Thickness Effect on the Optical Constants of Poly Methyl Methacrylate (PMMA) Doped by Potassium Iodide

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Abstract

Films of Poly Methyl Methacrylate (PMMA) doped by (1%) Potassium Iodide (KI) have been prepared using casting method at room temperature. Optical properties were investigated for different thicknesses by using spectrophotometeric measurement of absorption reflection transmission in the wave length range (200-800) nm. Both the refractive index (n) and absorption coefficient (α) were determined for the films. The optical dispersion parameters have been analyzed by single oscillator model. The value of E_o and E_d were found and the other parameters have been determined by Wemple-DiDomenico method.

Introduction

The optical behavior of materials is important to determine it's usage in optoelectronic devices [1]. Knowledge of optical constants of a material such as optical band gap, refractive index and extinction coefficient is quite essential to examine material's potential opto-electronic applications. Further, the optical properties may also be closely related to the material's atomic structure, electronic band structure and electrical properties, [2]. An accurate measurement of the optical constants can be easily performed on thin film specimens.

Poly-methyl Methacrylate (PMMA) is an important and interesting polymer because of its attractive physical and optical properties. PMMA contains both hydrophobic (methylene) and hydrophilic (carbonyl) groups in each unit. As a polymer waveguide, PMMA has attracted much attention for use as optical components in optoelectronic devices due to its low cost and volume productivity. In addition, it is found that it can produce a large refractive index difference with acryl amide-based photopolymer, [3].

In recent years, the doped polymers have been the subject of interest for both theoretical and experimental studies, because of the physical and chemical properties needed for specific application may be obtained by adding or doping with some dopant, [4]. Many studies reveal that the optical properties of PMMA is affected by using different dopants or by increasing the doping concentrations, [5, 6]. Recently thickness dependence of refractive index and optical gap of PMMA layers prepared by spin-coating and modified by electric field have been studied, [7].

In the present work, we report the effect of thickness on the optical absorption parameters of PMMA thin films, such as optical dispersion energies, E_0, and E_d, dielectric constant(ε), the average values of the oscillator strength S_0 and wavelength of single oscillator λ_0, have been evaluated as a function of thickness variation.

Experimental Work

Casting method is used to prepare films of pure Poly (Methyl Methacrylate) (PMMA) doped by KI salt at different thickness. PMMA solution was prepared by dissolving PMMA in Acetone, KI used as a dopant. The solution was stirred, using a magnetic stirrer for 6 h until the polymer completely dissolved. The solution was poured into flat glass plate dishes. Homogeneous films were obtained after drying in air for 48 h at room temperature. The thicknesses of the produced films (80, 140, 210, 250, 320) μm were measured using a Digital Caliper Vernier.

The optical properties of the samples were measured using (Shimadzu 1601 PC) spectrophotometer in the wavelength range 200-800 nm.

Results and Discussion

Optical measurements of the transmittance and the reflectance of the films at different thicknesses are shown in Figs. (1 and 2). These measurements have been taken in the wavelength range from 200 to 800 nm. One can notice from the Fig.(1) that the transmission intensity decreases with increasing of the film thickness. The reason for that behavior is that in case of thicker films more atoms are present in the film, so more states will be available for photons to be absorbed, [8].

When the film thickness increases the scattering of light increase, the coherence between the primary light beam and that reflected between film boundaries is lost and result in the disappearance of the interference which in turn decreases the transmittance of the film, [9].

The transmission spectrum rises and it became approximately constant at (93%, 76%, 68%, 48% and 30%) for the film thicknesses (80, 140, 210, 250, 320) μm respectively. It is noticed that the PMMA films have higher transmission values in the visible range of the spectrum. In all the figures we gave the labels a, b, c, d and e for thickness 80, 140, 210, 250, 320 μm respectively.

