

Effect of Doping Ratios of Rhodamine6G Dye on Optical Properties and FT-IR Spectroscopy of Polyvinyl Acetate Polymer

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Abstract

Optical properties such as absorption coefficient, refractive index, and extinction coefficients of pure polyvinylacetate (PVAc) and Rhodamine6G (Rh6G) laser dye doped with PVAc thin films where prepared using casting method, in order to study the effect of Rhodamine 6G additions on the optical properties of (PVAc) hosts.

These films were described using UV/VIS technique in order to assessment the type of transition which was found to be indirect transition.

Fourier Transform infrared (FT-IR) spectroscopy was used to identify the effect of (Rh6G) on the characteristic functional groups of PVAc.

Key Words: Optical properties, Rhodamine 6G, Polyvinyl acetate, Effect of Doping ratio.

تأثير نسب التطعيم لصبغة Rhodamine6G على الخواص البصرية والطيف FT-IR لبوليمر خلات البولي فينيل

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الخلاصة

الخواص البصرية مثل معامل الامتصاص، ومعامل الانكسار، ومعامل الخمود لافلام من بوليمر خلات البولي فينيل النقي (PVAc) والمطعمه بالصبغة الليزرية (Rhodamine6G (Rh6G) عند تحضيرها باستخدام طريقة الصب ، من أجل البحث في تأثير إضافات Rhodamine6G على خصائص البوليمر (PVAc). تم وصف هذه الأفلام باستخدام تقنية UV / VIS من أجل تقييم نوع الانتقال الذي وجد أنه انتقال غير مباشر.

تم استخدام مطياف فوريير لتحويل الأشعة تحت الحمراء (FT-IR) لتحديد تأثير (Rh6G) على المجموعات الوظيفية المميزة لـ PVAc .

1. Introduction

Generally, polyvinyl acetate (PVAc) is a thermoplastic polymer with chemical formula $(C_4H_6O_2)_n$. It is synthesized by the monomer of vinyl acetate (VAc) in the mixture of polyvinyl alcohol (PVA) as protective colloid, non-ion emulsifier, initiator, and water [1].

(PVAc) is a synthetic resin polymer, which, due its non-polar nature, is insoluble in water, oil, fats or gasoline. On the other hand, it is soluble in alcohols, ketones and esters [2].

It has many characteristics, being non-poisonous, non-harmful, easily produced, low price, convenient in application, economizing resources, etc. Because of these reasons, PVAc is widely applied in bonding of many porous materials, such as wood processing, furniture packaging, building decoration, texture bonding, and print bonding.

Lasing dyes are generally defined as substances capable of emitting light when stimulated and typically have, as their lasing media, dye compounds composed of conjugated double bonds [3].

Xanthene dyes are those containing the xanthylium as chromophore with amino or hydroxy groups meta to the oxygen as the usual auxochromes. Rhodamines are commercially the most important amino xanthenes. The organic dye laser has found many applications in scientific research because of its unusual flexibility [4].

Many experimental and theoretical works concerning the spectral properties of xanthene dyes were done because of their great promising results in solar concentration and nonlinear optics device applications.

There are large amount of data about laser dyes from many authors, Alaverdyan¹ R. B. and co-workers studied Luminescence spectrum thermal properties of Rhodamine 6G doped Polymethyl methacrylate film sandwiched between cholesteric liquid crystal layers [5].

Kailasnath M. and co-workers studied the energy transfer and optical gain studies of FDS: Rhodamine B dye mixture investigated under CW laser excitation [6]. Bahattab M. A. and co-workers studied Photostabilty of Liquid Mixture Based on Rhodamine 590 dye in Vinyl Acetate Polymer Solution [7]. Ali B. R. studied the energy transfer in dye laser mixture (1-Fluorescien+1-Rh 6G) [8], Ali H. Al-Hamdani study the spectroscopic properties for Rhodamine 3GO [9], Rhodamine B [10] dissolved in chloroform, Fluorescein Sodium dye in Ethanol

[11], mixture of Rh6G and Rc dissolved in chloroform [12] and Rh6G doped PMMA [13].

Fourier Transform Infrared Spectroscopy (FTIR) provides specific information about chemical bonding and molecular structures, making it useful for analyzing organic materials and certain inorganic materials. Chemical bonds vibrate at characteristic frequencies, and when exposed to infrared radiation, they absorb the radiation at frequencies that match their vibration modes.

Infrared spectroscopy focuses mainly on the vibrational- rotational absorption bands occurring between $(4000- 400) \text{ cm}^{-1}$, [14, 15 and 16].

The aim of the present work is to concern with the investigation the optical properties of pure PVAc and doping PVAc with Rh6G with different doping ratio (5, 10, 15 and 25) ml.

The relationship between the intensity of incident and transmitted light is given by the equation (1) [17]:

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

Where(I_0) and(I) are the intensity of the incident and transmitted light respectively, (α) is the optical absorption coefficient, and(t) is the thickness of film and absorbance is defined by $A = \log (I_0/I)$.

