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Influence of gamma-ray irradiation on optical and thermal degradation of poly (ethyl-methacrylate) (PEMA) polymer

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ABSTRACT

Polymer based on (polyethyl- methacrylate) (PEMA) were exposed to different doses of gamma radiation up to 100 kGy and the physical properties have been studied. The effects of gamma irradiation on the optical spectrum of PEMA films have been investigated using spectrophotometric measurements of reflectance and transmittance in the wavelength range 200-1100 nm. The structure of the sample is analyzed by X-ray diffraction technique and is found to be amorphous and partially crystalline. TGA studies revealed that the thermal stability of polyethyl methacrylate, improved after irradiation doses up to 100 kGy. On other hand driving absorption coefficient $\alpha(\omega)$, consequently the band tail width E_c and optical band gap estimated. This behavior is believed to be associated with the generation of excess of electronic localized states. Also, Optical constants such as refractive index (n), extinction coefficient (K) have been determined using Swanepole method. Optical dispersion parameters and the dispersion parameters, such as E_o (single-oscillator energy), E_d (dispersive energy) are discussed in terms of the single-oscillator Wemple- DiDomenico model.

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KEYWORDS

Gamma radiation;
PEMA;
X-ray diffraction technique;
Optical parameters;
Dispersion parameters;
TGA thermogravimetric.

INTRODUCTION

Acrylic and methacrylic polymers have characteristics of brilliance, optical clarity, high transparency, improved mechanical properties, adhesion capability and chemical stability^[1]. The photostability of aliphatic acrylic and methacrylic polymers are generally very high. Applications for rigid methacrylate polymer products include signs and glazing substitute for safety glass and to prevent vandalism, optical fibers for light transmission, plastic eyeglass lenses, dentures and dental filling materials, and con-

tact lenses (hard and soft)^[2]. Polymethacrylates degrade to lower molecular weight compounds or to the monomers on heating or irradiation with high energy radiation. The decomposition or stability of methacrylate polymers is related to their structures such as type of ester groups molecular weight and its distribution, stereoregularity and copolymer composition. Although data have been reported on the glass transition temperature^[3-5] of poly (ethyl methacrylate), its thermal degradation has been studied^[6-8]. Malhotra et al. however in their isothermal weight loss studies report that up to 40% weight loss values, the thermal decomposi-

tion of PEMA is closely resembling that of PMMA. Their GPC analysis also shows that the decomposition of PEMA is dominated by depolymerization. The nature of relaxation mechanisms in amorphous PEMA is discussed on the basis of the TSDC and dielectric results^[9].

In general, thermal stability of the polymer composites play a crucial role in determining application, because it effects the final properties of the polymer composites such as the upper-limit use temperature and dimensional stability. For the fabrication of advanced composites with better balance in processing and performance, it is very instructive to characterize the thermal decomposition behavior of the polymer composites. In this regard, thermogravimetric analysis (TGA) is in common use to characterize thermal decomposition behavior and the kinetic parameters of thermal decomposition processes, because of its simplicity and useful information about thermal decomposition^[10-14]. Consequently, the understanding of the thermal stability and thermal decomposition kinetics of polymer composites make it possible to develop and extend their applications as various industrial fields. At the same time, the need to develop a molecular-level understanding of the thermal degradation of polymers is becoming increasingly important in areas of science and technology associated with the high-temperature processing and combustion of these materials.

Studies continue to focus on developing new methods for increasing the radiation resistance of polymeric materials since radiation exposure is a concern in many polymers applications. The smaller the extent of molecular changes due to irradiation, the more radiation resistant the material. Modification of polymers by irradiation, with ionizing radiation in particular, is an expanding field of research and application because of its technological implications. In addition, γ -irradiation has been proved to be a significant tool^[15] for such modifications. It is well known that γ -irradiation can amend the electrical, optical, thermal properties etc of the polymeric materials by changing their morphology through various processes of chain accessions and cross linking^[16-18]. The polymer irradiation leads to shift in optical absorption edges, which shows a lowering of the energy-gap. The decrease in energy band-gap infers an increase in conductivity of the irradiated polymers which

might be due to the formation of clusters with rings, or due to the formation of conjugated double bonds or quinonic structures^[19].