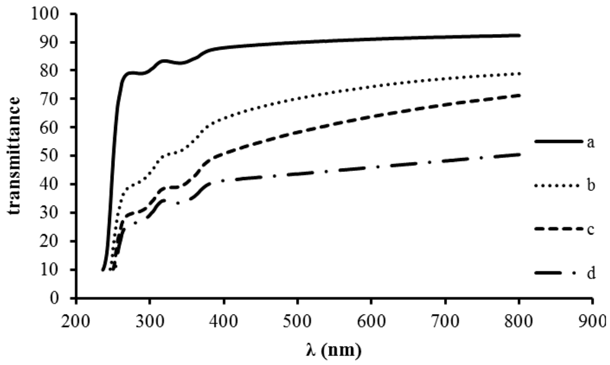

Fig.(1) Transmission spectra of (a-d) PMMA samples.

Fig.(2) illustrates the reflectance in the wavelength range (200-800) nm for different thickness of PMMA films. It is clear from this figure that the reflectance increases with the increasing film thickness. This is due to the increasing optical absorption and the increasing attenuation of incident beam, [10].

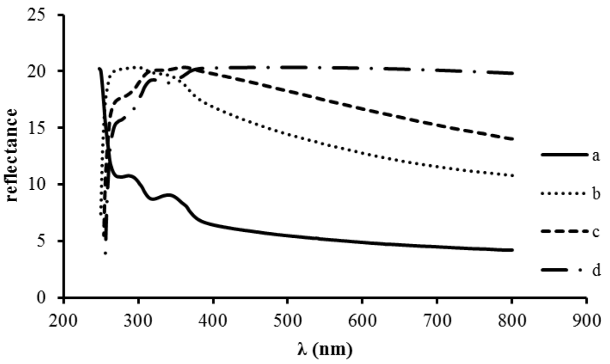

Fig.(2) Reflectance spectra of (a-d) PMMA samples.

The absorption coefficient (α) of the PMMA films was determined from transmittance measurements. The calculation of the absorption coefficient of the films in this region was calculated using the following expression: The absorption coefficient (α) = optical density/thickness, [11, 12].

$$\alpha(\nu) = \frac{1}{d}\ln\frac{1}{T} = \frac{A}{d} \quad \text{.......................................(1)}$$

where (d) is the sample thickness, (T) the transmittance and (A) is the absorbance. Fig.(3) shows the dependence of the absorption coefficient on the wavelength for the samples with different thicknesses, the absorption coefficient decrease with the increasing film thickness.

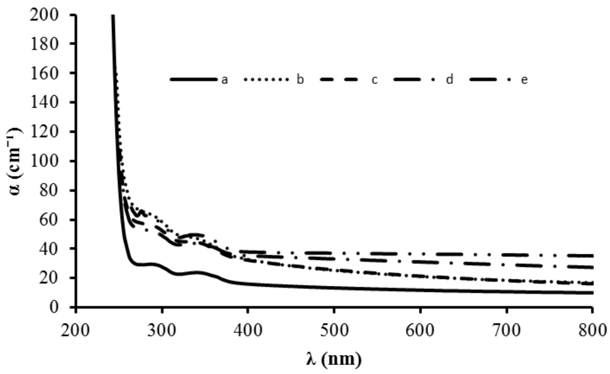

Fig. (3) Absorption coefficient versus wavelength for different thicknesses of PMMA films.

Determination of the dielectric constant could be defined using the dispersion relation of the incident photon. In literatures the refractive index was also fitted using a function for extrapolation towards shorter wavelength. The Moss model [13], which stated that: "the free carriers contribution to dispersion are relatively small". This means that data corresponding to the wavelength range lying below the absorption edge of the material has to be used, [14]. The properties of the investigated PMMA films could be treated as a single oscillator at wavelength at high frequency. The following equation which calculates the high frequency dielectric constant (ε) is:

$$n^2 - 1 = \frac{S_0\lambda_0^2}{1-(\lambda_0/\lambda)^2} \quad \text{.....................................(2)}$$

where S_o is the average oscillator strength and λ_0 an average oscillator wavelength. The values of refractive index (n) have been calculated from reference, [15]. Equation (2) can be written in the following form:

$$\frac{n_\infty^2-1}{n^2-1}=1-\left(\frac{\lambda_0}{\lambda}\right)^2 \qquad (3)$$

where n_∞ is the refractive index at infinite wavelength.

