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Spectroscopic Investigation of Optical Parameters of Pure PMMA and Azo - dye Doped PMMA films

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ABSTRACT

Casting technique was employed for preparation of pristine PMMA films and films that doped with different Azo-dye contents. UV/Vis. (200–2500 nm) and X-ray diffraction (XRD) were used to investigate optical properties of prepared samples. XRD spectra revealed some modifications, significantly sensitive to the doping level. Spectral absorption analysis showed presence of two absorption bands at 308 and 475 nm which attributed to the $\pi - \pi^*$ and $n - \pi^*$ transition of chromophore groups. The absorption coefficient and optical energy gap (E_g) have been obtained from the absorption edge in 200 - 900 nm range. It was found that E_g decreases with increasing the doping levels. The width of the tail of localized states in the band gap (ΔE) was evaluated using the Urbach edge method. Some optical parameters were determined from the reflection and transmission spectra in the spectral range 200-2500 nm. The dependence of the refractive index on the doping level has been discussed. A large variation in refractive index correlated to dye concentrations suggests the applicability of the studied system in optical devices.

Keywords: PMMA; azo – dye; doping; optical constants; refractive index.

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INTRODUCTION

Polymeric materials have attracted the interest of scientific and technological researchers. Various experimental studies have demonstrated that these materials have widespread applications [1, 2]. These applications such as solar energy conversion, coatings, adhesives, lithography, light emitting diodes, sensors, laser development, improved radiation stability and corrosion resistances, along with probable uses in the future. PMMA is one of the earliest polymers. This polymer unlike ionic and metallic crystals and low molecular weight substances consists of long chain molecules arranged in aggregates, which assume complex shapes and structures. Great attentions have been paid to PMMA due to its optical properties and its possible use in non - linear optics. It is extensively used in glazing applications as a replacement for glass in various applications with good weather resistance. PMMA exhibits photo refractive properties and has been used in rewritable / erasable three - dimensional bit data storage with an appropriate concentration of the doped compounds [3]. Moreover, PMMA is a plastic that is widely used in various industrial fields due to its stiffness and clarity. It can be used as a good keeper for rare earth iron garnets, which have a wide technological application in addition to its use in the field of insulation [4].

The introduction of metal ions into a polymer, particularly when the metal is linked chemically with a polymer chain, often imparts new or improved properties to the polymer. The modified films of pure and doped polymers are quite important for various engineering and technological purposes [5, 6]. The doping of polymers with metals salts causes changes in the structure and, therefore, in the physical and chemical properties [7, 8]. The changes in the physical properties of polymers due to doping depend on the chemical nature of the doping substances and the ways in which they interact with the host matrix [9, 10]. One may select the suitable type and doping level of a transition – metal halide to prepare a doped polymer with a desired physical property [11, 12].

In the study of physical properties of polymers, optical absorption spectrum is one of the most important tool for understanding band structure and electronic properties of pure and doped polymers. This technique depends on: when a photon with energy greater than the band gap, energy will be absorbed, a transition of an electron in the valence band (VB) to conduction band (CB) takes place. The transition is direct when the wave vector for the electron remains unchanged, but in the case of indirect transition, interaction with a lattice vibration (phonon) occurs (the minimum of the CB lies in different part of K-space from the maximum of the VB).

In all disordered materials, the allowed energy bands are not sharp, but have band tails into the mobility gap [13]. The exponential absorption edge, also known as the Urbach edge [14], is an important parameter for characterizing amorphous material and has implications for performance of electronic devices. The optical absorption spectra of many types of polymer has been reported [15-17], but to our knowledge a little attention has been paid to study the optical constants (refractive and absorption indices). Refractive index is an important optical parameter for the design of prisms and optical fibers [18].

The study of the optical absorption spectra in solids provides essential information about the band structure and the energy gap in the crystalline and non - crystalline materials. Analysis of absorption spectra in the lower energy part gives information about atomic vibrations, while the higher energy of spectrum gives knowledge about the electronic states of the atom [19].

In this work, we continue our efforts to study the doping effect of azo-dye on the structural and optical properties of PMMA using UV/Vis. and X - ray diffraction.

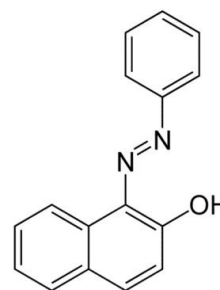
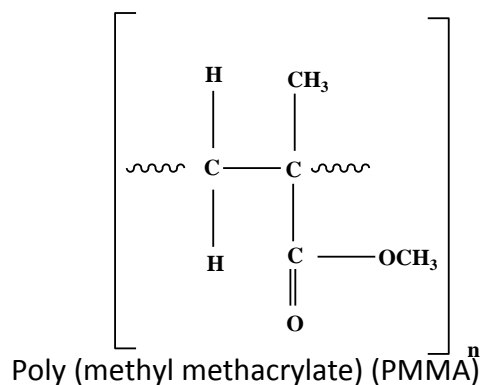
Experimental procedure

