Refractive Index Dispersion and Optical Properties of Dye Doped Polystyrene Films.

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ABSTRACT: The basic optical properties and optical constants of the polystyrene doped with methylene blue (mb) and methyl orange (mo) with thickness in the range (0.04-0.05) mm have been investigated by means of transmittance and reflectance spectra, were measured in the wavelength range (300-900) nm. The optical band gap $E_g$ was determined and the optical absorption spectra show that the absorption mechanism is an indirect allowed transition, it has been found that optical energy gap $E_g$ decreases with the increasing of the (mb) and (mo) concentrations. The $E_g$ decreased from 4.2 eV for pure PS films to 3.75 eV and to 3.64 eV for PS +0.06 (mb,mo) respectively. The optical constants (Refractive index, Extinction coefficient, Real and Imaginary parts of the dielectric constant) showed clear changes with increasing (mb) and (mo) doping concentrations. The refractive index, extinction coefficient at $\lambda$=600 nm changing from 1.716 and 5.6379 x10^{-5} for pure PS films to 4.56 and 7.92 x10^{-5} for PS + 0.06 mb, and to 2.52 and 1.27x10^{-4} for PS + 0.06 mo, respectively. The oscillator energy $E_o$, dispersion energy $E_d$ and other parameters have been determined by the Wemple–DiDomenico method. The study is to determine optical constants and optical band gap of dye doped polystyrene, which had been evaluated and compared between two types of dyes of different concentrations.

Keywords: polymer, polystyrene, optical constants, optical band gap, doping

1.0 INTRODUCTION

In recent years, polymers with different optical properties have been attracted much attentions due to their applications in the sensors [1], light-emitting diodes [2–4], and others [5,6]. The optical properties of these materials can be easily tuned by controlling contents of the different concentrations. Though a great deal of excellent work has been reported on such materials [7–9], it is still meaningful to extend the research of these polymers.

A polymer of a particular group is characterized by the molecular weight of the monomer unit. To study the interactions in the solid state of the polymers of few models have been suggested. One such model treats a polymer as an aggregate of fairly stiff tubes held together in approximately parallel bundles of forces arising from particle–particle potentials. The structure of polymers has been related to internal pressure and the same study has been extended to polystyrene solutions. Some of the interesting properties of polystyrene like the Gruneissen parameter, specific heat and bulk modulus have also been reported [10]. Polystyrene (PS) is amorphous polymer with bulky side groups. General purposes PS are hard, rigid, and transparent at room temperature and glass like thermoplastic material which can be soften and distort under heat. It is soluble in aromatic hydrocarbon solvents, cyclohexane and chlorinated hydrocarbons [11].

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The optical properties of PS thin films and the effect of doped concentrations by Anthraquinane copolymer on it studied by Al-Ramadhann [12] and found this films have direct and indirect allowed transition, also found that energy gap decreases with increasing the doped concentrations.

The study by Saeed [11] is focus on the modification of the properties of polystyrene with different additives, namely antimony oxide \( \text{Sb}_2\text{O}_3 \) tetra \( \text{Et}_4\text{N(ETsbCl}_2\text{Br}) \) and \( \text{Et}_4\text{N(ETsbBr}_2\text{Cl}) \) by preparing the composites system with different percentages (0.4,0.8,1.0,1.2,1.4) wt% of the above additives. He found the optical energy gap is slightly decreased with increasing of filler content, while in the wavelength range (400-2000 nm) the refractive index increased with increasing filler content.

However, in this paper we investigate the effect of incorporating additives or dyes, on the optical properties of PS films. Many researchers succeeded to prepare PS as films deposited on various substrates such as glass or silicon wafer [13,14], this interest was by the technological importance of film stability (e.g Toys and novelties, rigid packaging, refrigerator trays, boxes, cosmetic packs and costume jewelers, lighting diffusers, audio cassette and CD cases). The purposes of this paper are reporting some of our results about the effect on optical constants of pure PS as well as of doped PS films with methylene blue (mb) and methylene orange (mo) dye with different concentrations. Since the dyes or dopants 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 done in order to find doped polymer that will result in enhanced optical properties, thus increase the industrial application.

