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EFFECT OF SUBSTRATE ON REFLECTANCE SPECTRA AND OSCILLATOR PARAMETERS OF (AAS) : (PVP) FILMS

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ABSTRACT

(4-Acetaminophenol–[2-(4-Azo)]-4-Aminodipheyl-Sulfone)(AAS):Polyvinylpyrrolidone (PVP) films of thickness $32\ \mu m$ were prepared onto Pyrex, quartz and silica substrate . The effects of substrate types on optical properties of the film were investigated; the optical constants of the film were investigated too by spectrometric measurement. The optical band gap (E_g), statically refractive index ($n_\circ$), oscillator parameter ($E_\circ$) , dispersion parameter (E_d)of the films were determined using the transmittance (T) and reflectance (R) in the spectral range (340-700 nm). From this study we found that the type of substrates affects the optical constants.

KEYWORDS: Refraction Index, optical band gap, oscillator parameter, dispersion parameter

INTRODUCTION

Organic films are being explored as materials possessing many potential technological applications , such as microelectronics , photo conductors and nonlinear optical [1-3] .The properties of organic materials often depend on the macroscopic nature of the constituent organic molecules [1,2] . Therefore, the promise of controlling the properties of system by variation of the architecture , orientation , and density of the molecules within organized assemblies is currently an important driving force in many aspects of applied research [1,2] . Dyes are kind of organic compounds with a complex aromatic molecular structure that can bring bright and firm color to other substances. However, the complex aromatic molecular structure of dyes makes them more stable and more difficult to biodegrade [4].

Now, when photons of different wavelengths impinges on the material, the transmission characteristics of light typically depend on combination of absorption scattering, and reflectance properties. Absorption is the loss of photons and results in specific electron transition in the absorbing molecule of the materials. This absorbed radiation energy is typically converted into heat, and the amount of energy transformed, known as power of absorption, is expressed as a fraction of incident light energy on the material [5]. The part of incident light reflected back is known as reflection and results when the light is scattered in the direction opposite to that of incident light [6]. The power of reflection of the substance in the materials is also expressed as a fraction of incident light. Scattering is defined as a part of light energy that impinges at a definite direction on materials that is altered in all directions due to boundaries of refractive index [5].

The goal of the present work is the study of the effect of substrate include type (Pyrex, quartz, silica) on refractive index and oscillator parameter of (4-Acetaminophenol;–[2-(4-Azo)]-4-Aminodipheyl-Sulfone)(AAS):Polyvinylpyrrolidone (PVP) films in the wavelength range (340-700 nm).

EXPERIMENTAL

SYNTHESIS OF THE AZO DYES

The proposed azo dyes were prepared by a method similar to that described by Fox [7].Step (1) (0.006mole, 1.4899g) of amine was dissolved in 2ml of concentration. HCl and then 10ml of D.water was added, the mixture was stirrer and kept in ice bath. 0.456g of $NaNO_2$ was dissolved in about 5ml of D.water and kept in ice bath. Diazonium salt was prepared by adding sodium nitrite solution.In step (2) dropwise to the cold solution of amine in the step (1) with stirring and keeping the temperature below 50C. Coupler was prepared by dissolving (0.006mole, 1.4355g) of chromotropic acid disodium salt dehydrate in 25% sodium hydroxide solution and keeping in ice bath. The diazonium salt was added drop wisely to the couplers with constant stirring, keeping the temperature below 50C; the dyes were neutralized with dilute hydrochloric acid solution. The resulting crudes were re-crystallized from acetone the purity of the resulting azo dye , of 92% yield ,melting point 272 $^{\circ}C$. Azodye has been characterized by IR spectra. The structure of the azo dye is shown in Fig.(1).

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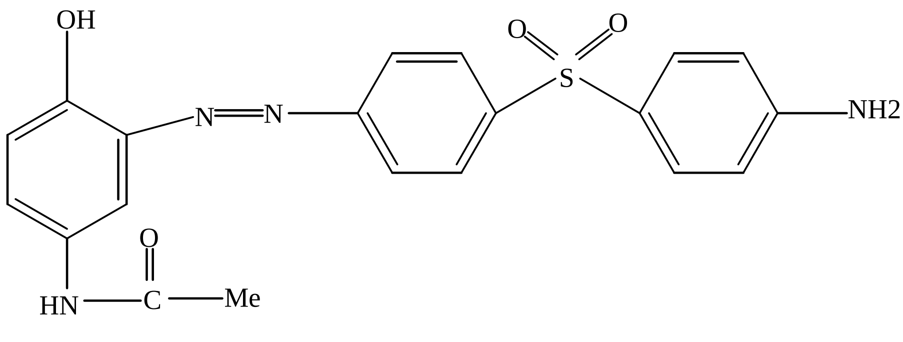


