Physical Properties of Rhodamine 6G Laser Dye Combined in Polyvinyl Alcohol films as Heat Sensor

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Abstract
Rhodamine 6G- polyvinylalcohol (Rh6G /PVA) films were prepared via casting route at room temperature with different volume of Rh6G dye solution (5, 10, 15, 20, 25 and 30 ml). The optical properties of as-prepared films were characterized using UV–Vis spectrophotometer at a wavelength range of 200-800 nm. The absorption peak of the pure PVA film does not affect by adding the Rh6G dye solution while exhibited increase in intensity of the absorption spectrum. Furthermore, the absorption peak of Rhodamine 6G demonstrated red-shift about 10 nm. Energy band gap slightly affected by adding Rh6G dye solution. The amazing influence of heat treatment on the physical properties of Rh6G/PVA films appeared due to red-shift and decrease the energy band gap. The results exposed that the best sensitivity calculated at temperature 40 °C for as-grown Rh6G (15 ml) /PVA film around 35.74%.

1. Introduction
The continuous development to discover new sorts of materials is influenced not only by the fabrication of materials in a practical field, but also for the assessment of their physical properties. These properties of materials are excellent in the field in which they will be used. The applications of the combination of laser dyes into the polymer material have made very good progress towards the development of the solid state dye laser. Polymers offer many advantages for use as a host matrix with organic laser pigments [1, 2].

Poly vinyl alcohol (PVA) is a polymer of great importance due to its many desirable properties, especially, for various pharmaceutical and biomedical applications [3]. It was applied in the industrial, commercial, medical and food sectors and was used to produce many products [2]. It is a linear polymer with a carbon chain back bone with hydroxyl groups connected to methane carbonate. These OH groups can be a source of the hydrogen bond and
thus aid in the formation of the polymer. Polyvinyl alcohol is not known as a natural product. The manufacture of the primary raw materials used in the manufacture of polyvinyl alcohol is vinyl acetate monomer [4, 5].

Furthermore, Rhodamine dye has a clinical value in itself, and is widely used as laser lithotripsy of bile micro-duct stones using the Rhodamine 6G dye laser with a visual detection system of stone tissue [6]. Rhodamine 6G is one of the very important laser dyes, so it uses as an active medium or gain medium. The wide utilization of Rhodamine 6G dye because the safest and effective properties. Thus, Rhodamine 6G is used in numerous applications such as (laser technology, optical conversion, solar cells with capacitors, light emission, diode, signal amplification in optics, optical communications, optical limiting power, and optoelectronics) as an active medium for dye lasers and photonics devices. [7, 8].

Many researchers studied physical characteristics of Rh6G dye solution alone and doped with different types of polymers or with other organic dyes, and reached to good results and applications [8-12]. The previous studies reveal that the Rh6G dye-doped with PVA polymer leads to happen strong effect on physical properties include absorption, transmission, absorption coefficient, and clearly shown changing the position of the maximum wavelength of solution spectrum due to adding polymer [8]. This study represents a synthesis of Rhodamine 6G-polyvinylalcohol (Rh6G/PVA) films via casting route at different volume of Rh6G dye solution (5, 10, 15, 20, 25 and 30 ml). The optical characteristics of as-synthesis films were described at a wavelength (200 to 800) nm.

2. Experimental

The Pure PVA film is prepared by casting method, the PVA solution is prepared by dissolving PVA (0.5 g) in distilled water (10 ml). The as-prepared PVA solution stirred very well by a magnetic stirrer until polymer dissolved and cast onto a clean glass petri dish (diameter: 7 cm). Homogenous pure PVA films obtained after drying at room temperature about (20 – 23 °C) for (3-4) days. The concentration (C in mole /liter) of Rh6G solution is $1\times10^{-5}$ mole/liter prepared by taking a specific amount of dye powder (in g) in known volume (V in ml) of distilled water according to Eq. (1) [13].

$$m = C \times V \times \frac{M_w}{1000}$$  \hspace{1cm} (1)

Where $M_w$ the molecular weight of Rh6G dye (479.01 g/mole).
To prepare Rh6G/PVA films for a different volume ratio of Rh6G dye solution (5, 10, 15, 20, 25, and 30) ml, added to PVA solution (0.5 g) with distilled water (10 ml). Followed, the mixture was stirred very well via magnetic stirrer until the Rh6G/PVA solution become a homogenous solution. The solution cast onto clean glass petri dish and leave at room temperature about (20-23) °C for seven days to obtain homogenous films. The thickness of as-synthesis films were measured, for PVA polymer films were around (0.063) mm, and for Rh6G/PVA films is given between (0.0088 - 0.0124) mm. Finally, to examined the as-prepared films as a heat sensor, temperature effect carried out of pure PVA and Rh6G/PVA (15 ml) films by electric oven type BINDER (USA) for 30 minute at different exposure temperatures (30, 40, 50, 60 and 70) °C.

