Influence of gamma radiation on Dispersion Parameters of Poly Methyl methacrelate (PMMA)

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Abstract:

The effects of γ- ray on the Dispersion Parameters of (PMMA) films, prepared by using casting technique, are studied by using Cauchy, Sellmeier and Wemple-DiDomenico models. Other optical parameters like Carrier concentration and Skin depth were calculated and correlated with irradiation.

Keywords: PMMA film, γ- ray, optical parameters, optical models.

Introduction:

Polymer materials have been widely used in various fields such as industrial products, optical communications, including polymer optical fibers, optical waveguides and optical connectors due to their ease of processing, relatively low cost and mass production compared to silica based optical materials [1].

The choice of poly (methyl methacrylate) PMMA was driven by theoretical and practical concerns as well as its technological applications. [2], it is a very attractive material, because it is easy to form a structure with desired optical properties.[3]. PMMA has been recognized as an excellent optical polymer for use in optical fibers, optical disks and lenses [4].It is used as a replacement for glass in many applications. This polymer is a hard, rigid, and transparent one with a glass transition temperature of 125 °C , also, It is a polar material and has large dielectric constant. Its physical durability is far superior to that of other thermoplastics. And it can be molten and molded into any shape we want [5].

The biological compatibility of PMMA allows its current use in bone cement, for replacement intraocular lenses in the eye and in black-light reactive tattoo ink. Its applications in micro fabrication include use as an x-ray resist, as a photo resist in lithography and as a high-aspect ratio resist for MEMS. . It is nonreactive and stable at room temperature. In it's a tactic form it does not crystallize at any temperature. PMMA is an ideal model system because of its simple chemical structure, its nonreactive nature, its resistance to crystallization, and the extensive experience in producing it in very thin film form [6].

The irradiation of polymeric materials with ionizing radiation (gamma rays, X rays, accelerated electrons, ion beams) leads to the formation of very reactive intermediates. These intermediates can follow several reaction paths, which result in rearrangements and/or formation of new bonds. The ultimate effects of these reactions can be the formation of oxidized products, grafts, scission of main chains (degradation) or cross-linking. The degree of these transformations depends on the structure of the polymer and the conditions of treatment before, during and after irradiation. The aim of this work is to investigate the optical properties of unirradiated and irradiate PMMA film with gamma ray by using Cauchy, Sellmeier and Wemple models.

Experimental procedure:-

Casting method is used to prepare (PMMA).The samples were prepared as films consist from of pure polymer which were supplied from Dentaurum company- Germany. Then PMMA is casted in glass dishes to obtain polymeric films with thickness 20 micron. Thicknesses of samples were measured by indicating micrometer 0.25 nm, they were in 20 micron. Sc^{137} is used as a source of gamma rays to irradiate the (PMMA) films under investigation. This source has half life 30.17 year and activity 12µCi.The samples were putted in front of the source at a distance 1mm for 240 hour.

Absorptance and transmittance measurements were carried out using double beam UV- VIS spectrometer (shimadzu Japan) in the wavelength range (190-1100) nm .

Results and Discussion:-

Wemple and DiDomenico have developed a model where the refractive index dispersion is studied in the region of transparency below the gap, using the single-effective oscillator approximation [8]. According to this model the optical data could be described to a very good approximately by the following formula[9]:

$$n^2 = 1 + \frac{E_d E_0}{E_0^2 - (h\nu)^2} \qquad \text{---------------} \quad (1)$$

Where, n is the refractive index, E_0 is the average excitation energy for electronic transitions, hν is the photon energy and E_d is the so–called dispersion energy. The dispersion energy E_d is a measure of the strength of inter band optical transitions and can be considered as a parameter having very close relation with the charge distribution within unit cell and therefore with the chemical bonding [10].

Plotting $(n^2-1)^{-1}$ against $(\text{photon energy})^2$ allows us to determine the oscillator parameters by fitting a linear function to the lower energy data as shown in Figure(1)

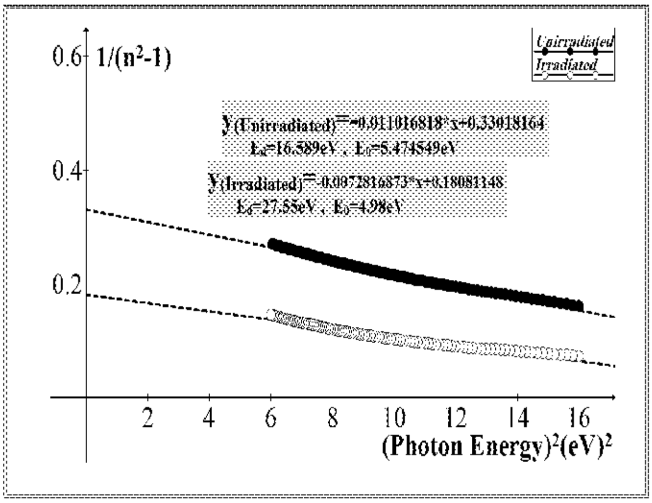


Fig. (1) The plots of the variations of $(n^2-1)^{-1}$ vs. $(h\nu)^2$ for the films.