Fig. 1. Chemical Structure of the Prepared Azo Dye Compound

FILM PREPARATION

Azo polymer films were prepared by dissolving 0.2gm of the azo dye in 1 ml of DMSO and then reduce the solution to 20 ml of distilled water. 0.1 gm from PVP and dissolved in 20 ml of distilled water thenmixedwith the azo solution. Then the solution of azo dyes: PVP was stirredat 70 C° for 1h,then the solution was filteredby filter of 0.2 µm. We attended the three substrates (Pyrex, quartz and silica)and used direct casting to cast three films with thickness of 32 µm. Finally, the films were heated from room temperature to50 C^{o}for 4hrs to evaporate the solvent used. The spectra of absorbance (A), transmittance (T) and reflectance (R) of (AAS): PVPof the films were recorded by CE-3055 PC dual beam Reflectance spectrophotometer in the wavelength (340-700nm).

RESULTS AND DISCUSSIONS

ABSORBANCE SPECTRA

Fig.(3) shows the absorbance(A) spectra of the (AAS):PVP film prepared on the different substrates (Pyrex, quartz, silica) in the UV range.The maximum absorption observed at wavelength region(340-380 nm) and then it decreases to zero at wavelength >625 nm, the absorption edges of the films occurs at wavelength region (500-550 nm) corresponding to photon energy (2.25-2.48 eV). The film prepared on the quartz substrate have optical absorption more than Pyrex and silica this, mean the film prepared on the quartz substrate have highelectronic excitation transition.

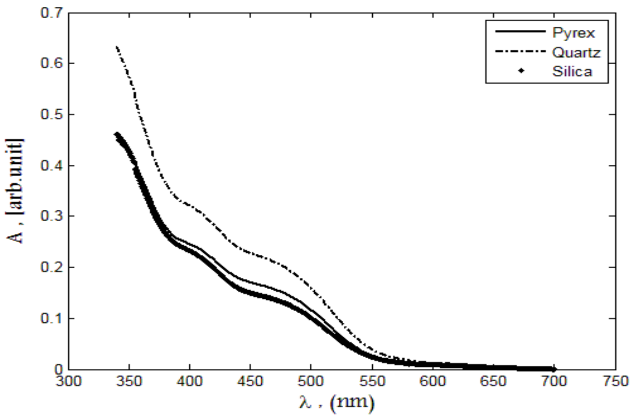


Fig.(3) The optical absorbance spectra vs. wavelength of the (AAS):PVP film prepared on the substrates (a) Pyrex (b) quartz (c) silica.

TRANSMITTANCE SPECTRA

The optical transmittance of the films as a function of the wavelength are shown in Fig.(4) , the transmittance spectra increases in the wavelength range (340-550 nm) and the curves reach's saturation above 550 nm. In addition, the higher transmittance in the visible range was observed from the film prepared on the quartz substrate. The average transmittance of the films on pyrex, quartz, silica are 85%, 90% and 70%, respectively.

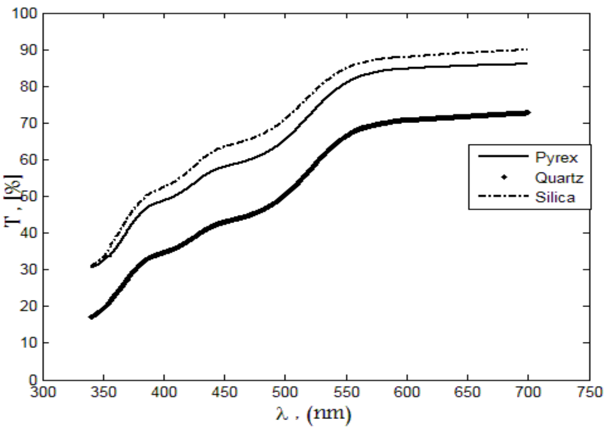


Fig. (4) The optical transmittance spectra vs. wavelength of the (AAS): PVP film prepared on different substrate (a) pyrex (b) quartz (c) silica.

REFLECTANCE SPECTRA

From the Fig. (5), we notes that there are three peaks for pyrex, quartz and silica at reflectance equals to 45.2%, 67.1% and 34.2% respectively, and they are decreasing in the wavelength region (355-550 nm). To our spectroscopic measurement the reflectance (R) , we have measure the back ground for each substrate need for the deferent thus.

