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Alpha –Ray Irradiation Effect on Optical Properties for Coumarin Doped Polystyrene Polymer Films

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Abstract : In this work, the effect of the alpha irradiation on optical properties for Coumarin dye doping different ratio in Polystyrene films has been studied. The absorption spectra increase with increasing doping ratio of dye solution and time of alpha irradiation, especially in doping ratio 60 ml. spectroscopy properties showed that the peaks to Coumarin dye for all samples after irradiation refer which have evaluated and compared with other researchers.
Keywords : Spectroscopy properties, Coumarin, Polystyrene Polymer, Dye Doped Polymer Films, Effect of Alpha irradiation.

Introduction

The large use of organic dyes and dye-doped polymers in optical and optoelectronic applications has produced a renewed interest in the area of laser dyes1. Dye laser Coumarin (2H-chromen-2-one) and several natural and synthetic derivatives of Coumarin are used in different applications in chemistry, biology, medicine and physics2. Polystyrene (PS) is an amorphous polymer with bulky side groups. General purposes PS is hard, rigid, and transparent at room temperature and glass like thermoplastic material which can be softened and distort under heat. It is soluble in aromatic hydrocarbon solvents, cyclohexane, and chlorinated hydrocarbons3.Americium-241 is an unsteady (radioactive) isotope with a half-life of 432.2 years. It decays tow energies of an alpha particle (5485.6 KeV and 5442.8 KeV). The americium-241 decay series ends with bismuth-209, a stable (non-radioactive) element.Alpha particles are one of the ionizing radiation which is a nucleus of an atom of helium and consist of two protons and two neutrons. Alpha particles are relatively slow and heavy.

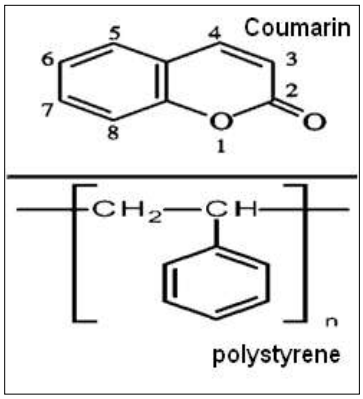


Figure (1) The chemical structure for Coumarin and polystyrene.

Experimental Work

Coumarin laser dye supplied by SIGMA-ALDRICHCHEMIE, Germany. The chemical formula of coumarin dye is ($C_9H_6O_2$), molecular weight (146.15) g/mole and the chemical structure shown in fig.(1-a)[4].Polystyrene PS polymer supplied from ICI Company. The chemical structure of PS polymer is shown in fig. (1-b)[5].The prepared Coumarin doped PS polymer films by a casting method. Weight the amount of PS was 0.5 g and make it as a solution by dissolved in 10 ml of Chloroform. Coumarin dye solution was prepared by dissolving in the same solvent of concentration 1×10^{-4}mol\liter[6]. In each case, the doping ratio of Coumarin dye solution (40, 50, 60) ml mixed with the polystyrene solution (10) ml and stirred very well to get regular mixture was poured into a clean glass Petri dish 10 cm diameter and dried at room temperature for 24hr to get homogeneous films. The time of irradiation by Alpha particles for all samples was for one and two minutes. The spectroscopy determined by UV-Visible spectrophotometer type (T70/T80) at the wavelength range (200-900) nm.