The absorbance (A) of a sample is defined by [15]

\[
A = \log \frac{I}{I_o} \quad \text{.................(1)}
\]

where, \( I_o \) is the intensity of incident light. \( I \) is the intensity of incident light at distance \( x \).

The absorption coefficient (\( \alpha \)) can be expressed by Lambert Beer's law [16]

\[
\alpha = \log \frac{A}{x} \quad \text{.................(2)}
\]

where, \( x \) is sample thickness.

The relation between the optical band gap, absorption coefficient and energy (hv) of the incident photon is given by [15,16]:

\[
\alpha hv = B (hv- E_g)^r \quad \text{.................(3)}
\]

where \( E_g \) the optical energy gap, \( B \) is a constant and \( r \) is an index which can be assumed to have values of 1/2, 3/2, 2 and 3, depending on the nature of the electronic transition responsible for the absorption. \( r =1/2 \) for allowed direct transition, \( r = 3/2 \) for forbidden direct transition and \( r =3 \) for forbidden indirect transition, with \( r =2 \) refers to Indirect allowed transitions [15,17].

2.0 EXPERIMENTAL

PS supplied by ICI with \( M_w =300,000 \text{ g.mol}^{-1} \), \( M_w/M_n = 1.06 \) and purity 99.995, was used as matrix. Chloroform (\( \text{CHCl}_3 \)) of purity 99.998 used as solvent was supplied by (BDH) Company Chemicals Ltd. Poole, England. For dopants, methylene blue (mb), \( \text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}, \ M_w= 319.85 \text{ g.mol}^{-1} \), and methylene orange (mo) \( \text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}, \ M_w= 327.33 \text{ g.mol}^{-1} \), were also purchased from BDH company. PS grains of weight (0.2) gm were dissolved in (5) Vl of Chloroform (\( \text{CHCl}_3 \)) to obtain solution of 4 % wt./vol. The
mixture was shaken well by stirring about 30 min. to obtain homogenous solution, (5ml) of the prepared solution was transferred into clean glass Petri dish with (6 cm) diameter and dried under temperature (50°C) in oven for at least 2 hours and then left to cool slowly to room temperature. The dried films were then removed easily using tweezers clamp. Other similar films were casted in order to ensure dried samples without bubbles and thermal damage. The thickness of prepared films were measured between (0.04 - 0.05) mm by using digital vernier.

Doped films were fabricated by dissolving mb and mo in Chloroform of concentrations 0.02, 0.04, 0.06w/w. The measurements of absorbance and transmittance spectra in the wavelength range (300-900) nm were carried out using UV-160A UV-VIS Recording Spectrophotometer.

The optical absorption and reflectance spectra were analyzed to determine the optical constants such as refractive index n, extinction coefficient k, and absorption coefficient $\alpha$. Analysis of the absorption coefficient was also carried out to determine the optical band gap and nature of transitions.

**3.0 RESULTS AND DISCUSSION**

**3.1 Optical Energy Gap**

Undoped and doped PS films obeys the role of indirect allowed transition and the optical energy gap of pure polystyrene while absorption of doped (mb) and (mo) with various concentrations were determined from straight line, fitting the plot of $(\alpha hv)^{1/2}$ as function of photon energy are shown in Figure 1 (A & B).

The present results were found to obey equation (3) with $r=2$ refer to indirect allowed transitions for all films. From Figure 1(A) the calculation of optical energy gap of doped PS sample with (mb) for different concentration showed which decrease with increasing of (mb) concentrations. The optical energy gap, $E_g$ decreased from 4.2 eV for pure PS films to 3.75 eV for PS +0.06 mb as shown in Table 1, this is ascribed to increase in absorption coefficient as a result of introducing dopant atoms and hence $E_g$ will be decreasing.

