International Journal of Engineering Research And Management (IJERM)
ISSN : 2349- 2058, Volume-02, Issue-10, October 2015

Study of the optical absorption edge and optical constants of poly alpha naphthyle acrylate thin films

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***Abstract*— Optical properties of poly alpha naphthyle acrylate thin films was deposited on glass substrate at room temperature by using cast method technique. The films properties investigated include their transmittance, reflectance spectra, absorbance spectra, extinction coefficient, optical conductivity and complex dielectric constant. The optical constants such as refractive index n the dispersion energy Ed the oscillation energy E0 the light frequency dielectric constant ε_∞ and energy bang gap Eg have been determined by reflection spectra in the wavelength range (200-1100) nm.**

***Index Terms*— PNA polymer, Absorption coefficient, Optical Conductivity, Complex dielectric constant**

I. INTRODUCTION

Amongst the new classes of materials, polymers are especially interesting because they combine the optical and electronic properties of semiconductors with the processing advantages and mechanical properties of polymers [1].

Semi conducting polymeric mixtures take a large area in different applications such as heating prevention of static electricity accumulation such as preventing dust attraction on electronic device cabinets and electrodes and used for electromagnanetic interference shielding of electronic devices and prevention of static electricity hazards in the handling of electronic chips and explosives[2,3].

Optical properties such as refractive indices for certain range of wavelength between ultraviolet and near infrared and optical band gap values becoming quite important criteria for the selection of application of the fabricated films. The refractive indices of optical materials are considerable importance for applications in integrated optic devices such as switches [4].

Many applications require the materials in thin form. Microscopic defect, which control surface smoothens and coating homogeneity, contribute to the scattering of light and associated degradation of the optical response. Similarly, structural disturbance at the atomic level can alter the optical properties through modifications to the complex refractive index of the material [5,6].

In the present study the optical properties of poly alpha naphthyle acrylate thin film in the wavelength (200-1100) nm.

The study included measurement of optical spectra, reflectivity, absorption coefficient, refractive index, optical band gap, optical dispersion parameter, loss function, and complex dielectric constant.

Manuscript received Sep 26, 2015

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II. EXPERIMENTAL PROCEDURE

Poly alpha naphthyle acrelate was synthesized and condensation polymerization adopting method previously reported [7]. Fig. 1 show the expected structure of the polymer under the present study.

0.1 M of polymer (0.1081) gm is first dissolved in Dimethyle Formamide (DMF) and stirred at room temperature for (4-6) h. The stirred solution was cast on the glass substrates cited horizontally to get a homogeneous thickness. The film was prepared onto a standard glass microscope slide with dimensions of 2.2 × 2.2 ×0.12 cm by the spin- coating method and dried at room temperature (RT) for (10 min). The solvent is allowed to evaporate slowly at room temperature. Current process was applied to the samples as a final process via increasing the temperature in the rate 10 C^o/hr up to 90C^o, then cooled gradually up to the room temperature. The thickness of the film is about 4 μm.

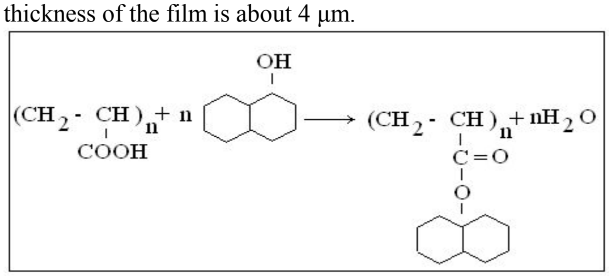

Fig.1. The chemical structure of polymer

III. RESULTS AND DISCUSSION

UV-Vis spectroscopy has been used to characterize the poly alpha naphthyle acrylate thin film in the spectral range (200–1100 nm). The absorbance, *A*, transmittance, *T*, and reflectance ,*R*, of poly alpha naphthyle acrylate film measurements were carried out using Cecil ReflectaScan CE 3055 Reflectance Spectrometer. These measurements were performed at room temperature. Figure 2 shows the spectral distribution of absorbance for poly alpha naphthyle acrylate film in the spectral range (200–1100 nm).