In the present work the affect of different gamma doses (10 to 100 KGy) on the optical and thermal decomposition character of PEMA has been studied by UV-Vis spectroscopy and TGA measurements. The affect of irradiation dose on the optical and thermal properties has been discussed in the light of the polymer's track registration sensitivity. The kinetics of decomposition of PEMA has been studied under non-isothermal conditions using thermo-gravimetry to determine the activation energy (E_a). Thermal behavioral analysis of PEMA as an affect of γ -irradiation have attracted much attention because of their application in optical devices, and has an important study in this direction.

EXPERIMENTAL

Materials

Poly (ethyl methacrylate) (PEMA) with a molecular weight of $\sim 280\,000\text{ g mol}^{-1}$ was purchased from Scientific Polymer Products, Inc (Ontario, NY) and used without further purification.

Method

The samples for these works were prepared by employing the solution casting technique. Films of PEMA were prepared by first dissolving 1-2 g of PEMA in approximately 20 mL of chloroform. The mixtures were stirred for 24 h using digital magnetic stirrers to ensure that the PEMA powders fully dissolved. After thoroughly dissolved, the sample was cast into Petri dish and let to dry at room temperature for 48 h to ensure complete evaporation of the chloroform without promoting thermal degradation. The resultant thin PEMA film (0.5 mm) was carefully removed from the molds for subsequent analysis.

Samples irradiation

Sample irradiation was carried out using a ^{60}Co gamma source model ISSLEDOVATEL manufactured by Russian irradiator and located at NCRRT, Egypt. The dose rate was 910 kGy/100 min and the temperature during irradiation was about 40°C. Irradiation doses ranged from 10 to 100 kGy in air.

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Structural characterization and thermal decomposition

X-ray diffraction (XRD) patterns were recorded using Shimadzu diffractometer XRD-6000 x-ray diffraction spectrometer with a copper target ($\lambda = 1.542 \text{ \AA}$) at operating voltage of 40 kV and an electric current of 30 mA. The optical absorbance and transmittance spectra were recorded against wavelengths of 200–1100 nm using UV / vis unikon 360 double beam spectrophotometer. Thermogravimetric analysis (TGA) were performed using Shimadzu-50 instrument (Japan) at heating rate of $10 \text{ }^\circ\text{C} / \text{min}$ under flowing nitrogen (20 ml/min) from ambient temperature to $500 \text{ }^\circ\text{C}$. The primary TGA thermograms were used to determine the kinetic parameters such as activation energy and order of the thermal decomposition reaction.

RESULTS AND DISCUSSION

X-ray diffraction studies

The X-ray diffraction pattern of (polyethyl-methacrylate) PEMA samples are shown in Figure 1. The patterns revealed that there are no sharp diffraction lines and the broadened background scattering area of PEMA suggests the presence of amorphous nature, which confirms its non-crystalline structure. Consequently, the increase in X-ray intensity may be resulting from grain growth. The particle consists of grains which are intensity interconnected, causing particles to be almost without porosity. This appears as boarding peaks. When PEMA films are irradiated with γ -rays, a cross-linked product is formed. The product is dimensionally stable and has increased thermal stability and a significant increase in tensile strength. So, it is well known that the interaction of radiation with polymer materials result in the formation of free radicals by dissociation of the excited states or by ion–molecular reactions.

Thermogravimetric analysis techniques (TGA)

The thermal stability of the polymer composites play a crucial role in determining the limit of their working temperature and the environmental conditions for use, which are related to their thermal decomposition temperature and decomposition rate^[20]. to study the affect of γ -irradiation on these kinetic parameters, TGA ther-

mograms of pristine and gamma irradiated samples of PEMA polymer at different doses have been recorded and are presented in Figure 2. TGA thermograms of PEMA polymer at 100 C/min under nitrogen is shown. TGA curves of PEMA polymer shifted toward higher temperature regions with γ - irradiation doses, which was explained by the fact that polymer molecules did not have enough time to exhaust the heat with increasing γ - irradiation doses, leading to slower decomposition rate and higher decomposition temperature due to slow diffusion of heat^[21]. TGA provides a method for thermal stability testing. It is observed that there are three stages of decomposition appearing in TGA curves as shown in Figure 2. The first stage at decomposition temperature $\approx 2300\text{C}$ is attributed to elimination of evaporated molecules in the side groups. The second stage of weight loss in the temperature range $\approx 230\text{--}4000\text{C}$ is attributed to quaternized graft chain degradation and the third stage of decomposition of the backbone polymer.