Samples preparation

The PMMA poly (methyl methacrylate) used in this work was supplied by Aldrich Chemical, CO, USA and the azo - dye is prepared in the laboratory. The present PMMA films doped with different amounts of azo - dye were prepared by the casting method as follow: PMMA was dissolved in chloroform for about two days at room temperature. Azo - dye was dissolved in chloroform also and added to the polymeric solution. The solutions were left to reach a suitable viscosity. The mixture was casted in glass dishes and kept in a dry atmosphere at room temperature for two weeks to ensure the removal of the solvent traces. The thickness of the obtained films is in the range 0.1 – 0.2 mm. PMMA films doped with mass fractions 0%, 0.25%, 0.50%, 0.75% and 1% of azo - dye were prepared. The dopant concentration W (wt %) is calculated from the equation :

$$W(\text{wt}\%) = \frac{W_f}{W_p + W_f} \times 100, \quad (1)$$

where W_p and W_f represent the weight of polymer and dopant, respectively. The molecular structure of PMMA and azo - dye are shown as



(1-Phenylazo-2-Naphthol) (Azo - dye)

Physical measurements

X - ray diffraction (XRD) scans were obtained using Philips diffractometer with $\text{CuK}\alpha$ -radiation (where, $\lambda = 1.5418 \text{ \AA}$). The tube operated at 30 KV, the Bragg's angle (2θ) is in the range $5 - 55^\circ$. The transmittance $T(\lambda)$ and the reflectance $R(\lambda)$ of PMMA films and PMMA doped films with azo - dye were measured using a double - beam spectrophotometer JASCO model V-570-UV-VIS-NIR. The transmittance and reflectance spectra were measured in the wavelength range 190 - 2500 nm. A deuterium discharge tube (190 - 350 nm) is used in the UV region and a tungsten iodine lamp (340 - 2500 nm) is used in the VIS / NIR region as light source.

RESULTS AND DISCUSSIONS

X - ray diffraction analysis:

X - ray diffraction patterns of pure PMMA and PMMA films doped with various fractions of azo - dye are presented in Fig.1. It is apparent from this figure that X - ray pattern of pure PMMA matrix shows three broad diffraction halos at $2\theta = 13.06, 29.62$ and 41.7° indicating the amorphous nature of PMMA [20, 21]. The X - ray patterns of PMMA films doped with azo - dye show the absence of the sharp peaks which are present in azo - dye with the broadening and decreasing the intensity of the first halo and disappearance of the second and the third halos of PMMA. This indicates that the amorphous nature of PMMA films doped with azo - dye. This amorphization of PMMA films doped with azo - dye may be due to the formation of interpenetrating network between azo - dye and PMMA chains in which the local ordering of azo - dye is destructed [22]. A similar type of XRD (three amorphous halos) results was observed [23, 24] in PMMA and they argue that the first broad peak is due to the intermolecular component, whereas the second and third peaks represent intermolecular separation in PMMA.

From the XRD patterns, the d-spacing can be calculated from the following Bragg's law:

$$d = \frac{n\lambda}{2\sin\theta} , \quad (2)$$

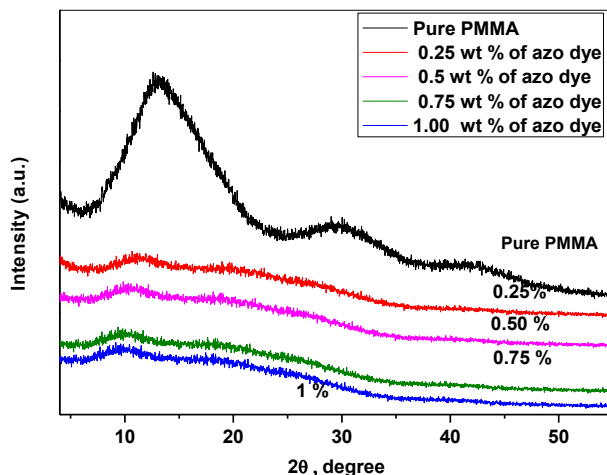


Figure (1): X - ray diffraction of pure PMMA and PMMA films doped with various fractions of azo - dye.

where n is order of reflection, θ is the Bragg's angle and λ is the wavelength of the radiation. The interchain distance between polymer chains in the present system is calculated from the first peak. It is found that this distance increases with increasing doping level of azo - dye (Table 1). These results indicate that the azo – dye addition can cause structural modification in the PMMA network.

Table (1) Values of interchain distance between polymeric chains in the present system.

W (wt %)	d (Å°)
0.00%	6.79
0.25%	7.98
0.75%	8.97
1.00%	9.35
0.00%	9.87

Optical properties:

Absorption spectra:

The absorption of light energy by polymeric materials in the UV / VIS region involves promotion of electrons in σ , π and n - orbitals from the ground state to higher energy states which are described by molecular orbitals [25]. Many of the optical transitions, which result from the presence of impurities, have energies in the visible part of the spectrum; consequently the defects are referred as color centers [26]. Doping the polymers leads to the formation of new adfects and new charge states.

