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Investigating the effects of the different rhodamine 6G laser dye volume ratios on the optical properties of PMMA/PC films

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Abstract

Rhodamine 6G – polymethylmethacrylate/polycarbonate (Rh6G–PMMA/PC) were prepared by a casting method at room temperature with diverse volume ratios of Rh6G dye solution (5, 10, 15, 20 and 25) ml. The as-prepared films were categorised via UV–Vis spectrophotometer, and the optical properties were investigated in the wavelength range of (200-800) nm. The absorption peaks for pure PMMA/PC film were affected by inserting Rh6G dye solution, the wavelength of absorption peak of pure PMMA/PC film is at 300 nm and 340 nm while there are different behaviour at different concentration of RG6 after mixing with PMMA/PC films; there are red shift for concentrations (10 and 25 ml) of RG6 after mixing with PMMA/PC films by appear another peaks at 530 nm and 535 nm respectively.

In addition, there is a blue shift for concentrations (15 and 20 ml) of RG6 after mixing with PMMA/PC films, as evidenced by the appearance of new peaks at wavelength 265 nm.

Furthermore, new peaks appeared and were absorbed while the energy band gap was influenced, with values ranging from 4.3 eV for pure PMMA/PC film to 4.18 eV for mixtures 10 & 25 ml concentration of Rh6G/ PMMA/PC belonging to the red shift to 4.9 eV and 4.85 eV for mixtures 15 and 20 ml concentration of Rh6G/ PMMA/PC belonging to the blue shift.

Keywords: Dye doped polymer; laser dye; optical properties; PC polymer; PMMA polymer.

1. Introduction

The continuous efforts to find new types of materials as well as the physical properties, such as the optical characteristics of materials with remarkable efficacy in their corresponding field, influence material manufacturing.

Dye-doped polymer solid lasers can be attributed to the incorporation of laser dyes into polymer materials. Using polymers as a host matrix for organic laser dyes has many advantages.

One of the most important laser dyes is Rhodamine 6G, which is used as a gain medium (Th. G. Pavlopoulos,2002). In addition, Rhodamine 6G is widely utilised in photocoagulation therapy and ocular photodynamics due to its large number of wavelengths of high output power laser lithotripsy. Thus, Rhodamine 6G dye is the most commonly used because of its safety and effectiveness (V. I. Gavrilenko *et al,*2006; M. F H. Al-Kadhemy *et al.,2020a)*.

Considering optical properties, the polymethylmethacrylate (PMMA) polymer has its specific optical features. This uncrystallised polymer exhibits remarkable transparency (92% light transmission) in the visible range from 380 nm to 780 nm. Thus, this material can be used to create light conductors, such as fibre optic filaments and films. PMMA can also be utilised in the manufacture of optical products due to its refractive index of 1.49 (V. Raja *et al.*, 2003; C. Hall,1989).

Polycarbonate (PC) polymers are characterised by their clarity, good electrical properties, high thermal stability and excellent impact strength. Moreover, these polymers are thermoplastic; that is, they are amorphous and transparent. PC polymer have excellent mouldability, low-temperature toughness and flame-retardant properties and are available in a variety of special grades (C. Hall,1989; H. M. Nasser & O. D. Ali, 2010). Many researchers investigated the optical properties of PMMA, PC and Rh6G alone; they doped these materials with each other or with other organic dyes and obtained notable outcomes and applications (N. J. Hameed & M. R. Fraih, 2011; Asrar A. Saeed *et al*., 2017; Asrar A. Saeed *et al.*, 2018).
Doping the Rh6G dye with the PMMA/PC polymer substantially affected the physical properties, such as absorption, transmission, reflection spectra, refractive index, extinction coefficient and indirect energy gap compared with other parameters, resulting in varying positions of the max wavelength of solution spectra due to the addition of two polymers (PMMA and PC) (R. A. Al-Mousawi *et al*.,2019). Films that are more stable than the dye solution used as an active medium in the solid laser where the properties of polymer PMMA are nearest to polymer PC are obtained by applying the aforementioned method (H. M. Zidon *et al.*,2003; Mahasin F. H. AL-Kadhemy *et al.*,2020b). PMMA/PC films with different Rh6G volume ratios will be investigated in this paper.