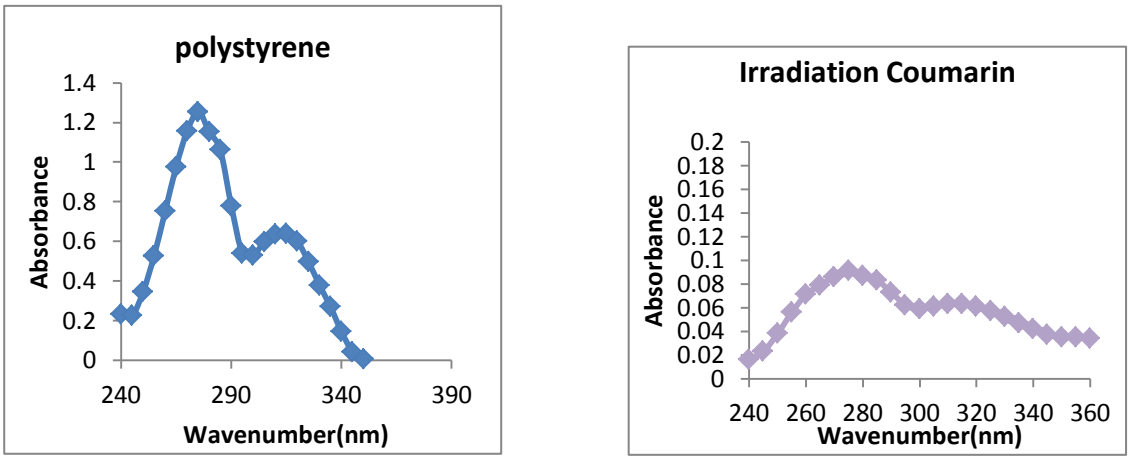


Figure (2) Absorption spectrum before and after irradiated for Coumarin Solution.

Theoretical Part

The intensity of energy propagation through an absorbing homogenous medium is described by lamberts law, which states that the intensity falls off exponentially with distance[7].

$$\mathbf{I = I_0 e^{-\alpha x}} \dots\dots\dots\dots\dots\dots\dots\dots\dots (\mathbf{1})$$

(**α**)refer to the absorption coefficient (cm^{-1}) and (**x**)refer to the thickness of sample (cm).

$$\alpha x = 2.303 \log \frac{I}{I_0} \dots\dots\dots\dots\dots\dots (2)$$

The term (log I /I_O) has been placed equal to the quantity absorbance (A):

$$\alpha = 2.303 \log \frac{A}{x} \dots\dots\dots\dots\dots\dots\dots (3)$$

The electronic transitions are described by Tauc formula [8]

$$\alpha\, h\upsilon = B(h\upsilon - E_g)^r \dots\dots\dots\dots\dots\dots (4)$$

Where

B is constant

ris constant depending on the material and the type of optical transition (direct or indirect).

The reflection spectra (R), were calculated from using the well-known equation (6):

$$R + A + T = 1 \dots\dots\dots\dots\dots\dots (6)$$

Therelation between reflectivity (R) and refractive index (n) is given by flowing equation[9]:

$$R = \frac{(1-n)^2+\kappa^2}{(1+n)^2+\kappa^2} \dots\dots\dots\dots\dots\dots (5)$$

krefer to the extinction coefficient (k≈0) that refractive index shown by equation (7)[10]

$$n = \sqrt{\frac{4R}{(R-1)^2} - R^2} - \frac{(R+1)}{(R-1)} \dots (7)$$

The extinction coefficient (K) was calculated using the following equation (8)[11]:

$$K = \frac{\alpha\lambda}{4\pi} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

λ,refer to the wavelength of the incident light.

The real part (ε_1) and imaginary part (ε_2) of the dielectric constant of the samples were determined by the relations[12]:

$$(n - iK)^2 = \varepsilon_1 - i\varepsilon_2 \quad \ldots\ldots\ldots\ldots (9)$$

And

$$\varepsilon_1 = n^2 - K^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (10)$$

$$\varepsilon_2 = 2nK \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (11)$$

Results and Discussions

1. Absorption Spectrum before and after irradiate for Coumarin dye solution

The concentration of Coumarinis $1x10^{-4}$mol/liter in chloroform solvent. The performance of absorption spectrum shown in fig.(2) .It has two peaks agree with (NIST) Standard[13]. Maximum wavelength absorption for two peaks is situated at (275,310)nm with intensity (0.06 and0.035), respectively. The electronic transitions formed through n–π* and π–π* are connected to an excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital the (LUMO)[14].The effects of Alpha –ray irradiation changed some optical parameters, such as a decrease in optical density on the absorption spectrum compared before irradiation are characteristic for essential Coumarin skeletons and are linked to the charge transfer from the benzenic cycle to the pyranone moiety [15].

