Effect of Adding Coumarin Dye on Optical Properties of PolyCarbonate Films

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Abstract

Pure and doped polycarbonate (PC) films with various doping ratio of coumarin dye were prepared by using casting method. The absorption and transmission spectra for these films were measured using UV/VIS spectrophotometer technique in order to assessment the type of transition which was found to be indirect transition. The optical energy gap of polycarbonate (PC) was (4.24eV) and coumarin dye was (4.08eV), after doping PC polymer with coumarin dye the maximum energy gap is(4.26eV) in volume ratio(4ml). Also, the results showed that absorption coefficient, refractive index, extinction coefficient and real- imaginary part of conductivity slightly affects by doping.

Key words: polycarbonate, coumarin dye, optical properties, Dye Doped Polymer.

تأثير اضافة صبغة الكومارين على الخواص البصرية لأغشية البولي كاربونيت

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الخلاصة

تم تحضير اغشية البولي كاربونيت النقي والمطعم بنسب تطعيم مختلفة من صبغة الكومارين بطريقة الصب. تم قياس اطياف الامتصاص والنفاذية لهذه الاغشية باستخدام تقنية مطياف الاشعة فوق البنفسجية–المرئية لتحديد نوع الانتقال الذي وجد بأنه انتقال غير مباشر. فجوة الطاقة للبولي كاربونيت وجدت(4.24) الكترون فولت ولصبغة الكومارين هي (4.08) الكترون فولت. بعد التطعيم

اصبحت اعلى فجوه طاقة هي (4.26) الكترون فولت بنسبة حجمية (4) مل كذلك بينت النتائج بان معامل الامتصاص، معامل الانكسار، معامل الاخماد، والجزء الحقيقي والتخيلي للتوصيلية الكهربائية تأثرت قليلا" بالتطعيم.

1- Introduction

The polycarbonate name is come from its carbonate backbone. The Chemical structure of polycarbonate is shown in the fig. (1) ,[1].

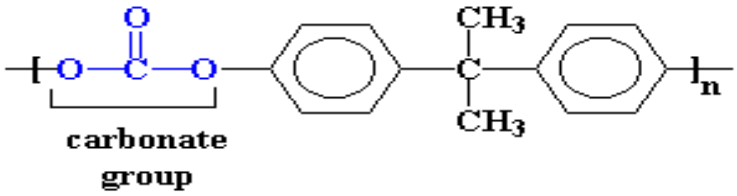

Fig. (1) Chemical structure of polycarbonate [1]

The Polycarbonate is amorphous, obvious polymers that presentation excellent dimensional settlement, the electrical properties is perfect, and thermal stability is good, superb impact might. They offer else stellar mold ability while extrude ability, toughness in low-temperature. Polycarbonate exercised in production curtains for supersonic aircraft, break-resistant windows, and helmets for spaceman, also in the field of protection uses bullet resistant slides for banks and painted cars. Also, applies in computer where electrical mechanical, fire-resistance properties and utilized in sterilizable food processing tools by fume [2]. Polycarbonate has good out-doors reluctance in the UV-stabilized form, but it resort to turn yellow by long exposition to sunlight [3]. Because of its good properties, polycarbonate is an ideal material for use in exacting applications where it is often exposed to environmental parameters.

PC is considered significant engineering plastics with a vast assortment of applications because the mechanical properties are superb and high influence power, and resistance in heat and modulus of elasticity is high. Polycarbonate has been studied in terms of degradation by many researchers, such as the

solidity, ability to recognize of the properties to lid the entire lifecycle of this Polymer, and likewise the degradation mechanism whose pass at the molecular level [4- 6]. It turns out that unto low clamminess content during processing adversely affects in mechanical properties of the eventual product. The effect of recycling on the properties of injection cast polycarbonate has been studied by J. W. Shea et al [7], which assessed the extent of degradation by measuring the rate of impact, molecular weight and flow rate of solubility [8]. On the other hand, they have scoured the effect of the transparency of polycarbonate with ultraviolet rays. The effect of UV radiation on the internal structure of polycarbonate and its optical properties was studied and found that irradiation affects the energy gap and causes its decrease. They concluded that this decrease causes photo degradation of PC and forms defects, aggregation of molecules in these materials [8, 9].

The Coumarin dye or other names such as benzo-α-pyrones, is a large family in terms of installed. Its composition or structure consists of the combination of the benzo-α-pyrones rings with the pyrone carbonyl group, which in turn leads to class of heterogeneous compounds and the sludge named benzopyrones and called chromes, the latter differing from the prior only in the position of the carbonyl group in the heterocyclic ring as shown in fig. (2), [10, 11].

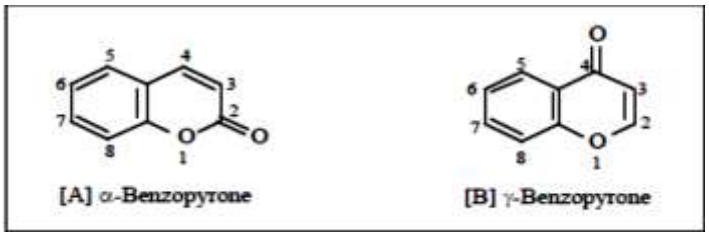

Fig. (2) Chemical structure of (A) Coumarin and (B) chromones[11]

Coumarin has medical benefits through itself to induce macrophages to disgrace outside the cell albumen by Coumarin and other benzopyrones, like 5, 6 benzopyrone, 1, 2 benzopyrone, diosmin. So permit faster desorption of edematous blob [12]. In the several dye lasers the Coumarin is too used as an active medium [13, 14], and in the field of photovoltaic technology is used as

a sensor [15]. This research aimed to study the effect of adding coumarin dye on physical properties of polycarbonate.

