The Effect of Gamma Irradiation on the Optical Constants of (HDPE-PP) Blends

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Abstract

The influence of gamma radiation and blend ratio on the optical constants (refractive index (n), extinction coefficient (k), and real & imaginary parts of dielectric constants (ϵ_1) & (ϵ_2)) for high density polyethylene (HDPE) Polypropylene (PP) blends using the transmittance and reflectance spectra have been discussed. For unirradiated samples the results showed that (n) increases in rich PP sample while (k) declared strong dependence on blends ratio and revealed systematic variation. It was found that (n) increases as a result of irradiation by gamma-ray with doses (80 and 240) kGy indicating that polymer chain crosslinking is the dominate phenomena , while for irradiation with dose 160 kGy (n) is found to decrease indicating that polymer degradation is the dominate phenomena (chain scission).

الخلاصة

تم مناقشة تأثير نسب الخلط والتشعيع باشعة كاما وبجرع مختلفة على الثوابت البصرية (معامل الانكسار (n)، معامل الخمود (k) وثابت العزل الكهربائي بجزأيه الحقيقي (ϵ_1) والخيالي (C_2)) لخلطات من البولي اثيلين عالي الكثافة والبولي بروبلين باستعمال طيفي النفادية والانعكاسية .أظهرت النتائج للنماذج غير المشعة زيادة معامل الانكسار (n) في النماذج ذات التركيز العالي للبولي بروبلين بينما اظهر معامل الخمود (k) تغيراً متناغماً مع نسب الخلط نسبة لتركيز البولي بروبلين.

لقد وجد ان التشعيع باشعة كاما وبجرع 80 و 240 kGy يزيد من معامل الانكسار مشيراً الى هيمنة ظاهرة تشابك السلاسل البوليمرية بينما عند التشعيع بجرعة 160 kGy وجد ان قيم(n) تقل مشيرة الى تغلب ظاهرة التهدم (قص السلاسل البوليمرية) .

Introduction

Polyethyelene is considered one of the best – known plastics and it comes in three classification based on density: Low medium and high. these density ranges are (0.91 - 0.925,0.925 - 0.94 and 0.94 - 0.965) respectively [1].The content of the crystalline phase in LDPE , MDPE and HDPE are 55-65%, 93%, and 80-90% respectively [2].PE is an important material because of its mechanical, electrical, optical and chemical properties. Absorption and reflection [3-7] have provided information about PE optical properties over the spectral range from the fundamental absorption in vacuum ultraviolet (VUV) to the core excitation in soft x-ray.

Many theoretical studies of PE optical properties [8, 9] have been carried out. On the other hand polypropylene (PP) can be obtained in three forms: Isotactic , syndiotactic and atactic . The isotactic and syndiotactic forms are crystalline [10] while the atactic PP is partially crystalline. PE and PP can be considered as the first two members of alarge group of polymers known as polyolfins which based on ethylene structure [1]. Indeed polyolfins are commercially important because of their relatively low cost, recently blending of PE and PP has become as away to improve other mechanical properties. It was found that the physical properties of crystalline polymers and their blends are influenced by their thermal history [11].

The effect of ionization radiation on polymers is known as the major sources to altering their internal structures which leading to wide range of interrelated change in their properties. The aim of this work is to calculate the optical constants (refractive index (n), extinction coefficient (k), real and imaginary parts of dielectric constants (ϵ_1) and (ϵ_2)) of (HDPE-PP) blend samples which have been irradiated with gamma–ray in the presence of air at room temperature with different doses in appoint of view that the behaviour of these constants reflects the intire structure of material under test.

Basic Relations:

The complex refractive index (N) is given by the equation [12]:

$$N=n-ik \quad \text{.............................(1)}$$

Where n is the real refractive index.
k is the imaginary part of (N) is obtained from the relation :

$$k=\frac{\alpha\lambda}{4\pi} \quad \text{.....................(2)}$$

where α is the absorption coefficient.
λ is the wavelength.