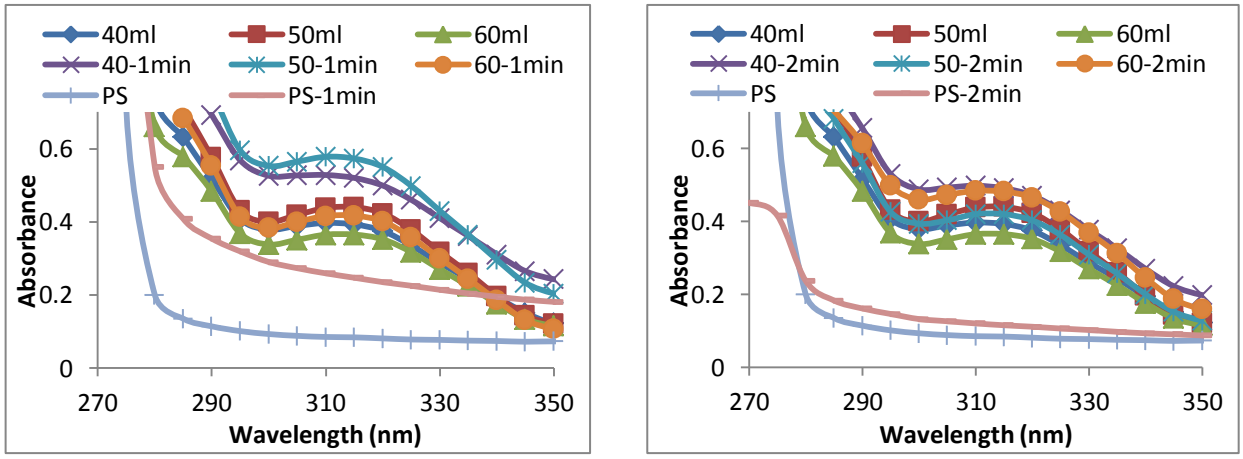


Figure (3) Absorption spectrum for pure PS and Coumarin doped PS films before and after irradiated

2. Absorption Spectrum before and after irradiate dye Doped Polymer Films

The effect of irradiation on the absorption spectrum of pure polystyrene film clearly showed in fig.(3).There is 5 nm blue shift after alpha irradiation; the maximum absorption wavelength of pure PSis265 nm before irradiation and became ≈ 270 nm after alpha irradiation and the absorbance less in two minutes of irradiation. Coumarin dye doped polystyrene films has noticeably appeared single peak at 315 nm in all doping ratio and after irradiation the peak shift to reach (310)nm in doping ratio (40,50)ml; as illustrated in fig.(3);this denote there was (short wavelength) blue shift about 5 nm compared with unirradiated samples. Before irradiation, the maximum intensity of absorption spectrum for all doping ratio increased till 60 ml will be decreased because formed the dimmer and trimmer[16]. The effect of irradiation observed to increase absorbance for all doping ratio in one minute and in two minutes. Increased the absorbance of each sample after irradiation, where the doping ratio 40 ml is stable during irradiation, but doping ratio 50 ml less than during the two minutes of irradiation that referred

the same behavior polymer films. The absorbance of doping ratio 60 ml film increased in two minutes more than in one minute after irradiation because of the increasing number of dye molecules that referred the same behavior of dye molecules.