2- Theoretical Part

In optical applications such as optical fiber, reflective coatings and interference filters, the use of materials in these applications requires precise knowledge of their optical constants and over a large range of wavelengths. All materials may be related to their atomic composition in the optical, electrical and electronic properties. Employ eq.(1) practically the absorption coefficient factor known as the function of the wavelength of the vector can be calculated from optical absorbance spectra [16].

$$\log (I/ I_0) = 2.303\, A = \alpha\, d \qquad (1)$$

Absorbance is defined A=log(I/ I_0) , α is the optical absorbance, and d is the film thickness, I and I_0 are the intensities of the incident and transmitted beams, respectively.

From eq.(2) The extinction coefficient which symbolizes the K is related to the absorption coefficient α [17]:

$$k = \alpha\lambda/4\pi \qquad (2)$$

The wavelength of light is λ.

From eq.(3) can be calculated the transmission coefficient [18]:

$$T = \exp[-2.303A] \qquad (3)$$

From the values of absorbance and transmission coefficient can be obtained the Reflection by the eq. (4) [18]:

$$R = 1 - (A + T) \qquad (4)$$

From the reflection coefficient data R and the extinction coefficient K can be determined the refractive index by eq. (5) [19].

$$n = \sqrt{\frac{4R}{(R-1)^2} - K^2} - \frac{(R+1)}{(R-1)} \qquad (5)$$

It can be obtained the absorption edge for direct and indirect transitions from eq.(6) [20]:

$$\alpha h \upsilon = C_o (h \upsilon - E_g^{opt.})^n \quad (6)$$

where C_o is an energy - independent linked to the properties of the conduction and valance bands , h υ is known as the photon energy, where α is a absorption coefficient, (E_g^{opt}) is known the optical energy band gap for material , and n = 1/2 , 3/2 , or 3 for direct allowed and forbidden, indirect allowed and forbidden transitions, respectively .

A part of (α h υ)$^{1/n}$ contra (h υ) yields often a reasonably kindly straight line fit to the absorption edge and the extrapolated (h υ) that (α h υ) $^{1/n}$ = 0 provides a good experimental standard for the optical band gap ($E_g^{opt.}$) . The absorption coefficient (α (υ)) near the band edge shows an exponential dependence on photon energy (h υ) [20]:

$$\alpha(\upsilon) = \alpha_\circ \exp (h \upsilon / Et) \quad (7)$$

α_0 is constant and E_t is concerning to the width of the band tails of localized states in the forbidden band gap . It is worth noting that this eq. does not apply in any area is applicable only in the absorption region except the absorption region (α=10^3 - 10^4 cm^{-1}).

It can calculate the dielectric constant by real and imaginary (ε_r and ε_i), respectively [21]:

$$N^* = n - I k \quad (8)$$

$$\varepsilon^* = \varepsilon_r - i \varepsilon_i \quad (9)$$

Where N* is the complex refractive index and (ε*) is the complex dielectric constant. Through the relationship N=$\sqrt{\varepsilon^*}$, there are so:

$$(n - i k)^2 = \varepsilon_r - \varepsilon_i \quad (10)$$

$$\varepsilon_r = n^2 - k^2 \quad (11)$$

$$\varepsilon_i = 2 n k \quad (12)$$

3- Experimental work

The process of casting was done to prepare a polycarbonate film made from the company (Sabic) and the coumarin dye made from company (SIGMA-ALDRICH CHEMIE, Germany). Polycarbonate and coumarin dye were dissolved in the Chloroform solvent. The amount of polycarbonate used in this work is (0.5g) dissolved in (10ml) chloroform and then put it on hotplate magnetic stirrer to shake well, and then pour into glass petri dish then put it in the oven for 24 hours, in order to get homogeneous films.

Dye solution has been prepared with different concentrations and this achieved by dissolving certain amount of dye in certain volume of solvent used in the preparation of the solution and the material is weighted according to the following relationship [22]

$$\mathbf{m} = \frac{\mathbf{M_W \times V \times C}}{\mathbf{1000}}. \qquad (13)$$

Where m: the amount of coumarin dye (g), M_W: Molecular weight of the coumarin dye (g /mol) ,V: the volume of the solvent and it is measured in unity (ml), C: the coumarin dye concentration (mol/liter). Concentrations were attended for Coumarin: $1x10^{-5}$ (mol/liter). Different volume ratio from this dye solution in chloroform was chosen: (4 - 40) ml with increment 4ml to add to polymer solution. The dye doped polymer films were cast by allowing the mixed dye solution with polymer solution on hot plate magnetic stirrer to shake well and then pour into glass petri dish and put it in the oven for 24 hours. After these processes, homogeneous dye doped polymer films were obtained. Absorption and transmission spectra can be measured by using UV – Visible spectrophotometer, type (T70/ T80 Spectrophotometer).