2. Experiment

The Rhodamine 6G laser dye processed by Sigma-Aldrich Company is characterised as follows: chemical formula $C_{28}H_{31}N_2O_3Cl$ and molecular weight (M_w = 479.02 g/mol) (C. Adnan, 2011). The PMMA with the chemical formula $(C_5O_2H_8)_n$ and molecular weight (200,000 g/mole) is made in Spain. The second polymer is the polycarbonate polymer with molecular formula $[C_{16}H_{14}O_3]_n$ and is processed by the Sabic Company (E. S. Guerra & E. V. Lima, 2013). The two polymers were chosen as host materials for Rh6G due to their excellent optical properties.

The cast procedure was used to prepare the pure PMMA/PC and Rh6G– PMMA/PC films. This casting method consediring easy for prepering samples, have stable results and can done in normal environment (Mahasin F. H. AL-Kadhemy *et al.*, 2020c). The PMMA/PC solution was organised by dissolving 0.3 g of PMMA with 0.2 g of PC in 10 ml of chloroform. The PC solution was stirred properly with a magnetic stirrer till the polymer was dissolved and cast onto glass Petri dishes with a 10 cm diameter and then left to dry at room temperature approximately (25 – 30) °C for one day. The Rh6G solution with 1×10^{-5} mole/litre concentration was prepared along with the illustrated method in Ref. (Mahasin F. H. AL-Kadhemy *et al.*, 2020a, W. H. Abbas, 2012). The dissimilar ratios of this dye solution (5, 10, 15, 20 and 25) ml were then added to PMMA/PC solution and mixed well using a magnetic stirrer. Similar to the case using the above-mentioned method, the mixture cast aimed to obtain homogeneous Rh6G–PMMA/PC films. The UV-Vis spectrophotometer type (T70/T80 Series UV/Vis Spectrometer) was used in 200–900 nm of wavelength range to measure the absorption and transmission spectra.

3. Results and Discussion

Figure (1) displays the absorption spectra of pure PMMA/PC and Rh6G–PMMA/PC films for the different volume ratios (5, 10, 15, 20 and 25 ml). The pure PMMA/PC film demonstrated the following two peaks: the maximum wavelength of the 1st peak at 300 nm with 1.504 absorbance and that of the 2nd peak at 340 nm with 1.345 absorbance. This finding matched the results in ref. (Mahasin F. H. Al-Kadhemy, *et al.*, 2020b). The intensity of the peaks decreased with the addition of 5 ml Rh6G dye solution as illustrated in Figure (1) and Table (1).

In addition to the emergence of a peak for the Rh6G dye at 530 nm with 0.683 absorbance, the additional 10 ml dye solution increased the two peaks and resulted in the 530 nm red-shift for the second peak. A split in the peaks of the two polymers was observed at 15 and 20 ml of the dye solution. These peaks became three (265, 300 and 340 nm) with maximum absorbance for the new peak of 265 nm to the concentration of Rh6G (15 and 20 ml). The increased dye solution additive to 25 ml led to the disappearance of 265 nm peak and apeare the peak at 335 nm. Meanwhile, there are a red shift for concentration (10 and 25 ml) of Rh6G after mixing with PMMA/PC and blue shift for concentration (15 and 20 ml) of Rh6G after mixing with PMMA/PC .

The Rh6G dye played a role in splitting the peaks of PMMA/PC films and makes some changes in energy gap by whilst increasing the volume ratio of the dye solution because it raised the number of dye molecules that reduced the role of polymers.