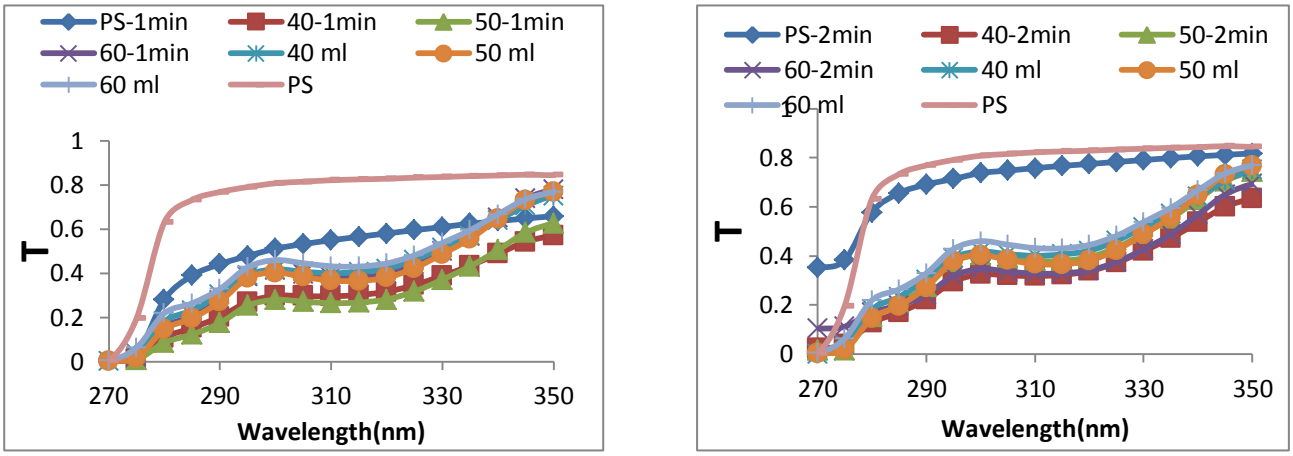


Figure (4) Transmission spectrum for pure PS and Coumarin doped PS films before and after irradiated

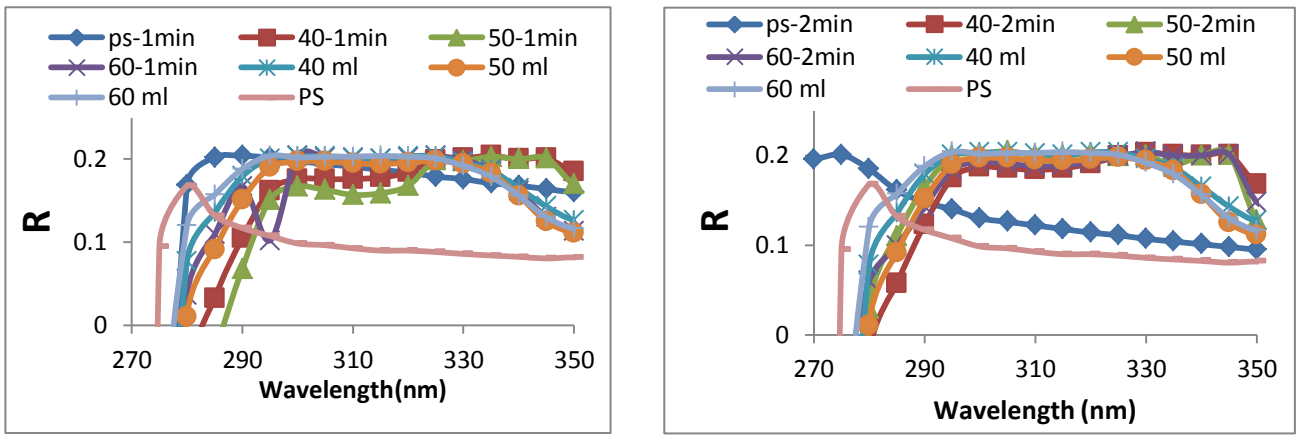


Figure (5) Reflection spectrum for pure PS and Coumarin doped PS films before and after irradiated

3. Transmission Spectrum

The spectral transmittance of pure polystyrene and Coumarin doped polystyrene films shows in Fig.(4) with different irradiation times. The transmission spectrum decreased with increasing doping ratio and irradiation times but in doping ratio C=50ml increasing after two minutes.

4. Reflection Spectrum

Through absorption and transmission spectrum, it can be calculated reflection spectrum from eq. (6). Fig. (5)shows reflection spectrum for films contain pure polystyrene and Coumarin doped polystyrene films for different doping ratio and two irradiated time. Increased Reflection spectrum with increasing irradiation times and doping ratio of Coumarin dye till reach doping ratio 60 ml in one minute and 50 ml in two minutes.