The reflectance part (R) of incident electromagnetic plane wave can be obtained when the transmittance (T) and the absorbtance (A) parts are known since:

$$A+T+R=1 \quad \text{..................(3)}$$

Thus (R) can be calculated through applying the following equation :

$$R=1-(A+T) \quad \text{..................(4)}$$

For normal incident of plane electromagnetic wave the reflectance is given by the equation [12]:

$$R=\frac{(n-1)^2+k^2}{(n+1)^2+k^2} \quad \text{.....................(5)}$$

Which leads to:

$$n=\sqrt{\frac{4R}{(R-1)^2}}-K^2-\frac{(R+1)}{(R-1)} \quad \text{.................(6)}$$

Thus (n) can be calculated when the reflectance (R) and (k) values are known.

The transmittance part of incident light (T) is depending on (α) through the following equation [13]:

$$T=\exp(-\alpha\, d) \quad \text{................(7)}$$

Where (d) is thickness of sample, Thus the absorption coefficient (α) corresponding to any wavelength (λ)can be calculated by applying the relation :

$$\alpha=\frac{\ln\left(\frac{1}{T}\right)}{d} \quad \text{................(8)}$$

or:

$$\alpha=2.303\log\frac{\left(\frac{1}{T}\right)}{d} \quad \text{.............(9)}$$

The dielectric constant (ϵ) which represents the responsivity of electrons in matter to the incident electromagnetic field and depends on frequency [14].

The real part of dielectric constant which represents the polarization term (ϵ_1) and imaginary part of dielectric constant (ϵ_2) can be calculated from the equations [12]:

$$\epsilon_1=n^2-k^2 \quad \text{...... ....(10)}$$

$$\epsilon_2=2nk \quad \text{......... ...(11)}$$

Samples Preparation and Procedure:

High density polyethylene and isotactic polypropylene were supplied from Alamo polymer Corp. and Saudi basic Indust. Corp. respectively.

Brabender method was achieved to obtain blends of HDPE and PP with different ratios:
(100%PE , 85%PE+ 15 %PP, 50%PE+50%PP , 15%PE+85%PP, and 100%PP) . The mixing velocity of polymers granules was varied in the range (5-120) cyc/min. through automatic controller. The temperature of composition was controlled by temperature controller in the range (10-200) $\overset{\circ}{C}$. The velocity of mixing was raised to 60 cyc/min. in order to accomplish the mixing during 8 min...

Samples of disk shape (32) mm in diameter and (0.3)mm in thickness were molded for transmittance and absorptance measurements .

UV-VIS spectrophotometer was used to obtain the transmittance and absorbtance spectrums in the wavelength range (200-700)nm for (HDPE-PP) blends. The reflectance (R) were obtained using eq.(4),(k)can be calculated using eq. (2) ,(n) can be obtained using eq.(6) while ϵ_1 , ϵ_2 is calculated using eqs. (10 and 11) respectively.

Irradiation Procedure:

The irradiation was done in air at room temperature with gamma radiation from Co^{60} source which emitted photons with average energy (2.5) MeV.The irradiation was carried out for different times to obtain the desired doses:
80, 160, 240 kGy

Results and Discussion:

Using equation (6) the refractive index (n) of (HDPE _PP) blends unirradiated and irradiated with different doses was determined. Fig. (1 a, b, c, d, e) show the variation of (n) as function of wavelength (λ). It was found that (n) change with (λ) in the range (200-700)nm . On the other hand our data show that the values of n for unirradiated samples increases as PP content decreases from (0 to 15)wt. % . However (n) get to rise with increasing PP content from (15 to 100) wt. % .Indeed (n) increases from 2.109 to 2.572 at λ=450 nm when PP increases in the mentioned range as can be seen in table (1). This can be explained as follows:

In the blends with PP contents change from (50 to 100) wt.% the HDPE was always present as disperse phase. Then the crystalline behavior was dominated by the PP component [11]. Indeed many researchers pointed out that (n) values of crystalline polymers like PP exceeded the value of (n) of semicrystalline polymers [15]. Doroudiani [16] referred that the crystalline fraction of PP increased as HDPE component decreased.