4- Results and Discussions

The absorption spectrum for pure polycarbonate is shown in the Fig. (3), and absorption data are illustrated in table (1). The absorption spectrum for polycarbonate contains wide band with two clear peaks: at wavelength (305nm) with intensity (0.7) be the first peak, and the second peak at wavelength (345nm) with intensity (0.69).The different between two peaks is

(40nm) which refers to the same formation origin so these two peaks are due to the n→π* and π→π* transitions of the carbonyl group that matched with ref. [23].

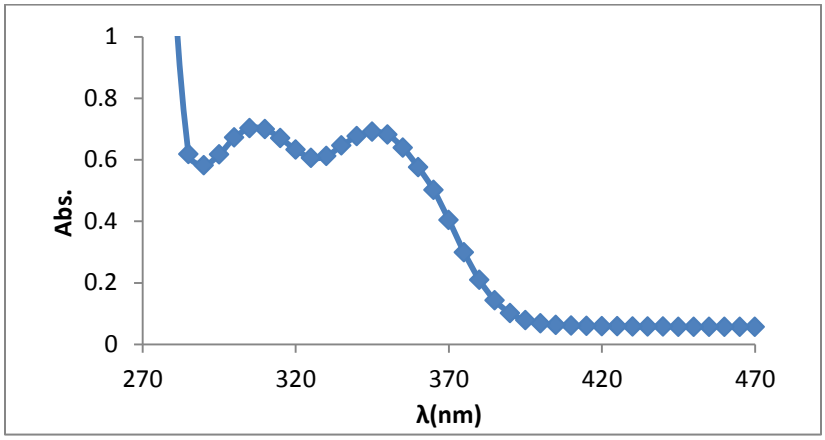

Fig. (3) Absorption spectrum of pure polycarbonate film

The absorption spectrum of coumarin in chloroform solution with concentration $1x10^{-5}$ mol/liter is shown in Fig. (4). The absorption spectrum of Coumarin has broad band with two peaks. First peak at (275) nm with intensity (0.12), second peak at (315) nm with intensity (0.064).The separation between two bands is (40) nm. The electronic transitions corresponding for these bands are n–π* and π-π*. Both transitions are typical for basic coumarin structure and are related to the charge transfer from the benzenic cycle to the pyranone, is agree with research [24].

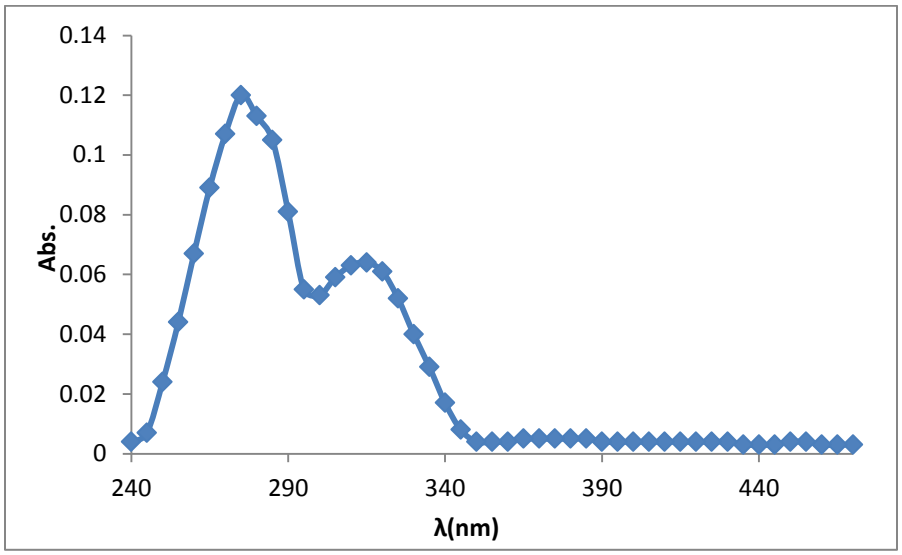

Fig. (4) Absorption spectrum of Coumarin dye solution in chloroform

The UV-VIS spectrum shows the absorption of pure polycarbonate film and polycarbonate with a different volume ratio of coumarin (4 - 40 ml) in fig. (5) along the wavelength length (270-470) nm. The maximum wavelength for the two peaks of PC-C with all volume ratio is at (305) and (345) nm, respectively, this indicated that polymer PC has the dominant role in this mixture process. The increase in the volume ratio of coumarin dye led to unevenly increase. Maximum intensity for these two peaks happened in the volume ratio (28 ml) of coumarin dye solution, this explained that increase absorbance of film. Whereas any additional increase in volume ratio of dye solution led to decrease in absorbance of these two peaks. This is explained to formation of aggregates of coumarin molecules such as dimmer and trimer as mentioned in ref. [25].