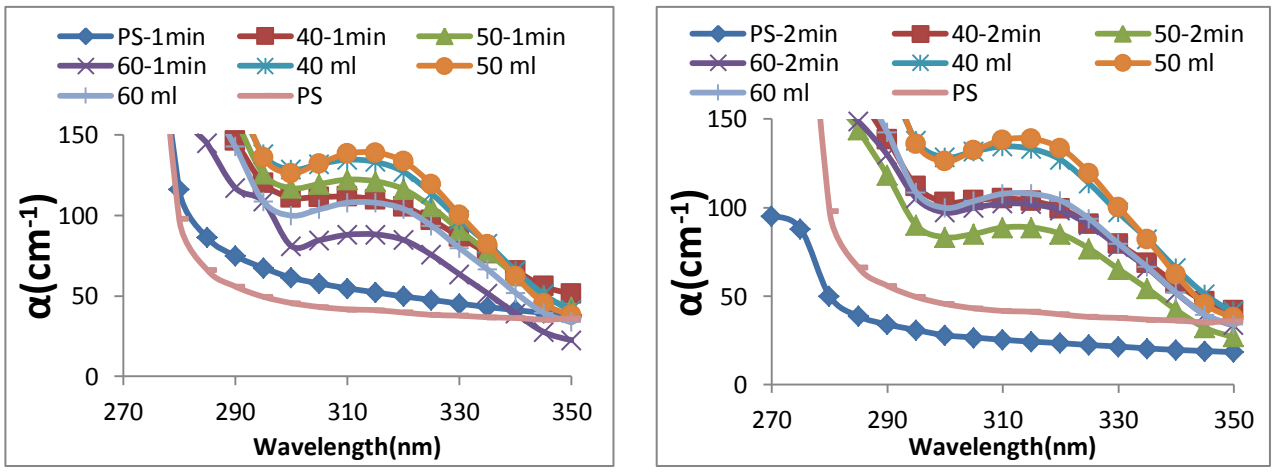


Figure (6) Absorption Coefficient spectrum for pure PS and Coumarin doped PS films before and after irradiated.