The value of E_o and E_d can be directly determined from the slope $(E_oE_d)^{-1}$ and the intercept on the vertical axis, (E_d / E_o). The oscillator energy, E_o is an average energy gap as pointed out in many references [10]. The oscillator energy E_o is related by an empirical formula to the optical gap value: $E_o \approx 2E_g$. The M_{-1} and M_{-3} moments of the optical spectra can be obtained from the relationship[12]:

$$E_o^2 = \frac{M_{-1}}{M_{-3}} \quad ; \quad E_d^2 = \frac{M_{-1}^3}{M_{-3}} \qquad \text{----------} \quad \textbf{(2)}$$

The obtained values are given in Table (1).

Table (1)

Type of Samples	E_o**(eV)**	E_d**(eV)**	**E$_g$ (eV)**	**M$_{-1}$**	**M$_{-3}$(eV)$^{-2}$**
Unirradiation (PMMA)	5.47	16.589	2.737	3.03	0.101
Irradiation (PMMA)	4.98	27.55	2.49	5.53	0.223

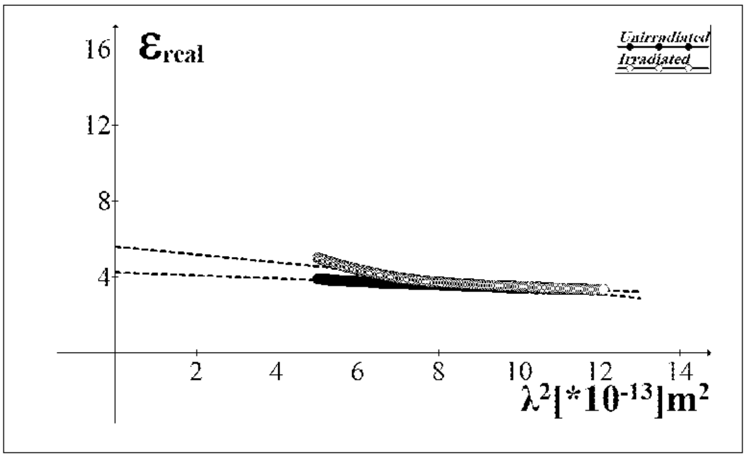
Our values of energy gap are closely to those which were obtained by Zainab et.al [13]

Gamma doses cause the breaking of bonds, leading in turn to the increase of dangling bonds and of defects, as well as the trapping of the generated carriers. This may be the cause for the increase in band tail width, and then decrease energy gap.[14]

The carrier concentration N_{opt} can be obtained using Drude's theory of dielectrics. The real dielectric constant ε_1, which results due to the contribution from the free carrier electric susceptibility, can be written by the following relation [15]

$$\varepsilon_1 = \varepsilon_i - [(e^2/4\pi^2 c^2 \varepsilon_0)(N/m^*)]\lambda^2 \qquad \text{- - - - - - - - - -} (3)$$

where ε_i is the residual dielectric constant due to the ion core, e is the electronic charge, c is the velocity of light, ε_o is the permittivity of free space ($\varepsilon_0 = 8.85 \times 10^{-12}$ C/N.m^2) and N/m* is the ratio of carrier concentration to the effective mass m^* [16].



According to the free electron Drude model[17], ε_1 should be a linear function of λ^2 as it shown in Figure (2). The values of carrier concentration N_{opt} for the films are $N_{opt(\textbf{Unirradiated})} = 2.326*10^{27}\ m^{-3}$, $N_{opt(\textbf{iraddition})} = 8.78*10^{26}\ m^{-3}$. The decreasing of N_{opt} might attributed to trapping carrier concentration by defects which increase with γ irradiation.

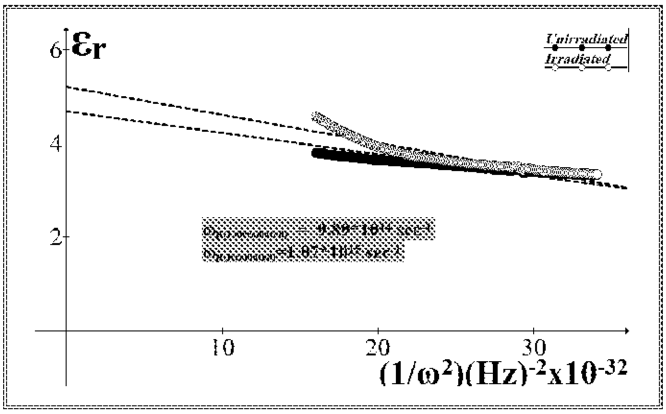


Fig. (2) dielectric constant vs. $(\lambda)^2$ for (PMMA) films.