The optical absorption coefficient (α) can be calculated from the optical absorbance spectra by using the relation (2) [17]:

$$\alpha = 2.303A/t \dots \dots \dots (2)$$

The extinction coefficient (K) is related to absorption coefficient (α), by the following equation [18]:

$$K = \frac{\alpha \lambda}{4\pi} \dots \dots \dots (3)$$

Where, λ is the wavelength of incident light.

The reflectance (R) can be calculated from the values of the absorbance and transmission coefficient from the equation:

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

The refractive index (n) depended on the reflectance (R) and extinction coefficient (K) and can be calculated from the following equation [19]:

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

The absorption edge for direct and indirect transition can be obtained in the view of the proposed by Tauc et al. [20]

$$\alpha h\nu = A(h\nu - E_g)^r \dots\dots\dots (6)$$

Where (h v) is the energy of photon, (A) is the proportional constant, (E_g) is the allowed or forbidden energy gap of direct and indirect transition and (r) is constant depended on the electronic transition, r = 1/2, 3/2, 2 or 3 for allow direct, forbidden direct, allow indirect and forbidden indirect transition respectively.

The Dielectric constant clarified the ability of material to polarization and can be express by the following equation:

$$\epsilon = \epsilon_r - \epsilon_i \dots\dots\dots (7)$$

The dielectric constant is divided into two parts real (ε_r) and imaginary (ε_i). They were described by the following equations:

$$\epsilon_r = n^2 - K^2 \dots\dots\dots (8)$$

$$\epsilon_i = 2nK \dots\dots\dots (9)$$

2. Experimental Work

Polyvinyl acetate (PVAc) used in this study was obtained from Sigma, Aldrich (Germany) and were reported to have molecular weights of 167000 g.mol⁻¹. Chloroform has purity 99.8% (HPLC) and was used as a common solvent for both PVAc and Rh6G.

Rhodamine 6G perchlorate from Exciton was prepared in chloroform solvent with different concentrations.

The cast technique was used to prepare the pure PVAc and Rh6G doping PVAc films. PVAc solution is prepared by dissolved (0.5g) of PVAc in (10 ml) chloroform. The PVAc solution is stirred very well at magnetic stirrer until polymer is dissolve and cast on to glass petri dish with diameter (10 cm) and then leave it dry at room temperature about (25-30) °C for 24hr. Dye solution (Rh6G) with concentration (1x10⁻⁵ mole/liter) 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

$$m = C V M_w \dots\dots\dots (10)$$

Where:

m: is the weight of the dye needed to obtain the desired concentration.

C: is the required concentration of the dye.

V: is the volume of solvent for the dye.

M_w : is the molecular weight of the dye.

Then, different ratio of Rh6G solution (5, 10, 15, and 25) ml were added to PVAc solution and mixed very well by use magnetic stirrer. The mixture cast on to glass petri dish with (10 cm) diameter and left to dry at room temperature for 24hr to get homogeneous films. The UV-Visible spectrophotometer type (T70/T80 Series UV/VIS Spectrometer) used to measure the absorption and transmission spectra in the wavelength range (200-900) nm.

FT-IR spectra were measured with a Fourier Transform Infrared Spectrometer (FT/IR – 460 plus) in the wave number range (400–4000) cm^{-1} .

3. Results and Discussions

3.1 Absorption Spectrum of Rhodamine 6G in Chloroform Solution:

Figure (1) show the relationship between absorbance versus wavelength with range of (200-800) nm at room temperature for Rhodamine6G (Rh6G). There are four peaks that can see for Rhodamine6G one at about (235-270) nm related to $\pi-\pi^*$. While the other is located at about (270-325) nm, (325-380) nm, and (450-580) nm. The maximum peak at (535) nm.

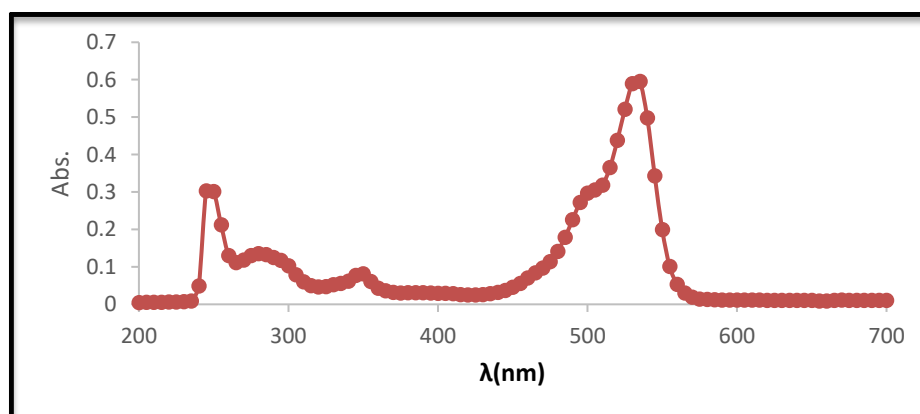


Figure (1) Absorption spectrum of Rhodamin6G with concentration (1×10^{-5} mol/liter)

3.2 Absorption Spectrum of Polyvinylacetate PVAc Polymer:

The absorption spectrum for PVAc polymer films show in figure (2). Polyvinylacetate, containing a phenyl ring in each repeat unit, absorbs

strongly over the (260-300) nm range (max 280 nm). These results are in good agreement with B. Jaleh, et al [21].

