Research Article

Optical Properies of Polystyrene Films Doped by Methyl Green Dye

Asrar A. Saeed, Nadia M. Sloomi

Department of Physics, College of Science, Mustansiriyah University, IRAQ. *Corresspondent email: asrarabdulmunim@yahoo.com

ArticleInfo	Abstract					
D 1	Effects of methyl green (MG) dye on the optical properties of polystyrene (PS) have been studied. Pure polystyrene and MG doned PS films were prepared by using costing method. These films					
Received	I use polystelle and two doped is mins were prepared by using casting include. These mins were prepared by using casting include. These mins were prepared by using casting include.					
11/5/2016	electric transition which was found to be indirect transition. The value of the ontical energy gap					
Assantad	was decreased with increasing doning ratios of methyl green dye. Absorption coefficient					
5/10/2016	extinction coefficient, refractive index and energy gap have been also investigated; it was found					
5/10/2010	that all the above parameters affects by doping dye.					
	Keywords: Methyl green, Polystyrene, Optical properties, Doping, and Energy gap.					
	تم في هذا البحث در اسة تأثير صبغة المثيل الأخضر على الخصائص البصرية للبولي ستايرين حيث تم تحضير اغشية من					
	البولي ستايرين النفي والبولي ستايرين المطعم بصبغة المتيل الأخضر بو اسطة استخدام طريفة الصب هذه الاغتنية ثم فحصها مأر تغدل تقنية جارك (UTV/VIS) لتعديد ندع الأنتقال الأاكترية حسن كان الأنتقال خسر براثه قدية فحد ترالحا لقة تتناقص					
	السلحدام تعليه مطيف (UV/VIS) للحديد فوع الإنتقال الالختروني حيث حال الإنتقال عبر مباسر بيمة حجوه الصحة تساخص ا بذيادة نسبة خلط صيغة المثنان الأخضر ، قد تم كذلك در اسة كان من معامان الأمتصباص ،معامان الأخماد، معامان الأنكسار					
	وفجوة الطاقة،حيث وجد أن هذه المعاملات تتأثر بالصبغة المضافة.					

Introduction

Dyes are widely used in various industries, such as textiles, leather, plastic, paper and cosmetics, for coloring their final products. The release of colored waste water from industry may produce an eco-toxic hazard and introduce potential danger of bioaccumulation, which may eventually affect humans through the food chain [1].

A.A.Saeed [2], focused on the modification of the properties of polystyrene with different additives, namely antimony oxide Sb_2O_3 , tetra Et4N (EtSbC₁₂Br) and Et4N (EtSbBr₂Cl) by preparing the composites system with different percentages (0.4, 0.8, 1.0, 1.2, 1.4) wt. % of the above additives and founded the optical energy gap is slightly decreased with increasing of filler content, while in the wavelength range (400-200) nm the refractive index increased with increasing filler content.

Alkahdemy *et al.* [3], studied optical energy gap for crystal violet doped polystyrene in different doping ratio of crystal violet solution (5, 10, 15, 25, and 40)ml from their optical absorption spectra in (390 - 900) nm for both irradiated and un irradiated with gamma radiation, and was found that the energy gap values shifted to low energies when irradiated with gamma radiation. W.M.Sachit [4], studied the polymeric thin films of polystyrene (PS) graft with Methyl red dye (MR) have been produced using casting method with different weight ratios (1g, 1.5g, 2.5g) from polystyrene and grafted it by (0.01g) from Methyl red, found that the absorption spectra at the weight ratio (2.5g) of polymer PS is different from another ratio where its minimum absorption, and the energy gap is (2.4eV) for ratio (1g) of PS and decreased to be (2.0eV) for ratio (2.5g).

The purpose of this research is reporting some of our results about the effect on optical constants of pure PS film and PS/MG films for different doping ratio. Since the dye absorb strongly in the visible range, the absorption of the spectra of cast, which doped PS films are analyzed. This study takes into account these constants. This is



Copyright © 2017 Authors and Al-Mustansiriyah Journal of Science. This work is licensed under a Creative Commons Attribution-NonCommercial 4.0 International License. done in order to find doped polymer that will result in enhanced optical properties, thus increase the industrial application.

When incident photon energy is less than the energy gap, photon will transmit and the transmittance for thin film is given by the relation [5]:

$$T = (1-R)^2 e^{\alpha t}$$
 (1)

Where: T: Transmittance, R: Reflectance, t: Thin film thickness.

The absorption coefficient (α cm⁻¹) is calculated in the fundamental absorption region using Lambert law:

$$I = I_o e \ge p(-\alpha t)$$
 (2)

Where I_o and I are the intensity of the incident and transmitted light respectively.

$$\alpha = (2.303 \times A)/t \tag{3}$$

Where A: Absorbance.