These broad emissions are attributed to deep-level emissions, which can be caused by structural defects in polymer films. The emission attributed to defects in the nanocrystalline of the host or could be due to add the dye depending on the availability of associated structural defects (Akeel M. Kadim, 2022)

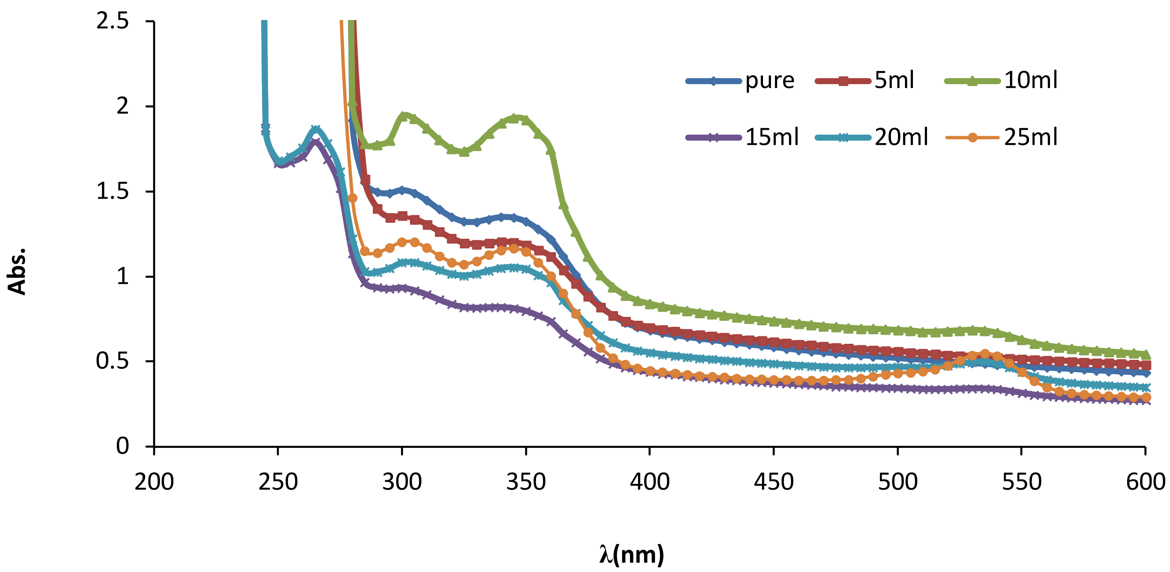

Fig. 1. Absorption spectrum of Rh 6G –PMMA/PC films for dissimilar volume ratios of dye

Table 1. Absorption data about pure PMMA/PC and Rh6G-PMMA/PC films

Samples	**$\lambda_{abs.}$ (nm)**	**Abs.**	**E_g (eV)**
Pure PMMA/PC	300	1.504	4.3
	340	1.345	
5ml Rh6G/ PMMA/PC	300	1.354	4.18
	340	1.2	
10ml Rh6G/ PMMA/PC	300	1.938	4.18
	345	1.928	
	530	0.683	
15ml Rh6G/ PMMA/PC	265	1.786	4.9
	300	0.93	
	340	0.816	
20ml Rh6G/ PMMA/PC	265	1.862	4.85
	300	1.078	
	345	1.051	
25ml Rh6G/ PMMA/PC	300	1.199	4.18
	345	1.161	
	535	0.546	

Figure (2) exhibits the transmission spectra for all samples. The transmittance reveals a reduction in its value with an increase in the absorption spectra and the volume ratio of the dye solution. This finding indicates that the films became blackout or less transparent with the increase in the volume ratio of the dye solution.

