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Optical Properties of Methyl Green and Methyl Red Polycarbonate Films

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Abstract: This research aimed to study the effect of incorporating additives (organic dyes) on the optical properties of polycarbonate (PC) films by investigating some of their optical constants. The casting method was chosen to prepare films from pristine PC mixed with either methyl green (MG) or methyl red (MR) in doping ratios of 5, 10, 15, 20, and 25 ml. The results showed that both the MG/PC and the MR/PC mixtures exhibited the same two absorption peaks as the pristine PC at wavelengths of 310 and 350 mm. The addition of the dyes did not shift the positions of the absorption wavelengths; however, the absorption coefficients, as peak values, of the mixtures were decreased, while the energy gaps were increased. This indicated that the dyes attenuated the conductivity of the PC.

Keywords: optical properties, organic dyes, polycarbonate polymer, doped dyes.

甲基绿和甲基红聚碳酸酯薄膜的光学特性

摘要：本研究旨在通过研究聚碳酸酯 (个人电脑) 薄膜的一些光学常数来研究加入添加剂（有机染料）对聚碳酸酯 (个人电脑) 薄膜光学性能的影响。 选择流延方法从原始个人电脑与甲基绿 (MG) 或甲基红 (MR) 以 5、10、15、20 和 25 毫升的掺杂比混合制备薄膜。 结果表明，MG/个人电脑和 MR/个人电脑混合物在 310 和 350 毫米的波长处表现出与原始个人电脑相同的两个吸收峰。 染料的加入没有改变吸收波长的位置； 然而，作为峰值的混合物的吸收系数降低，而能隙增加。 这表明染料减弱了个人电脑的导电性。

关键词：光学特性、有机染料、聚碳酸酯聚合物、掺杂染料。

1. Introduction

The optical properties of materials indicate their response to light and ability to conduct it, and several changes to electronic and vibrational states occur during absorption and emission processes. As with most chemistry and physics processes, the overall kinetics of a process can be important for determining which processes will be favored. Recently, the optical properties of various polymers have been studied due to their consideration for many applications [1].

2. Materials and Methods

2.1. Polycarbonate

Polycarbonate (PC), a polymer with prominent mechanical and optical properties, is used, to a great extent, for water bottles, screens, and car light covers [2]. Used in design, PC has great lucidity and effect [3]. Being a thermoplastic polymer, PC has good thermal and impact resistance, so it has numerous applications [4].

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2.2. Methyl Green and Methyl Red Dyes

We used methyl green (MG) dye. It is a fundamental triphenylmethane-type dicationic dye, generally used for the recoloring of medications and in science as a photo chromophore to sensitize gelatinous films [5]. This water-solvent dye yields shared cations in arrangement, which is why it is called a cationic dye. Being resistant compounds, dyes used by many industries end up in industrial effluent, which creates unfavorable environmental issues [6, 7]. Fig. 1 shows the sub-atomic structure of MG dye [6].

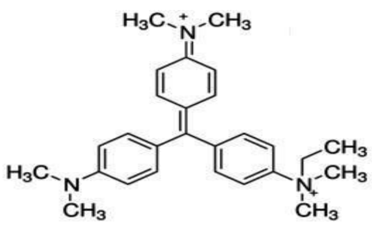

Fig. 1 Structure of methyl green dye

Most dyes used for the pigmentation of materials, including cowhide, paper, pottery, and food preparation, are azo dyes, which are discharged with water after their use [8, 9, 20]. This represents an extraordinary hazard to human and ecological wellbeing because of the lethality of azo dyes [10].

Methyl red (MR) dye, was chosen as a model framework due to its extraordinary color in a watery framework and low biodegradability due to the presence of benzene rings. MR, or dimethylamino, is an azo dye. It is an indicator dye, being red in a pH under 4.4, yellow in a pH over 6.2, and orange in between. The sub-atomic structure of MR dye is shown in Fig. 2 [11]. The molecular formula of MR is $C_{15}H_{15}N_3O_2$, and it has a molar mass of 269.31 g/mole and a melting point between 179°C and 182°C [12].

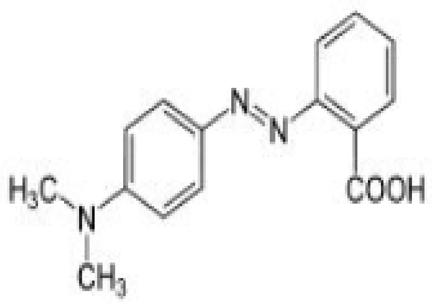

Fig. (2) Structure of Methyl Red dye

In this study, the optical properties of mixtures of PC/MG and PC/MR were verified. The optical properties included absorption, transmittance, some optical constants, and the energy gaps of MG and MR dye solutions mixed with PC. The effect of changing the dye solution concentration in the mixtures on the UV-VIS spectra of the PC film was investigated.

