The optical properties of Poly methyl methacrylate (PMMA) polymers doped by Potassium Iodide with different thickness

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Abstract :

Films of pure Poly (methyl methacrylate) (PMMA) doped by potassium iodide (KI) salt with percentages (1%) at different thickness prepared by casting method at room temperature. In order to study the effect of increasing thickness on optical properties, transmission and absorption spectra have been record for five different thicknesses(80,140,210,250,320)µm. The study has been extended to include the changes in the band gap energies, refractive index, extinction coefficient and absorption coefficient with thickness.

Key words: PMMA polymers, potassium iodide, optical properties.

Introduction :

Polymeric materials have attracted the scientific and technological researchers, because of their wide applications. This is mainly due to the lightweight, good mechanical strength, optical properties and makes them to be multifunctional materials. Moreover, these polymers are traditionally considered as an excellent host material for composites. In recent years, the doped polymers have been the subjects 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. It is observed that doping a polymer with metal salts has significant effect on their physical properties including optical, thermal, electrical properties [1].

PMMA is one of the earliest and best known polymers. PMMA was seen as a replacement for glass in a variety of applications and is currently used extensively in glazing applications. The material is one of the hardest polymers, and is rigid, glass-clear with glossy finish and good weather resistance. PMMA is naturally transparent and colorless. The transmission for visible light is very high. Polymeric composites of PMMA are known for their importance in technical applications. Studies of doping transition metal halides into PMMA are important for determining and controlling the operational characteristic of the different PMMA composites. The addition of transition metal halides to the PMMA network will cause a remarkable change in their properties. In the study of physical properties of polymers, the optical absorption spectrum is one of the most important tools for understanding band structure, and optical constants (transmission and absorption indices) of pure and doped polymers. Recently studied the Influence of $AlCl_3$ on the optical properties of new synthesized

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3-armed poly(methyl methacrylate) films [2], optical properties of pure and doped PMMA-CO-P4VPNO polymer films was studied[3] as well as the optical properties of poly aniline doped PVC-PMMA thin films have been studied [4].

In this paper, the optical properties of PMMA polymers doped by Potassium Iodide with different thickness have been studied.

Theory :

The absorption coefficient (α) has been estimated from the equation (1):

$$\alpha(\upsilon) = 2.3 \log(Ii/It) / d = 2.3A/d \quad \ldots(1)$$

Where Ii and It are the intensity of the incident and transmitted light, respectively, A is the absorbance and *d* is the film thickness.

It is well known that the relationship between the absorption coefficient (α) and the optical band gap (E_g), obeys the classical Tauc's expression. The optical energy band gap is determined by translating the spectra into Tauc's plots. To translate the absorption spectrum in to Tauc's plot, we use the frequency dependent absorption coefficient given by Mott and Devis [6].

$$\alpha h\nu = B(h\upsilon - E_g)^r \quad \ldots (2)$$

Where *B* is a constant and the exponent *r* is an empirical index, which is equal to 1/2 for direct transition ($\alpha > 10^4$) in the quantum mechanical sense, responsible for optical absorption.

The optical gap was estimated from the intercept on the energy axis of the linear fit of the large energy data of the plot. The absorption spectra [7] clarify an extending tail for lower photon energies below the band edge, which can be described by (3)

$$\alpha = \alpha_{\circ} \exp(\frac{E}{E_u}) \quad \ldots\ldots(3)$$

Where E_u is the energy of Urbach corresponding to the width of the band tails of localized states in the band gap.

The absorption coefficient (α) of the medium provides valuable optical information for material identification. The attenuation coefficient (k) [8] is directly proportional to the absorption coefficient (α) as seen in(4)

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

Where λ is the free space wavelength of light.

$$n = \left\{ \left[\frac{4R}{(R-1)^2} - k^2 \right]^{\frac{1}{2}} - \frac{R+1}{R-1} \right\} \quad \ldots\ldots (5)$$

For normal incidence, the reflection coefficient (R) [9] is given by (5)

The measurements of specular reflection and the absorption are using to calculate the optical constants (n,k) by the equations (4) and (5).

Material and Methods :

In the present research work, casting method has been adopted to prepare films of pure Poly (methyl methacrylate) (PMMA) doped by KI salt with percentage (1%) at different thickness.