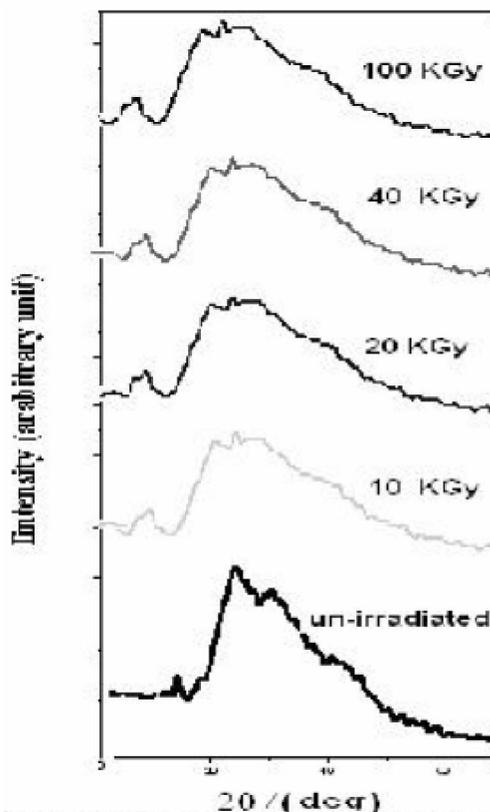


Fig (1): X-ray diffraction patterns of PEMA films before and after irradiation

TGA thermograms, various kinetic parameters of degradation reaction have been determined by adopt-

ing most commonly used method of Horowitz – Metzger^[22-27]. The activation energies of virgin and γ -irradiated samples of PEMA polymer corresponding with the major degradation process have been deduced using the expression^[27]

clear cut increase in the values of activation energy with the increasing irradiation dose. Such an increase may be attributed to the initialization of chain scissioning, possible evaporation of volatile side groups resulting in significant reduction of packing density, reorganization