2.3. Theoretical Background

The optical properties of a material are significant because they impart information about the structure of the material and indicate the types of electronic transitions the material undergoes. The optical properties of a material can be characterized as any property that includes interaction between electromagnetic radiation or light and its issue, and from the outcome of these interactions, the nature of the material can be determined.

Absorbance episode beams occur when a photon's donated energy is equivalent to or greater than the forbidden energy gap (Eg) of a conduction band as follows [13-15]:

$$h\,v \geq Eg, \tag{1}$$

where v is the frequency in Hz and h is Planck's constant.

The absorbance (A) of a sample is defined as follows [16]:

$$A = \log I/I_o, \tag{2}$$

where I_o is the intensity of incident light and I is the intensity of transmitted light at distance x.

The absorption coefficient (□) can be expressed by the Lambert–Beer law [17] as follows:

□□□□ $\log A/x$, (3)

where x is the sample thickness.

The relationship between the optical band gap, the absorption coefficient, and the energy (hv) of the incident photon is given as follows [16, 17]:

□□□□□□ $hv = B\,(hv\text{-}Eg)^r$, (4)

where Eg is the optical energy gap, B is a constant, and r is an index that can be assumed to have values of 1/2, 3/2, 2, or 3 depending on the nature of the electronic transition responsible for the absorption: r = 1/2 refers to allowed direct transition, r = 3/2 refers to forbidden direct transition, r = 2 refers to indirect allowed transitions, and r = 3 refers to forbidden indirect transition [16, 18].

2.4. Experimental Work

MG and MR dye solutions with concentrations of 0.5×10^{-4} mol/l were prepared with distilled water depending on the weight of the MG or MR dye according to Eq. (1) [19] as follows:

$$W = (M_w \, x \, C \, x \, V)/1000 \tag{5}$$

where W is the weight of the dissolved dye (g), M_W is the molecular weight of the dye (g/mol), V is the volume of the solvent (ml), and C is the dye concentration (mol/l).

MG/PC and MR/PC films were prepared from 0.5 g of PC polymer, with a molecular weight of 11,000 g/mol, in 10 ml distilled water and stirred with a magnetic stirrer for 3–4 h until well dissolved. Then, a certain volume ratio of dye solution (5, 10, 15, 20, and 25) ml was added to the PC solution. The mixture was put in a glass plate with a diameter of 3 cm and left to cast for 3-4 days to get homogeneous films.

An ultraviolet-visible spectrophotometer is an instrumental technique type (T80 Series UV/VIS spectrometer) used to measure all films' absorption and transmission spectra.

3. Results and Discussions

The absorption spectrum of pristine polycarbonate (PC) and the different volume ratios of methyl green (MG) are represented by a mixture of PC/MG films where the volume ratio for MG varies between 5, 10, 15, 20, and 25 ml as represented in Fig. 3. The results show that there are two peaks of absorption for pristine polycarbonate at different wavelengths: the first is 1.136 at wavelength 310 nm, and the second is 1.127 at wavelength 350 nm. But after mixing with a different doping ratio of MG, there were variable values depending on the variable doping ratio of the dyes. The first peak change ranged between 0.989 for a doping ratio of 10 ml at wavelength 310 nm to 0.69 for a doping ratio of 25 ml at the same wavelength. For the second peak, at a wavelength of 350 nm, the peak drop ranged between 0.924 for a doping ratio of 10 ml to 0.578 for a doping ratio of 25 ml. A similar behavior, as shown in Fig. 4, was seen for PC mixed with MR in which the maximum absorption for pristine PC is 0.976 at wavelength 310 nm and 0.952 at wavelength 350 nm, but after mixing with a different doping ratio of MR, the peak drop ranged between 0.897 at wavelength 310 for a doping ratio of 10 ml to 0.721 with a doping ratio of 25 ml. On the other hand, the peak of pristine PC (0.952) showed a drop with the value ranging from 0.897 at wavelength 350 for a doping ratio of 10 ml to 0.682 for a doping ratio of 25 ml as shown in Table 1 which represents the values of all the optical parameters of pristine PC and the mixture (MG, MR)/PC.