On the other side Fig.(1 a , b , c , d , e) declares that n exhibit to change in non systematic sequence (i.e increasing then decreasing) when samples irradiated with different doses .

Donnell [17] proposed the following classification for the changes in polymers structures due to irradiation:

1-Scission and cross linking of polymer molecules resulting in decrease or increase in molecular weight.

2-Evaluation of small molecules products such as H_2 , CO , CO_2 and CH_4 .

3-Modification of molecular composition and structure.

Crosslinking and chain scission (degradation) are simultaneous events and the relative extent of both reactions depends on the chemical nature of polymers.

Thus the increasing in (n) is attributed to crasslinking of molecular chains which lead to increase in cystallinity, many researchers [18] was observed that radiation induced increasing in degree of crystallinity.

While the decreasing in (n) values is attributed to chain scission which lead to decreasing molecular weight [19, 20].

In order to compare our results with the published data [21] many researchers referred that (n) values for PP exceeded the value of(n) for HDPE and this is in agreement with our n values in the absence of radiation. .

The dependence of the extinction coefficient (k) on wavelength obtained using equation (2) is shown in Fig. (2 a,b,c,d,e) . It is remarked that the values of (k) are reduced i.e. become smaller at the region near absorption edge. On the other hand (k) values for unirradiated samples exhibit to decrease with increasing PP content. Indeed k decreases from (1.554×10^{-4} to 3.035×10^{-5}) at λ=450 as PP increases from (0 to 100) wt.%. This can be ascribed to the reduction in absorption as a result of dominating crystalline phase and reduce the density of localized states [22].

The behavior explanation of (k) with irradiation doses (similar to n) can be related in terms of crosslinking and chain scission. The increasing in(k) values can be ascribed to high absorption coefficient [23] (i.e. increasing the density of localized states)as a result of polymer chain scission while decreasing in k value can be ascribed to increasing in degree of cystallinity which leading to eliminate the density of localized states by the effect of polymer chain crosslinking.

Our data for irradiated samples are in agreement with Kostoski [24] who referred that crosslinking reaction occurred in PE as a result of irradiation by gamma ray doses (80) kGy which is return to occurs in PP at dose (80) kGy.

The real and imaginary parts of dielectric constant (ϵ_1 and ϵ_2) of (HDPE-PP) blends unirradiated and irradiated with different doses are calculated using eqs. (10 and 11). The dependence of (ϵ_1 and ϵ_2) on (λ) are shown in

Fig. (3 a, b, c, d, e) and Fig. (4 a, b, c, d,e) . They are considered that the variation of (ϵ_1) mainly depends on the value of (n^2) while the imaginary part of dielectric constant (ϵ_2) for pure sample (100%PP) and blend sample (15%PE+85%PP) mainly depends on (k) values, which are related to the variation of absorption coefficient (α) while for residual blend samples (ϵ_2) is observed to depend on (n) values.

We can see from table (1) for pure samples (100%PE and 100%PP) irradiated with 240 kGy and the blend sample (50% PE+50%PP) irradiated with 80 kGy although the polymer chain crosslinking is the predominate phenomena (k) value was observed to increase with irradiation dose, this can be explained as follows: High energy radiation is absorbed in polymers by interaction with the valence electrons of the atoms within the molecules. In polymers containing Hydrogen atoms the chemical reaction is followed by abstraction of H atom and formation of radical and ionic sites along the length of molecules and this is the reason for crosslinking. The formation of C=C bonds by radiation with simultaneous elimination of H_2 can lead to reaction with radicals forming secondary parts and the absorptions of these parts are responsible for increasing in (k) values [19].