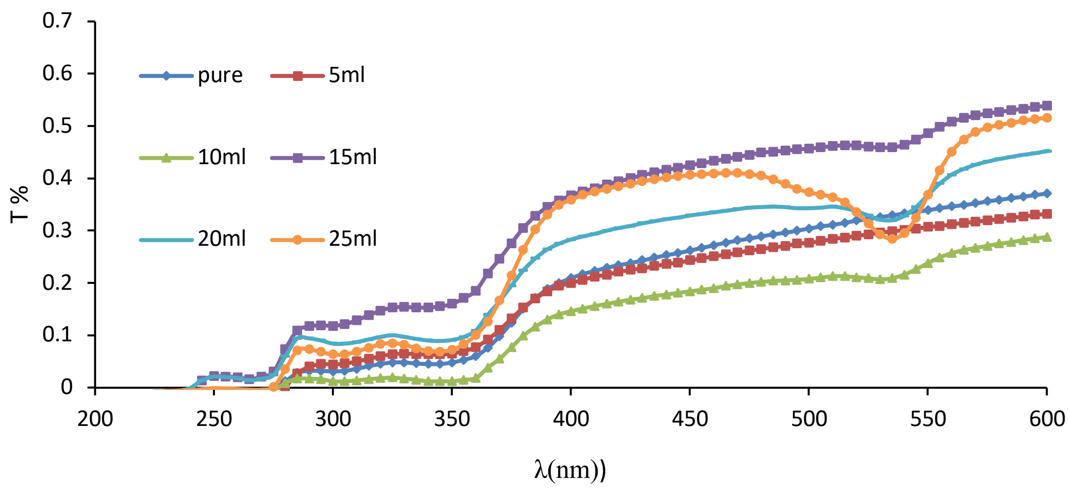

Fig. 2. Transmission spectra of Rh6G –PMMA/PC films for diverse volume ratios of dye

The reflection spectra can be calculated on the basis of absorption and transmission spectra in accordance with the following law in Equation (1) (L. K. Chopra, & I. Kaur, 1983) as shown in Figure (3).

Figure (3) reveals the high ratio of dye (25) ml; the reflection value increased due to the increased amount of impurities.

$$R+T+A=1 \quad \ldots\ldots\ldots\ldots \qquad (1)$$

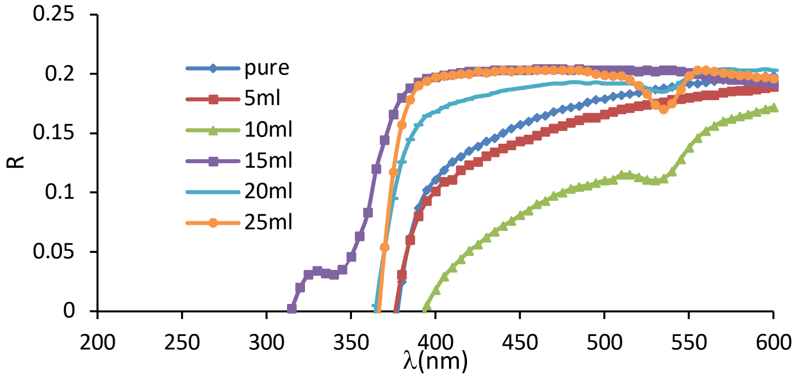

Fig. 3. Reflection spectra of Rh6G –PMMA/PC films for dissimilar volume ratios of dye

The behaviour reflects an increment in the refractive index (n) (Equation (2)) as demonstrated in Figure (4). An extinction coefficient (k) can be computed from Equation. (3); this coefficient represents an amount of energy loss due to the interaction between the spectrum and the charging mediums as shown in Figure (5) (J. L. Pankov, 1971; Asogwa PU, 2011).

$$\mathbf{R} = \frac{(\mathbf{1-n})^2+\mathbf{xK}^2}{(\mathbf{1+n})^2+\mathbf{xK}^2} \qquad (2)$$