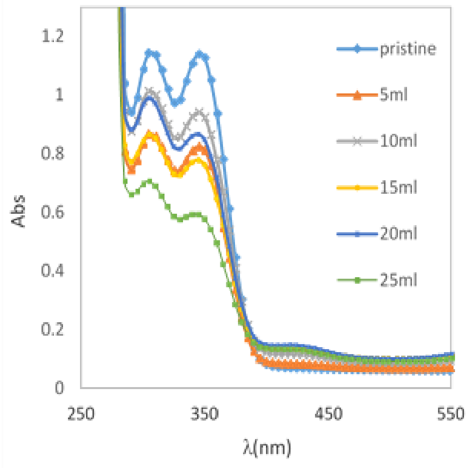

Figure (3): *Absorption spectra of pristine PC and mixture of MG / PC films with different doping ratio of MG dye different doping ratio of MR dye solution*

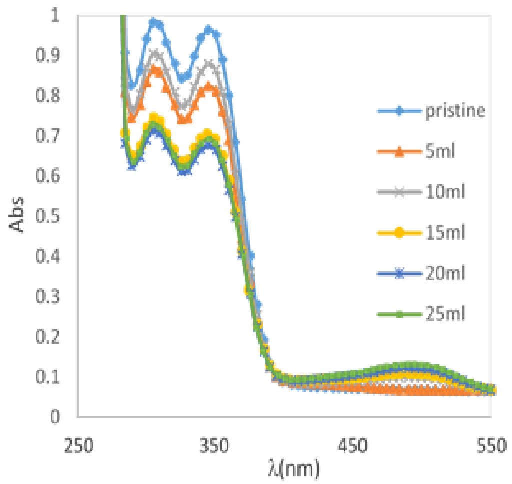

Figure (4): *Absorption spectra of pristine PC and mixture of MR / PC films with different doping ratio of MR different doping ratio of MR dye solution*

The reason behind the decrease in the intensity of the absorption spectrum of the mixture (MG, MR)/PC compared with the pristine PC is due to the increase in the number of molecules of the dyes per volume (increasing the concentration) which leads to an aggregation of dyes. This decreases the intensity of the absorption of polymer especially if we know the absorption wavelength of green color is between 500 and 565 nm, and for red color, it is between 625 and 740 nm. This, in turn, leads to a change in the energy levels.

Fig. 5 shows that the transmittance of pristine PC is more than the transmittance of mixture MG/PC film. The first peak of PC is 0.083 at wavelength 315 nm, and the second is 0.075 at wavelength 350 nm, while for MG/PC mixture, the first peak is 0.103 at wavelength 305 nm, and the second peak is 0.136 at wavelength 345 nm for 20 ml concentration. Fig. 6 shows that the transmittance of pristine PC is more than the transmittance of mixture MR/PC film. The first peak of pristine PC is 0.106 at wavelength 310 nm, and the second is 0.112 at wavelength 350 nm. For MR/PC, the first peak is 0.126 at wavelength 310, and the second is 0.136 at wavelength 350 nm for 10 ml concentration. The results show that the transmittance increases with dye because the MG and MR show more transparency than PC.

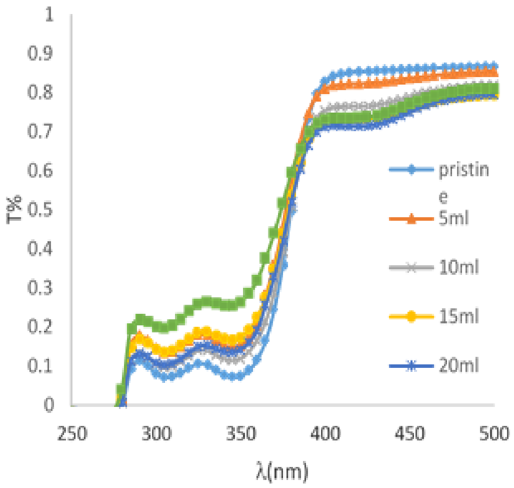

Figure. (5): *Transmittance spectra of pristine PC and mixture of MG / PC films with different doping ratio of MG*

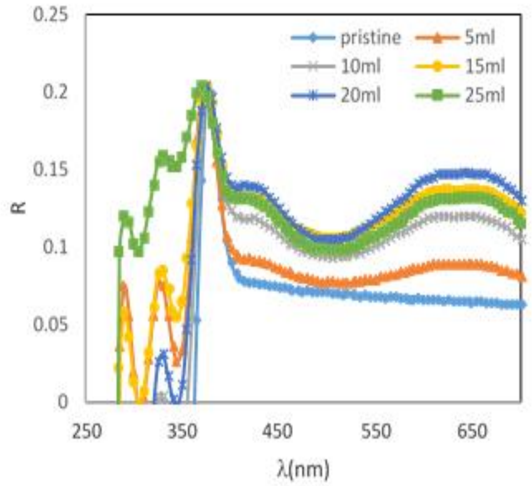

Figure (7): *Refraction spectra of pristine PC and mixture of MG / PC films with different doping ratio of MG*