Conclusion:

The optical constants measurements (n,k, ϵ_1,and ϵ_2) for unirradiated and irradiated (HDPE-PP) blends were carried out using the transmittance and reflectance spectra in the wavelength range (200-700)nm .Our results for unirradiated samples showed that (n) increases in PP rich blend samples (that which with PP content from 50 to 100 wt.%), as a result of dominating the crystalline phase of PP, while (k) decreases one order of magnitude when PP content increases from (0-100) wt.%. . For irradiated samples the data showed that (n) increases and decreases (while (k) decreases and increases) as a result of polymer chain croslinking and degradation respectively.

Table (1) The values of (n,k, $\epsilon_1$and ϵ_2) at λ =450nm for (HDPE-PP) blends unirradiated and irradiated with different doses

The blends ratio %	Irradation dose (kGy)	n	K	ϵ_1	ϵ_2
100% PE	0	2.397	1.5540×10^{-4}	5.745	7.449×10^{-4}
	80	2.635	1.1150×10^{-4}	6.943	5.876×10^{-4}
	160	1.885	1.2613×10^{-4}	3.553	4.755×10^{-4}
	240	2.097	1.8897×10^{-4}	4.397	7.922×10^{-4}
85% PE+15% PP	0	2.109	1.0930×10^{-4}	4.447	4.610×10^{-4}
	80	2.597	1.0930×10^{-4}	6.744	5.677×10^{-4}
	160	1.959	1.4050×10^{-4}	3.837	5.504×10^{-4}
	240	2.046	1.1538×10^{-4}	4.186	4.718×10^{-4}
50% PE +50% PP	0	2.537	6.478×10^{-5}	6.436	3.286×10^{-4}
	80	2.618	8.982×10^{-5}	6.853	4.702×10^{-4}
	160	2.636	6.478×10^{-5}	6.948	3.415×10^{-4}
	240	2.64	5.226×10^{-5}	6.969	2.759×10^{-4}
15% PE +85% PP	0	2.572	4.550×10^{-5}	6.615	2.340×10^{-4}
	80	2.525	3.298×10^{-5}	6.375	1.665×10^{-4}
	160	2.537	7.211×10^{-5}	6.436	3.658×10^{-4}
	240	2.545	4.785×10^{-5}	6.477	2.435×10^{-4}
100% PP	0	2.572	3.034×10^{-5}	6.615	1.560×10^{-4}
	80	2.572	2.987×10^{-5}	6.615	1.536×10^{-4}
	160	1.984	1.156×10^{-5}	3.936	0.458×10^{-4}
	240	2.647	3.973×10^{-5}	7.006	2.103×10^{-4}