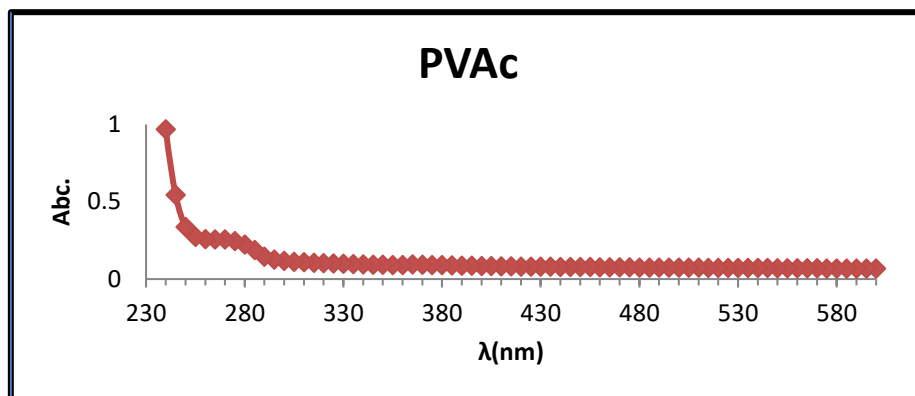


Figure (2) Absorption spectrum for polyvinylacetate (PVAc)

3.3 Absorption Spectrum of Rhodamine 6G Doping PVAc Polymer Films:

Figure (3) shows that the absorption spectrum to the polymer polyvinylacetate and its doping with different ratios of dye Rhodamine 6G (Rh6G) thick films respectively. There are three peaks that can be observed for all doping ratios, the first one at (270-300) nm related π - π^* while the other peaks are located at about (335-370) nm and (480-580) nm related to Rhodamine6G. From the table (1) we can see that absorption increase with increasing doping ratios of polymer doped with Rhodamin6G.

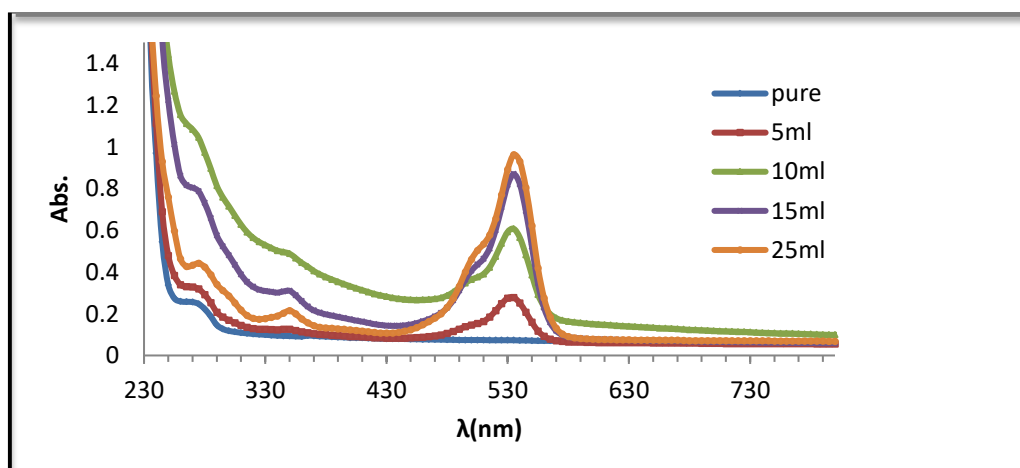


Figure (3) Absorption spectrum for different doping ratios of Polyvinyl acetate (PVAc) with Rhodamine6G

Table (1) The absorption and wavelength for different doping ratios of Polyvinylacetate (PVAc) with Rhodamine6G

	PVAc pure	(PVAc +5ml Rh6G)	(PVAc +10m Rh6G)	(PVAc +15ml Rh6G)	(PVAc +25ml Rh6G)
λ_{max}	275	275	275	275	275
Abs	0.247	0.319	1.083	0.787	0.442
λ_{max}		505	500	505	505
Abs		0.153	0.406	0.503	0.533
λ_{max}	535	535	535	535	535
Abs	0.073	0.278	0.607	0.869	0.962

3.4 Transmission Spectrum:

Figure (4) shows an optical transmittance spectrum as a function of incident wavelength on polyvinylacetate (PVAc) doped Rhodamine6G films. The transmittance obvious that behavior of the transmission spectrum of pure polyvinylacetate (PVAc) and different doping ratios films are opposite to that of the absorption spectra.