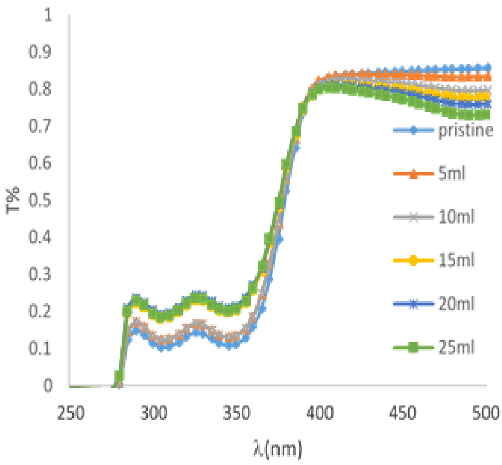

Figure. (6): *Transmittance spectra of pristine PC and mixture of MR / PC films with different doping ratio of MR*

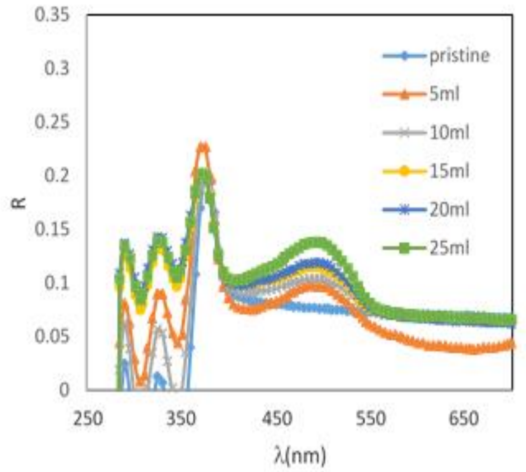

Figure (8): *Reflection spectra of pristine PC and mixture of MR / PC films with different doping ratio of MR*

Fig. 7 refers to the reflection spectra. The maximum reflection belongs to the mixture MG/PC for the concentration of 25 ml. The peak is 0.204 at wavelength 370 nm, while for pristine PC, the peak is 0.199 at wavelength 380 nm. Fig. 8 refers to the reflection spectra, which is the maximum reflection belonging to the MR/PC mixture with 5 ml concentration. The peak is 0.227 for a 375 nm wavelength; for pristine PC, the reflection is 0.195 for a 380 nm wavelength.

Fig. 9 refers to the extinction coefficient. The results show the first peak is 0.001724 for a 310 nm wavelength, and the second peak is 0.00169 for a 350 nm wavelength. Both peaks belong to the MG/PC mixture with 20 ml concentration: the first peak for pristine PC is 0.00130 for a 315 nm wavelength, and the second peak is 0.00150 for a 350 nm wavelength.

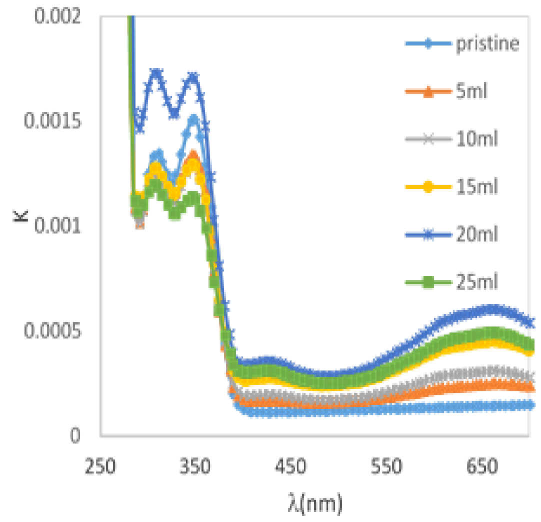

***Figure (9):** Extinction coefficient of pristine PC and mixture of MG / PC films with different doping ratio of MG*

Fig. 10 refers to the extinction coefficient. The results show that the maximum first peak is 0.00112 for a 315 nm wavelength, and the second peak is 0.00127 for a 350 nm wavelength; both peaks belong to pristine PC. The other two peaks belong to the 20 ml concentration. The first peak is 0.001 for a 310 nm wavelength, and the second peak is 0.0011 for a 350 nm wavelength (Table 1).