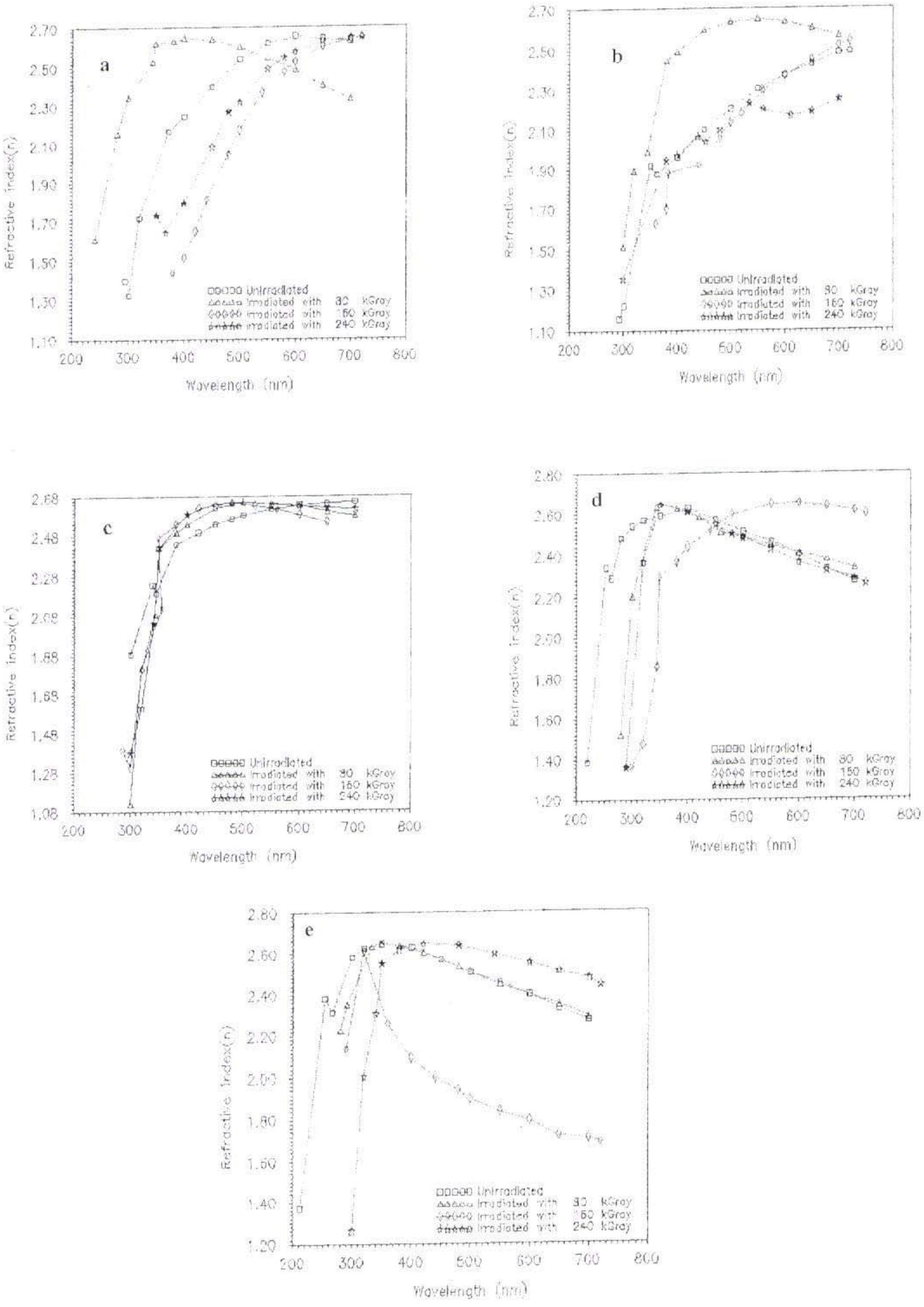

Fig.(1) Refractive index (n) as function of wavelength for (HDPE-PP) blends unirradiated and irradiated with different doses.
(a)100%PE ,(b)85%PE+15%PP, (c)50%PE+50%PP, (d)15%PE+85%PP, (e)100%PP.

