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Spectral Properties of Hybrid of Rhodamine (6G) Dyes Doped Epoxy Resin Dissolved in Chloroform

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Abstract:

The research is dealing with the absorption and fluorescence spectra for the hybrid of an Epoxy Resin doped with organic dye Rhodamine (R6G) of different concentrations ($5*10^{-6}$, $5*10^{-5,}$ $1*10^{-5}$, $1*10^{-4}$, $5*10^{-4}$) Mol/ℓ at room temperature. The Quantum efficiency Q_{fm}, the rate of fluorescence emission K_{fm} (s^{-1}), the non-radiative lifetime τ_{fm} (s), fluorescence lifetime τ_f and the Stokes shift were calculated. Also the energy gap (Eg) for each dye concentration was evaluated. The results showed that the maximum quantum efficiency 62 % and maximum stokes shift 96 nm was obtained in dye concentration $5*10^{-6}$ and $1*10^{-4}$. The energy gap ranges between 1.066 eV to 1.128 eV depending proportionally on the dye concentrations.

Key words: Absorption, Energy gap, Fluoresces, Hybrid polymer, Rhodamine 6G dye**.**

Introduction:

The strength of the absorption band in the visible spectrum is considered as a special merit of the organic dyes which is existed just in organic compounds; these compounds contain an expanded arrangement of both the single bonds and double bonds alternately. Dye's absorption bond of long wavelength is caused by transmission between electronic states with a large unity order moment. This process leads to particle absorption from the ground to the first excited state ($S_0 \rightarrow S_1$). While transmission from S_1 to S_0 results spontaneous and stimulated emissions in such lasers (1,2). Organic molecules in solid state dye lasers are distributed in a homogeneously uniform matrix. Such as Polymer Epoxy Resin. The demonstrated solid state dye lasers of a tunable wavelength from UV to NIR regions have a photostability issue to be studied. Dyes can be used to take possession of high quantum fluorescence and reduced triplet-triplet absorption within the lasing range (3). Due to several features, solid state hosts have been synthesized for such kinds of dyes. They are characterized by thermal stability, resistivity to specific solvent types and hydrolytically.

Polymers of high damage threshold played a critical role in dye laser development. Also, these polymers provide an appropriate choice of organic dye lasers hosts. Hermes and his colleagues have relied on polymeric hosts for dyes doping (4). Some fluorescent dyes are exploited as a lasing medium of dye lasers.

Organic polymers are often used as solid matrices for organic dyes. Semiconductors (conjugated) polymers are considered as an attractive solid stated laser gain material. Shift of stokes between absorption and emission wavelengths makes them exhibit a small self absorption in addition to their high efficient photoluminescence and large areas for stimulated emission to occur (4).

This work is dealing with the evaluation of absorption and fluorescence spectra for the hybrid of an epoxy resin doped with organic dye Rhodamine (R6G) of different concentrations ($5*10^{-5,}$ $1*10^{-5}$, $1*10^{-4}$, $5*10^{-4}$) Mol/ℓ. The spectral properties include quantum efficiency Q_{fm}, the rate of fluorescence emission K_{fm} (s^{-1}), the non-radiative lifetime τ_{fm} (s), fluorescence lifetime τ_f and the stokes shift is calculated. Also the energy gap (Eg) for each dye concentration is evaluated for each dye concentration.

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Materials and Methods:

Preparation of R6G/Epoxy Polymeric Composite Films

Xanthine's family involves Rhodamine dyes along with fluorescent and eosin dyes. Xanthine chromophore (A) and Rhodamine dyes (B) structures shown in Fig. 1.

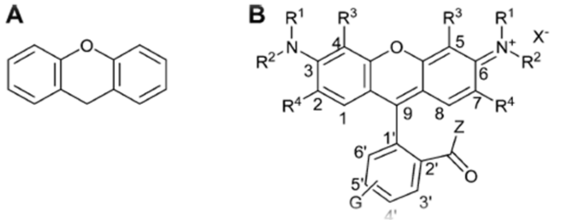

Figure 1. Molecular structure of Xanthenes (A) and Rhodamine 6G dye (5).

Photostability and photophysical of rhodamines make them to be used extensively as a laser dye (5-7), quantum yield fluorescence criteria (8), polarization (9), pigments and fluorescent probes to describe polymer nanoparticles surface (10) and in polymer-bioconjugates detection (11).