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

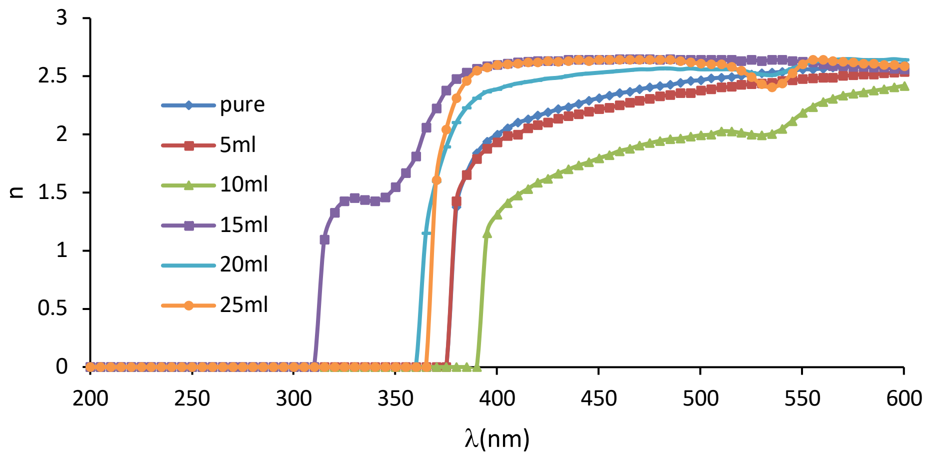

Fig. 4. refractive index (n) as function to wavelength for Rh6G –PMMA/PC films for different volume ratio of dye

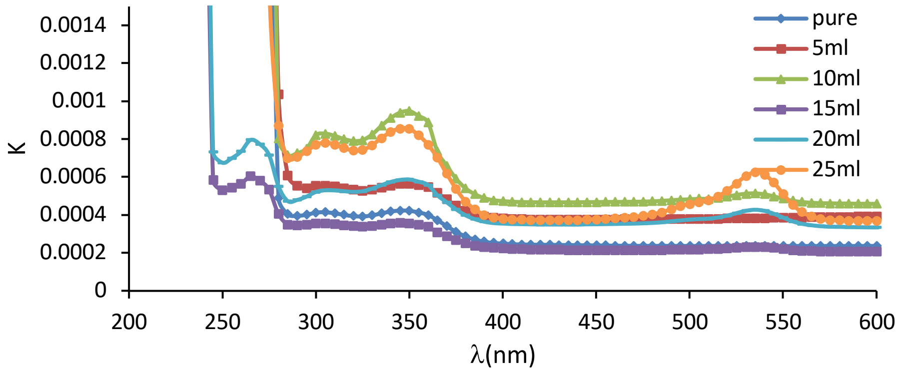

Fig. 5. extinction coefficient (k) based on the wavelength for Rh6G –PMMA/PC films for different volume ratio of dye

Equation (3) illustrates that the coefficient stands for a wavelength function; it depends on the absorption coefficient (α) offered by the coefficient in Equation (4) and defines the capability of materials to reduce the light that provides the wavelength alone, as shown in Figure (6) (Asogwa PU.,2011; Mahasin F. Hadi Al-Kadhemy *et al.*, 2017; Jahja Kokaj, 2011).

$$\boldsymbol{\alpha} = \frac{\mathbf{2.303A}}{\mathbf{t}} \tag{4}$$

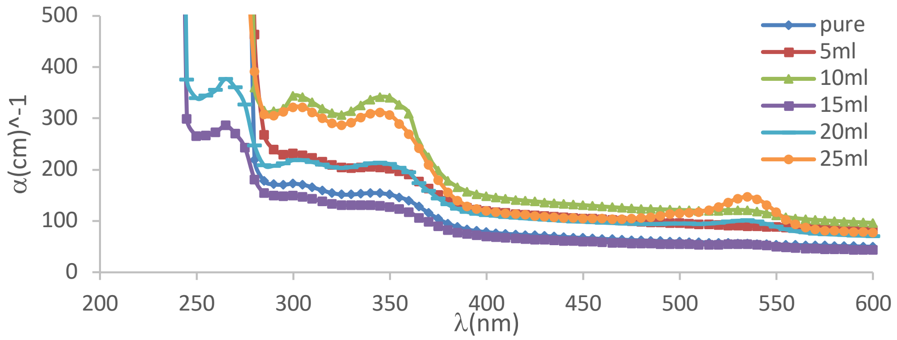

Fig. 6. Absorption coefficient (α) as function to wavelength for Rh6G –PMMA/PC films for different volume ratio of dye

The optical band gap can be estimated from Equation. (5) (L. K. Chopra, and I. Kaur, 1971; Mahasin F. Hadi Al-Kadhemy *et al.*, 2017).

$$(\alpha h\upsilon)^{1/r} = m(h\upsilon - E_g) \tag{5}$$

where m stands for constant, E_g represents the optical band gap energy, hυ stands for the incident photon energy and the exponent r is subject to on the transition kind. n = 1/2, 2, 3/2 and 3 based on allowable direct, allowable indirect, prohibited direct and prohibited indirect transitions, respectively.