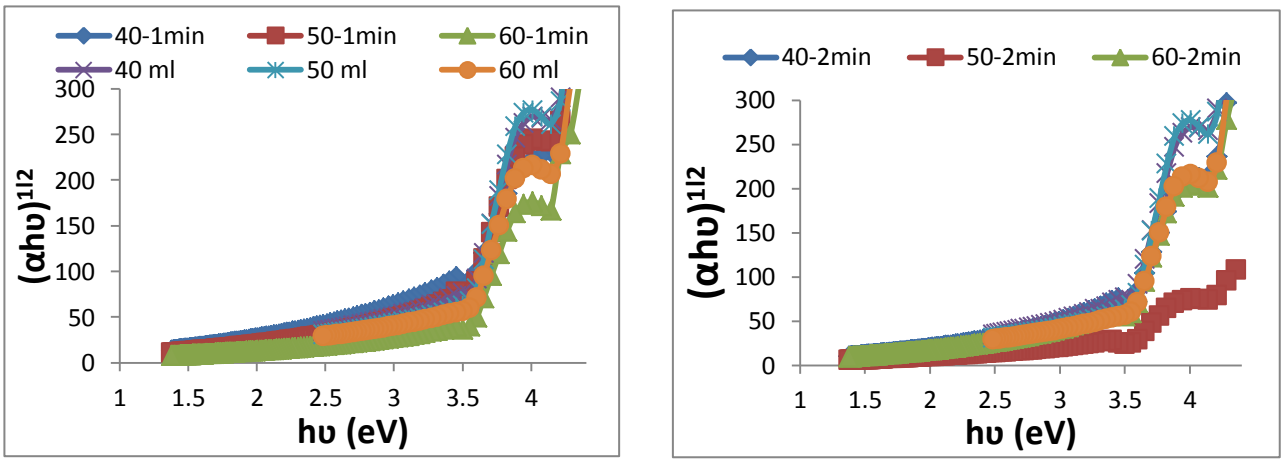


Figure (7) Energy gap for Coumarin doped PS films before and after irradiated

5. Absorption Coefficient

The absorption coefficient considered from eq. (3). Fig.(6) demonstrates the absorption coefficient(α) of polystyrene and Coumarin doped polystyrene films for varies doping ratio and effect alpha irradiation on these films. The type of electronic transitions determines by absorption coefficient. At higher energies the high values of absorption coefficient ($\alpha>10^4 cm^{-1}$) owing to direct electronic transitions of the energy and momentum of the electron and photon, even aslow energies the low values of absorption coefficient ($\alpha<10^4\ cm^{-1}$), due to indirect electronic transitions of the energy and momentum of the electron and photon by phonon helps[17].In these samples, the value of absorption coefficient for films less than $10^4\ cm^{-1}$,so that electronic transitions are the indirect electronic transitions.

6. Optical Energy Gap

The optical Energy gap is necessary to expand the electronic band structure of film material. It can be determined from a straight line, obtained by plotting $(\alpha h\nu)^{1/r}$as a function of photon energy (hν) shown in fig.(7). The energy band gap was calculated from eq.(4) with r=2 refer to indirect allowed transitions for all films, the value energy gap for pure PS film equal to (2.8) eV which is corresponding to the result[18,19].After alpha irradiation and effect of adding Coumarin to polystyrene by ratio (40,50,60) ml; the energy band gap ranged in the table.

Table: energy gap for coumarin dopoed polystyrene films before and after irradiated.

Coumarin doped PS films	Energy gap E_g (eV)		
	At room temp.	After irradiation for 1min.	After irradiation for 2min.
40 ml	3.4	3.3	3.3
50 ml	3.5	3.4	3.4
60 ml	3.5	3.5	3.4

7. Refractive Index

Fig.(8) shows the behavior of refractive index (n)before and after alpha irradiation for pure polystyrene and Coumarin doped polystyrene films. The value (n) of polystyrene was (2.4) [18]. When increasing doping ratio of Coumarindye in polystyrene films, the refraction index (n) highest value with increasing doping ratio of Coumarinand after alpha irradiation to be (2.6) while decreasing in all doping ratio with increasing wavelength.

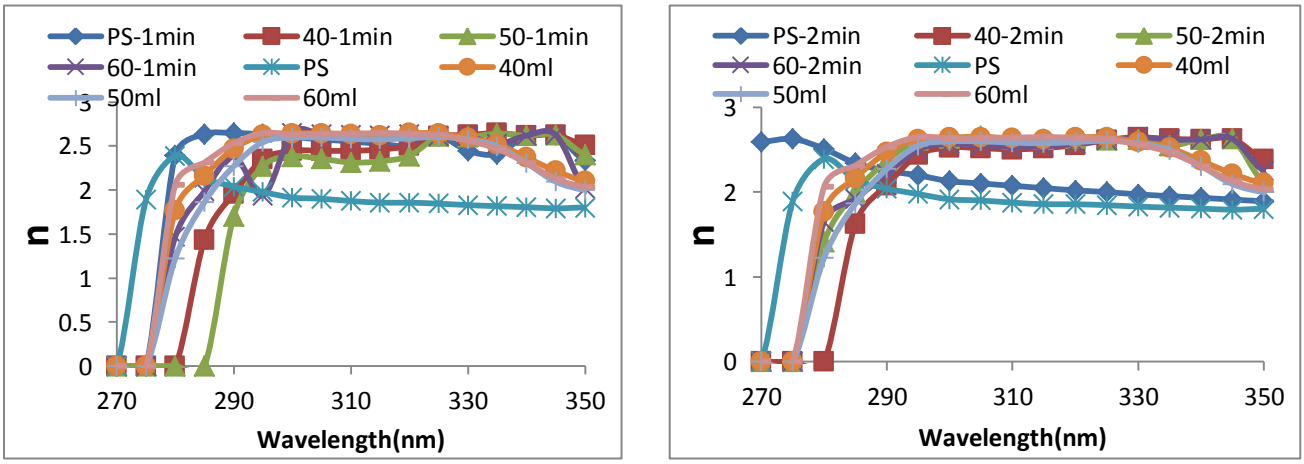


Figure (8) Refractive Index for pure PS and Coumarin doped PS films before and after irradiated.