Table (1) shows the values of λ_0 and S_0 they were obtained from the slope and intercept of $(n^2-1)^{-1}$ versus λ^{-2} curves at different thicknesses as in the Figure 4. The intersection with $(n^2-1)^{-1}$ axis is $(n_\infty^2-1)^{-1}$ and hence, n_∞^2 at λ_0 equal to ε_∞. Figure 4 shows the variation between $(n^2-1)^{-1}$ and λ^{-2} at different thicknesses.

Table (1)
Optical parameters of PMMA thin films with different thickness.

thick μm	$S_0.10^{13}(m^{-2})$	$\Lambda_0(nm)$	ε	$E_0(eV)$	E_d (eV)	M_{-1}	$M_{-3}(eV)^{-2}$
80	4.6899	76599	1.36	1.614	4.483	0.36	0.0179
140	13.3	89746	2.191	4.916	4.125	1.191	0.07
210	19.39	92216	2.885	8.4015	4.457	1.885	0.094
250	20.6	8584	4.489	46.69	13.38	3.489	0.019

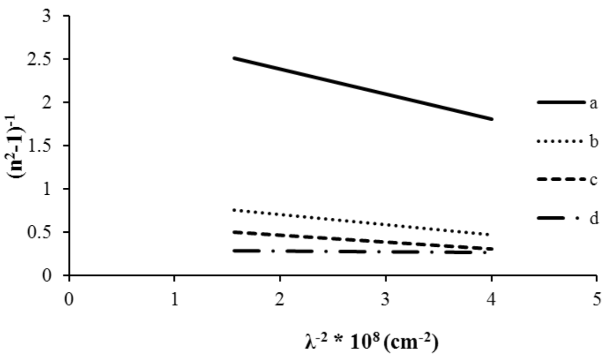

Fig. (4) Variation of $(n^2-1)^{-1}$ versus λ^{-2} for PMMA films.

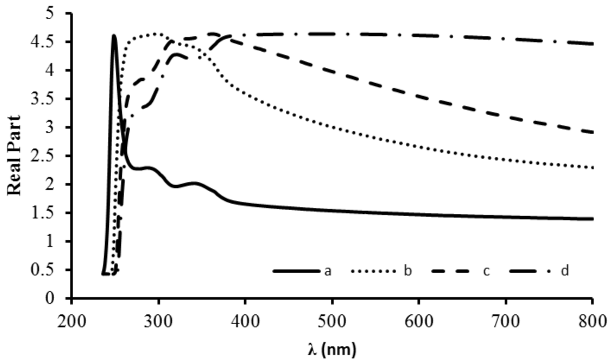

Fig. (5) Real part of dielectric constant versus wavelength.

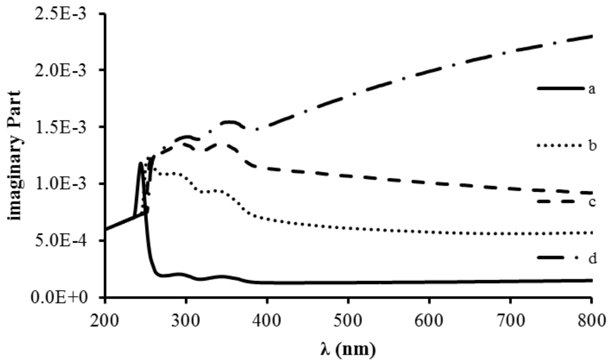

Fig. (6) Imaginary part of dielectric constant versus wavelength.

The real (ε_r) and imaginary (ε_i) parts of the dielectric constant related to (n) and (k) values. The (ε_r) and (ε_i) were calculated using the formulas [15, 16]:

$$\varepsilon^* = \varepsilon_r + i\varepsilon_i \qquad (4)$$

$$\varepsilon_r = n^2 - k^2 \qquad (5)$$

$$\varepsilon_i = 2nk \qquad (6)$$

Figs. (5) and (6) show (ε_r) and (ε_i) values dependence on wavelength. These values for the films increase as the film thickness increases. The real and imaginary part of the dielectric constant follows the same pattern curves but the values of the real part are higher than the values of the imaginary part.