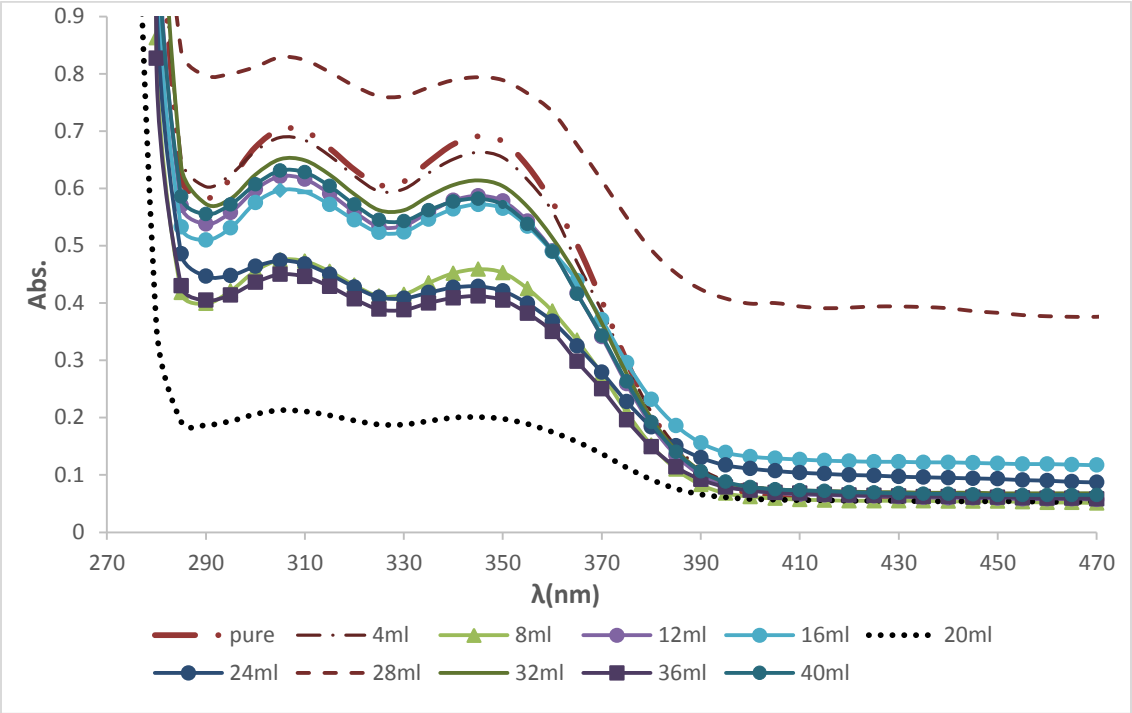

Fig. (5) Absorption spectra of pure polycarbonate film and Polycarbonate with different volume ratio of coumarin dye.

The spectral transmittance for pure PC and coumarin dye mixture PC films for different volume ratios (4-40ml) are shown in the fig. (6).It is obvious that behavior of the transmission spectrum of pure PC and coumarin dye mixture PC films for different mixture ratio of coumarin dye are opposite to that of the absorption spectra. In the sense The maximum intensity appeared in the volume ratio (20) ml at (305) and (345) nm, the minimum intensity appeared in the volume ratio (28) ml at (305) and (345)nm .

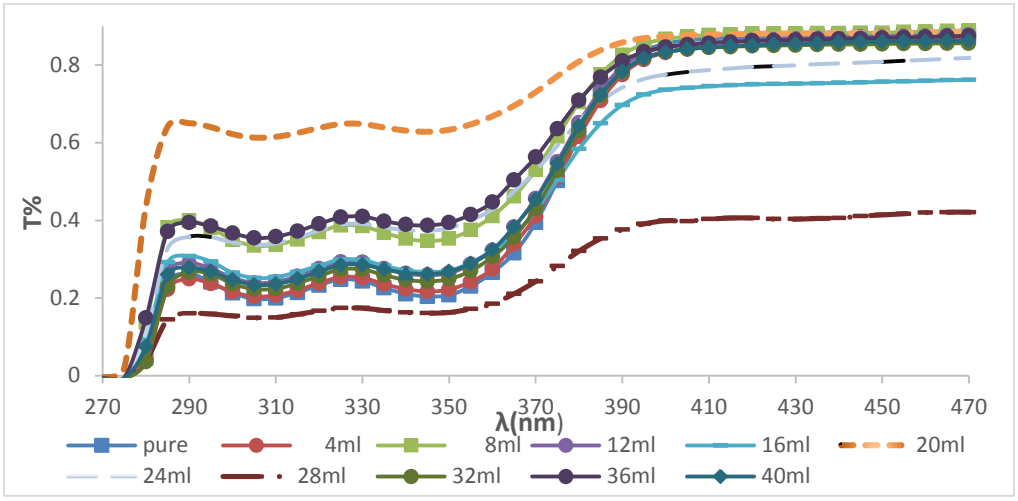

Fig. (6) Transmittance spectra of pure polycarbonate film and Polycarbonate with different volume ratio of coumarin dye.

For pure PC polymer and PC-C films; the Reflection spectra for different volume ratio are illustrated in fig.(7), R can be calculated from absorption and transmission spectrum according to eq. (4).The best reflectance which be obtained from this work in doping ratio (36ml) and(28ml). While all reflectivity peaks for other films is a slight change, which is a little reflection and then show the peaks of reflection is clear and that the increase of access is due to decreased reflection of the surface of the films according to eq. (4).