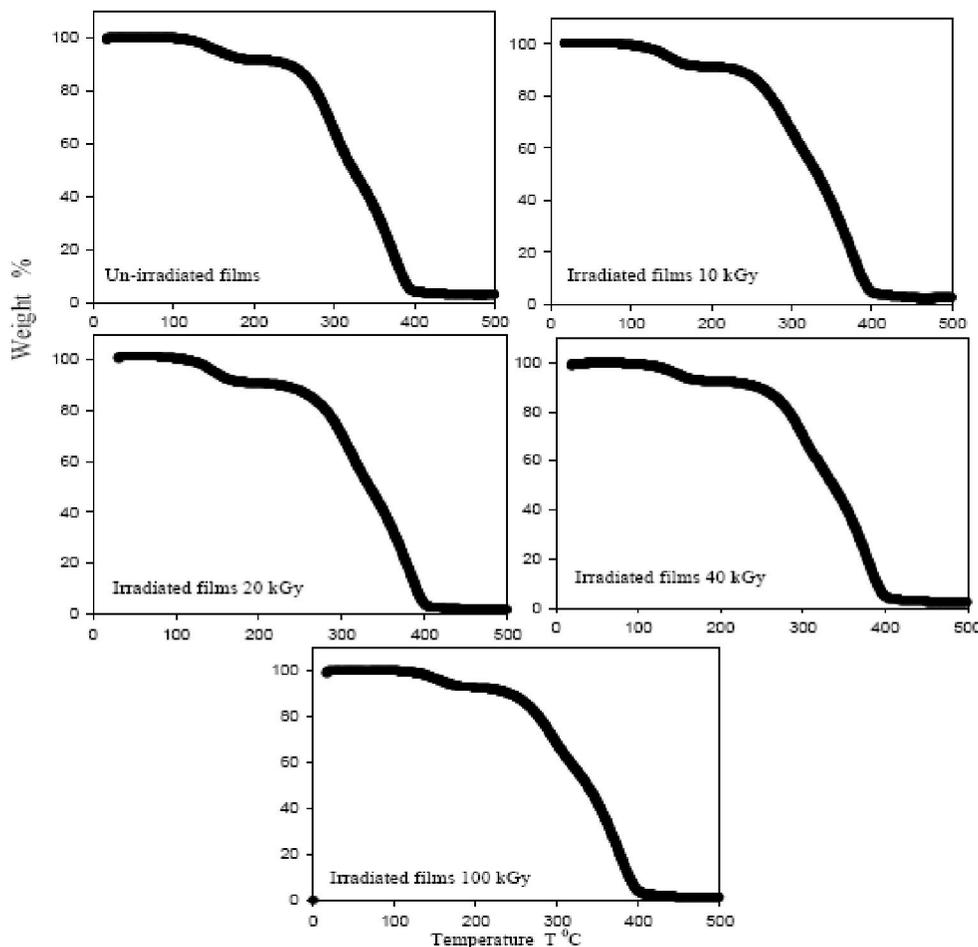


Fig. 2 TGA Thermograms for for un-irradiated and irradiate PEMA films

$$\ln(\ln[W_0 - W_f / W_t - W_f]) = E_a \theta / RT_s^2 \quad (1)$$

where W_0 , W_f are the initial and final weights, W_t is the remaining weight at temperature T , E_a is the activation energy, R is gas constant ($R = 8.314 \text{ J k}^{-1} \text{ mol}^{-1}$), and $\theta = T - T_s$ with T_s as the reference temperature corresponding to $W_t - W_f / W_0 - W_f = 1/e$. In the light of the equation (1), the activation energy E_a can be calculated from the slope of the linear fitted line between $\ln(\ln[W_0 - W_f / W_t - W_f])$ and θ as illustrated in Figure 3., for virgin and γ -irradiated samples at doses 10, 20, 40, 60 and 100 kGy. The values of activation energies so determined for pristine as well as γ -irradiated samples have been enlisted in TABLE 1. There is a

of molecular arrangements etc. in the polymeric sample which signifies the decrease in thermal stability of the polymer^[22,23,28].

Optical studies

The optical absorption edge

The study of the optical absorption and particularly the absorption edge is an useful method for the investigation of optically induced transitions and for the provision of information about the structure and energy gap in both crystalline and non-crystalline materials. The principle of this technique is that a photon with energies greater than the band gap energy will be absorbed. The absorption coefficient $\alpha(\omega)$ depends exponentially on the photon

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energy $h\omega$. The absorption edge in many disordered materials follows the Urbach (1953) rule^[29] given by:

$$\alpha(\omega) = \beta \exp\left(\frac{h\omega}{\Delta E}\right) \tag{2}$$

where α is the absorption coefficient at an angular fre-

quency ω . It is clear from Figure 4. that blank shows one absorption bands. The absorption at 325 nm is identified as the soresst band (B-band). These bands are attributed to the carbonyl group in polymeric macromolecule. It is observed that dose dependence UV has a