The dispersion energy plays an important role in the research for optical materials because it is a significant factor in optical communication and in designing devices for spectral dispersion. The dispersion of refractive index in PMMA films were analyzed using the concept of the single oscillator and can be expressed by Wemple and DiDomenico relationship, [17]:

$$n^2 - 1 = \frac{E_d E_0}{E_0^2 - E^2} \quad (7)$$

Where E, E_0 and E_d are the photon energy, the oscillator energy and the dispersion energy, respectively. The parameter E_d, which is a measure of the intensity of the inter-band optical transition, does not depend significantly on the band gap. A plot of $(n^2-1)^{-1}$s versus E^2 of PMMA films for different thicknesses as shown in Fig.(7). It is clear that, the effect of thickness on the refractive index and dispersion profiles were exhibited a linear displacement in the shape of the dispersion profile with increasing of refractive index. The values of E_d and E_0 were obtained from the slope and the intercept, respectively, resulting from the extrapolation of the lines. The individual errors in the calculated E_d and E_o should be significantly small to make the proposed method significant. The values of the parameters E_0 and E_d presented in Table (1) were calculated by the fitting procedure. The values of E_d and E_o was found to be increased with increasing the thickness.

A simple connection between the single-oscillator parameters of E_o and E_d and the imaginary part of the dielectric constant (ε_i), spectrum can be expressed in terms of moments of the (ε_i) as follows, [19]:

$$E_0^2 = \frac{M_{-1}}{M_{-3}}$$

and

$$E_d^2 = \frac{M_{-1}^3}{M_{-3}}$$

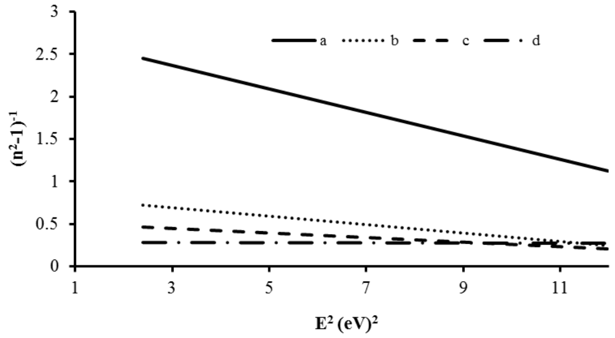

Fig. (7) Variation of $(n^2-1)^{-1}$ versus E^2 for PMMA films of different thicknesses.

The oscillator energy E_o, which was independent of the scale of ε_i is consequently an ''average'' energy gap, whereas E_d depends on the scale of ε_i and thus serves as an interband strength parameter. Since the M_{-1} and M_{-3} moments are involved in computation of E_d and E_o and the values of M_{-1} and M_{-3} are listed in Table (1).

Conclusion

- PMMA thin films doped by KI salt are prepared by using casting method at room temperature with different thicknesses
- The optical absorption parameters have been measured depending on single-oscillator model.
- Dispersion energy E_d, single oscillator energy E_o and average oscillator wavelength λ_o increase with increasing thickness.
- The real and imaginary part of the dielectric constant (ε_r) and (ε_i) values of the films increase as the film thickness increases and indicate the same pattern.

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الخلاصة

حضرت اغشية بولي مثيل ميثكرلايت (PMMA) المشوبة بملح يوديد البوتاسيوم (KI) بنسبة (1%) بطريقة الصب وفي درجة حرارة الغرفة.درست الخواص البصرية للاغشية المحضرة باسماك مختلفة من خلال قياس الامتصاصية والنفاذية للاطوال الموجية nm (200-800) وحدد معامل الامتصاص (α) ومعامل الانكسار (n). تم تحليل عوامل التشتت الضوئي باستخدام نموذج التذبذب الاحادي وحددت طاقة التذبذب E_0 وطاقة التشتت E_d المطورة وعوامل اخرى بطريقة ويمبل وداي دومينكو.