Ultraviolet–visible (UV-Vis) spectrophotometer (Type T70/T80) is an instrument used for measure the absorption and transmission spectra in the wavelength range (200-800) nm. The thickness of films were measured by digital micrometer (0.001) mm measurement accuracy the range of measure (0-150) mm (Type Tesha).

3. Results and Discussions

The absorption spectrum of Rh6G in distilled water with concentration (1x10⁻⁵) mole/liter illustrated in Fig. (1). The behaviors of the absorption spectrum is broadband with a peak position at (525) nm with associated intensity (0.421). These results agree with the standard research mentioned in [14]. The type of electronic transition is π-π*, this transition is typical for basic Rhodamine 6G dye and related to the charge transfer from the benzene cycle to the pianos moiety. This transition is associated to an excitation from the HOMO (the highest occupied molecular orbital) and the HOMO orbital, respectively, to the LUMO (the lowest unoccupied molecular orbital) [15].

The absorption coefficient (α) of this dye solution calculated from Eq. (2) [16], as shown in Fig. (1). The behaviors of absorption coefficient is as the same of absorption spectrum, but with greater value (0.969).

\[
\alpha = 2.303 \frac{A}{t}
\]  

Where A is absorbance and t the thickness of the film.

Fig. (2) illustrates the optical energy gap of Rh6G solution, the finding reveals that the energy gap is equal to (3.87) eV.
The absorption spectrum of pure PVA and Rh6G/PVA films with different volume of Rh6G dye solution (5, 10, 15, 20, 25 and 30) ml with concentration \((1 \times 10^{-5})\) mole/liter demonstrated in Figure (3). As well as, the absorption information is illustrated in Table (1). When, Rh6G dye doped with PVA polymer, the noticeable change in the spectrum of absorption wavelength for Rh6G dye. Clearly appearing absorption peak at 525 nm for Rh6G solution, in contrast, reach to 535 nm for doping film with PVA. That mean there is red-shift toward long wavelength about 10 nm with increasing doping ratio of dye solution.

In PVA film, it can see that the absorbance increase with increasing doping ratios of Rh6G dye. The intensity at first increases, becomes maximum at 0.389 for doping ratio 25 ml, while the absorbance decreased at (20 and 30) ml, this result can be attributed to forming aggregates. This may discussed as increasing the number of dye molecules as mentioned by Birks and Berlman in previous studies [15, 18].

\[
\alpha h\nu = B (h\nu - E_g)^\tau
\]

(3)

Where \((h\nu)\) is the photon energy, \((B)\) is constant which depends on the type of material and \((E_g)\) is the forbidden energy gap of direct transition. \((\tau)\) exponential constant and its value depended on the type of transition [17].
The value of absorption coefficient less than $10^4$ cm$^{-1}$ suggests that the occurrence of vertical transition at fundamental absorption edge and is indicated to indirect transition, as clarified in Fig. (4) and Eq. (3). Fig. (5) shows the variation of energy gap for pure PVA and Rh6G- PVA films, it can be noticed that the value of energy gap of the PVA films decreased with increasing the volume ratio of dye solution. This decrease due to the creation of new band gap, lead to facilitate the transition of electrons from valance band to these local levels to the

![Absorption spectra of pure PVA and Rh6G/ PVA films with different volume of Rh6G solutions](image)

**Fig. (3) Absorption spectra of pure PVA and Rh6G/ PVA films with different volume of Rh6G solutions**

**Table (1) Absorption information of pure PVA and Rh6G/ PVA films with different volume of Rh6G solution**

| Samples         | PVA  | Rh6G            | $E_g$ (eV) |
|-----------------|------|-----------------|------------|
|                 | $\lambda_{Abs.}$ | $\lambda_{Abs.}$ | Abs. | $\lambda_{Abs.}$ | Abs. |         |
| Pure PVA        | 280  | 0.163           | -----     | -----           | 5.12 |
| Rh6G solution   | ----- | -----           | 525       | 0.421           | 3.87 |
| PVA +5 ml Rh6G  | 280  | 0.268           | 535       | 0.222           | 5.22 |
| PVA +10 ml Rh6G | 280  | 0.272           | 535       | 0.322           | 5.21 |
| PVA +15 ml Rh6G | 280  | 0.304           | 535       | 0.512           | 5.21 |
| PVA +20 ml Rh6G | 280  | 0.235           | 535       | 0.401           | 5.2  |
| PVA +25 ml Rh6G | 280  | 0.389           | 535       | 0.791           | 5.18 |
| PVA +30 ml Rh6G | 280  | 0.208           | 535       | 0.471           | 5.16 |

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conduction band. Table (1) summarized the value of the optical band gap for pure PVA, Rh6G solution, and Rh6G- PVA films.

