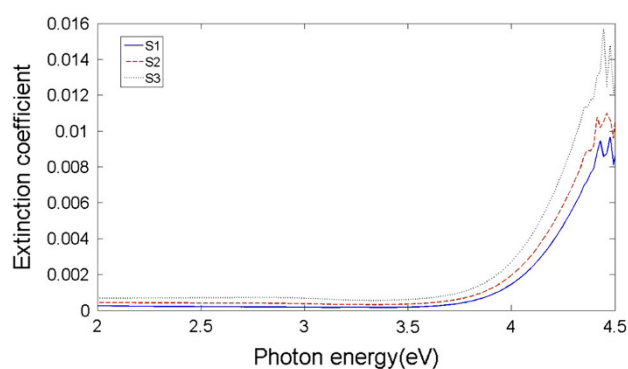
Fig. 6 Extinction coefficient of samples

in which $k = \lambda\alpha/4\pi$, is the extinction coefficient. Extinction coefficient is the imaginary part of complex refractive index. Figures 5 and 6 shows the photon energy dependence of refractive index and the extinction coefficient for pure PVA (S1) and red BS dye-doped PVA thin films. It can be discerned from Fig. 4 that the refractive index of doped samples (S2, S3) is lower than the refractive index of pure PVA and it decrease with increasing concentration of red BS dye in PVA matrix. One reason for the variation of the refractive index of samples creates bonds is polarized. Since thin films contains electronegative oxygen and nitrogen atoms, C–O and C–N (stretching) and N–H (bending) bands are polarized, resulting in specific interactions occurring at the inter phase. The dipole–dipole nature, which leads to the rearrangement of polymeric chains and induction of the photochemical processes at the PVA surface, can also be a reason for the variation of the refractive index of samples.

The extinction coefficient k describes the properties of the material with respect to light of a given wavelength and indicates the absorption changes when the electromagnetic wave propagates through the material. In Fig. 5, the

extinction coefficient k of samples at UV region began to rise and increases with increasing concentration of red BS dye in PVA dielectric medium. It can be observed that there is anomalous dispersion regions when $3.5 < E < 4.5$ eV and, as well as normal dispersion when $3 < E < 3.5$ eV for doped samples. So the normal dispersion is seen to occur everywhere expect in the neighborhood of a resonant frequency.

Conclusion

In this experimental work we have investigated the effects of thickness and dye concentration on the optical properties of dye-doped PVA thin films. Using transmittance and reflectance of films, their several optical parameters have been extracted and studied. From S1 to S3 transmittance of samples specially in the range of visible spectrum is decreased, which is the effect of dye increment in the structure of films. Also the absorption coefficient of samples is increased. Adding dye in the structure of PVA has been leaded to decreasing the band gap energy of films because of smaller band gap energy of dye. Increasing the absorption of samples is due to decreasing the real part of their refractive index and increasing its imaginary parts.

References

1. Dorranian, D., Abedini, Z., Hojabri, A., Ghoranneviss, M.: Structural and optical characterization of PMMA surface treated in low power nitrogen and oxygen RF plasmas. J. Non-oxide Glasses **1**, 217–229 (2009)
2. Dorranian, D., Zahedi S.: Investigation of pulsed laser effects on the structure of poly methyl methacrylate polymer. Res. Rev. Polym. **1**, 2–7 (2011)
3. Zahedi, S., Dorranian, D.: Effect of laser treatment on the optical properties of poly(methyl methacrylate) thin films. Opt. Rev. **20**, 36–40 (2013)
4. Zahedi, S., Dorranian, D.: The effects of pulsed laser irradiation on the nonlinear optical properties of PMMA film. Laser Eng. **26**, 243–254 (2013)
5. Hallensleben M.L.: Polyvinyl compounds, others in ullmann's Encyclopedia of Industrial chemistry. Wiley, weinheim (2000)
6. Shadi, S., Ghoranneviss, M., Mazzenchi, B., Rashidi, A., Dorranian, D.: Effect of using cold plasma on dyeing properties of polypropylene fabrics. Fibers Polym. **8**, 123–129 (2007)
7. Rashidian, M., Dorranian, D., Ahmadi, S., Saghafi, S., Ghorranneviss, M.: Nonlinear responses and optical limiting behavior of basic violet 16 dye under CW laser. Optik **120**, 1000–1006 (2009)
8. Hojabri, A., Dorranian, D., Hadavi, N.: Investigation of the effect of nitrogen plasma treatment on the properties of red-BS dye doped PMMA film. J. Appl. Chem. Res. **10**, 13–19 (2009)

9. Jafari, M., Dorranian, D.: Surface modification of PMMA polymer in the interaction with oxygen–argon RF plasma. JTAP **5**, 59–66 (2009)

10. Dorranian, D., Golian, Y., Tahmasebi, F.S., Rashidian, M.: Effect of RF plasma treatment on the nonlinear refractive index and susceptibility of PVC film. Iran. Phys. J. **3**, 6–11 (2009)

11. Tauc, J.: States in the gap. J. Non-Cryst. Solids **8–10**, 569–585 (1972)