The absorption spectra with UV/ VIS spectrophotometer carried out on pure PMMA and PMMA films doped with different amount of azo - dye are present in Fig.2. The observed spectrum of pure PMMA film has no absorption band. On the other hand the spectra of the

PMMA films doped with different amount of azo – dye contain two absorption peaks at about 308 and 475 nm. It is reasonable to assign the observed bands to the $\pi - \pi^*$ and $n - \pi^*$ transitions of chromophoric groups (the extended conjugated double bond system including the diazo group). It is found that the position of the azo - dye peaks is slightly shifted towards the longest wavelength, while the intensity (A) increases with increasing the doping level. The dependence of the intensity of the bands at 308 and 475 nm on the doping level is shown in Fig.3, providing an evidence for the incorporation of azo - dye into PMMA matrix. It is noticed that the exposure of the studied films to UV irradiation has no influence on their UV spectral features; therefore, it can be used as a photo stable materials (the figure is not shown here).

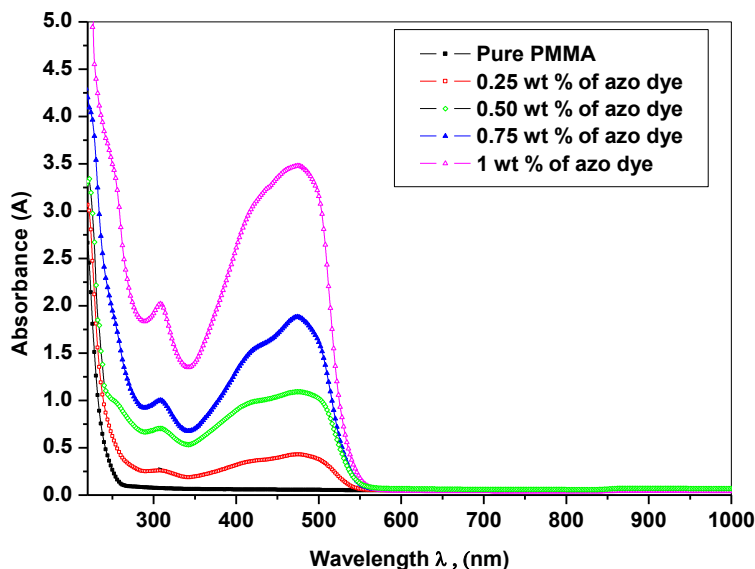


Figure (2): UV/Vis. scan for pure PMMA and PMMA films doped with different levels of azo – dye

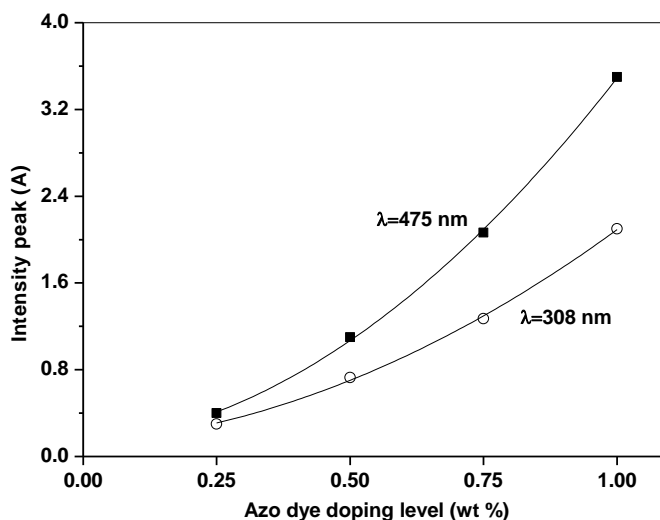


Figure (3): The dependence of intensity peak versus the azo - dye doping level at $\lambda = 308$ and $\lambda = 475$ nm.

Optical energy gap:

Significant changes of different amounts have been observed in optical response of the polymers after doping. UV/Vis. spectroscopy can be used for the investigation of the optically induced transitions and can provide information about the energy gap in crystalline and non-crystalline materials [27]. The fundamental absorption shows a sudden rise in absorption, known as absorption edge, which can be used to determine the optical energy gap. It is clear that the absorption spectra for the present system Fig.2 exhibit one absorption edge for the sample free from azo - dye, while the azo - dye contained samples revealed two absorption edges. These edges are shifted towards longer wavelength as the doping level increases. Also, the edges are not sharply defined, signifying the glassy nature of the films. The absorption coefficient (α) can be calculated from the optical absorption spectrum using the relation:

$$\alpha = \frac{2.3A}{X} \quad , \quad (3)$$

Where X is the film thickness in cm and A is defined by $A = \log \left(\frac{I_0}{I} \right)$ where I_0 and I are the intensities of the incident and transmitted beams, respectively.

The optical band gap is determined from the analysis of the spectral dependence of the absorption near the absorption edge. The absorption coefficient for non-crystalline materials has the following frequency dependence [28].

$$\alpha = B \frac{(h\nu - E_g)^r}{h\nu} \quad , \quad (4)$$

Where $h\nu$ is the energy of the incident photons, E_g is the value of the optical energy gap between the valence band (VB) and conduction band (CB) and r is the power, which characterizes the transition process in the K-space. Specifically, r has the values 1/2, 3/2, 2 and 3 for transitions direct allowed, direct forbidden, indirect allowed and indirect forbidden, respectively. The factor B depends on the transition probability and can be assumed to be constant within the optical frequency range. The usual method for the determination of the value of E_g involves plotting $(\alpha h\nu)^{1/r}$ against $(h\nu)$. The dependence of $(\alpha h\nu)^{1/r}$ on photon energy $(h\nu)$ is plotted for the studied films using different values of r . The best fit is obtained for $r = 2$. This indicates that the transition energy for electron is indirect in K-space and interactions with lattice vibration (phonons) take place.