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Fig. (4) Absorption coefficient of PVA/ Rh6G films with different volume of Rh6G solutions

Fig. (5) Optical energy gap of PVA/ Rh6G films
The absorption spectra of the thermally treated PVA polymer with 15 ml of Rh6G solution dye at different temperatures (30 - 70°C) of step 10°C for (30) min are shown in Fig. (6). At all temperatures, the ($\lambda_{\text{max}}$) value was appeared at the same position, except 50°C, maximum wavelength display red-shift in the wavelength from 535 nm to 540 nm as seen in Table (2). While, the slight changes in the value of absorption intensity. The absorbance decreases at 30°C and 40°C and then increase 50°C, and back to decrease at 60°C finally slight increase in 70°C.

![Absorption spectra of Rh6G (15ml) /PVA film at different temperatures](image)

**Fig. (6) Absorption spectra of Rh6G (15ml) /PVA film at different temperatures**

| Temp.(°C) | PVA | Rh6G | $E_g$ (eV) |
|-----------|-----|------|------------|
|           | $\lambda_{\text{Abs.}}$ (nm) | Abs. | $\lambda_{\text{Abs.}}$ (nm) | Abs. |          |
| R. T.(20-25) | 280 | 0.304 | 535 | 0.512 | 5.16 |
| 30 | 280 | 0.249 | 535 | 0.403 | 5.18 |
| 40 | 280 | 0.218 | 535 | 0.329 | 5.16 |
| 50 | 285 | 0.311 | 540 | 0.516 | 5.1 |
| 60 | 280 | 0.260 | 535 | 0.423 | 5.09 |
| 70 | 280 | 0.279 | 535 | 0.457 | 5.08 |

**Table (2) Absorption information of Rh6G (15 ml)/PVA film in different temperatures**
Moreover, Fig. (7) shows the absorption coefficient for Rh6G(15ml)/PVA after thermal treatment from (30-70) °C for (30) min. Increasing temperature led to decrease the value of (α) for all applied temperatures, except 50 °C from 119.1 at room temp. to 120.03 at 50 °C. The lowest value at 40 °C is 76.5. The finding reveals that the temperature clearly effects on the value of the energy band gap by decreasing its value, as shown in Fig. (8) and Table (2).

![Fig. (7) Absorption coefficient of Rh6G (15ml)/PVA film in different temperatures](image1)

![Fig. (8) Optical energy gap Rh6G (15ml)/PVA film in different temperatures](image2)
A common way to express the relation between absorbance and temperature is using the sensitivity, which is defined as: the ratio between the change in the absorbance at the time of heating ($A$) and the initial absorbance ($A_0$):

$$|S| = \frac{A - A_0}{A_0} \times 100\%$$

(4)

Where, the results prove that the best sensitivity about (35.74%) at temperature treatment 40 °C, as demonstrated in Table (3).

| T °C  | $A$  | $A_0$ | Sensitivity |
|-------|------|-------|-------------|
| R. T. (20-25) | 0.512 | 0.512 | ---         |
| 30    | 0.403 | 0.512 | 21.28%      |
| 40    | 0.329 | 0.512 | 35.74%      |
| 50    | 0.516 | 0.512 | 0.78%       |
| 60    | 0.423 | 0.512 | 17.38%      |
| 70    | 0.457 | 0.512 | 10.74%      |

4. Conclusions

In summary, pure PVA and Rh6G /PVA films were prepared by simple casting method. Studied the effects of change volume of Rh6G dye solution on the physical properties of the as-synthesis films were achieved. The absorption peak of the pure PVA film does not affect by adding the Rh6G dye. In contrast, due to Rh6G dye adding clearly red shift is observed in the absorption spectrum and absorbance of Rh6G dye. Furthermore, the effect of exposure temperature on the energy band gap and the sensitivity of synthesis films was investigated. The energy band gap of Rh6G/PVA films exhibit red shift and decrease due to the influence of temperature treatment. Rh6G (15 ml) /PVA film shows the greatest sensitivity (35.74%) at temperature 40 °C.

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