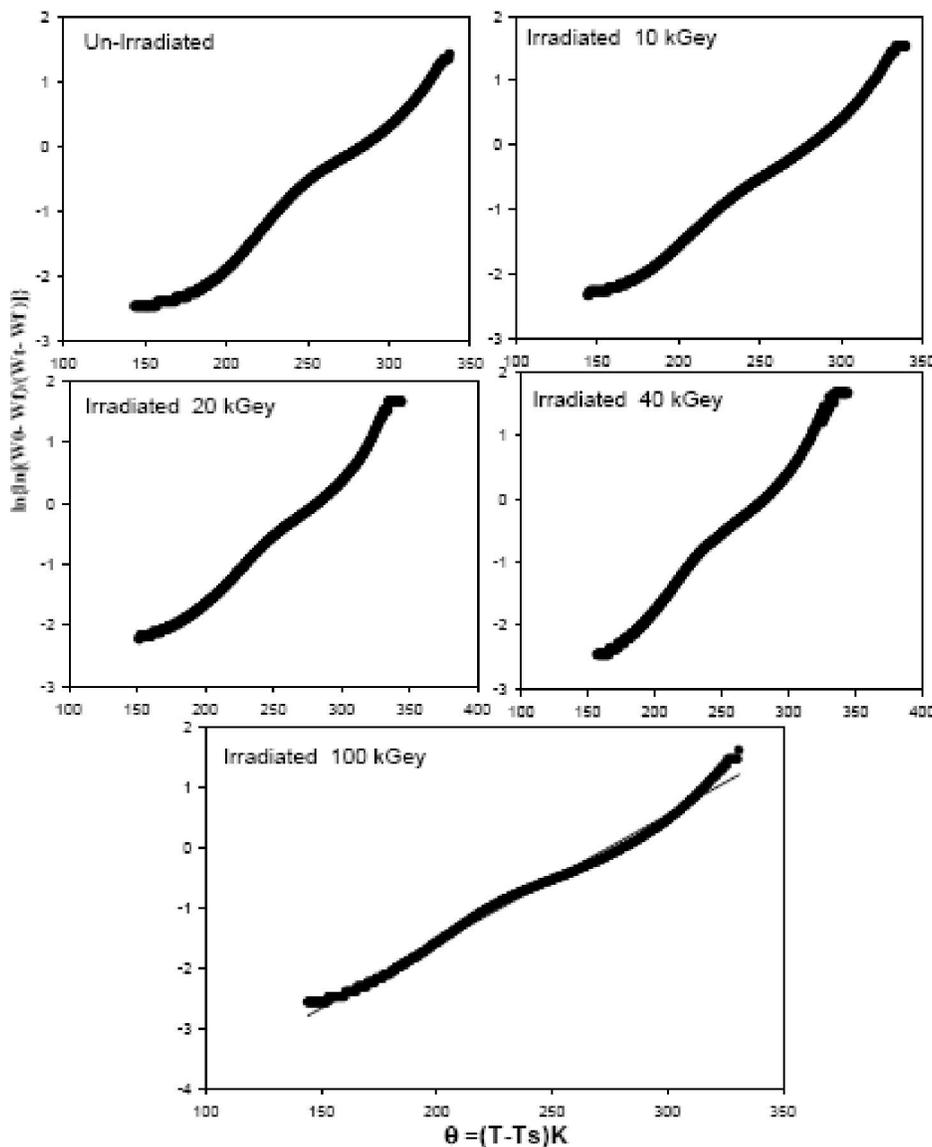


Fig 3. Plots of $\ln\{\ln[(W_0 - W_f)/(W_t - W_f)]\}$ versus $q = (T - T_s)K$ for un-irradiated and irradiate PEMA films

quency of $\omega = 2\pi\nu$ and β is a constant. ΔE is the width of tail of localized states in the band gap. The lower energy part of the absorption spectra gives information about the vibrations, and the higher part of the spectrum gives information about electronic states in the normal material. Figure 4. shows the absorption characteristic for the un-irradiated and irradiated EPMA

films. It is clear from Figure 4. that blank shows one absorption bands. The absorption at 325 nm is identified as the soresst band (B-band). These bands are attributed to the carbonyl group in polymeric macromolecule. It is observed that dose dependence UV has a slight effect on the position and the intensity of this band for PEMA films. Moreover, the intensity of carbonyl group peak decreases by increasing irradiation doses whereas its position is slightly shifted for all films.

The optical band gap

A model based on the electronic transition between the localized states is not preferable. For higher values

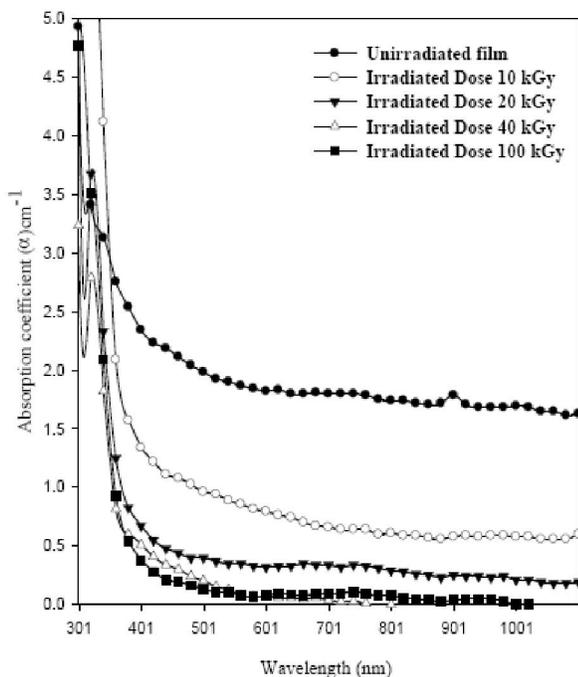


Fig. (4) Effect of the irradiation gamma doses on the absorption coefficient (α) with wavelength for PEMA films

TABLE 1 : The values of various activation energy E_a , initial and final weights (w_0, w_f) and remaining weight at temperature T (w_t) for virgin and γ - irradiated PEMA films