When [refractive index (n_0)]^2 >> [extinction coefficient (k_0)]^2 and 1 << $\omega\tau$. , where ω is the angular frequency of the lattice atoms, the real dielectric constant can be expressed as:[18]

$$\varepsilon_r = \varepsilon_L - [\frac{\varepsilon_L \omega_p^2}{\omega^2}] \quad ; \quad \omega_p^2 = \frac{e^2 [N/m^*]}{\varepsilon_0} \quad \text{-----------} \, \mathbf{(4)}$$

Where ε_L is the lattice dielectric constant (or limiting value of the high frequency dielectric constant), ω_p the plasma frequency, e is the electronic charge. Therefore, plotting ε_r vs. ω^{-2} in the NIR spectral region allow us to determine the values of the plasma frequency ω_p and lattice dielectric constant ε_L from the slope and intercept, respectively of linear parts of curves in Figure(3). These calculated values are listed in Table 2.

Fig.(3) Real dielectric constant vs. Reciprocal of square of angular frequency.

Table(2)

Type of samples	ε_L	$n=(\varepsilon_L)^{1/2}$	$\omega_p * 10^{14} s^{-1}$
Unirradiated (PMMA)	4.68	2.16	9.89
Irradiation (PMMA)	5.20	2.28	10.7

The refractive index can be analyzed to determine the long wavelength refractive index n_∞ and average oscillator wavelength λ_0 and oscillator length strength S_0 of the thin film. These values can be obtained using the single term Sellmeier oscillator [19]

$$n^2 - 1 = \frac{S_0\lambda_0^2}{1 - \lambda_0^2/\lambda^2} \quad \text{-----------------} \, (5)$$

Where $(n_\infty)^2 = 1 + S_0(\lambda_0)^2$ [20]. By drawing $(n^2-1)^{-1}$ verses $1/\lambda^2$ as in Figure (4), we obtained the values of λ_0 , S_0 and n_∞ for both films. These calculated values are listed in Table 3. .

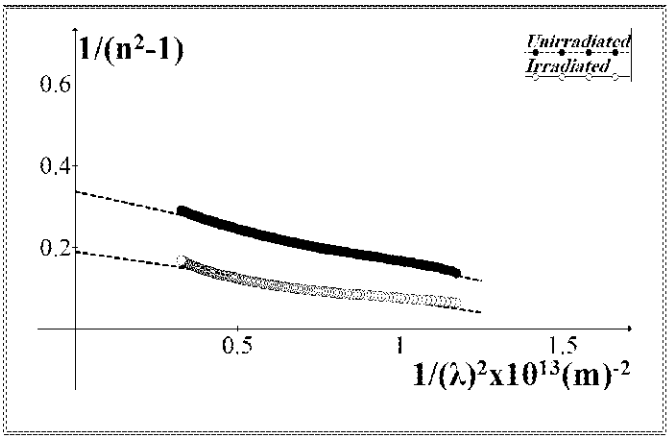


Fig. (4) $(n^2-1)^{-1}$ versus $(1/\lambda^2)$ for (PMMA) films.

Table(3)

Type of samples	n_∞	λ_0[nm]	$S_0[m^{-2}]$
Unirradiated (PMMA)	1.99	228	$5.71x10^{13}$
Irradiation (PMMA)	2.5	250	$8.40x10^{13}$

We studied the spectral dispersion of PMMA samples. The dispersion spectrum of the refractive index was fitted using the Cauchy formula [21]

$$n= \alpha + \beta \lambda^{-2} \quad ---------- (6)$$

where , **α** and **β** are cauchy's parameters .The fitted formula for both films are illustrated in figure(5).