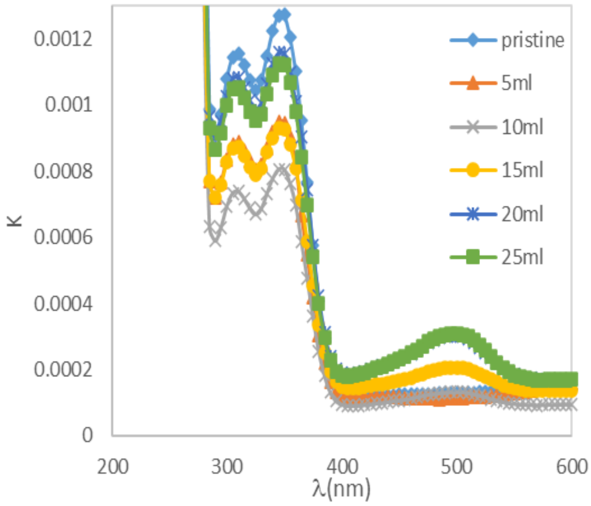

Fig. 10 Extinction coefficient

Fig. 11 shows the maximum refractive index for 25 ml concentration of 2.64 for a 370 nm wavelength, while the maximum refractive index for pristine polycarbonate is 2.610 for a 380 nm wavelength.

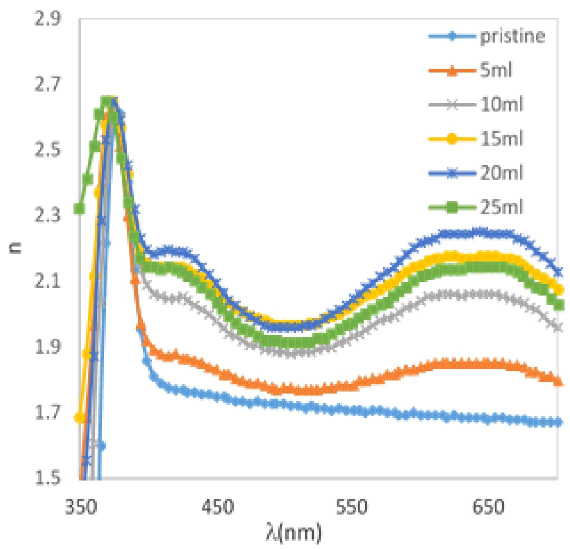

***Figure (11):** Refractive index of pristine PC and mixture of MG / PC films with different doping ratio of MG*

Fig. 12 shows the maximum refractive index for 5 ml concentration of 2.82 for a 375 nm wavelength, while the maximum refractive index for pristine polycarbonate is 2.581 for a 380 nm wavelength.

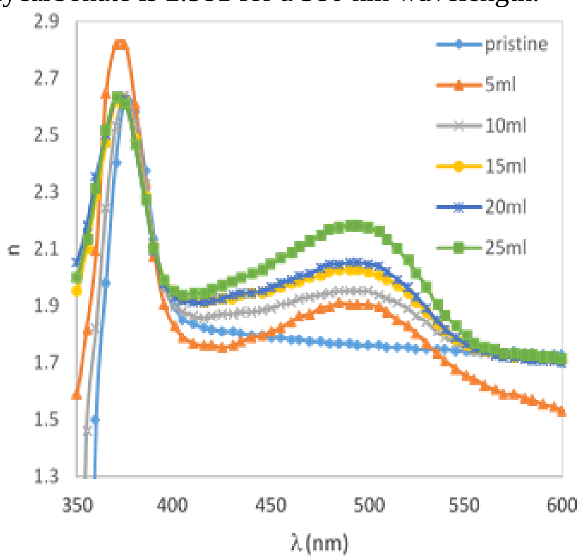

***Figure (12):** Refractive index of pristine PC and mixture of MR / PC films with different doping ratio of MR*

Fig. 13 shows the maximum real dielectric constant for 25 ml concentration of 7.00 for a 370 nm wavelength, while the peak of pristine PC is 6.81 for a 380 nm wavelength. Fig. 14 shows the maximum real dielectric constant is 7.952 at wavelength 375 nm for a 5 ml concentration, while the peak of pristine PC is 6.81 at wavelength 380 nm.