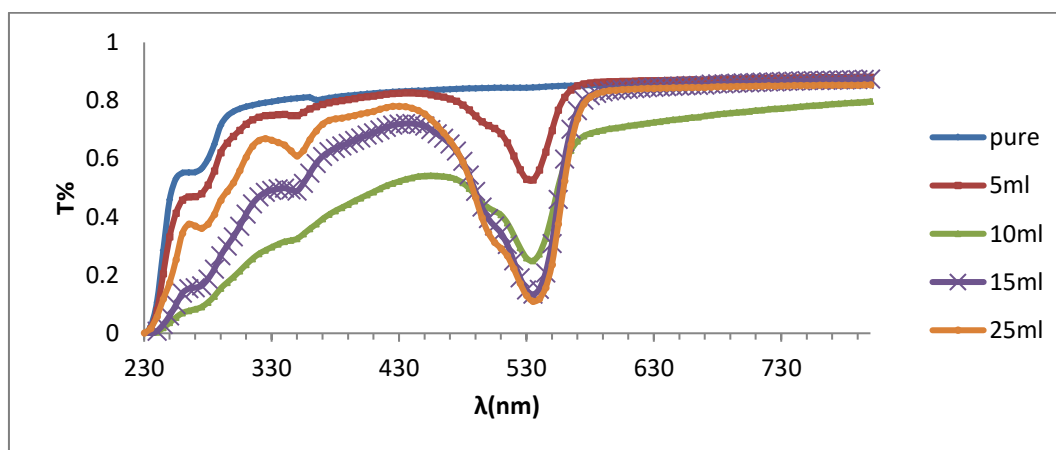


Figure (4) Transmission spectrum for different doping ratios of polyvinylacetate (PVAc) with Rhodamine6G

3.5 Reflection Spectrum

Reflection spectrum is calculated from absorption and transmission spectrum according to equation (4). The reflection spectrum of pure polyvinylacetate (PVAc) and different doping ratios are shown in figure (5). Increase the doping ratios of polymer polyvinylacetate with

Rhodamine6G lead to increase the reflection. The reflectance (R) can be calculated from the values of the absorbance and transmission coefficient from equation (4).

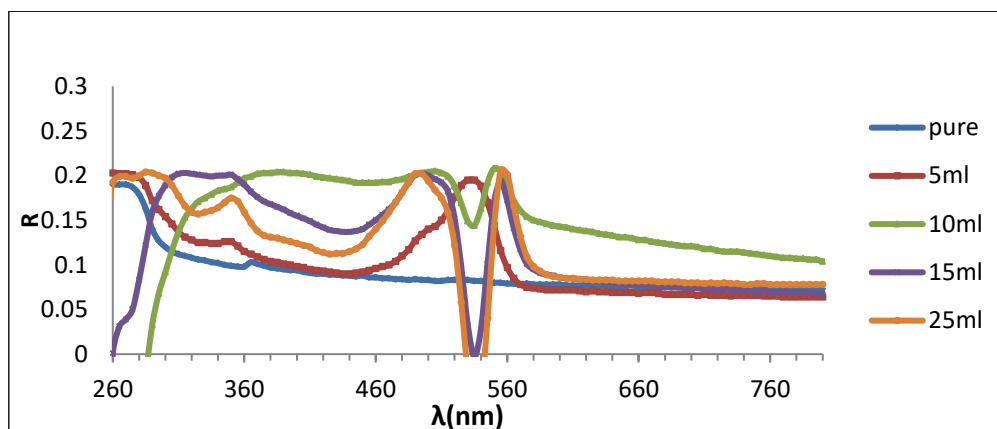


Figure (5) Reflectance spectrum for different doping ratios of polyvinylacetate (PVAc) with Rhodamine6G

3. 6 Absorption Coefficient:

The value of absorption coefficient less than 10^4 cm^{-1} suggests the occurrence of vertical transition at fundamental absorption edge and is related to indirect transition according to equation (1).The absorption coefficient can be calculated by equation(2).