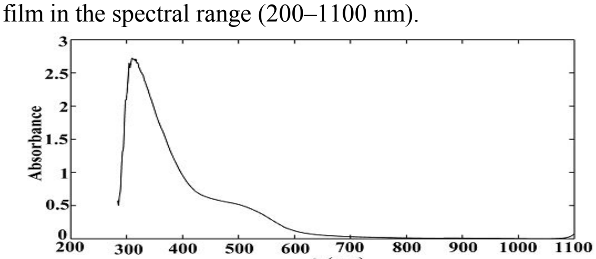

Fig.2. Spectral absorption vis. λ of poly alpha naphthyle acrylate thin film.

A close examination of the absorption band in the UV region which is known as the Soret band, reveals a peak at (λ =340 nm). The absorption band in the ultraviolet region is preceded by the ultraviolet absorption band edge of the titanium dioxide molecule. The other well-known band of the titanium dioxide molecule, namely Q band appears in the region between 400 and 900 nm. Transmission, *T*, and reflectance, *R*, measurements of poly alpha naphthyle acrylate film of thickness ,*d*, were used to determine the optical absorption coefficient ,α, refractive index ,*n*, and extinction coefficient, *k*, by using the following formulas [8–10].

$$\alpha = \frac{1}{d}\ln(\frac{1}{T}) \quad (1)$$

$$k = \frac{\alpha\lambda}{4\pi} \quad (2)$$

$$n = \frac{1+R}{1-R} + \sqrt{\frac{4R}{(1-R)^2} - k^2} \quad (3)$$

where λ is the wavelength of the incident light on the sample. The spectral distributions of *T*(λ) and *R*(λ) of poly alpha naphthyle acrylate thin film were measured at the normal incidence in the wavelengths range 200–1100 nm is shown in Figs. 3 and 4.

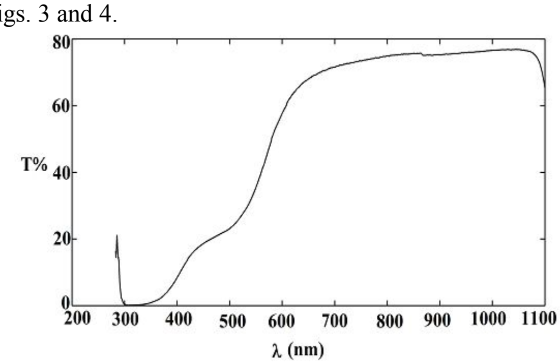

Fig. 3. Transmittance (*T*) vis. **λ** of thin film.

The spectral behavior of *T*(λ) shows a fundamental absorption band around λ ≈ 480 nm. The presence of such sharp band recommends that the prepared film is a good band pass or a good band stop optical filter depending on the wavelength. It is clear that at longer wavelengths (λ > 700 nm) poly alpha naphthyle acrylate film becomes transparent and no light is scattered or absorbed (i.e. $R + T = 1$). The inquality ($R + T < 1$) at shorter wavelengths (λ < 700 nm) known as the absorbing region.

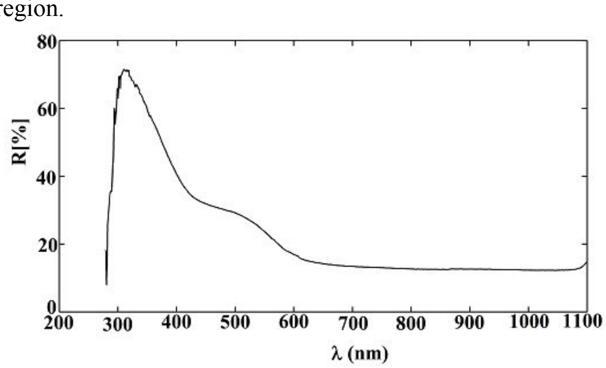

Fig. 4. Reflectance (*R*) vis. **λ** of thin film.