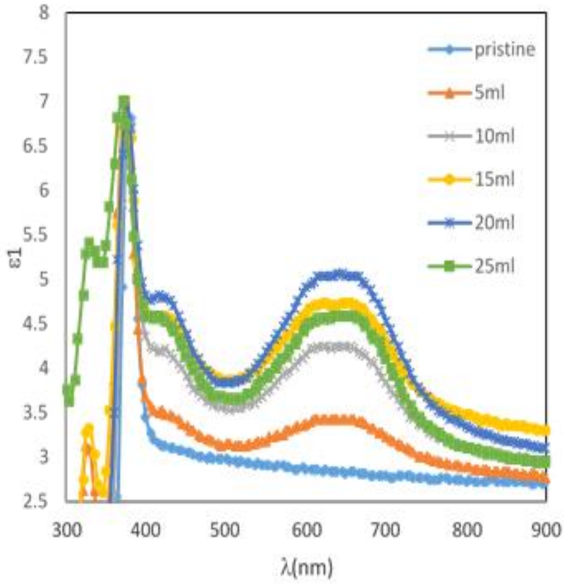

Figure (13): *Real dielectric constant of pristine PC and mixture of MG / PC films with different doping ratio of MG*

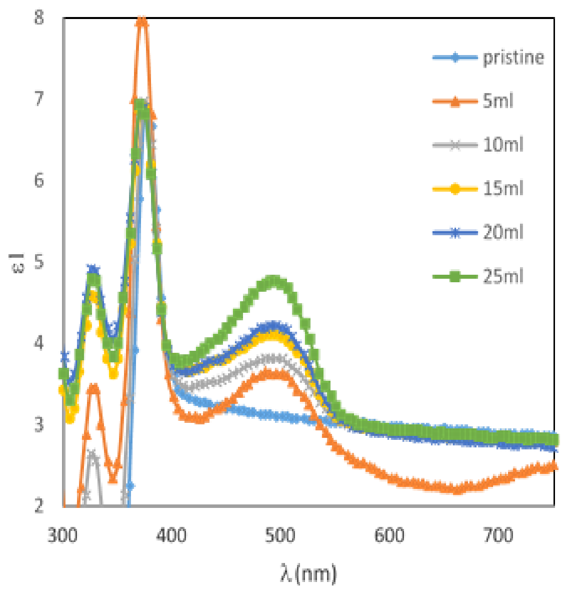

Figure (14): *Real dielectric constant of pristine PC and mixture of MR / PC films with different doping ratio of MR*

Fig. 15 shows that the peak of imaginary dielectric constant is 0.0056 at wavelength 365 nm for a 20 ml concentration, while for pristine PC it is 0.00383 at wavelength 370 nm. Fig. 16 shows that the peak of imaginary dielectric constant is 0.00132 at wavelength 365 nm for a 25 ml concentration.

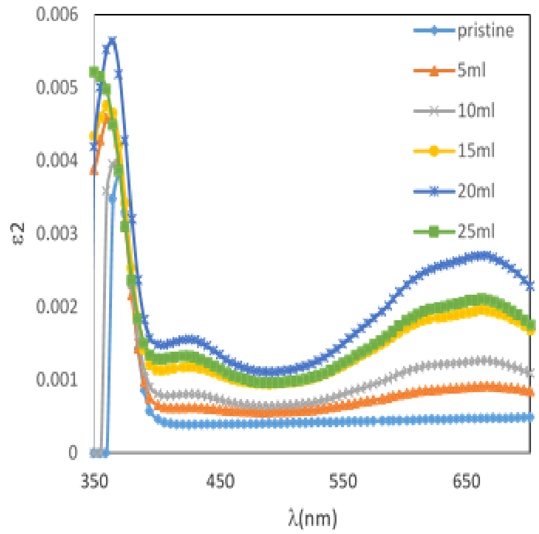

Figure (15): *Imaginary dielectric constant of pristine PC and mixture of MG / PC films with different doping ratio of MG*

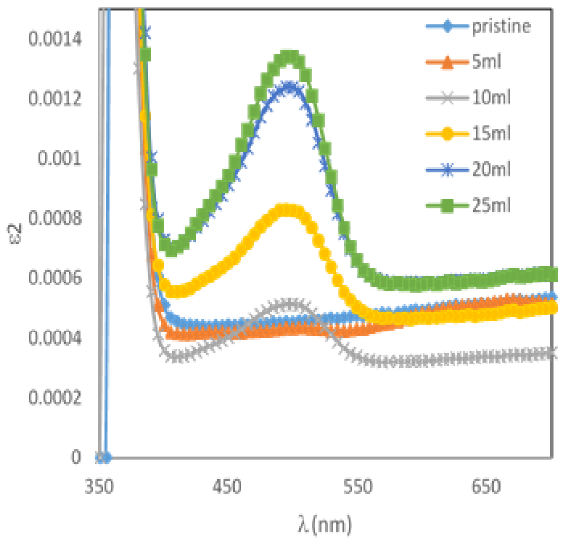

Figure (16): *Imaginary dielectric constant of pristine PC and mixture of MR / PC films with different doping ratio of MR*

Fig. 17 shows there are two peaks of absorption coefficient for a 20 ml concentration. The first one is 711.7 at wavelength 310 nm, and the second is 623 at 345 nm. For pristine PC, the first absorption coefficient is 545 for 310 nm, and the second is 540 at wavelength 350 nm.