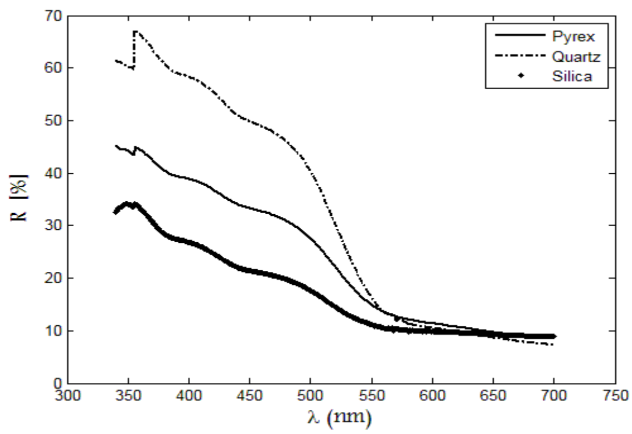


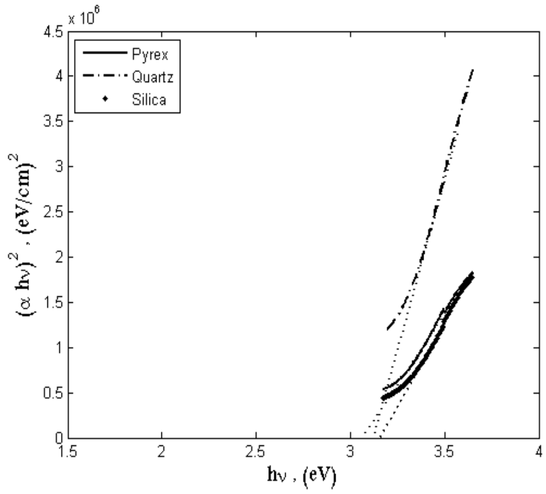
Fig.(5) The optical reflectance spectra vs. wavelength of the (AAS):PVP film prepared on substrate (a) Pyrex (b) quartz (c) silica.

DETERMINATION OF ENERGY GAP AND OSCILLATOR PARAMETER OF THE AZO FILMS

The optical absorption coefficient of the film was calculated from the relationship ($\alpha = \frac{1}{d}\ln(\frac{1}{T})$)[10]where (T) is the transmittance of the film and (d) is its thickness .The optical absorption method was used to determine the optical band gap of the film, which is the most direct and simplest method. The fundamental absorption refers to band to band transitions and it manifests itself by a rapid rising in the absorption used to determine the optical band gap. By using Tucc procedure the absorption coefficient related to the energy band gap by [11]:

$$\alpha h\upsilon = B(h\nu - E_g)^r \quad (1)$$

Where B is a constant and r is an index that characterizes the optical absorption process and it equal to 1/2, 2, 3/2 or 3 for direct allowed, indirect allowed, direct forbidden and indirect forbidden transitions, respectively [12]. We plotted $(\alpha h\nu)^{0.5}$and $(\alpha h\nu)^2$as functions of photon energy, as shown in Fig. (6). Thus, the direct and indirect optical band gapswere determined by the intercept on the energy by extrapolating the linear part of the curve to zero absorption value and shown in the table (2).



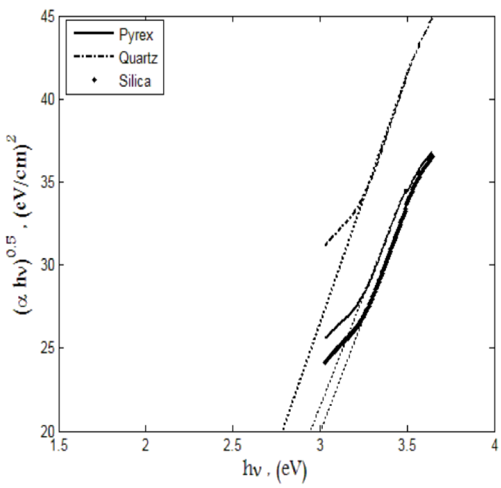


Fig.(6) (a)Plot $(\alpha h\upsilon)^2$ as a function to photon energy (b) plot $(\alpha h\upsilon)^{0.5}$ as a function to photon energy of the film.