The transmission through the film is relatively low at below band gap region, indicating high concentration of defects, free carriers. The transmittance decreases abruptly in the short wavelengths.

which is due to the band edge absorption. The incoming photons have sufficient energy to excite electrons from the valence band to the conduction band, resulting in strong absorption in poly alpha naphthyle acrylate film. The optical absorption edge was determined by the optical absorption, a simple method that provides explanation for the features concerning the band structure of the film. The optical absorption edge was analyzed by the following relationship [11],

$$\alpha h\nu = \frac{A}{h\nu}(h\nu - E_g)^m \quad (4)$$

where , α is absorption coefficient, *A* is an energy-independent constant and E_g is the optical band gap. The exponent *m* depends on the nature of the transition, *m*= 1/2, 2, 3/2 or 3 for allowed direct, allowed non-direct, forbidden direct or forbidden non-direct transitions, respectively. Eq.4 can be written as

$$\frac{d[\ln(\alpha h\nu)]}{d(h\nu)} = \frac{m}{h\nu - E_g} \quad (5)$$

The type of transition can be obtained by determining the value of *m*. A discontinuity in the $d[\ln(\alpha h\nu)]/d(h\nu)$ vs. $h\nu$ plot at the band gap energy, i.e. at $h\nu = E_g$ can be observed. The discontinuity at a particular energy value gives the band gap, E_g [12]. The curves of $\ln(\alpha h\nu)$ vs. $\ln(h\nu - E_g)$ were plotted using the E_g value to determine *m* value and it was found about 1/2 from the slope of plotted curves. Thus, obtained *m* value suggests that the fundamental absorption edge in the films is formed by the direct allowed transitions. It is well known that direct transition across the band gap is feasible between the valence and the conduction band edges in *k* space. In the transition process, the total energy and momentum of the electron-photon system must be conserved.

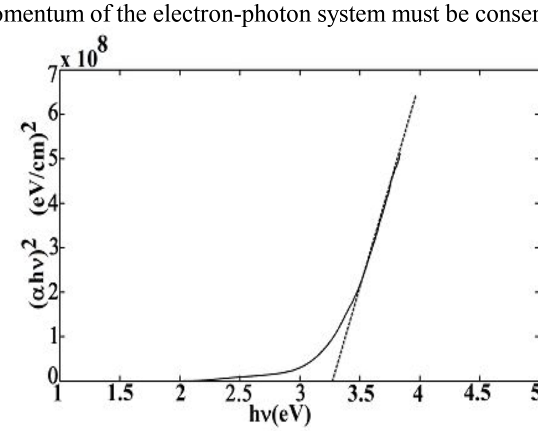

Fig.5. The plots of $(\alpha h\nu)^2$ vs. $h\nu$ of the film.

Fig.5. shows the plots of $(\alpha h\nu)^2$ vs. $h\nu$ of the films. The values of the direct optical band gap E_g are given in Table 1. The optical band gap values obtained by this method are suitable for many scientific studies and technological applications, such as gas sensors, heat mirrors, transparent electrodes, solar cells and piezoelectric devices. As seen from Table 1.

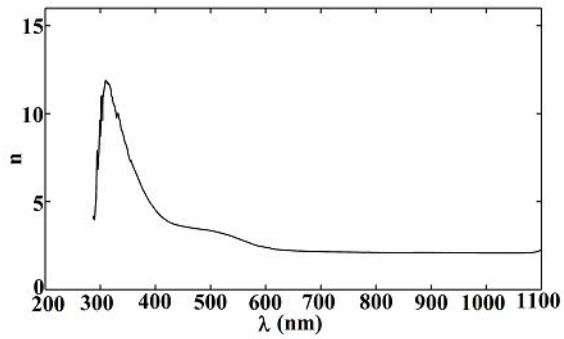

Fig.6. Refractive index (n) vs. λ of the film**.**

The extinction coefficient, k, and refractive index, n, values provide the optical properties of the film, are determined from Eq. 2 and 3. Figures 6 and 7 show the dependence of the refractive index, n and the extinction coefficient, k, on the wavelength. From these figures, one can see that in the region (300–400 nm), the values of refractive index, and k, increases with the increasing of wavelength, while the values of extinction coefficient, k, and n increase in the wavelengths region (410-520 nm) with the increase of wavelength.