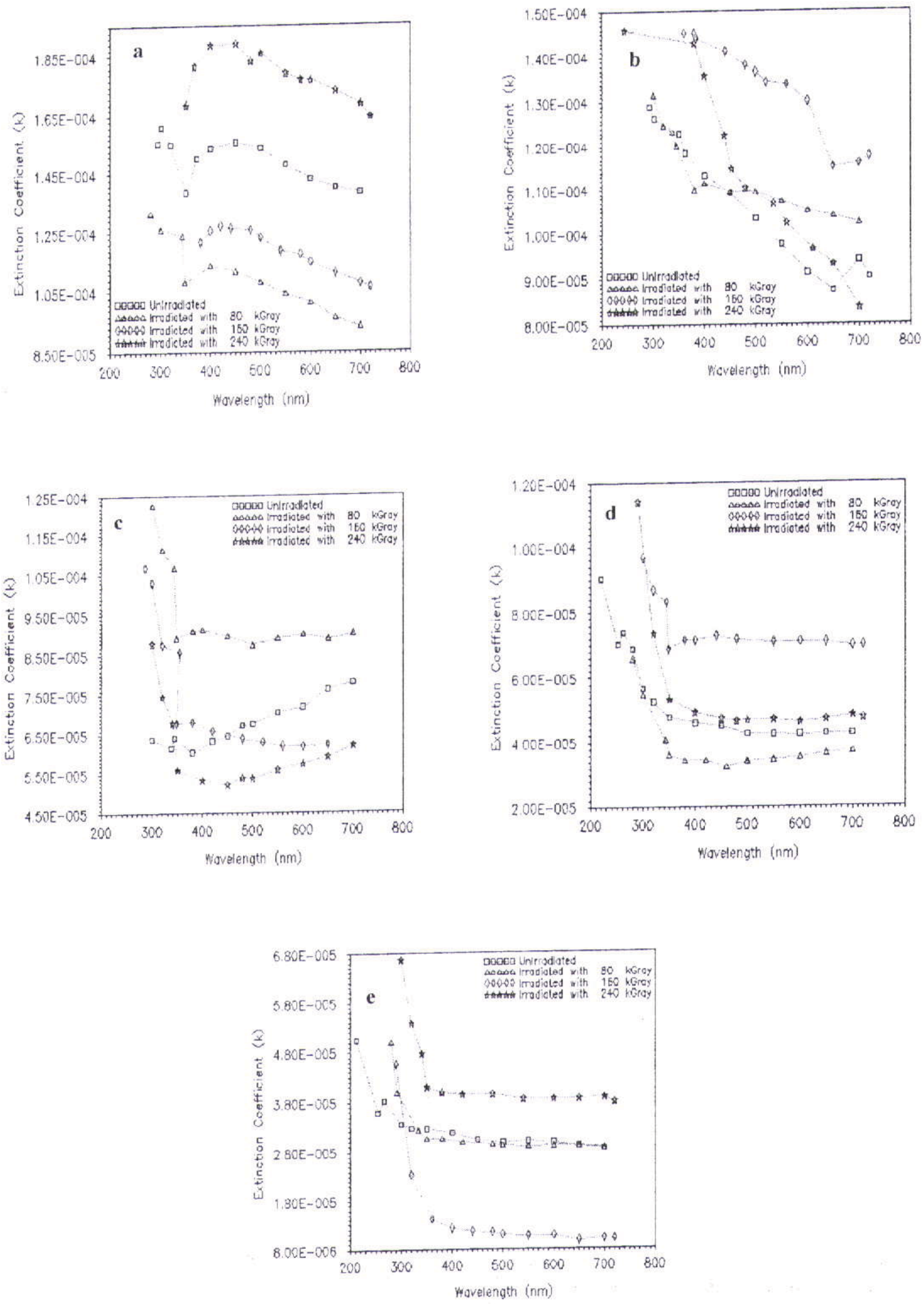

Fig.(2) Extinction coefficient (k) as function of wavelength for (HDPE-PP) blends unirradiated and irradiated with different doses. (a)100%PE ,(b)85%PE+15%PP, (c)50%PE+50%PP, (d)15%PE+85%PP, (e)100%PP.