The suitable transition was verified by approximating the power r that predicts indirect transition for PMMA/PC polymers under study. Nevertheless, the optical band gap was determined by drawing $(\alpha ht)^{1/2}$ set against hυ and extrapolating the straight-line portion of the curve to intercept the energy axis in Equation (5).

The magnitudes for E_g were obtained for the indirect transition of the samples (Figure (7)) and listed in Table (1). The values changed for the indirect transition from 4.18 eV to 4.9 eV as the volume ratio of Rh6G dye solution increased due to the expected partial dissociation of Rh6G dye attributable to polymer reduction (Asrar Abdulmunem Saeed *et al., 2020*).

The absorption shift to lower wave length (blue shift) means the absorption shifts to higher energy which has a positive accompanied by high degree of order which increases other parameters like band gap. A red shift in the absorption spectra of a material will increase its ability to absorb a wider spectrum of light (more in the visible region) and decrease the band gap. There for according to red shift done with concentration 15 and 20 ml of Rh6G which mixed with PMMA/PC films the energy gap changed from 4.3 eV for pure PMMA/PC films to 4.9 eV and 4.85 eV for mixture with concentration of Rh6G 15 and 20 ml. The opposite appear with blue shift wharas the energy gap decreased from 4.3 eV for pure PMMA/PC films to 4.18 eV for mixture with concentration of Rh6G 10 and 20 ml.

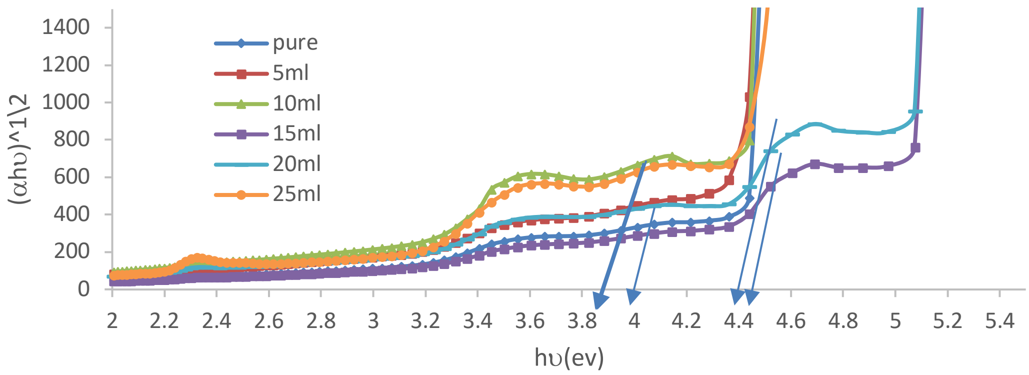

Fig. 7. energy band gap as function for Rh6G –PMMA/PC films for different volume ratio of dye

4. Conclusion

Overall, the paper highlighted the Rh6G-PMMA/PC films, which were primed by the casting technique. The effects of the change in the volume ratio of the Rh6G dye solution on the optical properties of the films had been carefully investigated. The results showed that the PMMA/PC films experienced an increase in intensity after adding the dye, resulting in the appearance of a new peak. Whare the intensity change from 1.504 and 1.345 for wavelength 300 and 340 nm respectively belonge to pure PMMA/PC film to 1.862,1.078, 1.051and 0.495 for wavelength 265, 300, 345 and 535 respectively belonge to mixture of 20ml Rh6G/ PMMA/PC. Furthermore, the energy band gap had demonstrate big difference after adding Rh6G by decreasing and increasing the energy gap, first of all the decreasing energy gap from 4.3 eV for pure PMMA/PC films to 4.18 eV for concentration of Rh6G (5,10 and 25 ml) which mixed to PMMA/PC film. The second showed the increasing energy gap to (4.85 and 4.9) eV for concentration (15 and 20) ml respectively for Rh6G after mixing the PMMA/PC films.

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