Plots of $(\alpha h\nu)^{1/2}$ versus $(h\nu)$ near the absorption edge for PMMA and PMMA doped with different contents of azo - dye produce a linear fit over a wide range of $(h\nu)$ as shown in Fig.4. Extrapolation of linear dependence to the abscissa yields the corresponding forbidden band width E_g . It is observed from Fig.4 that a linear dependence for pure PMMA in one region

representing one optical absorption edge, while azo - dye doped films give two regions representing the two optical absorption edges (E_{g1} and E_{g2}). These results are similar to that in previous work for PMMA films doped with $CrCl_3$ or $CoCl_2$ [29]. These absorption edges are characterized by higher optical energy gap E_{g1} and lower energy gap E_{g2} . A dual energy gap is reported for other polymers such as PVC films doped with $NiCl_2$ [10], PVC films doped with $MnCl_2$ [30] and PVA films doped with $MnCl_2$ and CrF_3 [31] and also in case of PMMA / PVAC irradiated blends [32]. The analysis of the optical absorption spectra for $Cu_xAg_{1-x}InTe_2$ thin films [33] revealed three energy gaps which are attributed to the optical transitions from the valence sub-bands to the conduction band minimum.

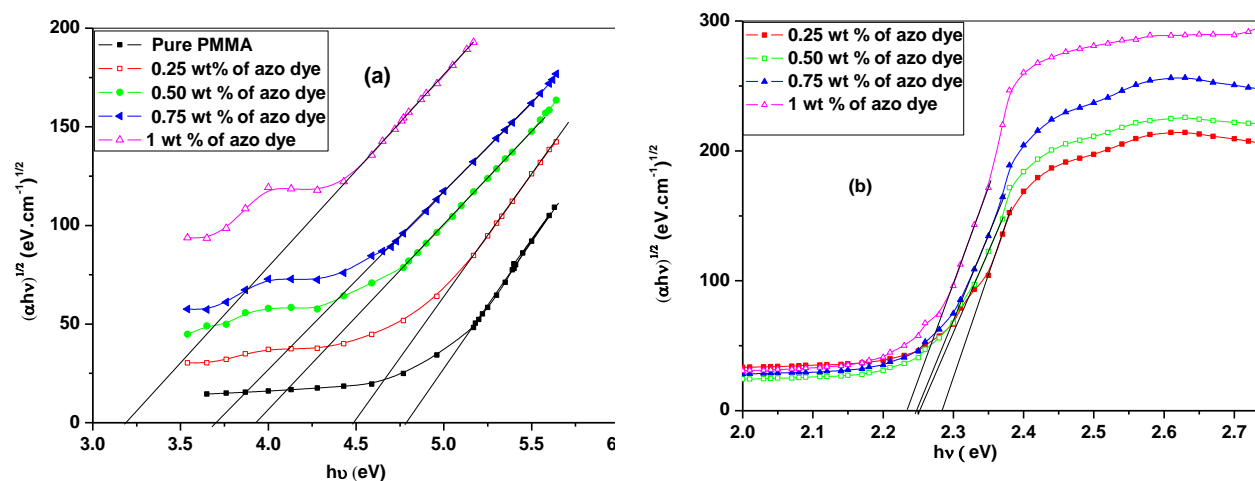


Figure (4): The dependence of $(\alpha h\nu)^{1/2}$ on $h\nu$ for PMMA films doped with different levels of azo - dye at (a) higher energy (b) lower energy.

The values of E_{g1} and E_{g2} for the studied films are calculated from Fig.4. The dependence of E_{g1} and E_{g2} on the azo - dye contents is shown in Fig.5. It is clear that E_{g1} and E_{g2} decreases as azo - dye contents (W) increase. The variation of the calculated values of both higher and lower optical energy gaps may reflect the role of azo - dye in modifying the electronic structure of the PMMA matrix due to appearance of various polaronic and defect levels. The density of localized state, $N(E)$, is found to be proportional to the concentration of these defects [34] and consequently, to azo - dye content. Increasing azo - dye content may cause the localized states of different color centers to overlap and extend in the mobility gap [13]. The overlap may give us an evidence for the decrease of energy gap when azo - dye content is increased in the polymeric matrix..

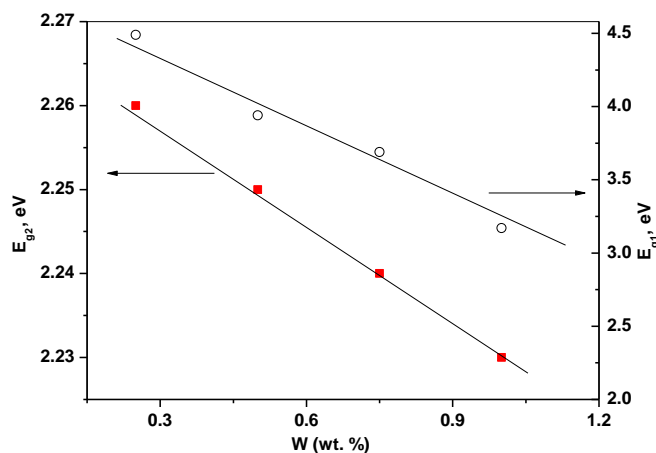


Figure (5): The dependence of E_{g1} and E_{g2} on azo - dye doping level.