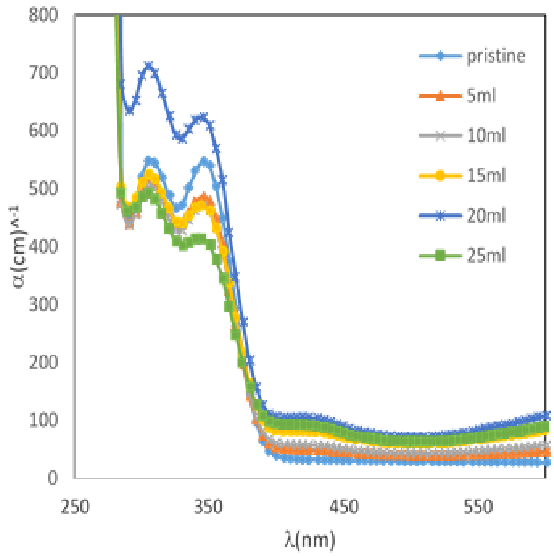

***Figure (17):** Absorption coefficient of pristine PC and mixture of MG / PC films with different doping ratio of MG*

Fig. 18 shows there are two peaks of absorption coefficient. For pristine PC, the first peak is 468.276 at wavelength 310 nm, and the second peak is 456.76166 at wavelength 350 nm. For the 20ml concentration, the first one is 439.437 at wavelength 310 nm, and the second is 421.386 at 345 nm.

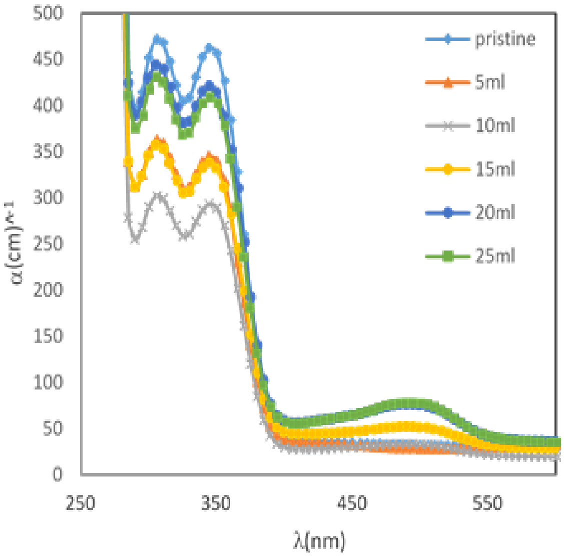

***Figure (18):** Absorption coefficient of pristine PC and mixture of MR / PC films with different doping ratio of MR*

The absorption coefficient for pristine PC and the mixture are less than 10^4 cm^{-1} so that the indirect electronic transition is dominant.

Fig. 19 shows the allowed indirect energy gap is 3.2, 3.5, 3.55, 3.58, 3.6, and 3.65 ev for 20, pristine, 5, 10, 15, 20, and 25 ml respectively. Fig. 20 shows the allowed indirect energy gap is 3.4, 3.49, 3.6, 3.6, 3.7, and 3.8 ev for pristine PC, 20, 25, 15, 5, and 10 ml respectively. Most of the results show there is an increasing and shifting in the energy gap related to the addition of dyes.

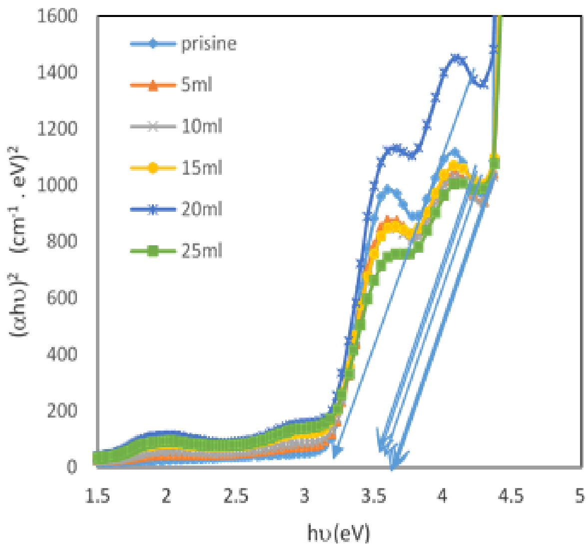

***Figure (19):** Allowed indirect energy gap of pristine PC and mixture of MG / PC films with different doping ratio of MG*