Dose kGy	E_a	w_0	w_f	w_t
0	19.412	2.01	0.06	0.907826
10	19.684	1.91	0.04	0.853043
20	20.5	1.78	0.05	0.802174
40	21.221	1.39	0.04	0.626957
100	21.996	1.53	0.03	0.682174

($\alpha \geq 10^{-4} \text{ cm}^{-1}$), the absorption coefficient (where absorption is associated with inter-band transitions)^[30,31] takes the form:

$$\alpha(\omega) = \beta(\hbar\omega - E_{opt})^M / \hbar\omega \quad (3)$$

E_{opt} the optical gap, and a number that characterizes the transition process. The value of the constant β in equation (3) can be evaluated from the slope of the straight part in Figure 4. In the high absorption region where absorption is associated with inter-band transitions, there are two kinds of optical transition at the fundamental edge of crystalline and non-crystalline, direct transitions and indirect transitions. Both of which involve the interaction of an electromagnetic wave with an electron in valance band, which is then raised across the fundamental gap to the conduction band.

For indirect transitions, interactions with lattice vi-

brations (phonons) take place; thus the wave vector of the electron can change in the optical transition and momentum change will be taken or given up by phonons. In other words, if the minimum of the conduction band lies in a different part of K-space from the maximum of the valence band, a direct optical transition from the top of the valence band to the bottom of the conduction band is forbidden.

For direct transition $M=1/2$ or $3/2$ while for indirect transition $M=1, 2$ and 3 which characterizes many amorphous or semi crystalline substances. The changes are strongly dependent on the internal structure of the absorbed substances. It may be expected that the gamma radiation can cause ionization or excitation of the optical electrons and possibly, displacement of atoms from their sites in the lattice of solid. When PEMA films are irradiated with radiation cross-linking and chain scission are formed.

The optical band gap, E_{opt} for un-irradiated and irradiated samples was determined using Eq. (3), from the intercepts of the extrapolated linear part of plots of $(\alpha h\nu)^{1/2}$ versus $(h\nu)$, as shown in Figure 5. The values of E_{opt} obtained are listed in TABLE 2 and it was found that E_{opt} decreases with increasing of the irradiation dose.

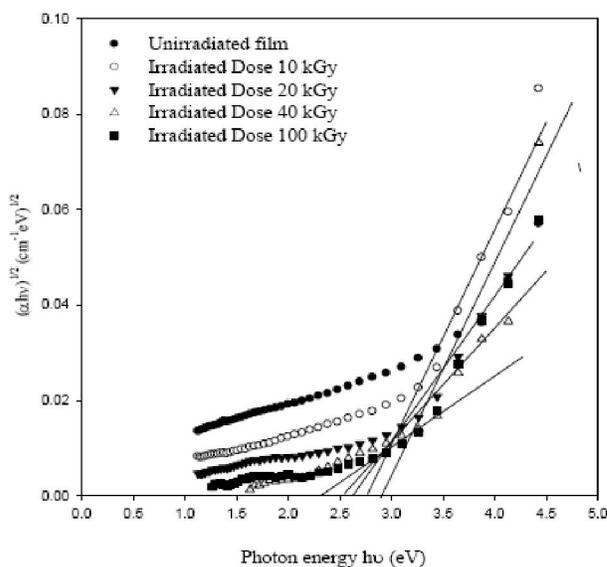


Fig. (5) The optical absorption coefficient edge plotted as $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) for as deposited and irradiated PEMA films with different doses

The band tail width

The band tail width was obtained using Eq (3) and then by plotting $(\ln \alpha)$ against $(h\nu)$ as shown in

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Figure 6. that should yield a straight line of a slope equals (1/). It should mention that Eq (3) is applied only in the low absorption region. The band tail width E_c is listed in TABLE 2, it increases with increasing dose; i.e. E_c exhibits an opposite trend with E_{opt} . This is could be due to the fact that, when polymer exposed to irradiation doses, it starts to crosslink, a formation of new covalent bonds can be produced. Then, different chains are obtained, i.e cross linking starts which are in turn hinder the motion of molecules and reduce its activities and in turn decrease the optical band gap. On further gamma doses, a formation of free radicals are obtained, which are causes a decrease in the optical band gap. As the gamma dose increases from 10 to 100 kGy, the crystalline structure is assumed to be perturbed and leading to an increase in the degree of disorder. At higher dose (100 kGy), the chains scission become predominant relative to the crosslinking. From the density-of-states model it is known that E_{opt} decreases with increasing the degree of disorder of amorphous phase Furthermore, the band tailing shifts to higher energies as shown in Figure 5. and extends into the forbidden band.