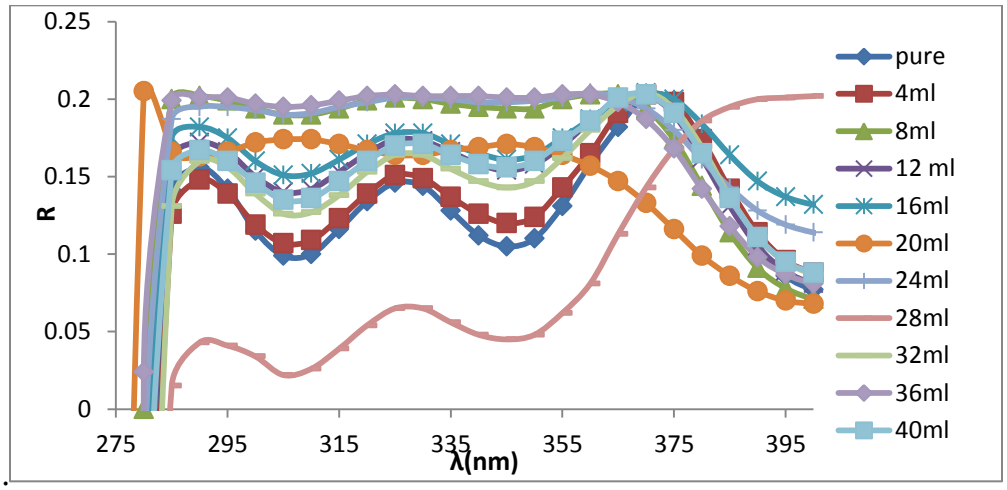

Fig. (7) Reflection spectra of pure polycarbonate film and Polycarbonate with different volume ratio of coumarin dye.

Absorption coefficient (α) can be defined as the ability of material to attenuate the light of a given wavelength per unit length. The value of (α) is calculated from eq. (1) for all samples (4-40) ml. The (α) for pure PC polymer and PC-C films for different doping ratio illustrated in Fig. (8). To deduce the nature of electronic transitions, the absorption coefficient can be used to known that. When the high absorption coefficient values ($\alpha > 10^4$ cm^{-1}) at higher energies their called direct electronic transitions, and the energy and momentum protect of the electron and photon. Whereas the values of absorption coefficient is low ($\alpha < 10^4$ cm^{-1}) at low energies there is called indirect electronic transitions, and the energy and momentum protect of the electron and photon by phonon helps. The value of α for all samples less than ($10^4 cm^{-1}$), so which means the indirect electronic transitions will be deduced [2ٔ].

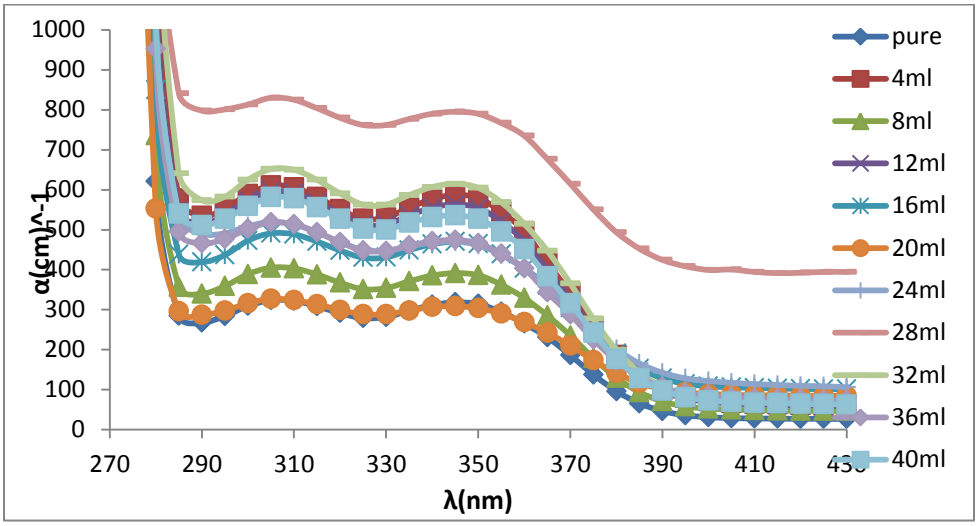

Fig. (8) The absorption coefficient (α) spectra of pure polycarbonate film and Polycarbonate with different volume ratio of coumarin dye.

The extinction coefficient can be calculated by eq. (2) in Fig. (9). The variation of extinction coefficient (k) values in wavelength range (270-470) nm for pure PC film and PC-C films in different volume ratio of coumarin dye. All curves for (k) is similar to absorption spectrum and the same absorption behavior because of their association with the same relationship. So the extinction coefficient depends on absorbance. Addition volume ratio of

coumarin dye (4-40) ml lead to the increase and decrease in extinction and absorbance coefficient.