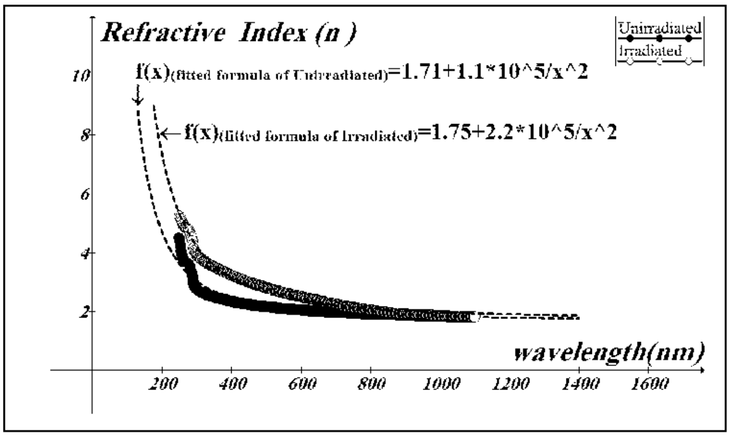


Figure (5) Dispersion curves for Unirradiated and Irradiated PMMA samples.

For **λ** →∞, the significance of the **α** parameters appears immediately as $\mathbf{n}_\infty$ .The values of the fit parameters **α** , **β** and the fit quality parameter χ are presented in Table(4).

Table(4)

Type of sample	**α**	**β*10^5**	χ^2
Unirradiated (PMMA)	1.71	1.1	0.924
Irradiation (PMMA)	1.75	2.2	0.9764

By Rewriting equation (5), and putting A= $S_0\,(\lambda_0)^2$ and B=$(\lambda_0)^2$,one obtain

$$n^2 = 1 + \frac{A\lambda^2}{\lambda^2 - B} \quad \text{-------------} (7)$$

Where *A* and *B* are the Sellmeier parameters [22]. Under these conditions we can see that $n_\infty = (1+A)^{1/2}$,and the calculated values are given in Table (5).Comparing these values (of n_∞) with the α values from Table(4), we find small disagreement which may be due to the inappropriate fitting curve.

Table(5)

Type of samples	A	B*10^{-14}	n_∞	A *(from eq.8)*	B*10^{-14} *(from eq.9)*
Unirradiated (PMMA)	2.97	5.19	1.99	3.03	5.14
Irradiation (PMMA)	5.25	6.25	2.5	5.53	6.21

Applying Sellmeier 's model and Wemple 's model on the same photon energy range , the A and B parameters can be expressed as [23]

$$A = (E_d/E_0) \quad \text{--------------} (8)$$

$$B = (h^2c^2/E_0^2) \quad \text{-------------} (9)$$

Where h is the Plank's constant and c is the speed of light in a vacuum .We calculated the A and B parameters values using equations (8 , 9),and the results are given in Table (5) .A comparison between them [A and B which are calculated from Sellmeier 's model "equation (7)" and their values calculated from Wemple 's model "equations (8 , 9)"] shows good agreement between the two optical models.

The electromagnetic wave will have amplitude reduced by a factor 'e' after traversing a thickness (called the skin depth χ) [24], a convenient form used widely is simply the inverse of α: [$\chi = 1 / \alpha$]. In long wavelength greater than absorption edge, skin depth increases with wavelength as shown in figure (6) ,this might be due to decrease the probability of absorption with increasing wavelength. In general skin depth for irradiated sample is lower than that of unirradiated sample especially at visible region, this might be attributed to increase the centers of absorbing light in irradiated sample.

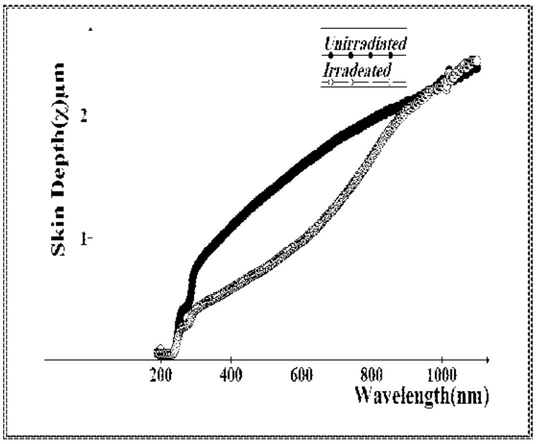


Figure (6) Skin depth (χ) as a function of wavelength.

Conclusions:

The content of this paper can be summarized by the following statements:

1-The normal dispersion of the refractive index was successfully fitted with the Cauchy, Sellmeier and Wemple *et al* .formula , and good agreement between the models is observed.

2- The optical gap and the dispersion energy values were determined using the Wemple and Di Domenico approximation.

3- Carrier concentration and skin depth decrease with gamma irradiation.

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الخلاصة :

درست تأثيرات اشعة كاما على معلمات التفريق لاغشية بولي مثيل ميثاكريلات (PMMA) المحضرة بطريقة الصب باستخدام موديلات Cauchy , Sellmeier و Wemple-DiDomenico . معلمات بصرية مثل تركيز الحاملات وعمق الأختراق حسبت وربطت مع التشعيع.