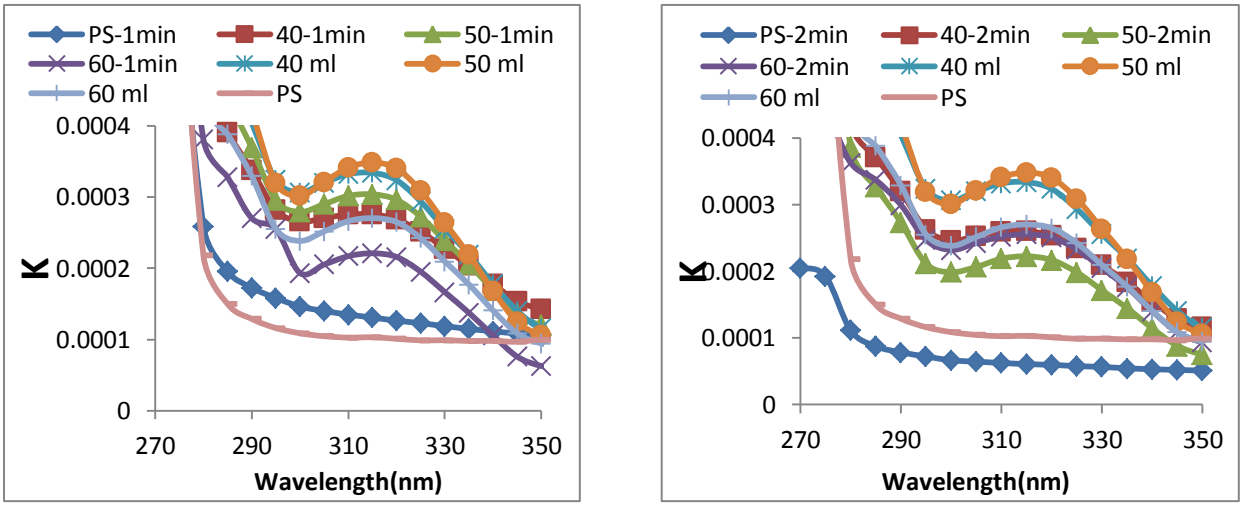


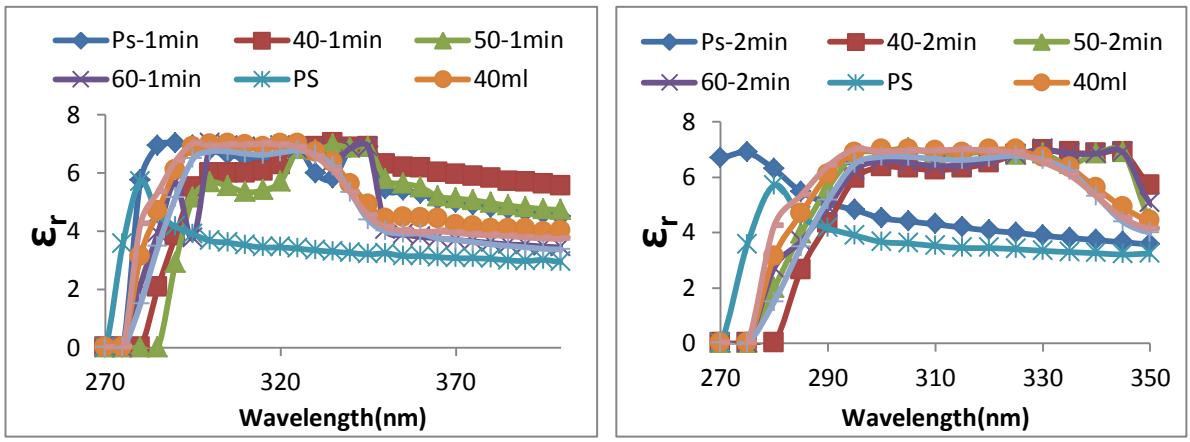
Figure (9) Extinction Coefficient for pure PS and Coumarin doped PS films before and after irradiated