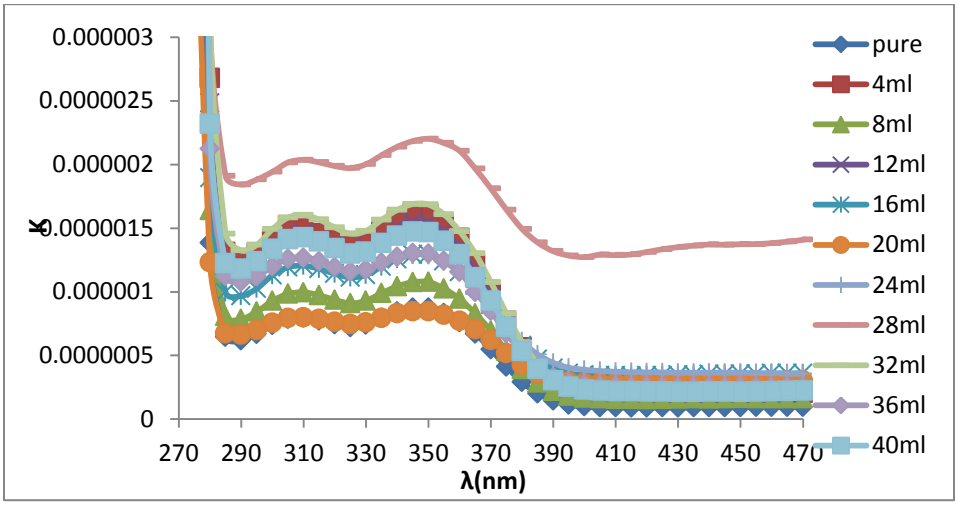

Fig. (9) The extinction coefficient spectra of pure polycarbonate film and Polycarbonate with different volume ratio of coumarin dye.

In Fig. (10) shows behavior of the refractive index for pure PC polymer and PC-C. The refraction index (n) It is related to transmittance and extinction coefficient by eq.(5). So that, the behavior of refractive index similar to behavior of reflection and extinction spectrum.

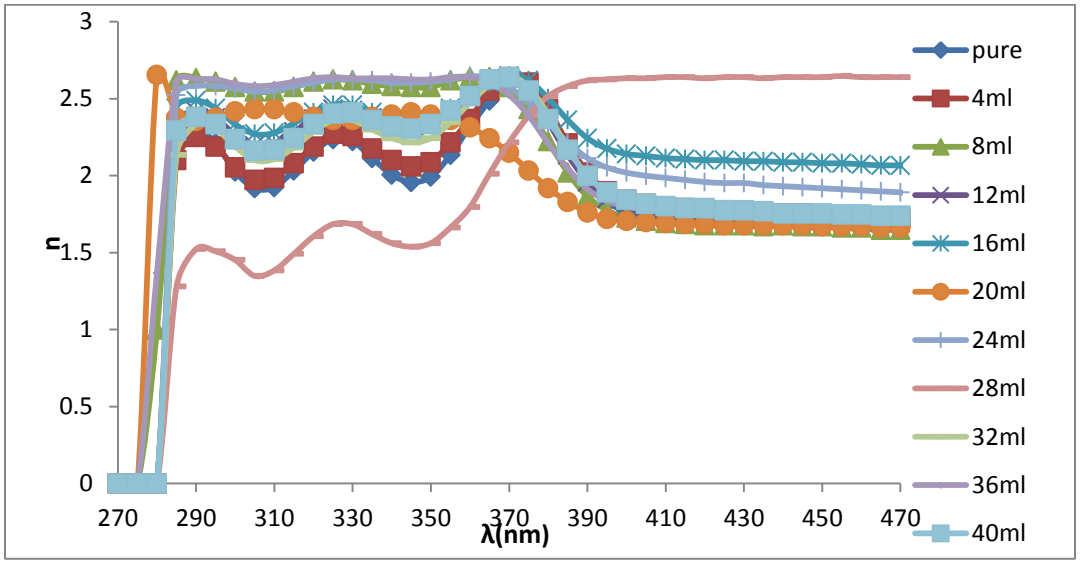

Fig. (10) The refractive index (n) spectra of pure polycarbonate film and Polycarbonate with different volume ratio of coumarin dye.

Transmission and refraction give the way to determine the dielectric constants, so the optical constant are very advantageous for the quantitative determine of the electronic band structure of solids from information of optical reflectivity. From eqs. (11) and (12) the real and imaginary parts of dielectric constants can be determine . Fig. (11) the real part of dielectric for pure Pc film and PC-C films in different doping ratio(4-40ml). For PC polymer, real dielectric constant increases to be maximum at wavelength (270) nm with increasing wavelengths, whereas the effect of addition coumarin dye will increase the real part of dielectric constant depends on the square of refractive index (n_2) because of small values of (k_2), so that the behavior of these figure are similar to refraction index. Imaginary part of dielectric constants for pure PC polymer and PC-C films in different doping ratio (4-40) ml are shown in Fig. (12). Imaginary dielectric constant for pure PC film increased with increasing wavelength, also as the real part, then ε_i depends on the (k) values which are related to the variation of (α) . The real part is higher than the imaginary part.