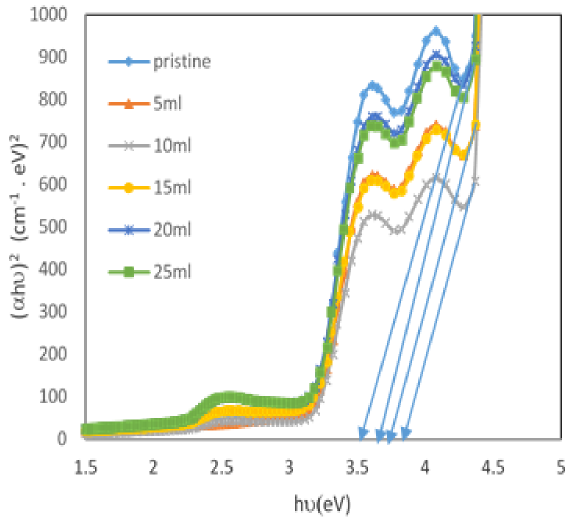

***Figure (20):** Allowed indirect energy gap of pristine PC and mixture of MR / PC films with different doping ratio of MR*

Table 1 shows the comparison for optical parameters between pristine PC and a mixture of PC/(MG, MR).

Table 1 The performance values obtained from the algorithm as a result of test processes

Pristine PC and Mixture PC/MG assays					Pristine PC and Mixture PC/MR assays				
Optical parameters	Pristine PC	Wavelength λ (nm)	Concentration of mixture MG with PC	Maximum peak	Wavelength λ (nm)	Pristine PC	Wavelength λ (nm)	Concentration of mixture MR with PC	Maximum peak
A	**1st peak 1.136 2nd peak 1.127**	**310 350**	**10 ml**	**0.989 0.924**	**305 350**	**0.976 0.952**	**310 350**	**10ml**	**0.897 0.866**
T	**1st peak 0.083 2nd peak 0.075**	**315 350**	**20 ml**	**0.103 0.136**	**305 345**	**0.126 0.112**	**310 350**	**10ml**	**0.126 0.136**
R	**0.199**	**380**	**25 ml**	**0.204**	**370**	**0.195**	**380**	**5 ml**	**0.227**
K	**1st peak 0.0013 2nd peak 0.0015**	**315 350**	**20 ml**	**0.00172 0.00169**	**310 350**	**0.0011 0.0012**	**315 350**	**20 ml**	**0.0010 0.0011**
N	**2.61**	**380**	**25 ml**	**2.64**	**370**	**2.581**	380	**5 ml**	**2.82**
ε1	**6.81**	**380**	**25 ml**	**7**	**370**	**6.81**	**380**	**5 ml**	**7.952**
ε2	**0.0038**	**370**	**20 ml**	**0.0056**	**365**	**0**	**0**	**25 ml**	**0.00132**
A	**1st peak 545 2nd peak 540**	**310 350**	**20 ml**	**711.7 623**	**310 345**	**468.27 456.76**	**310 350**	**20 ml**	**439.43 421.38**
αhυ	**3.622**		**10 ml**	**3.621**		**3.32**		**10 ml**	**3.6**

4. Conclusions

The study of optical properties is of great importance due to its technical uses. It provides us with information about the nature of changing optical constants such as absorption coefficient, refractive index, energy gap, and attenuation coefficient.

Thin films are also used to describe the nature or number of layers of the number of atoms of a substance with a thickness less than 1 μm.

The study of optical properties gives us important information in many practical applications such as solar cells, photodetectors, and electronic circuits. This information is important in science and technology and in the civil and military fields. It is also used in magnetic memory devices and integrated circuits.

The incorporation of dyes into polymer materials has made significant progress toward the creation of the solid-state dye. When used as a host matrix for organic pigments, polymers have numerous advantages. In summary, immaculate PC and (MG/PC, MR/PC) films were created using a simple casting process. The impact of changing the volume of the MG, MR dye solution on the optical characteristics of the as-synthesis films was investigated. After adding MG and MR dyes, the absorption peak and coefficient were reduced.

In contrast, the energy gap increased with the addition of MG and MR dyes. This indicated that the dyes (MG and MR) decreased the conductivity and optical characteristics of PC.

Acknowledgments

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