Devices and Measurements:

The main properties of epoxy are shown in Table 1, includes two materials. The first material is (epoxy resin (A)) and the second one is the (hardener (B)) which assists in polymer chains interlocking when two polymers are mixed. Both types of materials are mixed with a certain percentage by taking the epoxy type into consideration. The dye that is used belongs to xanthine family with chemical formula $C_{28}H_{31}N_2O_3Cl$ and molecular weight of 479.02 $g.mol^{-1}$. The appearance of pale red crystalline powder and its molecular structure is given in Fig. 1.

Composite films of Epoxy doped with Rhodamine (6G) were prepared with thickness (0.3 mm). The absorption spectra were recorded by using a UV–VIS spectrophotometer (Metertech, SP 8001). Spectrofluorometer (Model F96PR) was used for recording the emission spectra of R6G doped in Epoxy.

Table 1. Epoxy properties (12)

Traditional name	CONCRESIVE® 1320
Color	Limpid
Company	Badische Anilin-und Soda Fabrik (BASF), Germany
Boiling point	260 °C
Service temperature	(20-80) °C
Physical state	Liquid
Final cure	7 days (35 °C)

The casting solution technique was used to prepare a matrix consists of R6G dye in epoxy. Different weights of epoxy resin and R6G were dissolved in pure chloroform. A magnetic stirred at (25 °C) was used to mix R6G and resin for 2 hours. The obtained R6G/epoxy of different R6G contents were left in the Petri-dish glass for 3 days to evaporate the chloroform. The sample plate is of 2*9 cm^2 with 0.3 mm thickness and R6G ($5*10^{-6}$, $5*10^{-5,}$ $1*10^{-5}$, $1*10^{-4}$, $5*10^{-4}$) Mol. concentration.

Measuring of Quantum Efficiency (Q_{fm})

The quantum efficiency (Q_{fm}) is defined as the ratio between the number of quanta emitted and the number of quanta absorbed (13):

The quantum efficiency (Q_{fm}) is related to the spectral molecular fluorescence F(ύ), as :

$$Q_{fm} = \int_0^\infty F(\bar{\upsilon})d\bar{\upsilon} \quad \ldots 1$$

To evaluate the absolute quantum efficiency, both radiative and non-radiative processes taking place in the medium must be considered (14),

$$Q_{fm} = \frac{K_{fm}}{K_{fm} + \Sigma K_d} = \frac{K_{fm}}{K_{fm} + K_{IC} + K_{ISC}} \quad \ldots 2$$

Since $K_{fm} = \frac{1}{\tau_{fm}}$ ….3

And $\tau_f = \frac{1}{K_{fm} + \sum K_d}$ …4

where, K_{fm} is radiative emission probability, τ_{fm} is non-radiative life time, τ_f is fluorescence lifetime (15). Therefore,

$$Q_{fm} = \frac{\tau_f}{\tau_{fm}} = \int_0^\infty F(\upsilon')d\upsilon' \quad \ldots 5$$

The radiative emission probability can be determined from Bowen-workes equation by the following equation (16):

$$K_{fm} = \frac{1}{\tau_{fm}} = 2.88 \times 10^{-9} \times n^2 \times (\bar{\upsilon}^2) \int \varepsilon(\bar{\upsilon}) d\bar{\upsilon} \quad \ldots 6$$

Where n is the refractive index, ε is a molar absorption coefficient, $\acute{\upsilon}$ is wave-number.

Results and Discussion:

Beer–Lambert's law describes the relation between the medium absorption coefficient (α) and light intensity (I).

$I = I_0 e^{-\alpha t}$ …7

Where (I), is the output light, while (I_o) and (t) are the input light and the plate film thickness, respectively.

Or, $\alpha t = 2.303\, log\frac{I_0}{I}$ …8

and one can get $\alpha = 2.303\frac{Abs}{t}$ … 9

Where $Abs = log\frac{I_0}{I}$ …10

Abs: is the absorption.

The optical properties such as absorption and fluorescence have been studied for the hybrid samples (R6B/Epoxy) with dye concentrations ($5*10^{-6}$, $5*10^{-5,}$ $1*10^{-5}$, $1*10^{-4}$, $5*10^{-4}$) mol/l.

The absorption spectra of different concentrations of R6G/Epoxy matrix are shown in Fig.2. The absorption intensity increased as the R6G concentration increased. This is in agreement with Beer–Lambert's law. This absorption increment belonged to R6G made intermolecular bonds with epoxy resin. Figure 2 also shows that the peak intensity at (540 nm) doesn't shift in position.