The refraction index of the (AAS): PVP films is given by the following relation [13]

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

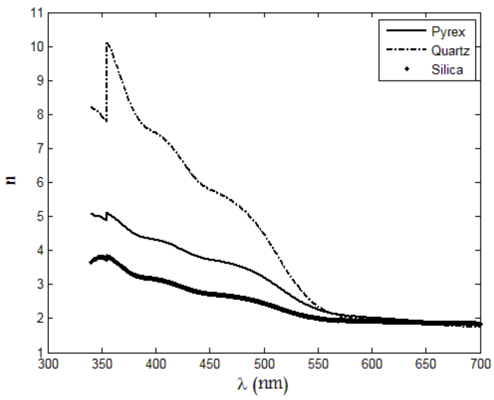


Fig. (7) Refraction index (n) as a function of wavelength of the (AAS): PVP film propertied on different substrate (a) Pyrex (b) quartz (c) silica.

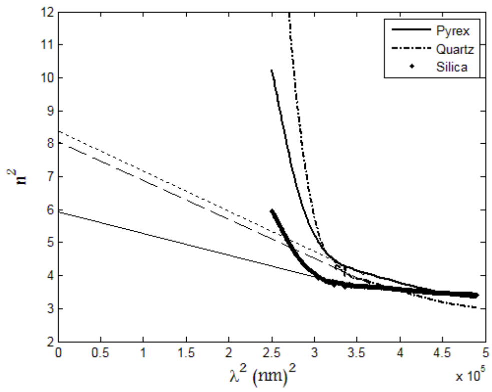


Fig. (8) Plot of n^2 as a function of wavelength for of the (AAS): PVP film propertied on different substrate (a) Pyrex (b) quartz (c) silica.

Where k is the extinction coefficient and we notes that therefractive index decreases with increasing the wavelength as shown in the Fig. (7),the decrease in the value of refractive index is due to that some interactions takes place between photons and electrons. The refractive index changes with the variation of the wavelength of the incident light beam due to these interactions, in another word, one is the optical loss caused by absorption and scattering, which decreases the amplitudes of the transmission intensity oscillations at shorter wavelengths. In this work it can be neglected because of the hightransparencyof(AAS): PVP film.

The optical dispersion characteristics play an important role in the research for optical materials, because it is a significant factor in optical communication and in designing optical devices. The dispersion of the refractive index (n) PVP– (4-ACETAMINOPHENOL – [2-(4-AZO)]-4-AMINODIPHEYL SULFONE)(AAS) Films were analyzed using the concept of the single oscillator and can be expressed by the Wimple and DiDomenico relationship as [14]

$$(n^2 - 1) = \frac{E_d E_\circ}{(E_\circ^2 - E^2)} \quad \textbf{(3)}$$

Where $E = h\nu$ is the photon energy, $E_\circ$ is the oscillator energy and E_d is dispersion energy. The parameter E_d which measures the intensity of the interband optical transition does not depend significantly on the band. A plot $(n^2 - 1)^{-1}$ as a function of photon energy $E = h\nu$ of (AAS): PVP film is illustrated in Fig. (7), the value of E_d and $E_\circ$ were obtained from the slope and the intersection obtained from extrapolation of the line to zero photon energy as the shown in the table (2).

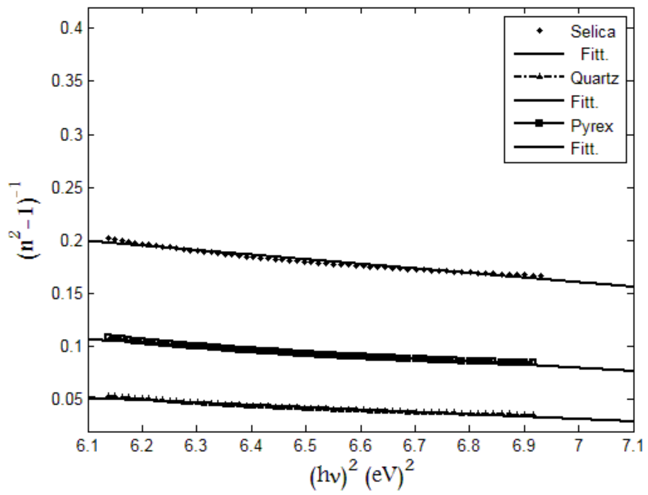


Fig.(9) Variation of (n^2-1) versus $(h\nu)^2$ for the (AAS):PVP film prepared on different substrate (a) pyrex (b) quartz (c) silica.