The Urbach tail is found to be related directly to similar exponential tail for the density of states of either one of the two band edges [35]. The width of the Urbach tail is an indicator of defect levels in the forbidden gap. The following relation is used to calculate the width of the Urbach tail [14]:

$$\alpha = \alpha_0 \exp (h\nu / E_t), \quad (5)$$

where α_0 is a constant and E_t is the width of the tail of the localized states due to the defect levels in the forbidden gap. Fig.6 shows the linear dependence of the natural logarithm of the absorption coefficient versus the photon energy for films of PMMA and PMMA doped with different contents of azo - dye. The reciprocal of the slopes yields the magnitude of E_t . The values of E_{t1} (for higher energy gap) and E_{t2} (for the lower energy gap) are calculated and listed in Table 2. The value of E_t for pure PMMA is 0.33 eV and for PMMA doped with azo - dye, E_{t1} lies between 0.46 and 1.11 eV, and E_{t2} lies between 0.045 and 0.086 eV. It is observed that the Urbach tail for pure PMMA is less than that for the doped ones.

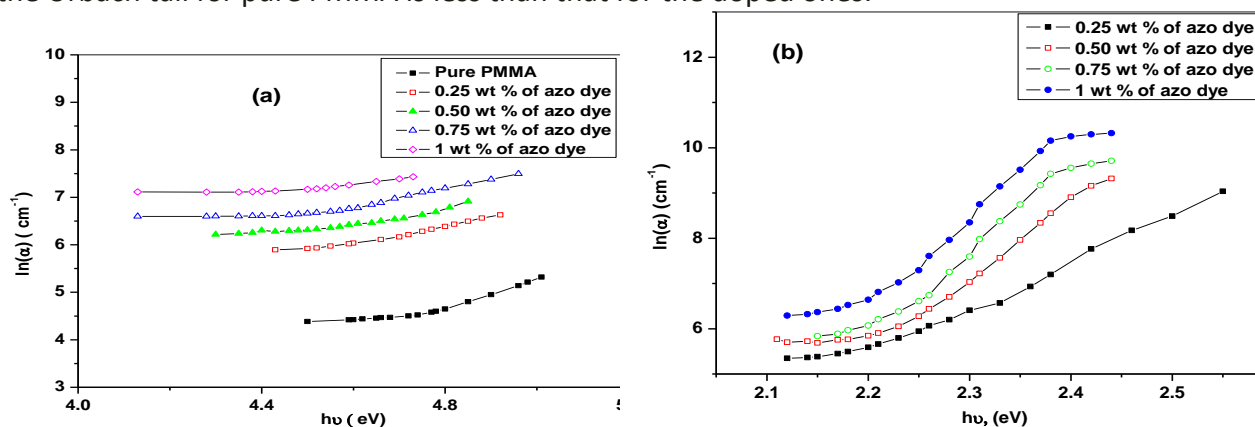


Figure (6): The dependence of $\ln(\alpha)$ versus $h\nu$ for PMMA doped with different contents of azo - dye at (a) higher energy (b) lower energy.

Table (2) Values of E_{t1} and E_{t2} for films of PMMA and PMMA doped with different contents of azo – dye.

W (wt %)	E_{t1} (eV)	E_{t2} (eV)
0.00%	0.33	–
0.25%	0.46	0.086
0.75%	0.56	0.055
1.00%	0.83	0.047
0.00%	1.11	0.045

Reflection and Transmission spectra

The optical properties obtained from the measurements of reflection and transmissions are studied. The spectral distribution of both reflectance $R(\lambda)$ and transmittance $T(\lambda)$ for the studied system in the wavelength range 200 – 2500 nm are shown in Fig.7. From the inspection of this figure, it is noticed that the pure PMMA film is transparent, that is, $T+R \sim 1$, and gives a normal dispersion region. On the other hand, the doped samples become transparent only at $\lambda > 1000$ nm. The inequality $T+R < 1$ at $\lambda < 1000$ nm is due to the existence of absorption. The peaks indicating the anomalous dispersion behavior are due to a rapid increase in the absorption mechanism in the fundamental absorption edge due to the presence of absorbing color centers induced as a result of the azo – dye group presence in the polymer matrix. This behavior obeys a multioscillator model.

The refractive index (n) for the studied samples are determined from the measured values of $T(\lambda)$ and $R(\lambda)$ according to the following equations:

$$T(\lambda) = (1 - R) \exp\left(-\frac{4\pi kx}{\lambda}\right), \quad (6)$$

$$R(\lambda) = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}, \quad (7)$$

where k is the absorption index.