PMMA solution was prepared by dissolving PMMA in Aceton, KI used as a dopant. The solution was stirred, using a magnetic stirrer for (6 h) until the polymer became completely soluble. The solution was poured into flat glass plate dishes. Homogeneous films were obtained after drying in air for (48h) at room temperature (27C°

)[5]. The thicknesses of the produced films (80,140,210,250,320)µm measured by Electronic Digital Caliper.

The absorbance and transmittance measurements of samples were measured by using (Shimadzu 1601 PC) spectrophotometer in the wavelength range (200–800) nm.

Results and discussion :

Figure.(1) shows the absorption spectra of the samples (a, b, c ,d and e) with different thickness (80, 140, 210, 250, 320) µm respectively under investigation in the range (200–800) nm which is the convenient spectral region. In the UV region, all the samples showed two absorption bands at the no same positions, which are related to energy absorption [10]. The absorption increases with increasing thickness of the samples

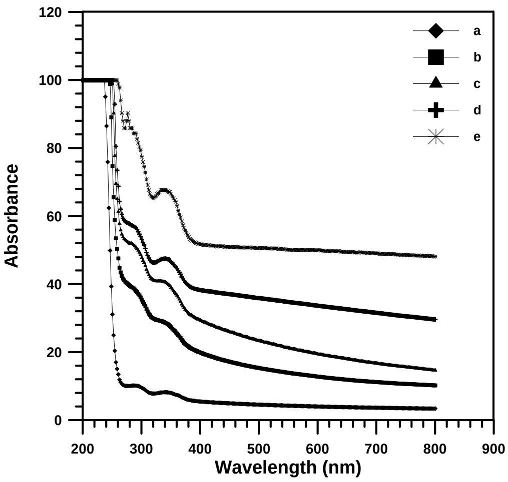

Fig.(1) Absorption spectra of (a-e) PMMA sample.

Figure (2) shows the dependence of the absorption coefficient (α) on the photon energy for the samples with different thickness at small energies (2-4.5)eV the absorption increase with increasing thickness while at higher energies (4.5-6)eV the absorption coefficient decrease. It can be seen from the figure that the position of the absorption edge slightly changes with increasing the film thickness. The Shift in the absorption edge may be attributed to the difference in grain size and /or carrier concentration for all samples [5]. The figure shows a tendency to shift irregularly to small energies.

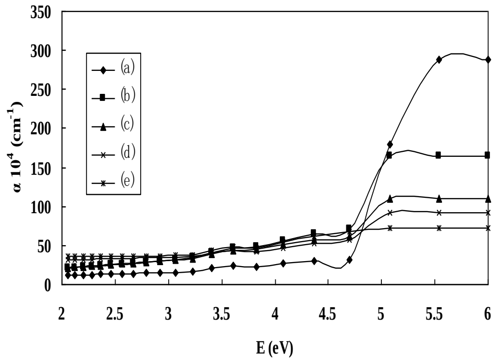

Fig.(2) Absorption coefficient versus photon energy for PMMA different thickness films.

The plot of the product of absorption coefficient and photon energy $(\alpha h\upsilon)^2$ versus the photon energy (hυ) at room temperature shows a linear behavior, which can be considered as an evidence for direct transition. Extrapolation of the linear portion of this curve to a point $(\alpha h\upsilon)^2 = 0$ gives the optical energy band gap (E_g) for the PMMA films with different thickness as shown in the Figure (3), for the films (a,b,c,d and e) with thickness(80,140,210,250 and 320)µm respectively. Here, the transition between the valence and conduction bands is assumed allowed transition. The figures show that the band gap decreases with the increase in the films thickness.

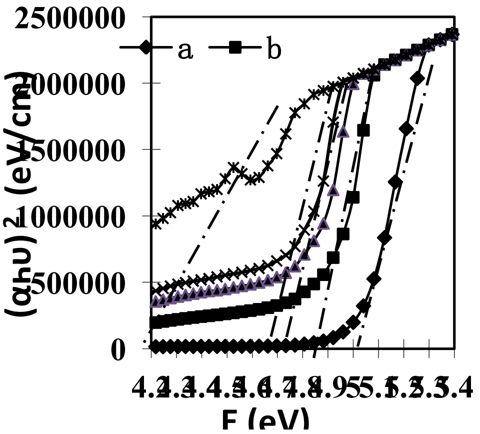

Fig.(3) Optical energy band gap of PMMA films .