Thedispersion data of the refractive index can be fitted by the single –effective oscillator model [15]

$$\frac{n_\circ^2-1}{n^2-1}=1-(\frac{\lambda_\circ}{\lambda})^2 \qquad \textbf{(4)}$$

$n_\circ$ is the refractive index at infinite wavelength $\lambda_\circ$, the plotting of $(n^2-1)^{-1}$ versus λ^{-2} shows linear part below the absorption edge as shown in Fig.(6) .The intersection with $(n^2-1)^{-1}$ axis is $(n_\circ^2-1)^{-1}$ and hence, $n_\circ^2$ at $\lambda_\circ$ equals ε_∞ . The average oscillator strength is given by,

$$s_\circ = \frac{n_\circ^2-1}{\lambda_o{}^2} \qquad \textbf{(16)}$$

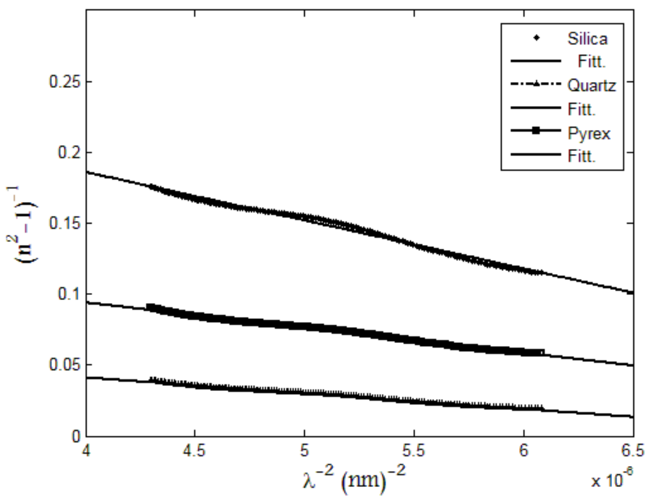


Fig.(10) Plot of $(n^2-1)^{-1}$ against λ^{-2} for the (AAS):PVP film propertied on different substrate (a) pyrex (b) quartz (c) silica.

The moments of optical dispersion spectra M_{-1} and M_{-3}, can be evaluated using the relationships [15],

$$E_{\circ}^{2}=\frac{M_{-1}}{M_{-3}} \quad \textbf{(6)}$$

$$E_{d}^{2}=\frac{M_{-1}^{3}}{M_{-3}} \quad \textbf{(7)}$$

The values of dispersion parameters and the optical moments of the films are presented in table 2 .

Table (2) the optical parameter of the film

Quantity	Silica	Quartz	Pyrex
	Value	**Value**	**Value**
$E_g^d (eV)$	3.18	3.1	3.14
$E_g^{ind} (eV)$	2.5	2.38	2.47
$E_{\circ} (eV)$	3.2707	2.9388	3.1091
$E_d (eV)$	7.1103	15.4672	10.7211
$M_{-1}(eV)^2$	2.1739	5.2632	3.4483
$M_{-3}(eV)^2$	0.2032	0.6094	0.3567
$n_{\circ}$	1.7815	2.5026	2.1091
$\varepsilon_{\circ}$	3.17	6.26	4.44
ε_{∞}	5.95	8.35	8
$\lambda_{\circ} (nm)$	325.9601	359.7385	335.4102
$S_{\circ}(m^{-2})$	2.9412X10^{+13}	9.0909 X10^{+13}	5.5556e X10^{+13}

Table (2) illustratesthe optical parameter of the (AAS): PVP film,we note that the value of the energy gap for the direct and indirect electronic transitionsare less of the film prepared on quartz and the film prepared on silica has high valueof the direct and indirect electronic transition,this mean that the quartz substrate haseffects more than silica and pyrex.From the table (2),we note that the value of oscillator parameter for the film prepared on the silica is the highest, while the dispersion parameter has maximum value for the film prepared on quartz.As a result the film prepared on quartz has high parameters than pyrex and silica, this means the film exhibit more interaction between photonsand electronswhich reflect high optical response.Then if we want to take the substrate effectiveness into accountwe must chose the quartz substrate and chose silica substrate if we want neglect substrateeffect because it has lower optical parameters.

CONCLUSIONS

The optical properties of the (AAS): PVPfilmprepared on different substrates including pyrex, quartz and silica were investigated. The variation of optical absorption edges and refractive index with type of the substrate wereexamined. The dispersion of refractive index was analyzed by single effective oscillator model. The oscillator parameter $E_\circ$and the dispersion parameterE_d were calculated and changed by the type of the substrate.Thedirect and indirect energy gaps of the film changes found to be3.14, 2.47 (eV) respectively for (AAS): PVP/Pyrex, 3.1, 2.38 (eV) for (AAS): PVP/Quartz and3.18, 2.5 (eV) for (AAS): PVP/Silica.The film prepared on quartz have high optical parameters than Pyrex and silica, this means that the film exhibit strong interaction between photons and electron so this reflect high optical response. But if we want to neglect the substrate effect we must chose the silica as the best.

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