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Effect of gamma ray on the optical properties $Zn(ext)_2$ doped poly(methylmethacrylate) films

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ABSTRACT

In this work there is the films of $Zn(etx)_2$ doped PMMA films were investigated for gamma-irradiation dosimeter purpose. Samples were fabricated using cast method. PMMA doped by $Zn(etx)_2$ films were exposed to a (^{137}Cs) gamma-radiation source at different dose rate (0, 1, 2 Gy) at room temperature. Transmittance and absorption spectra for films were recorder and the values of the optical band gap and energies of localized states for unirradiated and gamma-irradiated samples were calculated. It was found that the optical band gap values were decreased as the radiation dose increased. The observed change in the optical properties suggest that $Zn(etx)_2$ doped PMMA films may be considered as an effective material for room temperature real time gamma-radiation dosimeters.

KEYWORDS

Poly(methylmethacrylate);
Gamma irradiation;
Optical properties.

INTRODACTION

Radiation method is largely used polymer modification, since irradiation induces transformations in the structure of materials which can be exploited to improve their performance. On the other hand, combined action of ionizing radiation and oxygen may lead to degradation of the polymer, with worsening of properties such as mechanical strength or electrical insulation resistance. Therefore, the change of the chemical and physical properties of polymers under irradiation is a dynamic topic of research[1].

Irradiation in polymers destroys the initial structure by way of cross linking, free radical formation, irreversible bond cleavages etc. These result in the fragmentation of molecules and formation of saturated and unsaturated groups. All these processes introduce the so called defects inside the material that are responsible for change in the optical, electrical, mechanical and chemical properties of the material[2].

One of the polymers applied most successfully to dosimetry is PMMA, know commercially as plexiglass. Radiation dosimeters using induced optical changes in clear plexiglass with particular reference to the effect of radiation[3].

In the study of physical properties of polymers, optical absorption spectrum is one of the most important tool for understanding band structure and electronic properties of pure and doped polymers. This technique depends on: when a photon with energy greater than the band gap, energy will be absorbed, a transition of an electron in the valence band (VB) to conduction band

(CB) takes place. The transition is direct when the wave vector for the electron remains unchanged, but in the case of indirect transition, interaction with a lattice vibration (phonon) occurs (the minimum of the C.B. lies in a different part of K-space from the maximum of the V.B.)[4,5].

The main goal of this work has been mainly concentrated on the determination of the optical properties of $Zn(ext)_2$ doped PMMA films before and after gamma irradiation. It has been suggested that $Zn(etx)_2$ doped PMMA films can be used as dosimeters.

EXPERMENTAL

poly(methylmethacrylate) (PMMA) is supplied by ICI with M_w = 100 g.mol^{-1}, Mw/Mn = 1.06 and purity 99.995, was used as matrix. Chloroform ($ChCl_3$) of purity is 99.98 used as solvent was supplied by (BDH) Company Chemicals Ltd. Poole. England). For dopant used the $Zn(etx)_2$, that preparation by this steps, 25ml of ethanolic solution of 0.01 mol, $NnCl_2.6H_2O$ was added, with constant stirring. After that 0.02 mol of Potassium, ethyl xanthate dissolved in 25ml of water was added. This mixture was then stirred until white crystalline solid was obtained. The product was recrystallized from a mixture of Petroleum ether and acetone to yield white crystals of $Zn(etx)_2$.

PMMA grains of weight (2) gm were dissolved in (10) Vl of Chloroform ($CHCl_3$) to doped was fabricated by dissolving $Zn(etx)_2$ in Chloroform of concentration 0.02 w/w. The mixture was shaken well by stirring about 30 min. to obtain homogenous solution, (10 ml) of the prepared solution was transferred into a clean glass Petri dish with (6 cm) diameter and dried at room temperature for 2 days. The dried films removed easily using tweezers clamp. Other similar films were cast in order to ensure dried samples without bubbles and thermal damage. The thicknesses of prepared films were(0.14 mm) measured by using digital vernier.

The films irradiations by used the (^{137}Cs) source. For each dose the film samples were placed simultaneously at the centre of the chamber surrounded for radiation equilibrium purposes. Samples were irradiated with various doses ranging 0, 1, 2 Gy at room temperature.

The measurements of absorbance and transmittance spectra in the wavelength range (275 - 900) nm were carried out by using UV-160A UV-VIS (Shimadzu Japan) Recording Spectrophotometer.

RESULT AND DISCUSSION

The absorptions and transmittance spectra of $Zn(etx)_2$ doped PMMA films are illustrated in Figure (1a-b). The absorptions spectra exhibit opposite behavior in spectra of transmittance. The absorption spectra, which are the most direct and perhaps the simplest method for probing the optical band structure.

