Optical properties of Xanthene Dye Doped Polymer Blend

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Abstract. The optical characteristics of blend polyvinylacetate / Polymethylmethacrylate (PVAc/PMMA) films doped with rhodamine6G (Rh6G) with different ratios of (5ml , 10ml , 15ml , 20ml , 25ml , 30ml) were studied. The thin films prepared by using casting technique. Many optical constant are calculated depending on absorption spectrum in the wavelength rang (200-800) nm, such as refractive index(n), absorption coefficient(α), optical energy gap(Eg) as well as real and imaginary part of dielectric constants.

Key words: polymer blend, Rhodamine 6G, doping ratios.

1- Introduction

The study of optical absorption spectra in solids provides essential information about the band structure and the energy gap in the crystalline and non-crystalline materials [1]. The analysis of the absorption spectra in the lower energy part gives information about atomic vibration while the higher energy part of the spectra gives knowledge about the electronic states in atom [2]. Optical properties such as refractive indices for certain range of wavelength between ultraviolet and near infrared, and optical band gap values, are becoming quite important criteria for selection of application of the fabricated films; the refractive indices of optical materials have considerable importance for applications in integrated optic devices such as switches [3].

The absorption coefficient near fundamental absorption edge in both of crystalline and amorphous semiconductors is dependent on the photon energy. For direct transitions, the absorption coefficient was taken on the following more general form as a function of photon energy [4, 5].

\[ \alpha h = A (\alpha h - E_g)^r \]   \hspace{1cm} (1)

for indirect transition

\[ \alpha h = B (\alpha h - E_g)^r \]   \hspace{1cm} (2)

where \( \nu \) is the frequency of the incident photon, \( r \) is the number which characterizes the optical processes, \( r \) has the value 1/2 for the direct allowed transition, 3/2 for forbidden direct transition and 2 for the indirect allowed transition, 3 for forbidden indirect transition. \( A \) and \( B \) are constants and \( E_g \) is the optical energy gap. When the straight portion of the graph of \( (\alpha h)^{1/2} \) against \( (h) \) is extrapolated to \( \alpha=0 \), the intercept gives the transition band gap [6].
The optical absorption coefficient $\alpha$ (cm$^{-1}$) which is a function of wavelength can be calculated from the optical absorbance spectra by using the relation:

$$I = I_0 e^{-\alpha t}$$  \hspace{1cm} (3)

Where $I$ is the incident intensity and $I_0$ is the penetrating light intensity, and $t$ is the thicknesses of matter (cm) and $\alpha$ is the absorption coefficient (cm$^{-1}$) where the amount of $\log(I/I_0)$ represents the absorbance (A).

The absorption coefficient can be calculated by:

$$\alpha = 2.3 \cdot \frac{A}{t}$$  \hspace{1cm} (4)

The reflectance ($R$) can be calculated from the values of the absorbance and transmission coefficient from the equation [8]:

$$R = 1 - (A + T)$$  \hspace{1cm} (5)

The extinction coefficient can be calculated by:

$$k = \frac{\alpha}{4}$$  \hspace{1cm} (6)

The refractive index $n$ can be expressed by:

$$n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}}$$  \hspace{1cm} (7)

Where $\lambda$ is the wavelength of the incident ray. The relation between the complex dielectric constant and the complex refractive index $N$ is expressed by:

$$\varepsilon = N^2$$  \hspace{1cm} (8)

It can be concluded that:

$$(n - ik)^2 = \varepsilon_r - i \varepsilon_i$$  \hspace{1cm} (9)

The real and imaginary complex dielectric constants can be expressed by Equation 9 and 10, respectively:

$$\varepsilon_r = n^2 - k^2$$  \hspace{1cm} (10)

$$\varepsilon_i = 2nk$$  \hspace{1cm} (11)

N.J.Hameed & M.R.Fraih (10) studied the optical constants of PMMA/PC blends. The Samples are casted as films from PMMA and PC homopolymers and blend. The energy gap for PMMA is (5eV) and the energy gap for PC is (4.25 eV). The energy gap of 50% PMMA/ 50%PC (2.5 eV) which is less than the energy gap of PC and PMMA and the other binary blends.

Z.J.Neamah, et.al. (11) Studied and investigation the optical properties of pure PC and doping PC with anthracene with different doping ratio (10, 20, 30, 40, 50 and 60) ml.