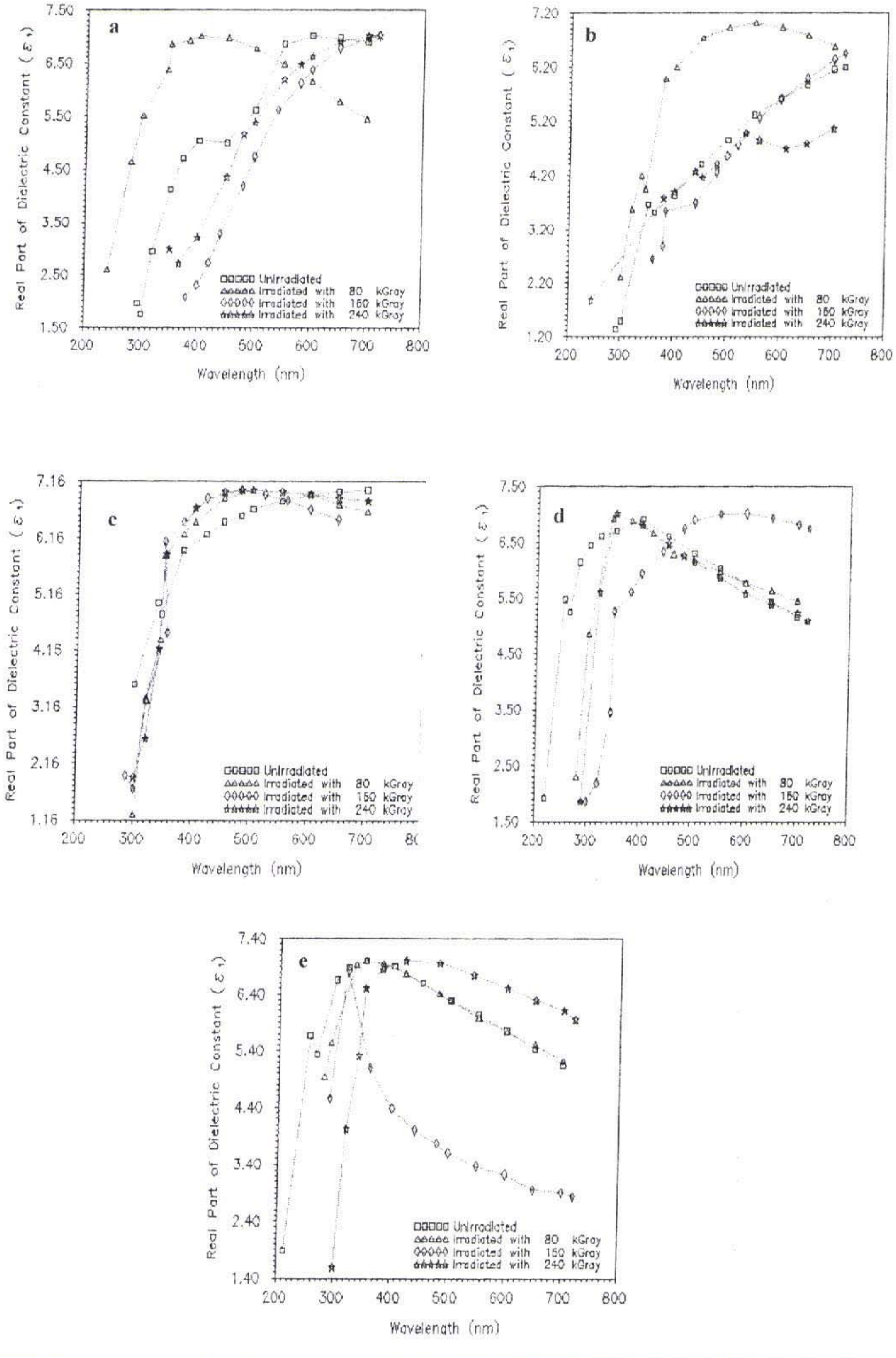

Fig.(3) Real part of dielectric constant (ϵ_1) as function of wavelength for (HDPE-PP) blends unirradiated and irradiated with different doses. (a)100%PE ,(b)85%PE+15%PP, (c)50%PE+50%PP, (d)15%PE+85%PP, (e)100%PP.