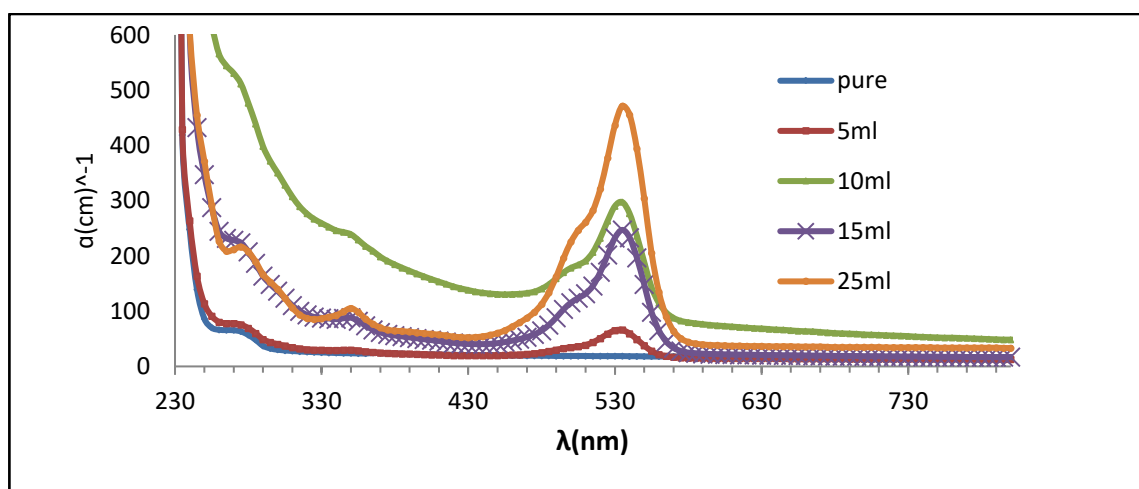


Figure (6) Absorption coefficient spectrum for different doping ratios of polyvinylacetate (PVAc) with Rhodamine6G

3.7 Optical Energy Gap:

According to equation the plot of $(\alpha h\nu)^{1/2}$ versus photon energy are shown in figures (7) from the figure, it can be noticed that the energy gap of the blend films decreases with increasing doping ratio. The value of indirect band gap energy with different doping ratio is tabulated in table (2).

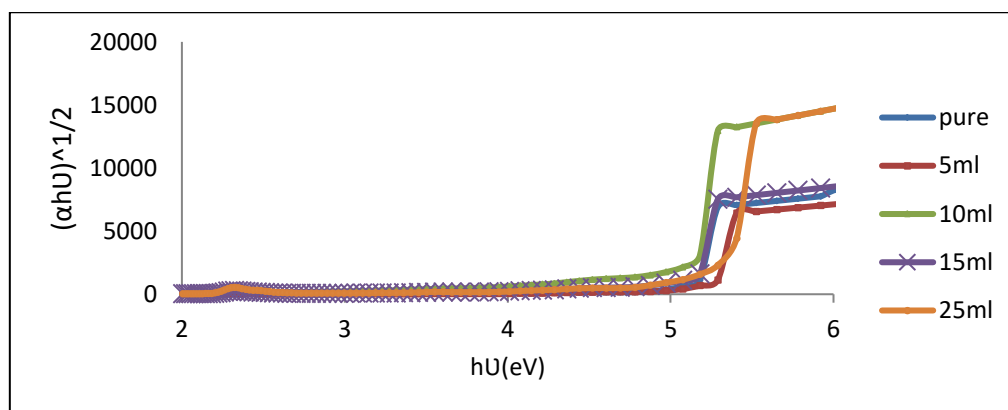


Figure (7) Optical energy gap for different doping ratios of polyvinylacetate (PVAc) with Rhodamine6G

Table (2) Indirect band gap energy (Eg) values for doping polyvinylacetate (PVAc) films with different doping ratios.

Doping ratios with Rh6G	Eg (eV)
(PVAc)	5.073
(PVAc)+5ml	4.875
(PVAc)+10ml	4.781
(PVAc)+15ml	4.691
(PVAc)+20ml	4.681
(PVAc)+25ml	4.604
(PVAc)+30ml	4.286

3. 8 Refractive Index:

The Refractive index (n) is important parameter. The Refractive index (n) of pure polyvinylacetate (PVAc) and different doping ratios with Rhodamine6G are shown in figure (8).The Refractive Index (n) is increased with increase the doping ratios. The refractive index n can be expressed by equation (5).

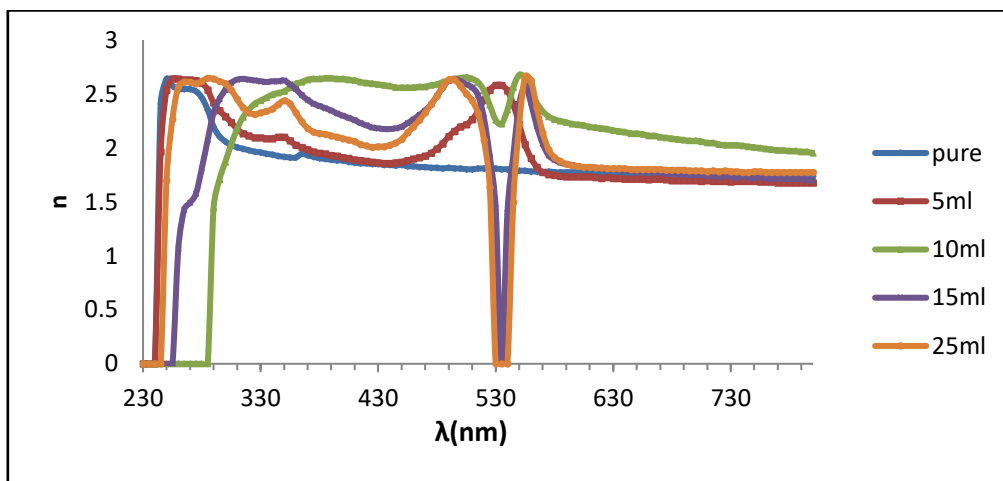


Figure (8) Refractive index spectrum for different doping ratios of polyvinylacetate (PVAc) with Rhodamine6G