The aim of the research is study the optical properties of polymer blend (PVAc / PMMA) with different ratios of Rhodamine6G (Rh6G).
2- Experimental Work

Materials:

The materials tested in this study were polyvinyl acetate (PVAc), polymethyl methacrylate (PMMA), chloroform solution and Rhodamine 6G were preparation of blend polyvinylacetate Polymethyl methacrylate "PVAc /PMMA".

Preparation of polymer blend doping with Rhodamine6G

The blend can be prepared by using(50%wt) polyvinyl acetate "PVAc" with (50%wt) polymethyl methacrylate "PMMA" and chloroform solution equipped with mechanical stirrer the solution were poured into glass Petri dishes and left for 24 hours at room temperature. Finally the films of the samples were removed and then cut as desired. It was observed that only for the concentration of Rh-6G (1*10^{-5} mol) doped in polymer blend. The doping of blend (PVAc /PMMA) with dye Rhodamine6G is carried out by adding the weight dye to the appropriate weight of polymer blend (PVAc/PMMA) then the mixture was dissolved in chloroform solution after the prepared directly to give a polymer / dye system contains (0, 5 ml, 10 ml, 15 ml, 20 ml, 25 ml and 30 ml) of doping reagent Rhodamine 6G [8]. The mixture was stirred well for (30 min) to guarantee that the homogenous distribution of dye in polymer blend, and then the solution were poured into glass Petri dishes at room temperature. The thickness of films was measured using micrometer. The spectrum of absorption was recorded for wavelengths 200-800 nm using UV-visible spectro photometer model (U-V-25400-38).

3- Results and Discussions

Absorption Spectrum

Figures (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 (Rh6G) one at about (235-270) nm related to π-π* 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}) M/L

Figure (2) show the Absorption spectrum to the Polymer blend and its doping with different ratios of dye Rhodamine 6G (Rh6G) thin films respectively. There are three peaks that can be observed for all doping ratios, the first one at (260-295) nm related π-π* while the other peaks are located at about...
330-360) nm and (480-570) nm related to Rhodamine 6G [9]. From the table(1) we can see that absorption increase with increasing doping ratios of polymer blend with Rhodamine 6G.

![Figure 2](attachment:image2.png)

**Figure (2)** The absorption spectrum for different doping ratios of polymer blends with Rhodamine 6G.

| PVAc/P(MMA) | (PVAC/PM MA) +5ml | (PVAC/PM MA) +10ml | (PVAC/PM MA) +15ml | (PVAC/PM MA) +20ml | (PVAC/PM MA) +25ml | (PVAC/PM MA) +30ml |
|-------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| λ<sub>max</sub> | 285 | 285 | 285 | 285 | 285 | 300 | 380 |
| Abs | 0.322 | 0.322 | 0.322 | 0.322 | 0.322 | 1.719 | 0.526 |
| λ<sub>max</sub> | 350 | 355 | 355 | 355 | 355 | 355 | 355 |
| Abs | 0.151 | 1.33 | 0.23 | 0.23 | 0.23 | 0.23 | 0.23 |
| λ<sub>max</sub> | 545 | 525 | 540 | 540 | 540 | 535 |
| Abs | 0.182 | 0.343 | 0.511 | 0.752 | 1.32 | 1.11 |

**Table (1)** The absorption and wavelength for different doping ratios of polymer blend with Rhodamine 6G.

**Transmission Spectrum**

Figure (3) shows an optical transmittance spectrum as a function of incident wavelength on polymer blend doped Rhodamine 6G films. The transmittance obvious that behavior of the transmission spectrum of pure blend and different doping ratios films are opposite to that of the absorption spectra.

![Figure 3](attachment:image3.png)

**Figure (3)** The transmission spectrum for different doping ratios of polymer blends with Rhodamine 6G.
Reflection Spectrum

Reflection spectrum is calculated from absorption and transmission spectrum according to equation (5). The reflection spectrum of pure blend (PVAc/PMMA) and different doping ratios are shown in figure (4). Increase the doping ratios of polymer blend (PVAc/PMMA) with Rhodamine6G lead to increase the reflection.

![Figure (4) The reflectance spectrum for different doping ratios of polymer blends with Rhodamine6G.](image)

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 eq (1).