The effect of (mo) on the optical energy gap for PS shown in Figure 1(B) shows that $E_g$ decrease with increasing (mo), doping concentration from 4.2 eV for pure PS films to 3.64 eV for PS + 0.06 mo. As referred to Table 1, similar interpretation can be given as in (mb).

The optical energy gap values in case of doped PS with (mb) as compared with optical energy gap of doped PS with (mo), it is clear that mo has greater effect on optical energy gap than mb of PS films, same this result agreement with Hasan [18] that he found that energy gap of PMMA decreased when he doped by mb and mr with different concentrations.
3.2 Refractive Index and Dispersion

The transmittance and reflectance spectra of the films are shown in Figure 2. The extinction coefficient can be calculated by the relation [19]:

\[ k = \frac{\alpha \lambda}{4 \pi} \quad \text{........................(4)} \]

Where \( \lambda \) is the wavelength, \( \alpha \) is the absorption coefficient.

The refractive index of the films was calculated by the following equation [19]:

\[ n = \sqrt{\frac{4R}{(R-1)^2-k^2}} - \frac{R-1}{R} \quad \text{...............(5)} \]

where \( R \) the reflectance and \( k \) the extinction coefficient and define as above.

Figure 1: The variation of \( (\alpha \cdot h \cdot \alpha)^{1/2} \) with \( (h \cdot \alpha) \) of pure and doped PS films. (A) for mb dye and (B) for mo dye, both for different concentrations.

Figure 2: The variation of Transmission and Reflective spectra with (Wavelength) of pure and doped PS films. (A) for mb dye and (B) for mo dye, both for different concentrations.
Figure 3 (A-B) shows the variation of refractive index (n) and extinction coefficient for doped and pure PS films, with wavelength at two types of dyes for different concentrations.

Figure 3(A) shown the refractive index n decreases with increasing wavelength. On the other hand, is observed that (n) of doped PS increases with increasing mb concentrations, indeed (n) changes from 1.716 to 4.56 at $\lambda = 600$ nm when mb concentration increases from 0.0 to 0.06 wt.%. The result of high photosensitivity of mo at the forementioned wavelength range [20].

Figure 3(B) shows the relation between the refractive index as function of wavelength for pure and doped PS with mo of different concentrations. In this figure, (n) exhibits to decrease with $\lambda$ for pure and doped films. Also the values of (n) showed increase with increasing mo concentrations. Moreover, (n) increases from 1.716 to 2.52 at $\lambda = 600$ nm (when mo concentration increases from (0 to 0.06) wt.%. In general, it is clear that (n) values of samples doped with mo are lower than values of samples doped with mb, this means that the former samples are more transparent than the latter.

The dependence of extinction coefficient (k) on the wavelength is shown in Figure 3 (A-B) for pure and doped samples. It is noticed that (k) value of pure sample has reduced, the behavior of pure sample has systematic with wavelength, where decrease with increasing $\lambda$, while (k) for doped sample with mb Figure 3(A), shows an increase with increasing wavelength. The maximum peaks belong to maximum absorption of mb [20] , on the other hand (k) exhibits clear changes with increasing mb concentrations, indeed (k) changes from $5.6379 \times 10^{-5}$ to $7.92 \times 10^{-5}$ at $\lambda = 600$ nm when mb concentration increases from (0-0.06) wt.%.

Figure 3(B) shows the variations of (k) with $\lambda$ of pure and doped PS with mo. (k) shows an increasing with increasing dopant concentration , moreover k increases from $5.63 \times 10^{-5}$ to $1.27 \times 10^{-4}$ at $\lambda = 600$ nm when mo concentration increases from (0- 0.6) wt.%. The behaviour of (k) can be ascribed to high absorption coefficient [18]. This result indicates that the dopant atoms of mo will modify the structure of the host polymer [20]. mo dopant has increased the absorbance in the visible region.

