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Effects of methyl red acidity and UV illumination on absorption coefficient of MR/PVA thin films

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ABSTRACT

The absorption coefficient spectra of poly(vinyl alcohol), PVA, mixed with methyl red (MR) thin films on glass substrates, prepared by the spin coating method has been investigated using scanning electron microscopy (SEM) and spectroscopic ellipsometry. SEM imaging indicates that the surface of the MR/PVA film is smooth, uniform, and no crack could be observed. Spectroscopic ellipsometry measurements of PVA and MR/PMMA thin films were carried out at three angles of incidence, over the wavelength range 400–800 nm. Optical models were used to obtain the absorption coefficients for the prepared samples. These models include Cauchy formula for the glass substrate and PVA film, Lorentz model with three oscillators for MR layer, and a Bruggeman effective medium approximation for MR/PVA films. Absorption coefficients were found to be in the range $5\times10^3-5\times10^4\,cm^{-1}$ with a maximum being at about 475 nm. Changing the absorption coefficient as a function of increasing the pH of MR causes a shift of the absorption band toward higher wavelengths. Our results show that the absorption coefficient of the film decreases upon increasing the UV illumination time.

1. Introduction

Poly(vinyl alcohol), PVA, is a non-toxic, water-soluble synthetic polymer and has good physical and chemical properties and film-forming ability [1]. The use of this polymer is important in many applications such as controlled drug delivery systems, membrane preparation, recycling of polymers, and packaging. PVA has bio-inertness, so it has many uses as, artificial pancreas, hemodialysis, nanofilteration, and synthetic vitreous and implantable medical device. Anti-thrombogenicity, cell compatibility, blood compatibility, and biocompatibility of PVA have been studied extensively [2–4].

Azo dyes in polymers have been intensively investigated in the last decade because of their potential applications in optical elements [5–7]. Azo dyes can undergo a photochemical process called photo-isomerization. In this reaction, upon absorbing light of sufficient energy, dye molecules undergo a spatial trans–cis isomerization through the rotation of an N=N double bond. Azo dyes are also used as a liquid crystal photo-aligning medium because of their molecular reorientation capability when subjected to electric fields [8,9].

Spectroscopic ellipsometry (SE) has been used to study many problems in composite polymer thin films at atmospheric conditions [10–14]. In spectroscopic ellipsometry, the change in polarization state of light reflected from a film is measured and used to determine the thickness, surface roughness, and the optical properties of the thin film and the substrate. Spectroscopic ellipsometry determines two parameters Ψ and Δ according to $\tan\Psi=|r_p|/|r_s|$, and $r_p/r_s=\exp(i\Delta)\tan\Psi$, where r_p and r_s are the complex Fresnel reflection coefficients for 'p' and 's' polarizations, respectively. However, the acquired data from SE (Ψ and Δ) must be analyzed to obtain useful information [15]. An optical model representing the assumed physical geometry and microstructure is developed, and Fresnel reflection coefficients are calculated, allowing predictions of ellipsometric parameters to compare with measured values. Model parameters, such as refractive index, n, extinction coefficient, k, and thickness, vary in regression until the comparator function, such as the mean square error (MSE), is minimized. The resulting parameters are the "best fit" values of n and k.

The aim of this paper is to present the effect of methyl red acidity, and the effect of UV illumination on the absorption coefficient of spin coated thin films composed of methyl red azo dye-in-polyvinyl alcohol using spectroscopic ellipsometry.

2. Experiment

0.4 mg of Methyl Red, $C_{15}H_{14}N_3NaO_2$, (S.D. Fine Chem., Mumbai, India) was dissolved in 100 ml chlorobenzene (99%), and 4 g of poly(vinyl alcohol), PVA, of linear formula, $[–CH_2CHOH–]_n$; MW=82,600 for GPC (Fluka–Aldrich) was dissolved in 100 ml of

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Table 1
Samples identification, composition, volume ratio, and MR pH.

Sample symbol	Composition	Volume ratio MR:PVA (v/v)	MR acidity (pH)
A	PVA	0:1	–
B1	MR//PVA	3:1	1
B2[a]	MR//PVA	3:1	4.54
B3	MR/PVA	3:1	8
B4	MR/PVA	3:1	11

[a] pH of MR is 4.54 and therefore HCL was not added.

de-ionized distilled water by heating up to 40 °C for 2.5 h, then allowed to cool to room temperature with continuous stirring. Different acidity degrees of MR were obtained by adding NaOH, and HCl. Different solutions of MR, and PVA were prepared with volume ratio of 3:1. Table 1, lists the prepared samples, their MR:PVA volume ratio and MR pH value. The solutions were then filtered using millipore filter to remove any insoluble impurities and dust before use. Before film preparation, microscope glass slides as substrates were washed with soapy water and distilled water (twice) in an ultrasonic path, then washed with acetone. A set of thin films was obtained of individual and mixture media using the spin coating method on glass substrates using a spin time of 20 s and a spin frequency of 1500 rpm. All samples were prepared at room temperature and left to dry inside an oven at 40 °C for 2 h. One sample was illuminated using low power UV lamp (250 μW/cm^2) filtered at wavelength 254 nm for 8, 16, and 24 h illumination time. The micrographs of PVA, and MR/PVA thin films were performed by the direct observation via a scanning electron microscope (SEM FEI Quanta 600). Ellipsometric parameters (Ψ and Δ) were acquired with a J.A.Woollam variable angle spectroscopic ellipsometer of the rotating analyzer type. Ellipsometric measurements were performed in air at room temperature for three angles of incidence 65°, 70°, and 75° over the wavelength range of 400–800 nm.