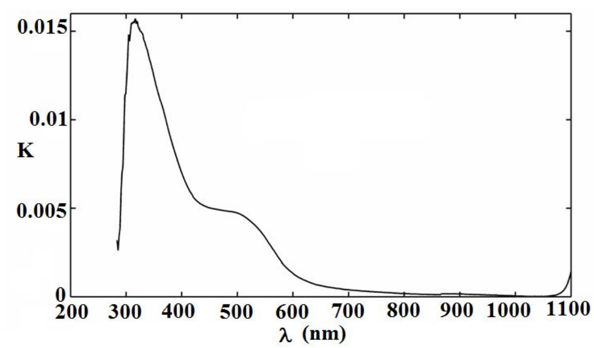

Fig. 7. Extinction coefficient (k) vs. λ of the film**.**

IV. DISPERSION CHARACTERISTICS OF FILM

Measured refractive indices were analyzed by employing the Wemple_DiDomenico single oscillator model [13, 14] in the region of normal dispersion (λ >400 nm) and the data were used to obtain the oscillator parameters. Equation 6 describe the relationship between the refractive indices, n, and the oscillator parameters.

$$\frac{1}{n^2-1}=\frac{E_0}{E_d}-\frac{(h\nu)^2}{E_0E_d} \qquad (6)$$

where, $h\nu$ is the photon energy, E_0 is the oscillator energy, and E_d is the oscillator strength or dispersion energy. Plotting $(n^2-1)^{-1}$ against $(h\nu)^2$ allows us to determine the oscillator parameters by fitting a linear function to the lower energy data. The point of intersection with the ordinate at $h\nu = 0$ yield the value of dielectric constant at higher wavelength (static dielectric constant), ε_0. The values of E_0 and E_d obtained from the intercept and the slope of the curve and the static refractive index, n_0, calculated using the relation, $[n^2(h\nu = 0) = (E_0/E_d) + 1]$. Fig. 8 shows the plot of $(n^2-1)^{-1}$ against $(h\nu)^2$.

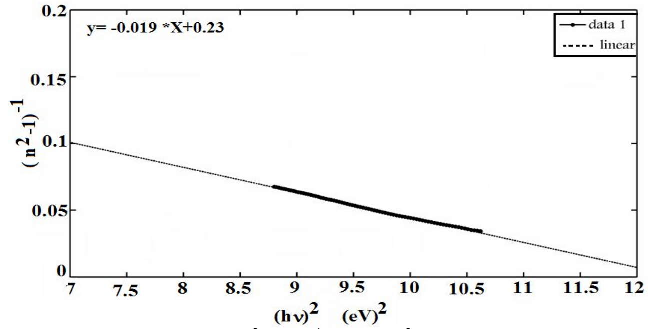

Fig.7. Plot of $(n^2-1)^{-1}$ vs. $(h\nu)^2$ of thin film.

The oscillator strength parameter, F, can be calculated using the following relation:

$$F = E_0E_d \qquad (7)$$

The moments of optical dispersion spectra, M_{-1} and M_{-3}, can be evaluated using the relations [14]

$$E_0^2=\frac{M_{-1}}{M_{-3}} \qquad (8)$$

$$E_d^2=\frac{M_{-1}^3}{M_{-3}} \qquad (9)$$

Table 1 shows the values of the static refractive index n_0, the static dielectric constant , ε_0,oscillator energy, E_0,disperse-ion energy, E_d, the oscillator strength, F, and the moments of optical dispersion spectra M_{-1}, M_{-3} .

E_0 (eV)	E_d (eV)	ε_0	n_0	F (eV)^2	M_{-1}	M_{-3} (eV)^2	E_g
3.47	**15.1**	**5.3**	**2.3**	**52.49**	**7.24**	**0.600**	**3.37**

Table 1. The estimated values of the oscillator parameters of poly alpha naphthyle acrylate film.

V. DIELECTRIC CHARACTERIZATIONS

The following relations have been used to calculate the values of the real part ε_1 and imaginary part ε_2 of the dielectric constant for a poly alpha naphthyle acrylate film, [15]:

$$\varepsilon_1 = n_2 - k_2 \qquad (10)$$

$$\varepsilon_2 = 2nk \qquad (11)$$

The dependences of ε_1 and ε_2 on the photon energy are shown in Figs. 8 and 9. The real and imaginary parts follow the same pattern and the values of the real part are higher than the imaginary part. The variation of the dielectric constant with the photon energy indicates that some interactions between photons and electrons in the films are produced in this energy range. These interactions are observed on the shapes of the real and imaginary parts of the dielectric constant and they cause the formation of peaks in the dielectric spectra which depends on the material type.