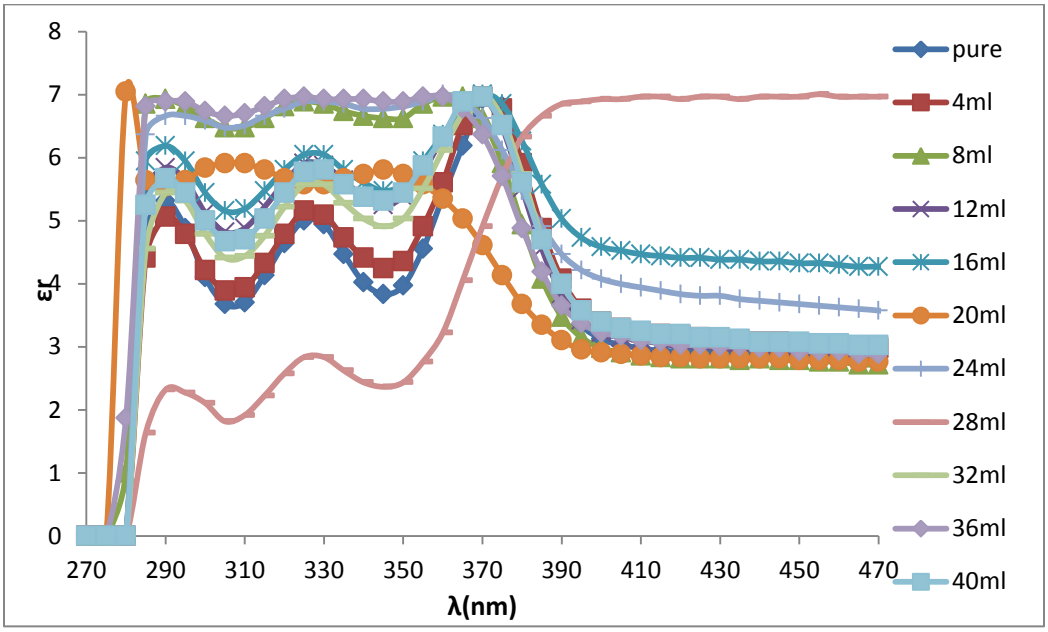

Fig. (11) real part of dielectric constants spectra of pure PC film and PC-C with different volume ratio of coumarin dye.

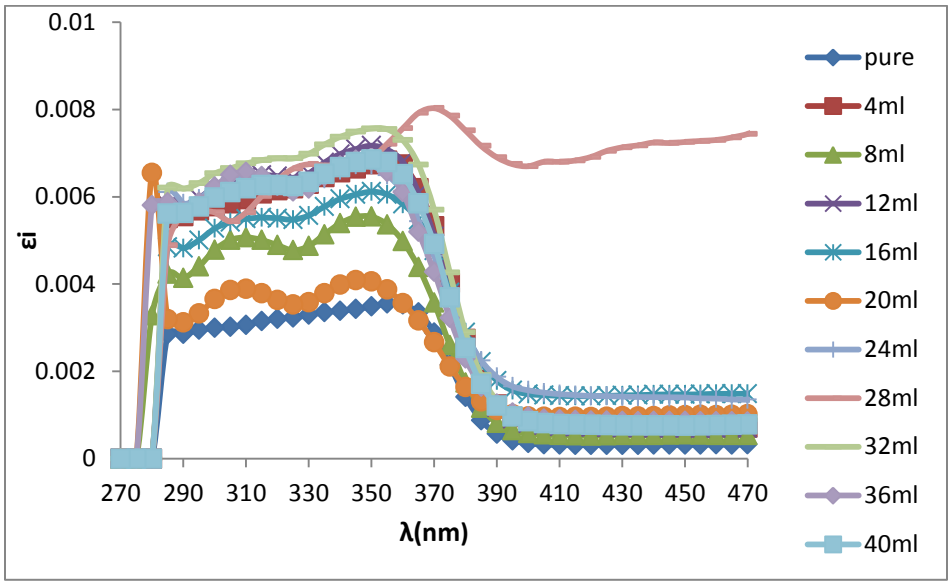

Fig. (12) Imaginary part of dielectric constants spectra of pure polycarbonate film and Polycarbonate with different volume ratio of

The optical band gap is necessary to develop the electronic band structure of film material. It can be get by planning $(\alpha\ h\ \nu)^{1/2}$ against (h ν) in the high absorption range followed by extrapolating the linear region of the plots to (αhν)=0 [17].The indirect transition will happened at r=2 From Fig. (13) and table (1) in the value of absorption coefficient of pure PC and coumarin dye mixture PC films, the E_g for pure PC film can be measured and its equal (4.24)eV. The indirect transition from the value of absorption coefficient can be calculated. Coumarin solution has energy band gap is (4.08) eV calculated from fig. (14). This is ascribed to increase in absorption coefficient as a result of introducing dopant atoms and hence E_g will be decreasing.