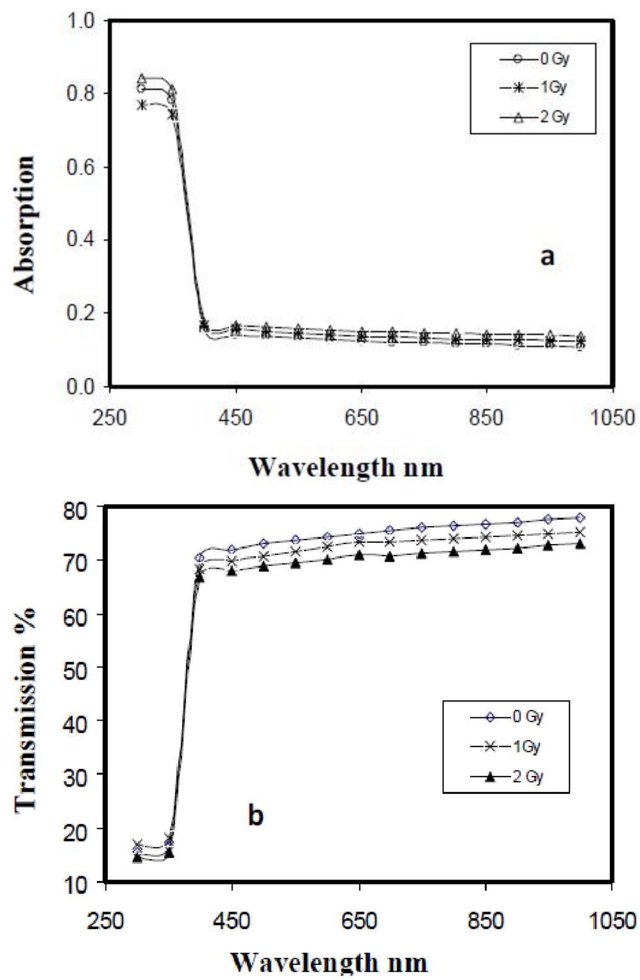

Figure 1 : The variation of a) Absorption and b) Transmission spectra with (Wavelength) of doped PMMA films at different doses irradiation.

Optical absorption measurement is a standard technique for investigating band structure and it is therefore of interest to study absorption in films. The absorption spectra in the lower region (IR) are useful in studying the molecular vibrations. The higher energy region (UV) can be useful to manifest the electronic state of the atoms and other important phenomena affected by irradiation[6]. The wavelength dependence 275-1000 nm of the optical absorbance spectra of $Zn(etx)_2$ doped PMMA at different gamma-dose are shown in Figure (1a). It is obvious from this figure, which the increasing of gamma-dose leads to increasing in optical absorbance; the radiation effects are strongly dependent on the structure of the absorbing substances. It is clear that the absorbance increases linearly with absorbed gamma-dose, it is evident that the optical absorption spectra distribution is sensitive to the radiation influence. It is believed that ionizing radiation causes structural defects leading to their density change on the exposure to gamma –rays[7,8].

The fundamental absorption is the most important absorption process involves the transition of electrons from the valence to the conduction band, which manifests itself by a rapid rise in absorption, can be used to determine the energy gap of the material. In fundamental absorption, an electron absorbs a photon (from the incident beam), and jumps from the valence to the conduction band. The photon energy (hυ) must be equal or more than energy gap (E_g). The absorption of radiation that leads to electronic transitions between the valence and conduction bands takes two mechanisms: direct and indirect process. The direct transition in general occurs between states of the same wave vector [K_{min}=K_{max}]. The allowed direct transitions refer to that transitions which occur between the top of the valence band and the bottom of the conduction band when the change in wave vector is equal to zero [ΔK=0]. If the transition occurs also between states of the same wave vector, but the wave vector does not equal to zero then these transitions are called "direct forbidden transitions". In indirect transitions there is a large momentum difference between the points to which the transition takes place in valence and conduction bands, this means that the conduction- band minima are not at the same value of K as the valence band maxima. Therefore, assistance of a phonon is necessary to conserve the momentum. Therefore $h\upsilon=E_g+E_p$ Where E_p is the energy of absorbed or emitted phonon. For an allowed indirect transition, the transition occurs from the top of the valence band to the bottom of the conduction band. While the forbidden indirect transitions occur from any point other than the bottom of C.B. The empirical relationship for this types of transition is given as

$$\alpha h\nu = B (h\nu - Eg)^r \quad (1)$$

Where E_g the optical energy gap, α absorption coefficient, B is a constant and r is an index which can be assumed to have values of 1/2, 3/2, 2 and 3, depending on the nature of the electronic transition responsible for the absorption. r = 1/2 for allowed direct transition, r = 3/2 for forbidden direct transition and r = 3 for forbidden indirect transition, with r = 2 refers to Indirect allowed transitions[4,5,9].