Reflectance can be founded from the absorption and transmission spectra in accordance with the law of conservation of energy by the following Equation [6]:

$$\mathbf{R} + \mathbf{T} + \mathbf{A} = 1 \tag{4}$$

The imaginary part of the complex refractive index n^* is called the extinction coefficient, as illustrated in the following Equation:

$$n^*=n-iK$$
 (5)

Where (n) is the real part of the refractive index. The extinction coefficient can be measured by using the following Equation [7]:

$$\mathbf{k} = \alpha \lambda / 4\pi \tag{6}$$

Where (λ) is the wavelength of incident ray. Dielectric constant represents the ability of material to polarization [5], whose expression is given by the following Equations:

$$\varepsilon = \varepsilon_1 - i\varepsilon_2 \tag{7}$$

$$\boldsymbol{\varepsilon} = (n^{*})^{2} \tag{8}$$

$$(n - iK)^2 = \varepsilon_1 - i\varepsilon_2$$
 (9)

$$\boldsymbol{\varepsilon} = (n^2 - K^2) - i(2nK) \quad (10)$$

Dielectric coefficient (ϵ) can be measured from refractive index (n), joining complex dielectric coefficient (ϵ) with complex refractive index (n*).

From Equations (11) and (12) real and imaginary complex dielectric coefficient can be written as in following Equation:

$$\varepsilon_1 = (n^2 - K^2) \tag{11}$$

$$\boldsymbol{\varepsilon}_2 = (2 \ n \ K \) \tag{12}$$

The refractive index (n) depends on the reflectance and extinction coefficient (k) according to the following Equations [8]:

$$R = \frac{(1-n)^2 + K^2}{(1+n)^2 + K^2}$$
(13)

Reflectivity can be calculated from Equation (13). Refractive index can be rewritten as [9]:

$$n = \sqrt{\frac{4R}{(R-1)^2} - K^2 - \frac{(R+1)}{(R-1)}}$$
(14)

Materials and Methods

Methyl Green has chemical formula C₂₇H₃₅N₃BrCl with molecular weight Mw=516.94g/mol [10]. Polystyrene polymer has been choosing as host material for laser dye due to its excellent optical properties. The molecular formula of PS is - [-CH (C₆H₅)-CH₂]_n, highly amorphous, melting temperature 270 °C and glass transition temperature 100 °C [11]. It is an aromatic polymer made from the aromatic monomer styrene, a liquid hydrocarbon that is commercially manufactured from petroleum by the chemical industry. Polystyrene is thermoplastic substance and one of the most widely used kinds of plastic [12].

Pure PS and MG/PS films are prepared by casting technique. PS solution is prepared by dissolving (0.5 g) PS in (10ml) dichloromethane. The PS solution is stirred very well at magnetic stirrer until polymer is dissolved and cast onto a glass petri dish with diameter (10cm). Homogenous pure PS films obtained after drying

at room temperature about $(25-30)^{\circ}$ C for 24 hr. To prepare MG/PS films for different doping ratio MG solution which has concentration 0.5 10-3 mol/liter, is chosen: (5, 10, 15, 20 and 25)ml, added to PS solution and stirred very well at magnetic stirrer until the (MG/PS) solution become homogenous solution. Then the solution cast onto glass petri dish and left at room temperature (25°C) for one day to obtain homogenous films.

Results and Discussion

In this section, absorption spectra of methyl green dye in dichloromethane solution, pure PS film, MG/PS films and all optical properties of samples are demonstrated.

Figure 1 shows the absorption spectrum of Methyl Green in dichloromethane solution with concentration (0.5x10-3) mole/liter. The behavior of absorption spectrum with three peaks: the first peak at (285nm) with intensity (1.033), second peak at (415nm) with intensity (0.473) and third peak at (635nm) with intensity (0.54).



Figure 1: Absorption Spectrum of Methyl Green in Dichloromethane Solution

Figure 2 illustrated the absorption spectrum for polystyrene; there is suddenly decrease in the absorption values observed above (285) nm with intensity (0.105), for PS the decrease was even slower.



Figure 2: Absorption Spectrum of Polystyrene Film

Figure 3 illustrated the change in wavelength of absorption spectrum of PS after doping MG is clearly illustrated by appearing double peak at the same wavelengths (410, 630)nm for doping ratio 5ml and 25ml. The intensity of absorption spectrum of all samples increased with increasing doping ratio for Methyl Green solution from (0.087, 0.0838) to (0.146, 0.167) at the same wavelengths (410, 630)nm for (25ml), the absorbance decreased; this is due to form aggregates (such as dimmers and trimmers).



Figure 3: Absorption Spectrum for Pure PS and Different Doping Ratio of MG/PS Films

Figure 4 showed the transmission spectrum of pure PS film and (MG/PS) films with different doping ratio of (MG) dye exhibit opposite behavior in absorbance spectra. The transmission decreased with increasing doping ratio of (MG) dye.