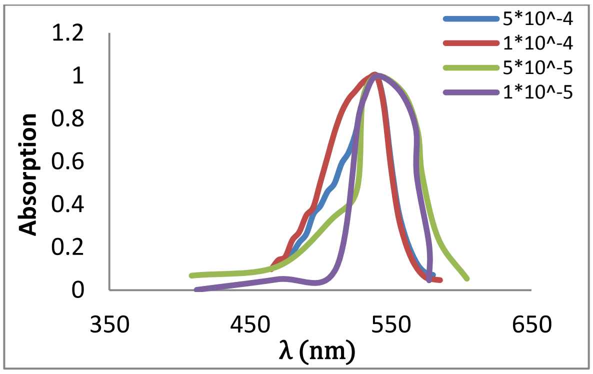

Figure 2. R6G/Epoxy absorption spectra of different dye concentrations as a function of wavelengths. (Sample thickness is 0.3 mm)

It is clear from Fig.3 that the fluorescence spectrum with a shifting toward longer wavelengths (Red Shift) with increasing concentration.

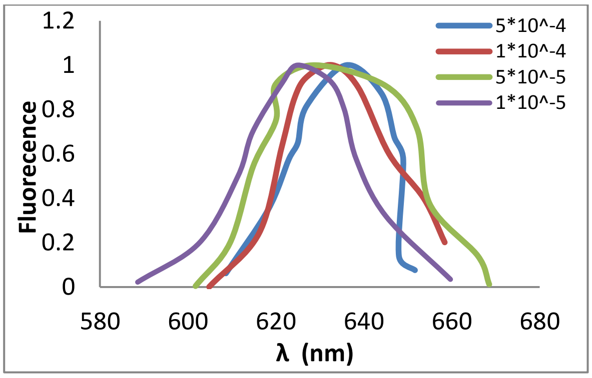

Figure3. Fluoresces spectra of R6G/Epoxy shows the effect of dye concentration variation as a function of wavelengths. (Sample thickness is 0.3 mm)

From Table 2, it is clear that increasing the stokes shift occurs with increasing concentration and its value is higher than for solutions of dye R6G, and also the Table shows an increase in the value of the (τ_{fm}) and the (τ_f) when increasing concentration, and the (τ_f) less than the (τ_{fm}) because of the non radiation processes are associated with the process of fluorescence. And the quantum efficiency (Q_{fm}) decreases as the dye concentration are increased, because of the decrease in the probability of non-radiative transition (inter system crossing) and (internal conversion).

Table 2. Optical properties of hybrid of Rhodamine 6G/epoxy.

Concentration (mol/l) $*10^{-4}$	Position of λ_{max} Fluoresces (nm)	Stockes shift (nm)	(Q_{fm}) %	τ_{fm} (μs)	τ_f (μs)
5	636	96	52	5.3	2.8
1	633	93	54	0.9	0.5
0.5	629	89	58	0.4	0.2
0.1	625	85	62	0.1	0.1

The relation between the absorption index (k) and (α) is (17):

$$k = \frac{\alpha\lambda}{4\pi} \quad \dots \quad 11$$

where λ is the light wavelength. The (k) values as a function of wavelengths for different R6G/ epoxy films contents have been investigated. The R6G/epoxy (k) behavior for different dye concentrations have been observed in Fig.4 which indicates that (k) increase as R6G content increase. The (k) peak position are at 538,540, 540 and 545 nm. There is a slight increment in absorption peaks with a R6G-doping increment. Table (3) shows that the k values vary between (42.9 - 43.1) as R6G dye contents vary between ($1*10^{-4}$- $5*10^{-6}$) in the polymer matrix.