Figure 3: The variation of n & k with (Wavelength) of pure and doped PS films. (A) for mb dye and (B) for mo dye, both for different concentrations.
The variation of $n$ and $k$ values wavelength region 300 to 900 nm as shows in Figure 3 (A-B), that some interactions take places between photons and electrons. The refractive index changes with the variation of the wavelength of the incident light beam due to these interactions [21].

The refractive index dispersion of the thin film is expressed as equation of Didomenico [22]:

$$n^2 = 1 + \frac{E_o E_o}{E_o^2 - (\hbar \nu)^2} \quad \text{………………(6)}$$

where $n$ is the refractive index, $h$ is Planck’s constant, $\nu$ is the frequency, $\hbar \nu$ is the photon energy, $E_o$ is the average excitation energy for electronic transitions and $E_o$ is the dispersion energy which is the measure of the strength of interband optical transitions. The dielectric response for transitions below the optical gap is described by this model. $E_o$ and $E_d$ values were calculated from the slope and intercept on the vertical axis of plot of $1/(n^2 - 1)$ versus $(\hbar \nu)^2$ Figure 4 and given in the Table 1.

The refractive index can also analyzed to determine the long wavelength refractive index $n_{\infty}$ and average oscillator wave length $\lambda_o$ and oscillator length strength $S_o$ of the thin film. These values can be obtained by using the single term Sellmeier oscillator [23]

$$\frac{n^2 - 1}{n - 1} = 1 - \left(\frac{\lambda_o}{\lambda}\right)^2 \quad \text{………………(7)}$$

From Figure 5 we obtained $n_{\infty}$ and $\lambda_o$ values from the linear of $1/(n^2-1)$ versus $\lambda^{-2}$ and are given in the table. Equation (7) can be rewritten as [24]

$$n^2 = 1 + S_o \lambda_o^2$$

$$n^2 - 1 = \frac{S_o \lambda_o^2}{1 - \lambda_o^2/\lambda^2}$$

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_o$ (eV)</th>
<th>$E_d$ (eV)</th>
<th>$E_g$ (eV)</th>
<th>$n_{\infty}$</th>
<th>$\lambda_o$ nm</th>
<th>$S_o$ (m$^{-2}$)</th>
<th>$E_o/S_o$ (eVm$^2$)</th>
<th>Thick -ness</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS + 0.0 mb</td>
<td>5.698</td>
<td>0.675</td>
<td>4.2</td>
<td>1.574</td>
<td>499.16</td>
<td>5.92*10^{-15}</td>
<td>9.61*10^{14}</td>
<td>0.044</td>
</tr>
<tr>
<td>PS + 0.02 mb</td>
<td>4.365</td>
<td>3.630</td>
<td>4.05</td>
<td>1.129</td>
<td>570.26</td>
<td>8.44*10^{-16}</td>
<td>5.17*10^{15}</td>
<td>0.042</td>
</tr>
<tr>
<td>PS + 0.04 mb</td>
<td>4.647</td>
<td>6.896</td>
<td>3.91</td>
<td>1.070</td>
<td>552.01</td>
<td>4.75*10^{-16}</td>
<td>9.78*10^{15}</td>
<td>0.048</td>
</tr>
<tr>
<td>PS + 0.06 mb</td>
<td>6.065</td>
<td>9.099</td>
<td>3.75</td>
<td>1.054</td>
<td>483.4</td>
<td>4.74*10^{-16}</td>
<td>1.27*10^{16}</td>
<td>0.044</td>
</tr>
<tr>
<td>PS + 0.02 mo</td>
<td>6.028</td>
<td>1.394</td>
<td>4.01</td>
<td>1.310</td>
<td>485.35</td>
<td>3.04*10^{-15}</td>
<td>1.98*10^{15}</td>
<td>0.047</td>
</tr>
<tr>
<td>PS + 0.04 mo</td>
<td>5.167</td>
<td>2.035</td>
<td>3.84</td>
<td>1.221</td>
<td>525.42</td>
<td>1.77*10^{-15}</td>
<td>2.90*10^{15}</td>
<td>0.047</td>
</tr>
<tr>
<td>PS + 0.06 mo</td>
<td>5.860</td>
<td>1.193</td>
<td>3.64</td>
<td>1.322</td>
<td>491.53</td>
<td>3.46*10^{-16}</td>
<td>1.69*10^{16}</td>
<td>0.046</td>
</tr>
</tbody>
</table>
The $S_0$ value for the thin film was calculated and given in the Table 1. The value of $E_0/S_0$ was found in order to $10^{14}$-$10^{16}$ eVm$^2$ for the films and this value is approximately the same order as that obtained by DiDomenico and Wemple [22] and Fahrettin [21] for a number of materials.