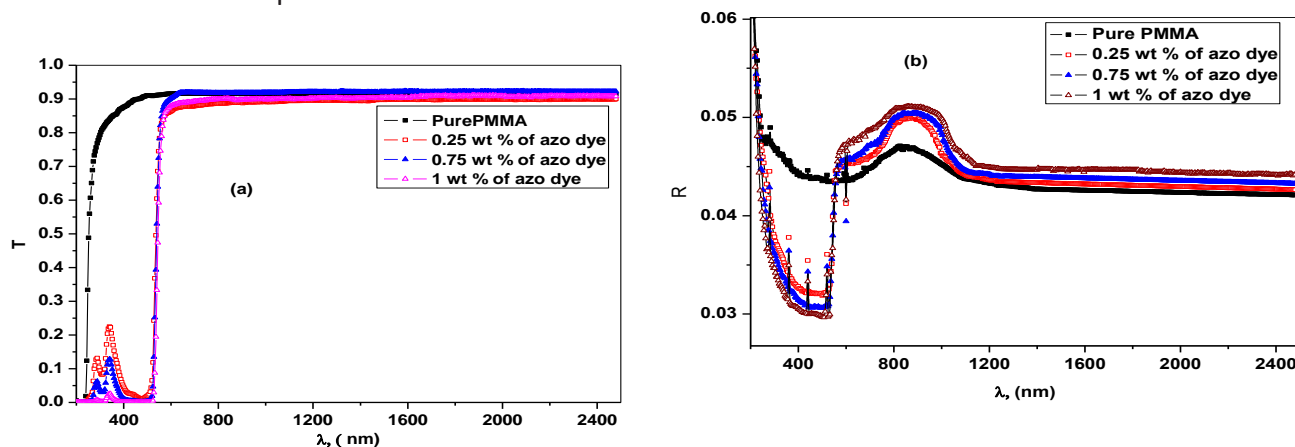

 Figure (7): The spectral distribution of (a) $T(\lambda)$ and (b) $R(\lambda)$ for pure PMMA and PMMA films doped with different contents of azo - dye.

Fig.8 shows the dispersion curve (n vs λ) in the wavelength range 900 – 2500 nm for the studied films. It is observed that the refractive index decreases with increasing the wavelength and reaches a nearly constant value at long wavelength, suggesting a normal dispersion. Also, it is found that for the doped films, the value of n increases with increasing the azo - dye doping level. The refractive index changes are large and show that the azo – dye doped PMMA films are suitable to applicability for optical devices.

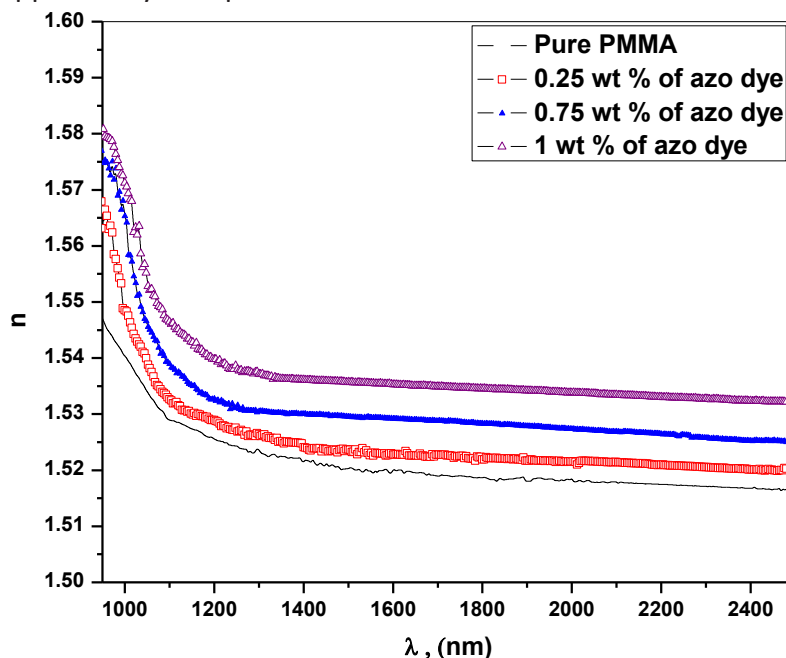


Figure (8): The dispersion curve of refractive index (n) for pure PMMA and PMMA films doped with different contents of azo - dye.

The obtained data of n can be analyzed to yield the long wavelength refractive index (n_{∞}) together with the average interband oscillator wavelength (λ_o) and the average oscillator strength (S_o) for the present samples using the single term Sellmeir oscillator [36]. The relation between the refractive index n and λ is given by

$$\frac{n_{\infty}^2 + 1}{n^2 - 1} = 1 - \left(\frac{\lambda_o}{\lambda} \right)^2, \quad (8)$$

where λ_o and n_{∞} can be evaluated from the plots of $(n^2 - 1)^{-1}$ against λ^{-2} as illustrated in Fig. 9. Equation 8 can also be rewritten as [37]

$$n^2 - 1 = \frac{s_o \lambda_o}{\left(1 - \frac{\lambda_o^2}{\lambda^2} \right)}, \quad (9)$$

where $s_o = \frac{n_\infty^2 - 1}{\lambda_o^2}$. The values of $n_\infty^2 = \epsilon_\infty$, λ_o and S_o can be obtained for the studied samples and are listed in Table 3.