![Figure (5) The absorption coefficient spectrum for different doping ratios of polymer blend with Rhodamine6G.](image)

Optical energy gap

According to equation the plot of $(\alpha h)^{1/2}$ versus photon energy are shown in figures (6) 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 (6) The band gap energy spectrum for different doping ratios of polymer blend with Rhodamine6G.

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

| Doping ratios with Rh6G          | Eg (eV) |
|---------------------------------|---------|
| (PVAc/PMMA)                     | 4.875   |
| (PVAc/PMMA)+5ml                 | 4.781   |
| (PVAc/PMMA)+10ml                | 4.691   |
| (PVAc/PMMA)+15ml                | 4.604   |
| (PVAc/PMMA)+20ml                | 4.604   |
| (PVAc/PMMA)+25ml                | 4.072   |
| (PVAc/PMMA)+30ml                | 4.520   |

**Refractive Index (n)**

The Refractive index (n) is an important parameter. The Refractive index (n) of pure blend (PVAc/PMMA) and different doping ratios with Rhodamine6G are shown in figure (7). The Refractive Index (n) is increased with increase the doping ratios.
Figure (7) The refractive index (n) spectrum for different doping ratios of polymer blend with Rhodamine6G.

The extinction coefficient

The extinction coefficient depended on absorbance and can be calculated by equation (6). The extinction coefficient of pure blend (PVA_c/PMMA) and different doping ratios with Rhodamine6G are shown in figure (8). The extinction coefficient increased with increase the doping ratios till (25ml) then the extinction coefficient decrease.

Figure (8) The extinction coefficient spectrum for different doping ratios of polymer blend with Rhodamine6G.

Dielectric constants

Figure (9) illustrates the relation between real parts (ε_r) of dielectric constant with wavelength for different doping ratios of polymer blend respectively. In the range of (250-600) nm the real part dielectric constant for blend 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 (595nm) for pure blend all different doping ratios.
Figure (9) The real dielectric constant spectrum for different doping ratios of polymer blend with Rhodamine6G.

Figure (10) show the relation between imaginary part($\varepsilon_i$)of dielectric constant with wavelength for pure blend and its doping with different ratios respectively its clear from the figure that the imaginary blend and all different doping ratios. Part is dependent on wavelength in range (250-595) nm for pure blend and for doping ratios. The imaginary part of dielectric constant was decreased sharply in high wavelength greater then (595nm) for pure.

Figure (10) The imaginary dielectric constant spectrum for different doping ratios of polymer blend with Rhodamine6G.

4- Conclusions

The blend doped with Rhodamine 6G thin films have been prepared by cast method technique. The optical transmission spectrum is used to calculate the optical parameters such as absorption coefficient, real and imaginary parts of dielectric constant where found to be increasing with increasing of doping ratios the energy gap of indirect transition decreases with increasing doping ratios.
5- References

[1] S. H. Deshmukh, D. K. Burghate, S. N. Schilaskar, G. N. Choudari and P.T. Deshmukh, Ind. J. Pure and Applied Phys. Vol. 46, (2008) 344-348.

[2] F. H. Abdel Kader, W. H. Osman, H. S. Ragab, J. Polt. Mater 21 (2004) 49.

[3] W. C. Tang, MSc. Thesis, University of Saskatchewan, (2006).

[4] T. M. Tsidelkovsk, Band structure of semiconductors, Pergamon Press Oxford (1982).

[5] H. N. Najeeb, A.A. Balakits, G. A. Wahab, A. K. Kodeary, Academic Research International, vol. 5 No. 1 (2011).

[6] F. I. Ezema, Turk J. Phys. 29 (2005) 105-114.

[7] M. A. Jabir, PhD. thesis, University of Basrah, (2003).

[8] E. Amir, P. Anton, L. M. Campos, Damiron, N. Gupta, R. J. Amir, N. Pesika, E. Droekennmullerand C. J. Hawker, Electronic Supplementary Material (ESI), The Royal Society of Chemistry Journal (2012).

[9] S. Singh, V. R. Kanetkar, G. Sridhar, V. Muthuswamy, K. Raja, J. Luminescence, 101 (2003) 285-291.

[10] N. J. Hameed & M. R. Fraih. Study of the optical constants of the PMMA/PC Blends, Eng & Tech. Journal, 29(4), 698-708 (2011).

[11] S. A. Asrar, M. F. Hadi and Z. J. Neamah (2017). The Effect of Anthracene on optical properties of polycarbonate films. Journal of College of Education, Ibn Al-Haitham – Baghdad University.