3.9 Extinction Coefficient:

The extinction coefficient depended on absorbance and can be calculated by equation (6). The extinction coefficient of pure polyvinylacetate (PVAc) and different doping ratios with Rhodamine6G are shown in figure (9). The extinction coefficient increased with increase the doping ratios. The extinction coefficient can be calculated by equation (3).

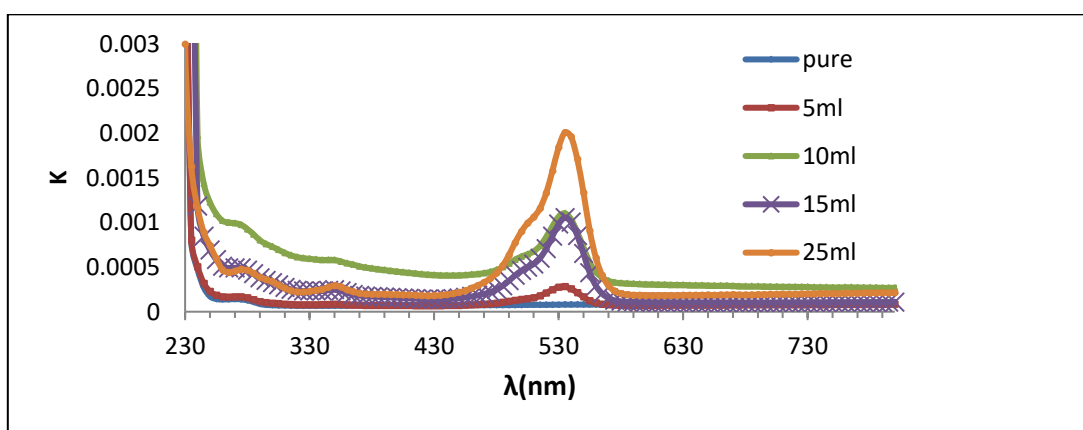


Figure (9) Extinction coefficient spectrum for different doping ratios of polyvinyl acetate (PVAc) with Rhodamine6G

3.10 Dielectric Constants:

Figure (10) illustrates the relation between real parts (ϵ_r) of real dielectric constant with wavelength for different doping ratios of polymer PVAc with Rh 6G. In the range of (250-600) nm the real part dielectric constant for polyvinylacetate (PVAc) is dependent on wavelength in this region which is corresponding to the high wavelength. The real part of dielectric constant was decreased sharply in the high wavelength greater then (590nm) for pure polyvinylacetate (PVAc) all different doping ratios. The real and imaginary complex dielectric constants can be expressed by equations (8) and (9), respectively.

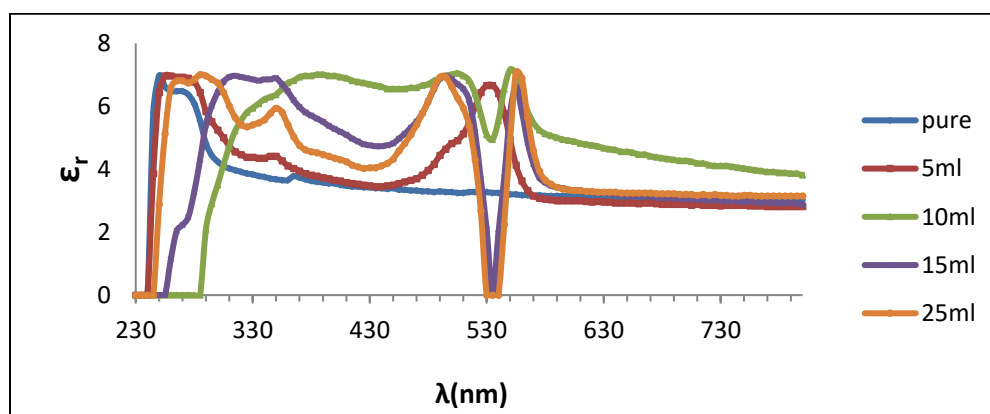


Figure (10) Real dielectric constant spectrum for different doping ratios of polyvinylacetate (PVAc) with Rhodamine6G

Figure (11) show the relation between imaginary part(ϵ_i)of dielectric constant with wavelength for pure polyvinylacetate(PVAc) and its doping with different ratios respectively its clear from the figure that the imaginary polyvinylacetate(PVAc) and all different doping ratios. Part is dependent on wavelength in range (260-580) nm for pure polyvinylacetate (PVAc) and for doping ratios. The imaginary part of dielectric constant was decreased sharply in high wavelength greater then (575nm) for pure.