### 3.3 Complex Dielectric Function

The complex dielectric constant ($\varepsilon^* = \varepsilon_r + i\varepsilon_i$) characterizes the optical properties of the solid material. The real and imaginary parts of dielectric constant for pure and doped PS with mb and mr with different concentrations were also determined by the following relations [25]:

$$\varepsilon_r = n^2 - k^2 = \varepsilon_0 - \frac{e^2}{4\pi^2 c^2 \varepsilon_0} \frac{N}{m} \lambda^2 \quad \ldots \quad (10)$$

and

Figure 4: The variation of $(1/n^2-1)$ with $hu^2$ (eV)$^2$ of pure and doped PS films. (A) for mb dye and (B) for mo dye, both for different concentrations.

Figure 5: The variation of $(1/n^2-1)$ with $\lambda^2$ (nm)$^2$ of pure and doped PS films. (A) for mb dye and (B) for mo dye, both for different concentrations.
\[ \varepsilon_i = 2nk = \frac{\varepsilon_\infty \omega_p^2}{8\pi^2 \varepsilon_0 c^2 \tau} \lambda^3 \]  

(11)

where \( \omega_p \) is the plasma frequency, \( \varepsilon_\infty \) is the high frequency dielectric constant, \( e \) is the electronic charge, \( N \) is the free carrier concentration, \( m^* \) is the effective mass of the free carrier, \( \tau \) is the optical relaxation time, \( c \) is the velocity of light. In Figure 6 it is seen that the real and imaginary parts of the dielectric constant increase with increasing the photon energy. The real part of the dielectric constant is higher than the imaginary part.

It is concluded that the variation of \( \varepsilon_i \) mainly depends on \( (n^2) \) because of small values of \( (k^2) \), while \( \varepsilon_i \) mainly depends on the \( (k) \) values which are related to the variation of absorption coefficients.

![Figure 6: The variation of \( (\varepsilon, \varepsilon_\infty, \varepsilon_i) \) with \( h\nu \) \( (eV) \) of pure and doped PS films. (A) for mb dye and (B) for mo dye, both for different concentrations.](image)

### 4.0 CONCLUSIONS

Prepared films samples of neat and doped PS with mb and mo with different concentrations have been investigated for their optical properties such as optical band gap, refractive index and extinction coefficient through transmittance and reflectance spectra.

The optical constants such as the real \( (n) \) and imaginary \( (k) \) are parts of the complex refractive index, the real and imaginary parts of the dielectric constant were also determined. The oscillator energy \( E_o \), the dispersion energy \( E_d \) and other parameters have been determined by the Wemple–DiDomenico method. The optical band gap was determined and the optical absorption spectra showed that the absorption mechanism is an indirect allowed transition.

Lower \( (n) \) values of PS doped with mo compared with those of PS doped with mb, means that mo has a high effect on the absorption in the visible range than films doped by mr dye.

**References**