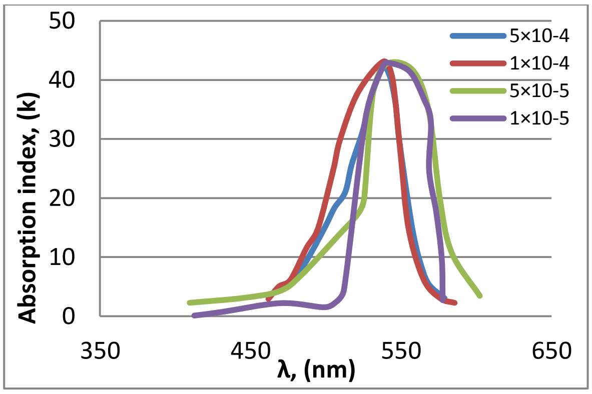

Figure 4. Absorption index (k) for R6G/Epoxy at different dye concentrations. (Sample thickness is 0.3 mm)

One can distinguishes between insulators and semiconductors from their energy gaps (Eg) which plays a major role in designing and modeling. Essential gaps are: (i) (HOMO): highest occupied molecular orbital to anti-bending, (ii) (LUMO): lowest unoccupied molecular orbital and (iii) (E_g) is the minimum energy of free electrons and holes belong to the singular particles transition within the solid. Pure epoxy and R6G/Epoxy polymeric films Eg values are evaluated by Tauc's law (17);

$$\alpha h\nu = \beta\left(h\nu - E_g\right)^r \qquad \dots\ 12$$

where β is a constant. r = 2 , 3, 0.5 and 1.5 belong to indirect allowed transition, indirect forbidden transition, direct allowed transition and direct forbidden transition, respectively. Figure 5 shows the linear dependence of $(\alpha ht)^2$ on $h\nu$ and the indirect transitions is contingent for these films. Band gaps of the Rh6G/Epoxy of different concentration are listed in Table 3. Variations of the optical band gap indicate that an additional energy states exists and are prompted by dye doping.

From this work, R6G dye modifies the electronic structure and epoxy structure due to defect levels formation when doping with R6G dye. Indirect Eg decrease as the content of R6G concentration increases in epoxy because the interaction occurs between dye and epoxy and new dipoles creation which is considered as a point defect (17). Figure.5, shows $(\alpha h\nu)^2$ plot vise energy of a photon ($h\nu$) achieved by by straight line curves extrapolating at α=0 (18), Where we noted, an increase of energy gap with increased concentration of the sample, as shown in the Table 3. This is due to the creation of the site levels in forbidden energy gap. The results are in agreement with research works (19, 20).

Table 3: Energy Gap (E_g), and absorption coefficient *k* for different concentrations.

Concentration (Mol/L)	Energy Gap (eV)	Peak absorption index (*k*)
$5*10^{-4}$	1.128	43.1
$1*10^{-4}$	1.124	42.9
$5*10^{-5}$	1.088	42.6
$1*10^{-5}$	1.086	42.5
$5*10^{-6}$	1.066	43.1