8. Extinction Coefficient

The difference of extinction coefficient (k) values in the wavelength range (270-350) nm can be calculated by eq.(8), for pure polystyrene and Coumarin doped polystyrene films as shown in fig.(9). The differences of extinction coefficient (k) support on absorbance, so that the extinction coefficient (k) resembles the manners of all curves for absorption spectrum. Increasing dopant of Coumarin dye and effect of alpha irradiation lead up to the increment in extinction coefficient, but contraction in 60 mlon two minutes irradiation.

9. Dielectric Constants

The real dielectric constant computed from eq. (10). It is concluded that the variation of ε_r mainly depends on (n^2) because of small values of (k^2)[12];fig.(10) gives the real part of dielectric constants (ε_r) for pure polystyrene and Coumarin doped polystyrene films in different doping ratio, increases real dielectric constant (ε_r).The polystyrene film at wavelength (280) nm and the dye doped polymer films at (295)nm and decreases with increasing wavelengths, and after alpha irradiation led to increasing at (285)nm and Coumarin doped polystyrene films at (300)nm.



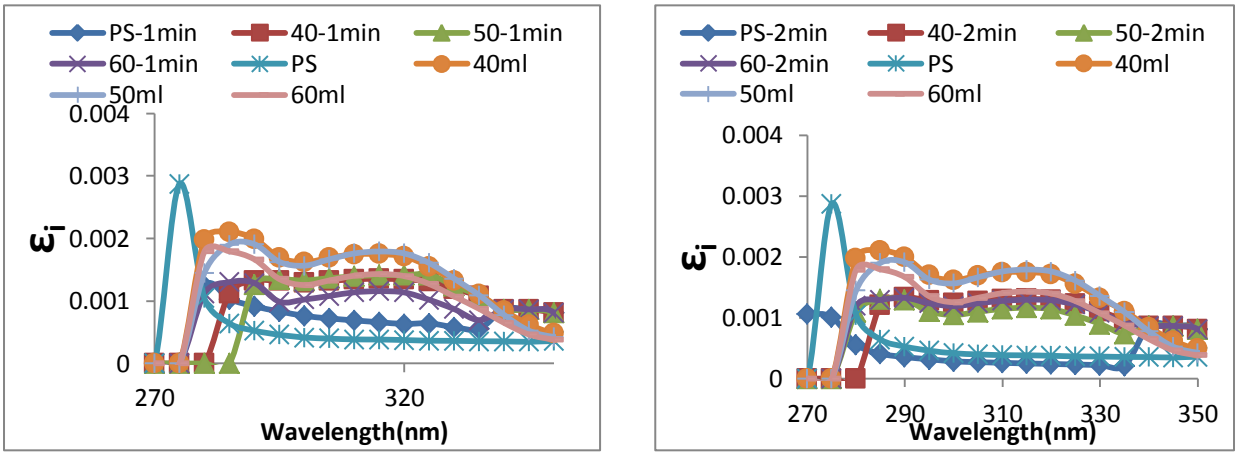


Figure (10) Real and imaginary part of dielectric constant for pure PS and Coumarin doped polystyrene films before and after irradiated.

While the imaginary dielectric constant computed from eq. (11) ε_i mainly depends on the (k) values which are related to the variation of absorption coefficients (α) [12]. The imaginary part of dielectric constants for pure polystyrene and Coumarin doped polystyrene films in different doping ratio are shown in fig.(10). Imaginary dielectric constant for all films decreased with the increasing wavelength by the effect of doping ratio and irradiation for polystyrene and Coumarin doped polystyrene films.

Conclusions

The effect irradiation times and doping in samples led to the stability of vaccination for coumarin doping ratio 40 ml but a decrease in doping 50 ml and increase in doping 60 ml with irradiation times.

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