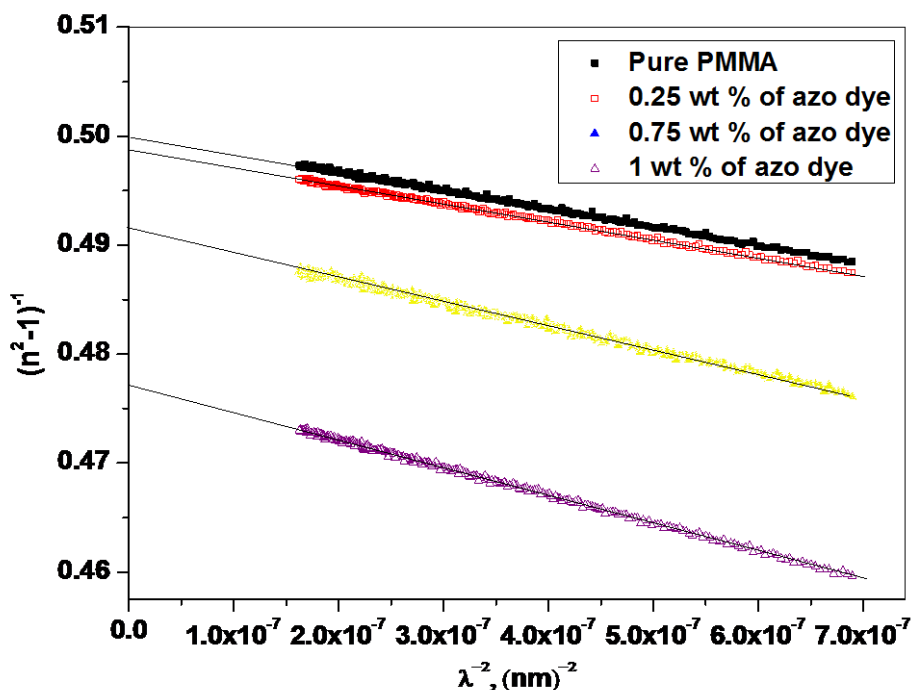


Figure (9): The plots of $(n^2 - 1)^{-1}$ versus λ^{-2} for pure PMMA and PMMA films doped with different contents of azo – dye

Table (3) The values of some optical parameters for films of pure PMMA and PMMA doped with different contents of azo – dye.

W (wt %)	ϵ_∞	λ_o (nm)	n_∞	$S_o \times 10^{13}$ (m ²)	E_d (eV)	E_o (eV)	$N/m^* (m^{-3}Kg^{-1})$	ϵ_i
0.00%	2.99	183	1.73	5,98	13.58	6.79	8.98×10^{39}	3.023
0.25%	3.01	180	1.704	5.15	13.79	6.68	1.0169×10^{40}	3.0030
0.75%	3.04	209	1.75	4.64	12.06	5.92	1.32557×10^{40}	3.0753
1.00%	3.1	231	1.76	3.93s	11.25	5.37	1.45215×10^{40}	3.138

In the normal dispersion region (the transparent region), the refractive index dispersion has been analyzed using the single oscillator model developed by Wemple and DiDomenico [37, 38]. They introduced dispersion energy parameter E_d to describe the dispersion of the refractive index. In terms of the dispersion energy E_d and a single oscillator energy E_o , the refractive index at frequency ν can be expressed by the following equation

$$n^2(\nu) - 1 = \frac{E_d E_o}{[E_o^2 - (h\nu)^2]}, \quad (10)$$

where $h\nu$ is the photon energy. Fig.10 shows the plot of $(n^2 - 1)^{-1}$ against $(h\nu)^2$. The values of E_o and E_d are determined from the slope $(= (E_o E_d)^{-1})$ of the straight line and the intersection $(= E_o/E_d)$ with the vertical axis. The calculated values of E_o and E_d are listed in Table 3.

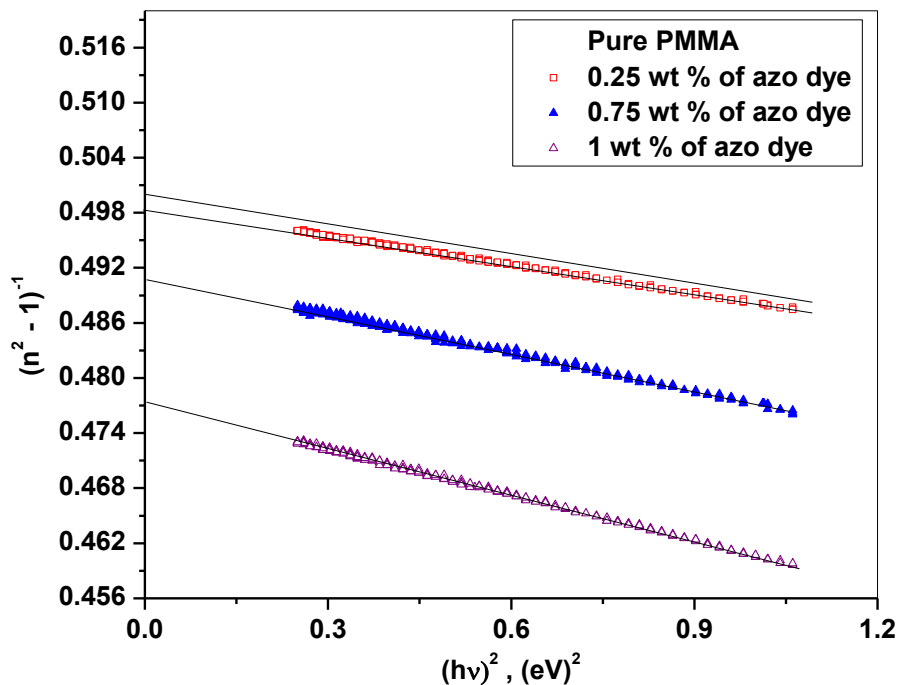


Figure (10): The plots of $(n^2 - 1)^{-1}$ versus $(h\nu)^2$ for pure PMMA and PMMA films doped with different levels of azo - dye.