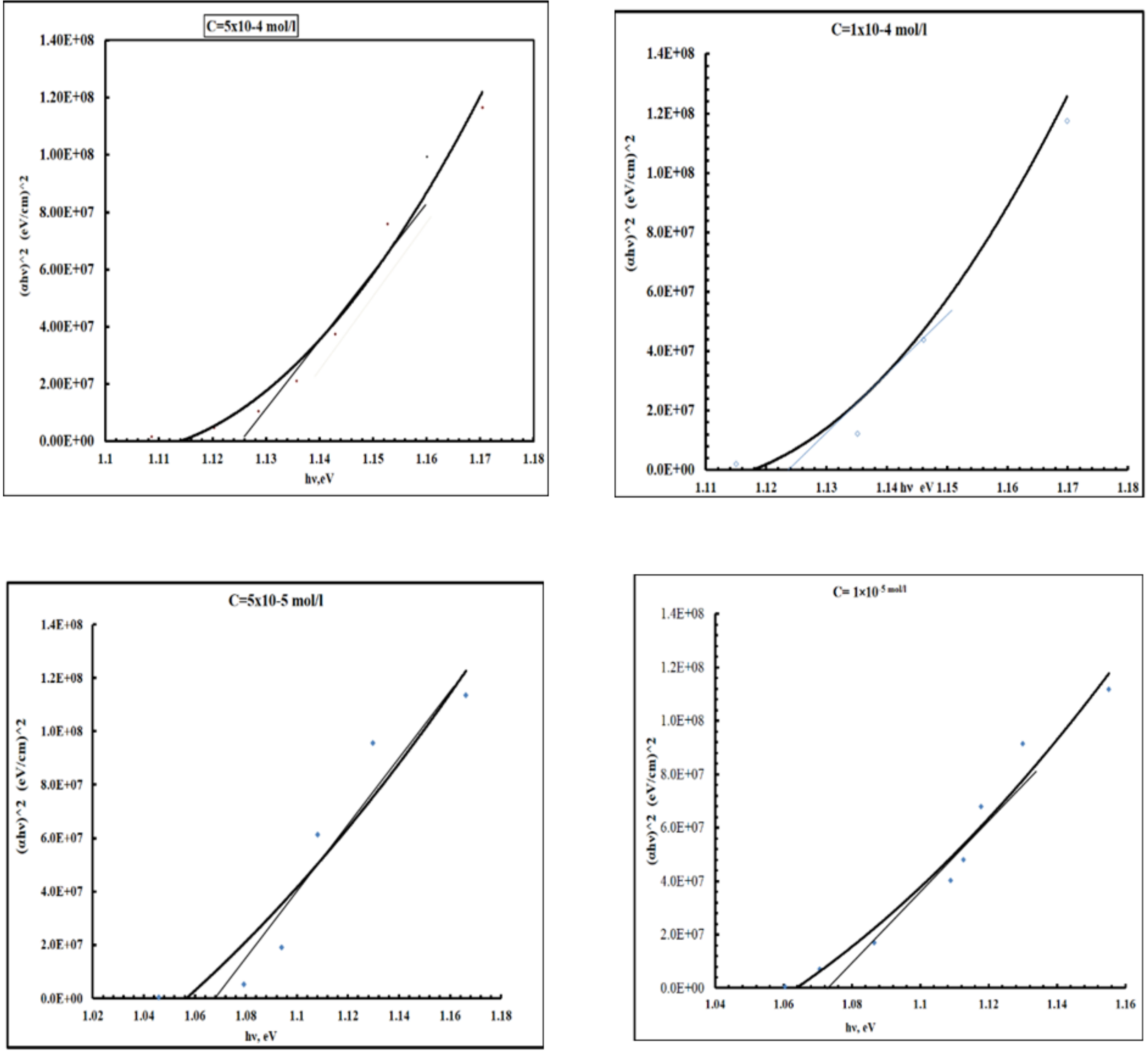

Figure 5. $(ah\nu)^2$ Vs ($h\nu$) of R6G/Epoxy for various R6G dye concentrations

Conclusions:

The research study shows the spectral characteristics of the hybrid of dye – Epoxy films. Their absorption and fluorescence spectra of these film shifts toward long wavelength (lower energies) more than those of liquid solutions of dyes. It has been found that the value of Stokes Shift ($\Delta\lambda=\lambda_{abs} - \lambda_{flu}$) of these films are large (reduction of absorption spectrum and the fluorescent film overlap relates to the stokes shift increment, in comparison with dye solution) so that we can get a small overlapping between absorption and fluorescence spectra, and a wide tuning range for dye lasers. In addition, this large stokes shift will be effective in the work area of solar cells and gives better efficiency when using this film as a solar concentration.

From this study, one concludes that structural modulations, linear and NLA of basic fuchsin doped epoxy. The peak intensity increases with the increasing the dye content. The optical energy gap analysis demonstrates the three optical band gaps presence for R6G/Epoxy. Finally, Eg varies with doping, which are explained by the defect levels existence within the R6G doped epoxy films.

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Conflicts of Interest: None.

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الخصائص الطيفية لهجين من صبغة العضوية الرودامين (6G) والأيبوكسي والمذابه بالكلوروفورم

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الخلاصة:

يتناول البحث طيف الامتصاص والفلورة لهجين من الايبوكسي واللدائن المذابة بالصبغة العضوية من الرودامين (6G) بعدة تراكيز ($5*10^{-4}$, $1*10^{-4}$, $1*10^{-5}$, $5*10^{-5}$) مول/لتر وبدرجة حرارة الغرفة. تم حساب كل من الكفاءة الكمية Q_{fm}، معدل انبعاث الفلورة k_{fm}، العمر الزمني الاشعاعي τ_{fm}، العمر الزمني للفلورة τ_f وازاحة ستوك. وكذلك تم حساب فجوة الطاقة (Eg) لكل تراكيز الصبغة. اظهرت النتائج ان اعظم كفاءة كمية 62% واعظم مقدار لازاحة ستوك 96 nm تم الحصول عليهم عند التركيز $5x10^{-4}$. وأن مدى فجوة الطاقة بين 1.086الى 1.28 eV ويعتمد تناسبيا على تراكيز الصبغة.

الكلمات المفتاحية: الأمتصاصيه، فجوه الطاقه، الفلوره، البوليميرات الهجينه، صبفه الروداماين.