Dispersion analysis

In this work, the polymer films are sufficiently thick compared to the beam wavelength to neglect the inter-

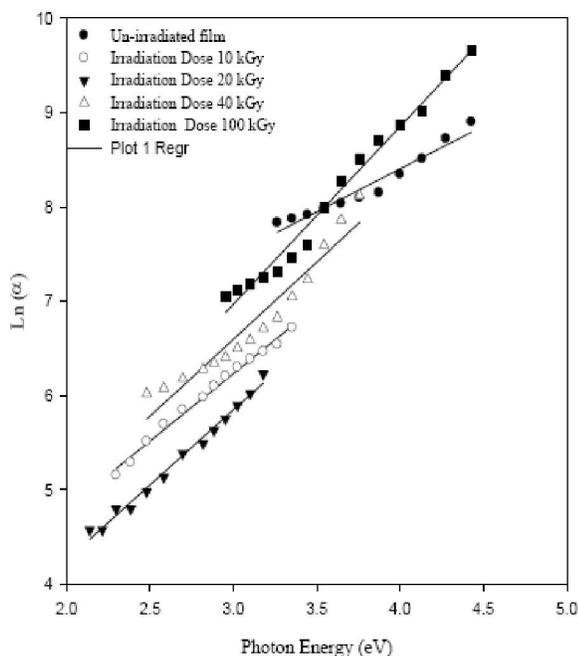


Fig. 6 The logarithmic variation of absorption coefficient $\ln(\alpha)$ versus photon energy for PEMA films irradiated with different doses

TABLE 2 : Optical parameters for PEMA films under different γ -irradiation doses

PEMA Films	Optical band gap (eV)	Band tail width (eV)
Un-irradiated films	2.95	0.53
Irradiation Dose 10 kGy	2.80	0.61
Irradiation Dose 20 kGy	2.65	0.63
Irradiation Dose 40 kGy	2.55	0.70
Irradiation Dose 100 kGy	2.45	1.1

ference phenomena. The air/polymer interface transmission T are expressed as functions of refractive index (n) and extinction coefficient (K)^[32].

$$T = \frac{4n}{(n+1)^2 + k^2} \quad (4)$$

Once the measurements T have been performed, an iterative procedure to calculate n and K is initiated. When the absorption α is known, the extinction coefficient K can be found the relation $K = \alpha\lambda/4\pi$. The real and imaginary parts of dielectric constant ϵ' and ϵ'' can be estimated if the refractive index and extinction coefficient is known from the relations $\epsilon' = (n^2 - K^2)$ and $\epsilon'' = 2nK$. The real part generally relates to dispersion, while the imaginary part provides a measure to the dissipative rate of the wave in medium^[33].

The refractive index and the single oscillation parameters have been calculated and discussed in terms of the Wemple-DiDmenico model^[34] Figure 7. That the parameters single-oscillation energy (E_o) and dispersion energy (E_d) have been calculated by knowing the refractive index (n) which is independent on the

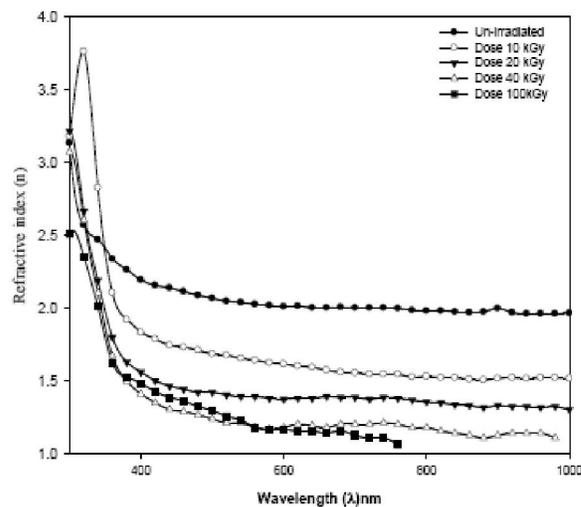


Fig. 7. Refractive index (n) against wavelength (λ) nm, for PEMA Film before and after irradiation with different dose.