The values of E_u were calculated as the reciprocal gradient of the linear portion of the plot. Moreover, figure(4) shows the plot of (ln α) versus photon energy E (eV) samples before exposure to light. Table (1) summarize the values of optical parameters E_u, E_g for different thickness.

Table (1) the values of optical parameters Eu , Eg for different thickness.

Sample	Thickness (μm)	(E_u) eV	(E_g) eV
a	80	0.491	5.3
b	140	0.471	4.9
c	210	0.444	4.8
d	250	0.197	4.75
e	320	0.145	4.35

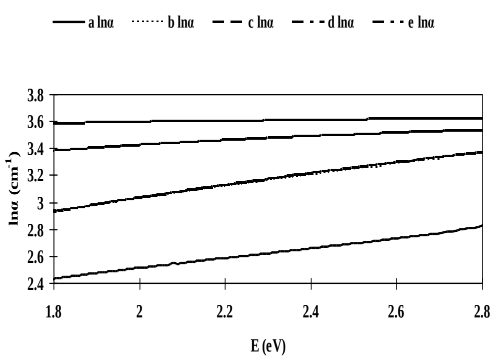

Fig.(4) Urbach plot of (Ln α) versus photon energy .

Fig.(5) shows the variation in K as a function of the wavelength, It can be notice that the extinction coefficient decreases as the film thickness increase (200-260) nm, At long wavelength (400-800) nm the extinction coefficient increase with thickness increase.

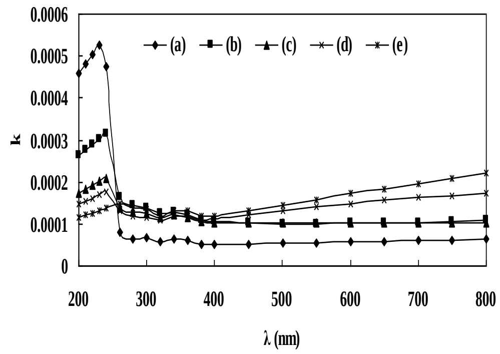

Fig.(5) Extinction coefficient versus wavelength for the PMMA different thickness films.

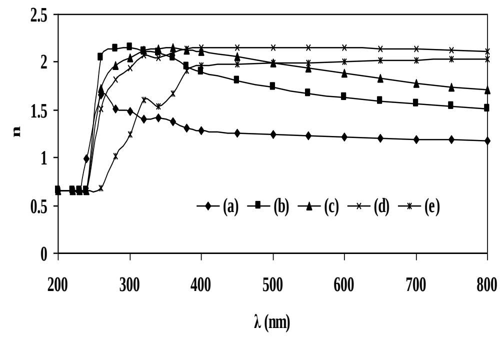

Fig. (6) Refractive index versus wavelength for PMMA different thickness films.

Figure(6) illustrates the refractive index versus wavelength for different thickness. It can be shown from this figure that the refractive index increases with increasing of the film thickness.

Conclusion :

We have studied the effect of thickness on the optical properties of PMMA films .

The band gap and energy of Urbach decrease with increase thickness . The refractive index increase with increase thickness , while the absorption coefficient increase with thickness at small energy but in the large energy decrease with increase thickness.

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الخصائص البصرية لبوليمرات البولي مثيل مثاكريلات (PMMA)المشوبة بيوديد البوتاسيوم بأختلاف السمك

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الخلاصة :

تم تحضير أغشية من البولي مثيل مثاكريلات النقية (PMMA) والمشوبة بملح يوديد البوتاسيوم (KI) بنسبة (1%) بطريقة الصب وفي درجة حرارة الغرفة . لغرض دراسة تأثير السمك على الخواص البصرية سجل طيفي الامتصاصية والنفاذية لخمسة اسماك مختلفة (80,140,210,250,320)µm . امتدت الدراسة لتتضمن تغيرات كل من فجوة الطاقة ،معامل الانكسار،معامل الخمود ومعامل الامتصاص مع زيادة السمك.