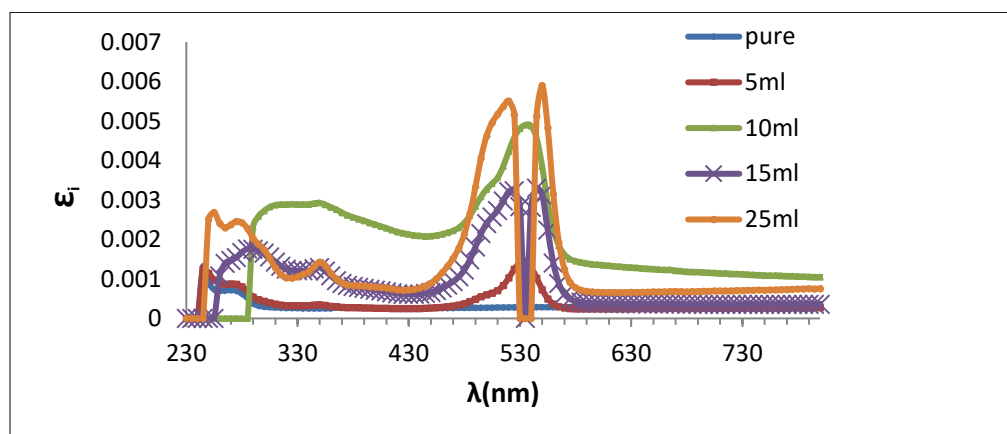


Figure (11) Imaginary dielectric constant spectrum for different doping ratios of polyvinylacetate (PVAc) with Rhodamine6G

3.12 FT-IR Characterization

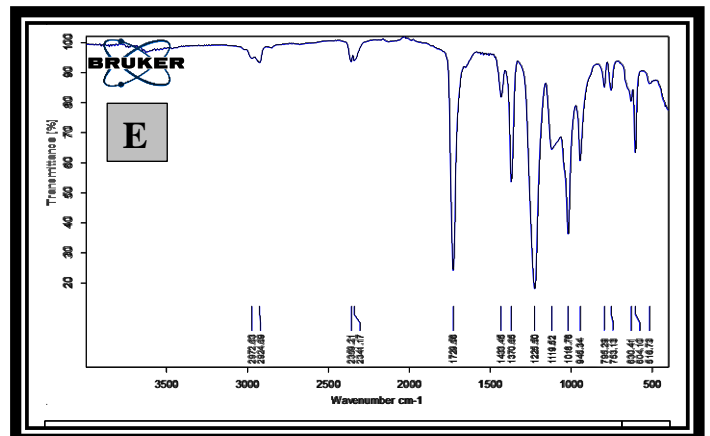
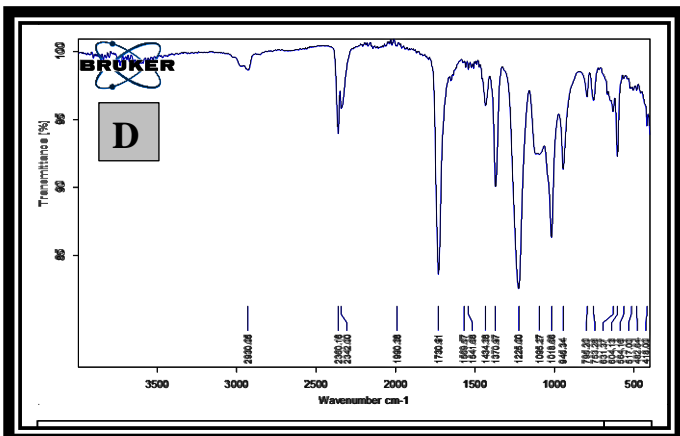
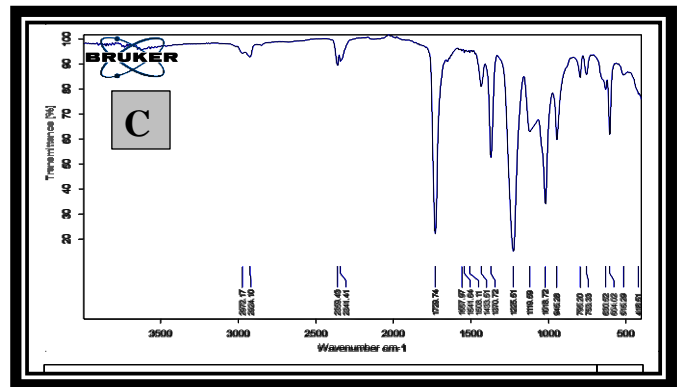
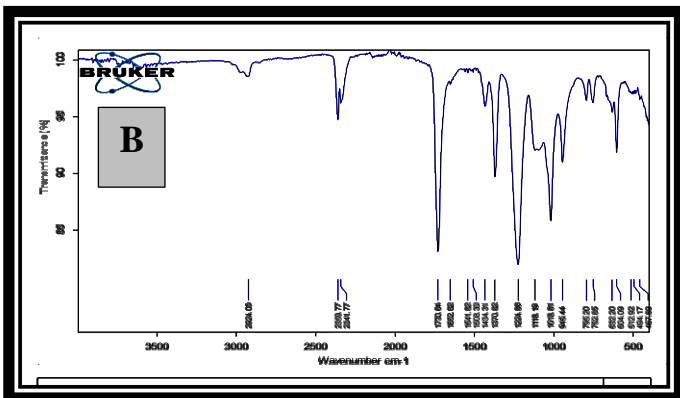
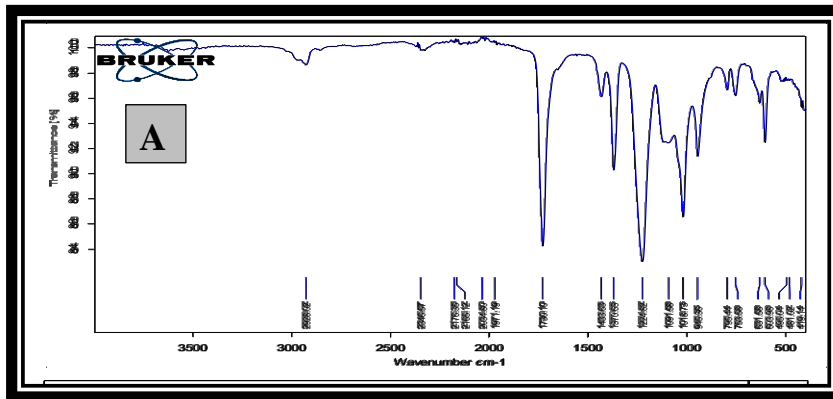
FTIR spectroscopy was used to discover the possible interaction between the functional groups of PVAc and Rhodamine6G (Rh6G) laser dye as shown in Fig (12).