The indirect allowed optical energy gaps $Zn(etx)_2$ doped PMMA films were estimated lie in the range 3.2 eV at 0 Gy to 2.79 eV at 2 Gy, and it is slightly decreased with increasing gamma doses. and the attributable to effect of gamma ray on the structure of polymer samples, The variation of E_g with gamma dos is tabulated in TABLE 1 and illustrated in Figure 2.

TABLE 1 : Optical parameters of doped PMMA films at different doses irradiation.

Doses	E_g (eV)	ΔE eV
0 Gy	3.2	1.52
1 Gy	2.84	1.65
2 Gy	2.79	1.67

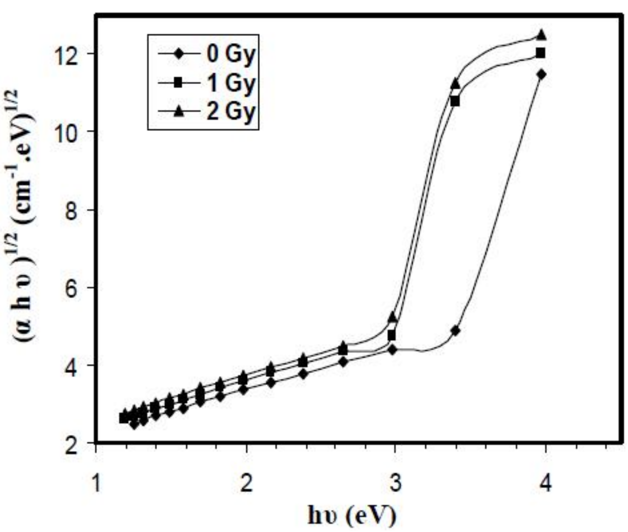

Figure 2 : The variation of $(\alpha h\nu)^{1/2}$ with (hν) of doped PMMA films at different doses irradiation.

The density of the localized states in the band can be evaluated from the Urbach energy (ΔE). There are absorption tails at energies smaller than Eg, and the absorption coefficient can exhibit exponential behavior. The Urbach energy can be calculated from the equa-

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tion[10,11].

$$\alpha = \alpha_o \exp(h\nu/\Delta E) \quad (2)$$

by plotting ln α as a function of hυ, the reciprocal slope of the linear part give the value of ΔE, the variation of ln α with hυ for Zn(etx)$_2$ doped PMMA films at different gamma dose, and the values of ΔE tabulated in TABLE 1, we can observe that ΔE is increased with increasing gamma doses.

The extinction coefficient can be calculated by the relation[12]:

$$k = \alpha \lambda / 4\pi \quad (3)$$

Where (λ) is the wavelength, and the refractive index (n) of the film was calculated by the following equation[13]:

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

Where k is the extinction coefficient and R is the reflectance.

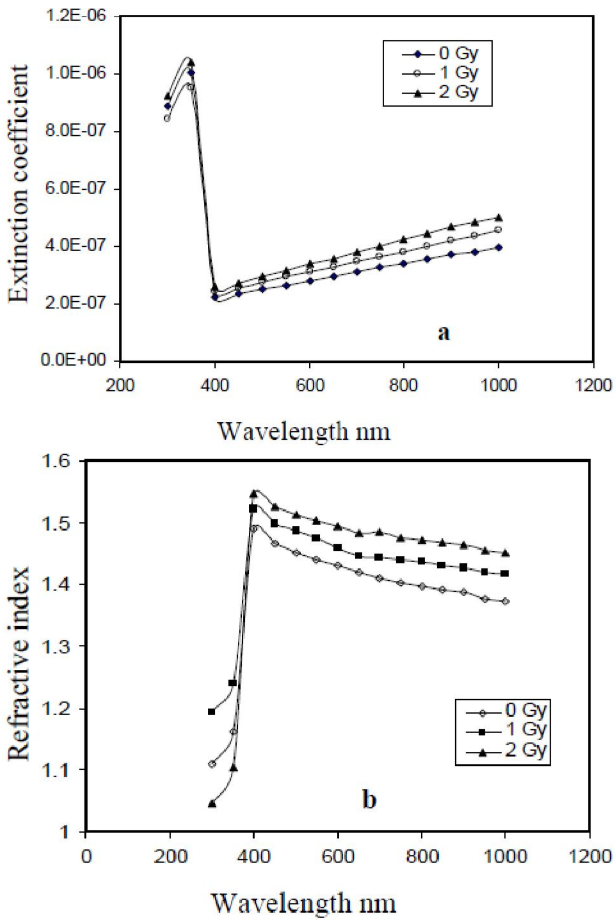

Figure 3 : The variation of a) k & b) n with (Wavelength) of doped PMMA films at different doses irradiation.