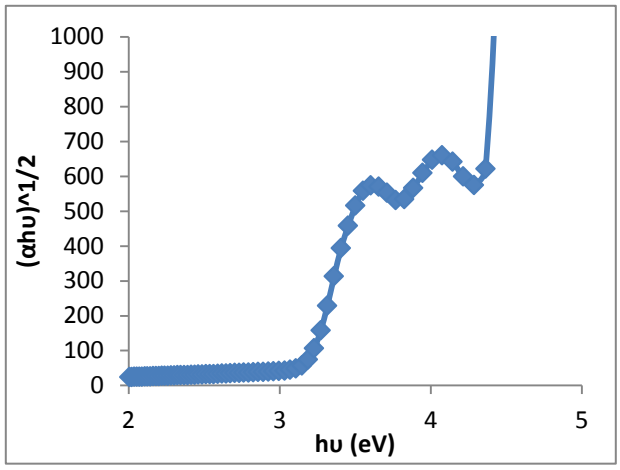

Fig.(13)Energy gap for pure PC film

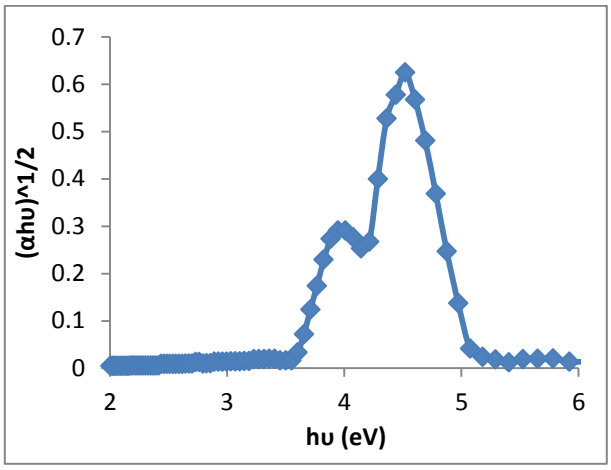

Fig.(14) Energy gap for coumarin dye

In fig. (15) for all samples (4-40)ml can be measure the energy band gap when coumarin dye added to PC with different volume ratio of dye. Note from the table(1), that the energy gap before adding the dye was (4.24eV) and after the addition of the dye was observed the maximum energy gap in volume ratio(4ml) is (4.26eV) and then begin to decrease this behavior is attribute to form a new levels between conduction and valance bands. So its drove to expedite the passage of electrons from the valence to the conduction band. It can also be attributed to the fact that coumarin dye affects the behavior of electrons within polycarbonate, which affects the way that atoms are arranged within the crystal lattice. If the coumarin can change the polymer from crystalline to random, so some of the free local levels of electrons will also change. As for the film that do not have a change, their molecules are stable and there will be no change in the energy gap when the coumarin dye is added to it, As shown in the table(1).

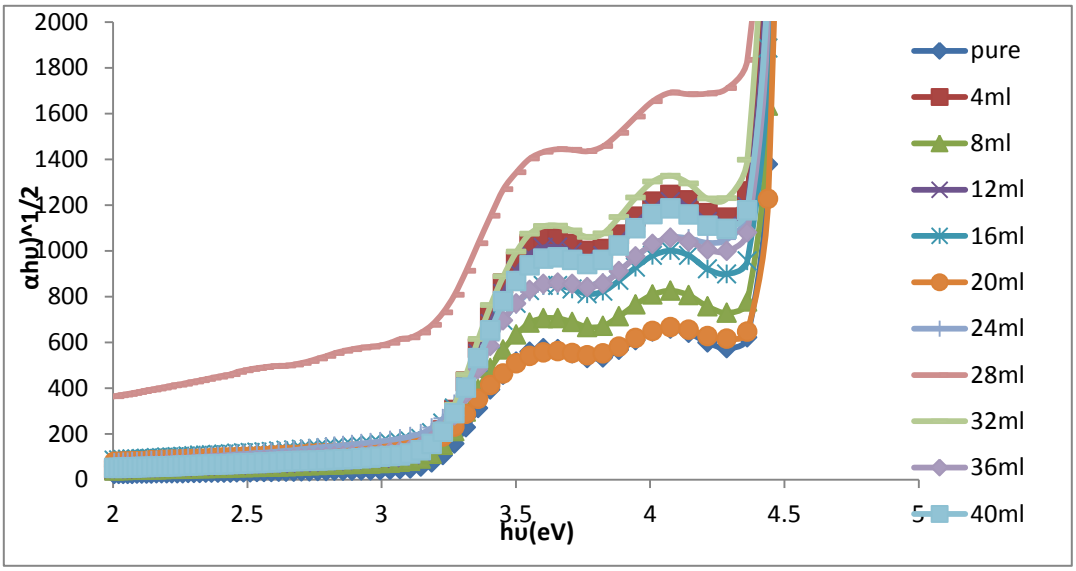

Fig. (15) Energy gap for pure PC and PC with different volume ratio of coumarin dye.

Table (1) Absorption information for pure PC, Pure Coumarin dye and (PC-C)

Sample	λ_{m1} (nm)	Abs.$_1$	λ_{m2} (nm)	Abs.$_2$	Energy gap(eV)
Pure PC	305	0.691	345	0.7	4.24
Pure Coumarin	275	0.12	315	0.064	4.08
Pc+4ml C	305	0.68	345	0.66	4.26
Pc+8 ml C	305	0.475	345	0.459	4.24
Pc+ 12ml C	305	0.621	345	0.587	4.24
Pc+16 ml C	305	0.597	345	0.572	4.25
Pc+20 ml C	305	0.213	345	0.201	4.23
Pc+24 ml C	305	0.474	345	0.429	4.22
Pc+28ml C	305	0.829	345	0.794	4.18
Pc+32ml C	305	0.651	345	0.614	4.24
Pc+36ml C	310	0.44	345	0.412	4.24
Pc+40 ml C	305	0.631	345	0.582	4.23

5- Conclusions

The effect of adding volume ratio of coumarin dye solution on optical properties of polycarbonate showed that variable changes in maximum absorbance with increasing volume ratio of dye solution. While, the maximum wavelength of two peaks don't change and the polycarbonate is the dominant material after mixing. Also, the value of energy gap after mixing has slightly changed from the value of energy gap of Polycarbonate. So that, coumarin dye doesn't have great effect on polymer.

6- References

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