Figure 4: Transmission Spectrum for Pure PS and Different Doping Ratio of MG/PS Films

The reflection spectrum can be calculated according to Equation 4 Reflection spectrum of pure PS films and (MG/PS) films for different doping ratio shown in Figure 5. Reflection increased for peaks of pure PS and (MG/PS) with





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increasing doping ratio of (MG) dye solution that similar to absorption spectra.



Figure 5: Reflection Spectrum for Pure PS and Different Doping Ratio of MG/PS Films

The refractive index (n) is an important optical parameter and determined from Equation 5. Figure 6 illustrated the behavior of refractive index as a function of the wavelength for pure PS film and (MG/PS) films in different doping ratio of (MG) dye solution. It might be showed that the refractive index increased with increasing doping ratio because of increasing reflectivity. This change in refractive index may be attributed to existence of defects [13].



Figure 6: Refractive index spectrum for pure PS and different doping ratio of MG/PS films

The extinction coefficient can be calculated from Equation 6. The variation of (k) values in wavelength range (280-710)nm and wavelength range (280-800) nm as shown in Figure 7 for pure PS film and (MG/PS) films in different doping ratio of (MG). The extinction coefficient depends on absorbance, so that the behavior of all curves is similar to absorption spectrum.



Figure 7: Extinction Coefficient Spectrum for Pure PS Film and Different Doping Ratio of MG/PS Films

Optical constant are very useful for the quantitative determination of the electronic band structure of solids from information of optical reflectivity, transmission and refraction provide the way to determine the dielectric constants of solid, which is related to the band structure. The real and imaginary parts of dielectric constants computed from Equations (11 and 12) respectively. Figure 8 gives the real part of dielectric constant for pure PS film and (MG/PS) films in different doping ratio.

For PS polymer, real dielectric constant increases to be maximum at wavelength (280) nm and decreases with the increasing wavelengths, whereas the effect of (Methyl Green) dye will increased the real part of dielectric constant depended on the square of refractive index, so that the behavior of these Figure are similar to refraction index. Imaginary part of dielectric constants for pure PS polymer and (MG/PS) films in different doping ratio are shown in Figure 9. Imaginary dielectric constant for pure PS film increased with the increasing wavelength. Also, the effect of doping ratio of (MG) solution decreased the imaginary dielectric constant for pure PS films.



Figure 8: Real Part of Dielectric Constant for Pure PS Film and Different Doping Ratio of MG/PS Films.



Figure 9: Imaginary Part of Dielectric Constant for Pure PS Film and Different Doping Ratio of MG/PS Films.

The value of absorption coefficient (α) is calculated from Equation 3 for all samples. The absorption coefficient helps to deduce the nature of electronic transition. Figure 10 showed the absorption coefficient (α) for pure PS films and (MG/PS) films for different doping ratio. When the high absorption coefficient values (α > 104cm-1) at higher energies, direct electronic transitions have been expected and the energy momentum preserve of the electron and photon. Whereas the values of absorption coefficients low ($\alpha < 104$ cm⁻¹) at low energies, indirect electronic transitions have been deduced. In this work the values of absorption coefficients were low energies and indirect electronic transitions have been deduced.



Figure 10: Absorption coefficient spectrum for pure PS film and different doping ratio of MG/PS Films

The optical energy gap is the value of optical energy gap that is necessary to develop the electronic band structure of film material. It can be obtained by plotting (α hv) 1/m versus (hv) in the high absorption range followed by extrapolating the linear region of the plots to (α hv) = 0 [14]. The energy gap for pure PS film can be measured; it is equal to (4.25eV). From the value of absorption coefficient, indirect transition will be calculated.

When Methyl Green added to PS polymer with different doping ratio, the energy band gap was calculated from Figure 11 for all doping ratio. It ranged from (4.25eV) to (2.74eV) from pure polystyrene to (25ml), respectively as shown in Table 1.



Figure 11: Energy gap for pure PS film and different doping ratio of MG/PS films.

Table 1: Energy gap of Methyl Green doped polymer polystyrene films for different doping ratio.

Doping Ratio of MG	Ps- Pure	5	10	15	20	25
Energy gap (EgeV)	4.25	3.9	3.12	2.9	2.86	2,74

Conclusion

From this work it can be concluded that: the absorption spectrum for all samples illustrate two peaks for MG/PS films, these peaks increased with increasing doping ratio of dye solution. The experimental results illustrated that the absorption coefficient for Pure PS and (PS/MG) films less than 104 cm₋₁ this indicates to allowed indirect electronic transitions. Methyl green dye doping ratio solution in polymer affected on the optical Energy gab and optical constants (A, K, n, ε_1 and ε_2) increase and optical energy gap decrease with increasing of Methyl Green solution.

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