Fig(12)give the characteriistics of FTIR spectra of pure PVAc. Many bands refer to the ring deformation vibration are observed at (631cm^{-1}). Also,the C-H deformation vibration band of benzene ring hydrogen's is apeared at(753.58cm^{-1}). The peaks at (1370.63cm^{-1})are assigned to CH_2 bending.While, the band(1730.10cm^{-1}) is to C=O stretch.The band at(2928.02cm^{-1})are corresponding to aliphatic C-H stretch Aliphatic .

The effect of the addition Rh6G dye to PVAc polymer on FTIR spectrum is shown in figs.(12-A,B,C,D,E)for different doping ratios(0,5,10,15,,25)ml there are two peaks(1557.98cm^{-1}) appeared in (10and25)ml and(2972.63cm^{-1})appeared in (15,25)ml refers to Rh6G dye and the other peaks as the same for pure PVAc polymer are tabulated in table (3).

Table(3) FTIR-characteristic of pure PVAc and all doping ratios with Rh6G

Bond	PVAc	PVAc +(5ml) Rh6G	PVAc +(10ml) Rh6G	PVAc +(15ml) Rh6G	PVAc +(25ml) Rh6G
C-H out phase bend (625-970)cm⁻¹	631.58	632.20	631.37	630.41	630.52
	753.58	752.85	753.28	753.13	753.33
	795.44	795.20	795.20	795.29	795.20
C-O stretch (880-1000) cm⁻¹	945.36	945.44	945.34	945.34	945.28
CH₂bending (1300-1380) cm⁻¹	1370.63	1370.82	1370.97	1370.65	1370.72
CH₂waggingC=C Stretch (1550-1610)cm⁻¹			1569.57		1557.97
C=O stretch (1550-1750) cm⁻¹	1730.10	1652.62 1730.64	1730.91	1729.56	1729.74
C-H stretch Aliphatic (2800-3000) cm⁻¹	2928.02	2924.03	2930.05	2924.69 2972.63	2924.10 2972.17
c-H stretch Aromatic (3000-3100)cm-1					



**Fig (12) FTIR Spectrum for PVAc and Doping Ratios of Rh6G
A-PVAc, B-5ml, C-10ml, D-15ml, E- 25ml**

Conclusions:

(PVAc) doped with Rhodamine 6G thin films have been prepared by cast method technique. The optical transmission spectrum is used to calculate the optical parameters:

- 1-** absorption coefficient, real and imaginary parts of dielectric constant where found to be increasing with increasing of doping ratios.
- 2-** the energy gap of indirect transition decreases with increasing doping ratios.
- 3-** The absorption intensity of PVAc is increase with increasing doping ratios of Rh6G.

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