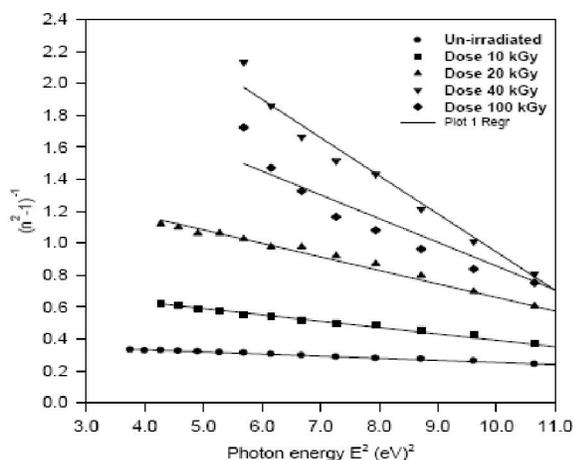


Fig (8) Plot of refractive index factor $(n^2-1)^{-1}$ versus E^2 for unirradiated and irradiated PEMA films

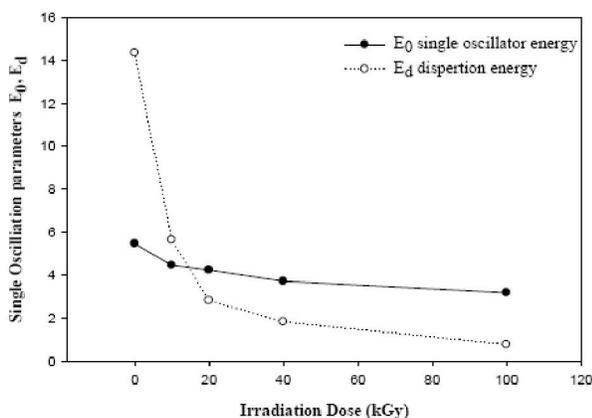


Fig.9 The variation of E_0 single oscillator energy and E_d dispersion energy with gamma irradiation dose for PEMA films

scale of optical dielectric constant (ϵ) and is consequently an “average” energy gap, whereas E_d depends on the scale of ϵ and thus serves as an interband strength parameters. Since the M_o and M_d moments are involved most heavily near the interband absorption edge^[35].

The dispersion of refractive index below the interband absorption edge according to the single oscillator model is given by^[34];

$$n^2(E) = 1 + \left[\frac{E_0 E_d}{E_0^2 - E^2} \right] \tag{5}$$

where the parameters E_o , E_d are the single-oscillation energy and dispersion energy respectively. By plotting $(n^2 - 1)^{-1}$ versus E^2 and fitting a straight line as shown in Figure 8; E_o and E_d are determined directly from the gradient, $(E_o, E_d)^{-1}$ and the intercept (E_o / E_d) , on the vertical axis, TABLE.3. and Figure 9^[35,36].

TABLE 3 : The calculated single-oscillation parameters values of PEMA films before and after γ -irradiation

Gamma Dose	E_o	E_d
Un-irradiated	5.083256	12.65121
10 kGy	4.4832	5.657539
20 kGy	4.22017	2.802622
40 kGy	3.803229	1.220061
100 kGy	3.598682	0.983112

CONCLUSIONS

From the results and discussion above it is possible to conclude that:

1. XRD obtained for PEMA films confirmed the amorphous nature and partially crystalline nature for different films. The XRD data suggested that the crosslinking process predominated during the irradiation of PEMA.
2. TGA studies revealed that the thermal stability of polyethyl methacrylate
3. Gamma-rays irradiation of PEMA films in the dose range of 10 up to 100 kGy has been investigated as a potential technique of refractive index modulating optical elements. There was a decrease in the refractive index in via the decrease in the dispersion energy for the irradiated films with different doses.
4. Single oscillator energies in the PEMA films were significantly influenced by gamma irradiation affects. It was observed a decrease in the dispersion energy and discussed in terms of the Wemple-DiDmenico model.
5. The affect of gamma irradiation on the optical band gap obtained from. Moreover, there was a decrease in the optical energy gap with increasing radiation dose up to 100 kGy. It was deduced that the energy of gamma rays, in the dose range from 10 up to 100 kGy, is suitable for the cross-linking of PEMA films.

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