The obtained data of refractive index can be also analyzed to obtain the lattice dielectric constant ϵ_L and the carrier concentration to effective mass ratio N/m^* which describes the contribution of the free carriers and the lattice vibration modes of the dispersion, via the following procedure.

The real part of the dielectric constant $\epsilon_r = (n^2 - k)$ is related to the wavelength λ in the non - absorbing region by the following relation [39]:

$$\epsilon_r = \epsilon_L - \frac{e^2 N}{4\pi\epsilon_o m^* c^2} \lambda^2 \quad (11)$$

where e is the electron charge, ϵ_o is the permittivity of the free space and c is the speed of light. Fig.11 shows the plots of ϵ_r vs λ^2 for the studied films. The intersection at linear part of this curve gives the value of ϵ_L and the ratio N/m^* can be calculated from the slope of the straight line. The calculated values of ϵ_L and N/m^* are listed in Table 3.

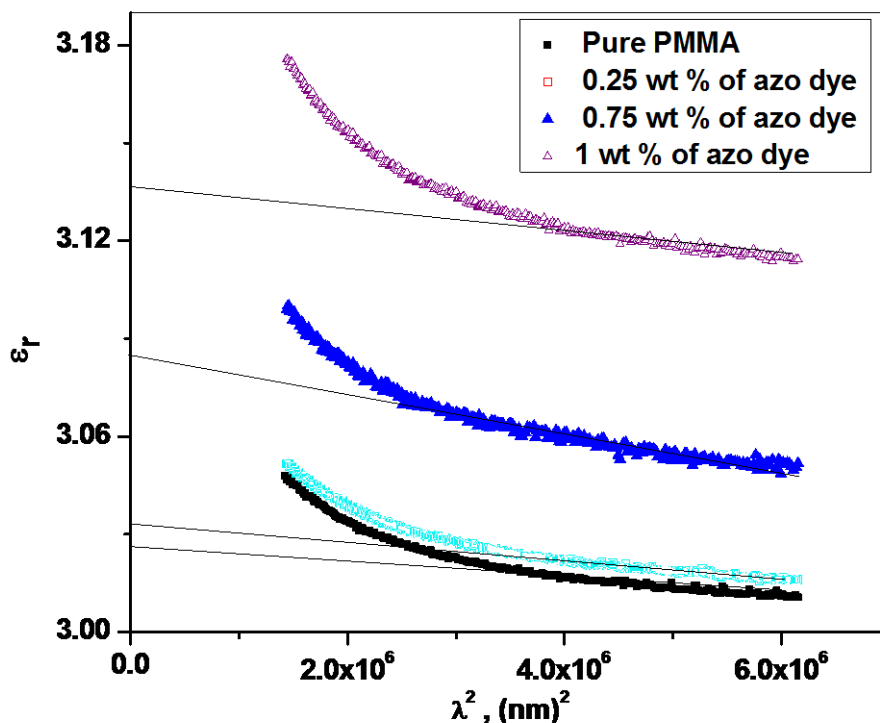


Figure (11): The plots of ϵ_r vs λ^2 for the pure PMMA and PMMA films doped with different levels of azo - dye.

CONCLUSIONS

In the present study the results demonstrate significant modification in the structure and optical properties in the PMMA films doped with azo – dye. From these results, the following conclusions were drawn:

1- The XRD shows the absence of sharp peaks indicating the amorphous nature of the studied films. It was found that the interchain distance between the polymer chain increases with increasing doping level of azo – dye.

2- UV / VIS spectra show that: (a) The spectra of doped films contain two absorption peaks assigned to the chromophoric groups of azo – dye. The intensity of these peaks increasing with increasing azo – dye indicating the incorporation of azo – dye into PMMA matrix. (b) The analysis of the calculated values of E_g evidences the presence of induced energy states due to azo – dye doping. (c) The width of the tail of localized states in the forbidden band gap for the studied system are calculated.

3- The spectral distribution of both $T(\lambda)$ and $R(\lambda)$ in the wavelength range 200 - 2500 nm evidences the following: (a) The pure PMMA film is transparent and gives the normal dispersion region. On the other hand the doped films become transparent only at $\lambda > 1000$ nm due to the presence of induced azo – dye color centers in the polymer matrix. (b) The long wavelength refractive index (n_∞) increases with increasing the doping level of azo – dye. (c) Refractive index changes due to azo – dye doping suggesting the applicability of PMMA films doped with azo – dye for the optical devices. (d) The optical parameters of the studied system such as n_∞ , λ_0 , S_0 , E_0 , E_d , ϵ_L , ϵ_∞ and N/m^* have been evaluated.

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