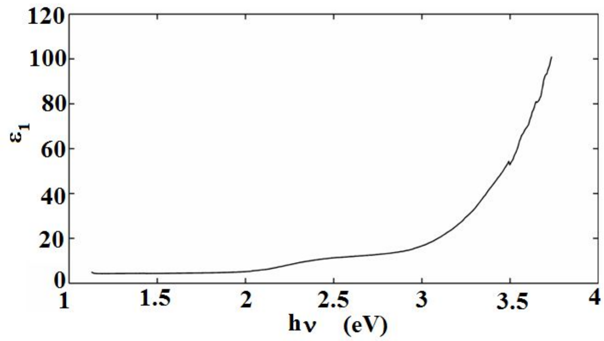

Fig.8. The variation of ε_1 vs. $h\nu$ of thin film.

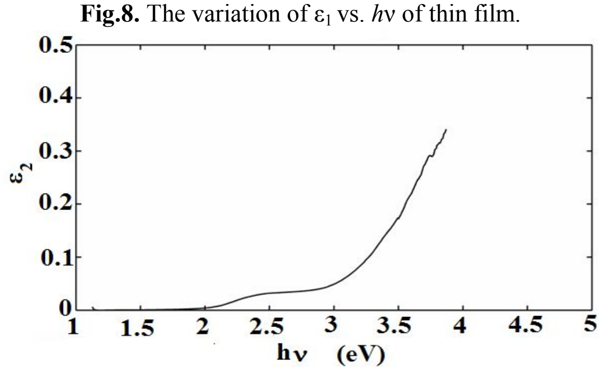

Fig.9. The variation of ε_2 vs. $h\nu$ of thin film.

VI. OPTICAL AND ELECTRICAL CONDUCTIVITY

The absorption coefficient α can be used to calculate the optical and electrical conductivity σ_{opt} , σ_e as follow [16]:

$$\sigma_{opt} = \frac{\alpha n c}{4\pi} \quad (12)$$

$$\sigma_e = \frac{2\lambda\sigma_{opt}}{\alpha} \quad (13)$$

where α is the absorption coefficient and c the velocity of light. Figs.10 and 11 shows the variation of optical conductivity σ_{opt} and electrical conductivity σ_e as a function of photon energy $h\nu$, it is worthwhile to note that the metal inclusion has greatly reduced the dielectric constant and increased the optical conductivity. The increased of optical conductivity at high photon energies is due to the high absorbance of sample thin films and also may be due to the electron excited by photon energy [17].

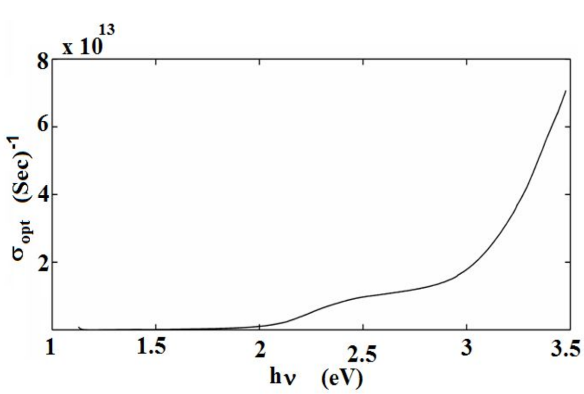

Fig.10. Optical conductivity vs. $h\nu$ of thin film.

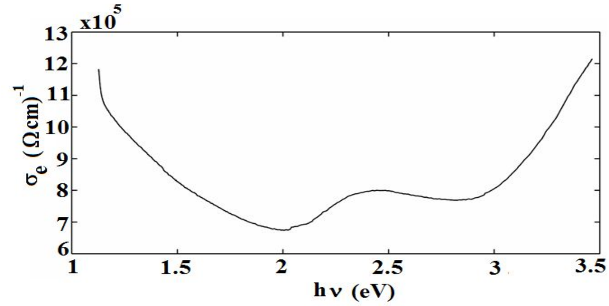

Fig.11. Electrical conductivity vs. $h\nu$ of thin film.

CONCLUSIONS

Optically smooth and homogeneous poly alpha naphthyle acrylate film was prepared at room temperature by the spin_coating method. The single oscillator Wemple–DiDomenico method was used to calculate their optical constants from the transmittance spectra and the refractive index dispersion of the film. The dispersion of the refractive index in film follows the single electronic oscillator mode relation. The UV_Visible spectroscopic studies showed that, the poly alpha naphthyle acrylate film have high refractive index, and high dielectric constant.

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