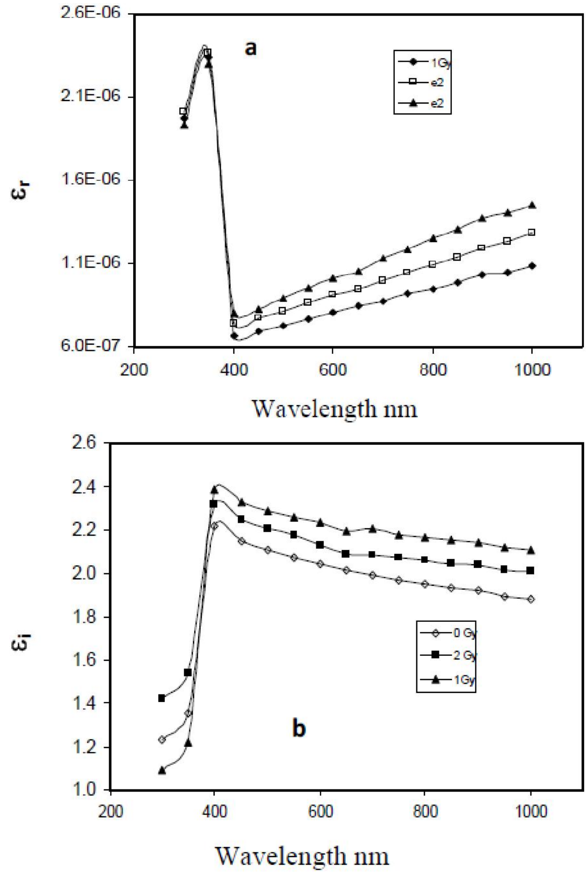

Figure 4 : The variation of a) ε_r, b) ε_i with Wavelength (nm) of doped PMMA films at different doses irradiation.

The evaluation of refractive index of an optical material is important for many applications especially in optical devices. Figures (3 a & b) shows the variation of refractive index n and extinction coefficient k with wavelength, from which it can be noticed that, in general noticed the values of n and k in increased with gamma dose.

The real (ε_r) and imaginary (ε_i) parts of the dielectric constant can be calculated using the from formulas[14]

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

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

Figures (4 a & b) presents the dependence of (ε_r) and imaginary (ε_i) on wavelength. The variation of (ε_r) and (ε_i) have similar trends as for refractive index extinction coefficient an according to Maxwell's equation[15]

Optical conductivity σ_o is calculated using the following equation[16]:

$$\sigma_o = \alpha\, n\, c / 4\pi \quad (7)$$

The plots of σ_o against hν of films with different gamma dose are displayed in Figure 5.

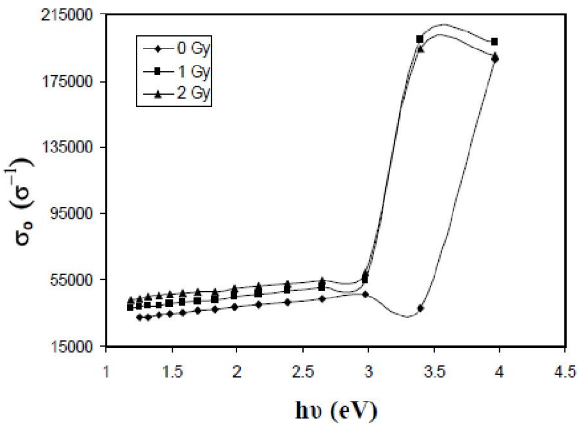

Figure 5 : The variation optical conductivity σ_o with (hν) of doped PMMA films at different doses irradiation.

All the change in optical parameters of for $Zn(etx)_2$ doped PMMA films after radiation can attribute to the effect of radiation on the structure of samples, which creates a localized energy states in the forbidden band gap acts as a tail to the conduction band which reduced the energy gap and all other optical parameters.

CONCLUSIONS

The results present above the absorbance as a function of wavelength for unirradiated samples as well as samples exposed to various gamma-doses in $Zn(etx)_2$ doped PMMA films. From these results, the following conclusions were drawn:

1- The Absorptions increases linearly with increasing gamma-dose.
2- the optical gap energy decreases with increasing gamma-dose.
3- Upon the results obtained,it is possible to use $Zn(etx)_2$ doped PMMA film as a dosimeter to measure the average dose rate of gamma-rays within the range (0,1, 2,) Gy.

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