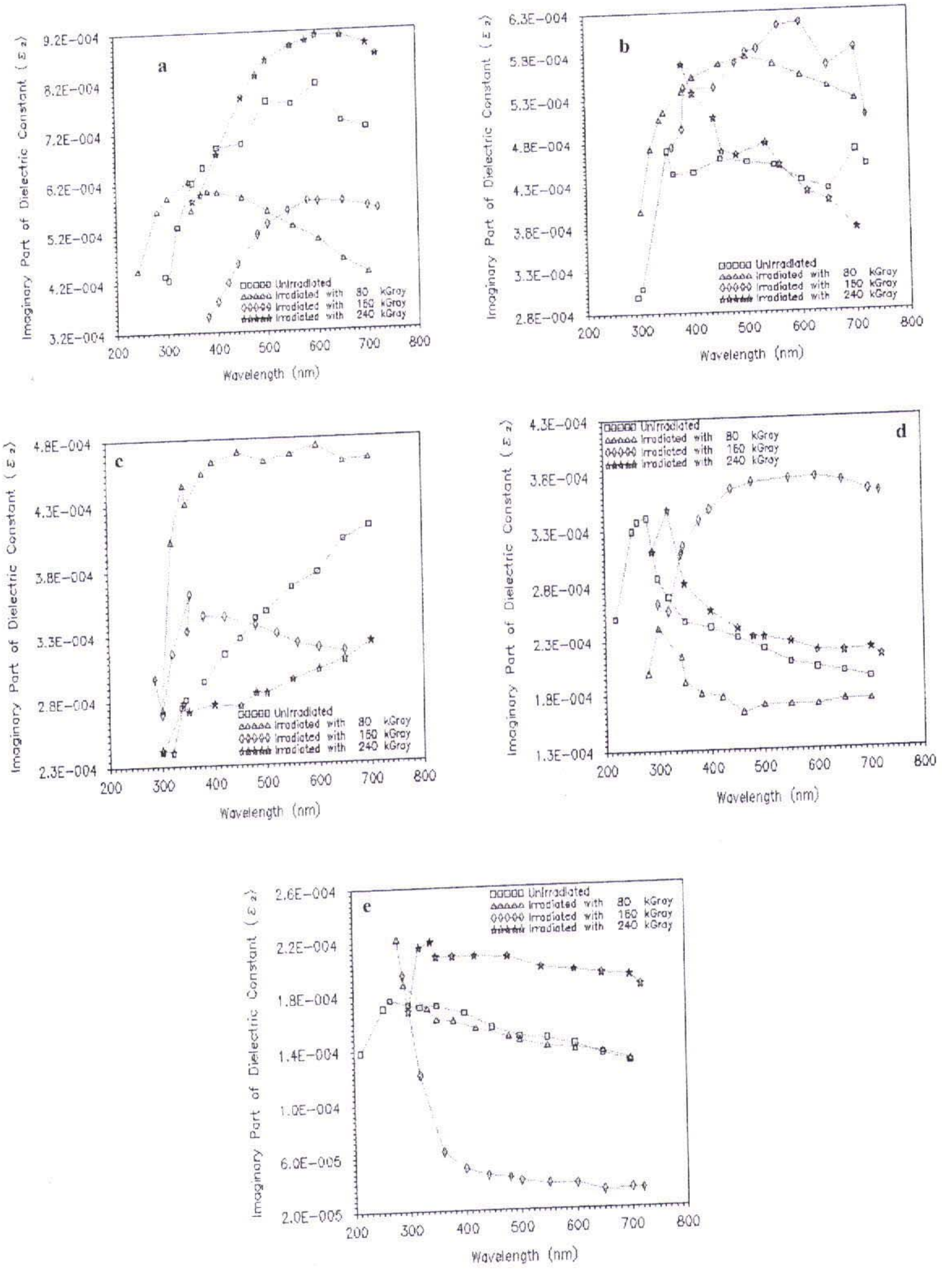

Fig.(4) Imaginary part of dielectric constant (ϵ_2) as function of wavelength for (HDPE-PP) blends unirradiated and irradiated with different doses. (a)100%PE ,(b)85%PE+15%PP, (c)50%PE+50%PP, (d)15%PE+85%PP, (e)100%PP.

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