3. Results and discussion

A glass was used as a substrate for thin films in this work. Its transparency in the visible range, and internal reflections, are of concern for ellipsometry. Since the light penetration depth is high, reflection from backside of a glass slide can be only suppressed either by abrading and/or blackening the backside surface, or by using suitable analysis software, which includes contributions of a second light beam (two reflected beams reach the detector from the top and back glass surfaces) [15,16].

The value of Δ is very high (close to 180°) or small (close to 0°) at incident angles that are below and above, respectively, to Brewster angle θ_B. Usually θ_B is near to 55–57° for most glasses. Because of difficulty in measuring delta near 180° or 0°, the data analysis can be made at different values of incident angle using only Ψ values and ignoring the Δ values. The dispersion model for bulk glass (substrate) is best modeled by the Cauchy dispersion relation that describes the index of refraction (n) as a function of incident light wavelength (λ) [17] by

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \quad (1)$$

where the Cauchy constants, $A = 1.4351$, $B = 0.00502$ nm^2, and $C = -0.00024$ nm^4 are the fitting parameters for the used glass substrate. Extinction coefficient (k) vanishes in the visible region (400–700 nm). The fitting parameters and the number of backside reflections from the backside surface of the glass substrate were set to vary in order to fit for the Ψ data only. An evaluation of good (90%) confidence for the regression analysis and the data fitting is calculated from the elements of the correlation matrix, which the Levenberg–Marquadrat algorithm produces during the minimization procedure using WVASE (J.A. Woollam Co.) software [18]. A procedure of calculation of the elements of the correlation matrix and the absolute error is described in Ref. [19].

Fig. 1a shows Ψ spectrum of PVA (sample A) film deposited by spin coating on glass substrates. The Cauchy formula for n shown above was used to analyze the spectroscopic ellipsometry data. For this purpose a single optical model was chosen as the Cauchy layer/substrate, the film thickness, and Cauchy parameters were fitted. The fitted parameters obtained from the Cauchy model have the values of $A = 1.5556 \pm 0.104$, $B = 0.1062 \pm 0.054$ nm^2, and $C = -0.0174 \pm 0.006$ nm^4. The resultant film thickness as a fitting

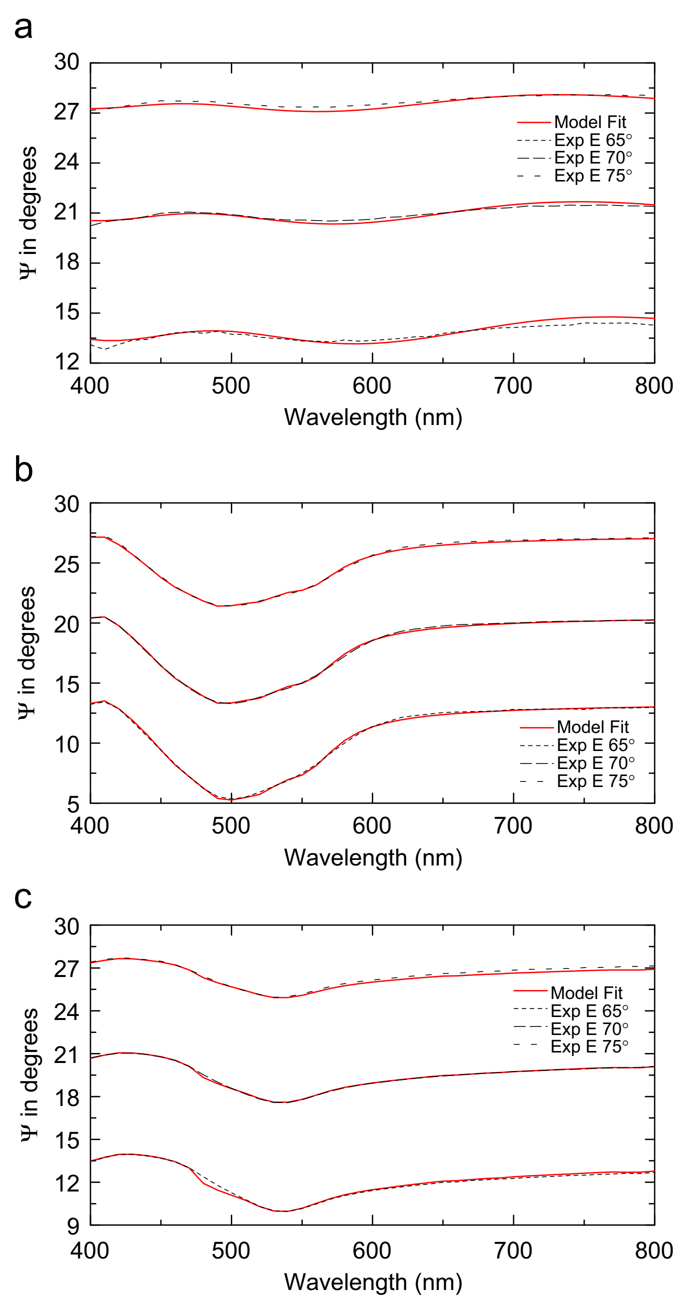

Fig. 1. Spectroscopic ellipsometric parameter Ψ versus wavelength, (a) PVA, (b) MR, and (c) MR/PVA thin films on glass substrate at angles of incidence of 65°, 70°, and 75°.