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Refractive Index Dispersion and Analysis of the Optical Parameters of (PMMA/PVA) Thin Film

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Abstract

The optical characteristics of (PMMA/PVA) thin films are investigated by spectrometric measurements. Sample with different percentage are prepared with constant thickness (110 μm) using casting technique. The real (n) and imaginary (k) parts of refractive index and dielectric constant of the thin films are determined. Some important parameters of optical absorption, such as the oscillator energy (E_0), dispersion energy (E_d), the average value of oscillator strength (S_0), wavelength (λ_0) of single oscillator and the ratio carrier concentration to the effective mass (N/m*) have been evaluated. The values obtained for the high frequency dielectric constant through two procedures are in the range of (6.31-7.35) for all ranges of the different concentrations.

Keywords: PMMA/PVA thin film, spectroscopic measurements, dispersion parameters, dielectric constant.

Introduction

Polymer materials have been widely used in various fields such as industrial products [1], optical communications, including polymer optical fibers, optical waveguides and optical connectors due to their ease of processing, relatively low cost and mass production compared to silica based optical materials [2]. They also have potential advantages for applications in optical storage systems, such as high thermal stability, low absorption loss and the ability of refractive index changing upon exposure to light.

Polymethylmethacrylate (PMMA) has drawn tremendous interest due to its remarkable physical and optical properties. literature studies reveals that the properties of PMMA depend on its molecular structure and could be modified by several methods such as external electric field, UV illumination and polymer blending [3-5].

Kaminska et al [6] studied the thermal and photochemical stability of poly (methyl-methacrylate)/poly (vinyl acetate) blends and revealed that poly (vinyl acetate) acts as stabilizer with respect to thermal and photochemical degradation when the processes take place in air. The electrical conductivity of polyaniline doped (PVC) and (PMMA) thin films have been measured by studying the I–V characteristics at various temperatures in the range (323–363) K^0 [7]. Ismail, L.N. et al prepare PMMA thin films with different concentration deposited on (ITO) substrate to investigate the effect on the dielectric, optical and morphology properties of PMMA thin film [8].

Because of its good compatible nature with other polymers, we reported in the present work, the effect of various concentrations of (PVA) on some important optical parameters of PMMA thin films. Such as refractive index, oscillator energy (E_0) dispersion energy (E_d), average value of oscillator strength (S_0) and the ratio carrier concentration to the effective mass(N/m*).

Experimental Work

1. Sample preparation:

The PVA polymer obtained in powder form (BDH) chemicals has approximately molecular weight (10000 g/mol) and PMMA polymer supplied by (Aldrich) were used in this study. The specimens with thickness (110 μm) were prepared by casting from solution, the polymers were separately dissolved in chloroform for 48 hour at room temperature and thoroughly stirred using a magnetic stirrer for about 4 hour. The solutions of different concentrations (100/0, 80/20, 60/40, 20/ 80, 0/100) of two polymers are poured in to clean glass Petri dish.

2. Optical measurements:

Optical properties of samples were measured by using (Shimadzu 1601 PC) spectrophotometer in the wavelength range (200–900) nm. The spectroscopic behavior of materials is utilized to determine their optical constants (refractive index (n), extinction coefficient (k), real and imaginary parts of dielectric constants ($\varepsilon_r,\varepsilon_i$)). Several methods were proposed to determine these optical constants; they involve measurements of absorbance (A), reflectance (R) and transmittance (T).

The absorbance (A) is defined as the logarithm of the ratio between absorbed light intensity (I) by material and the incident intensity of light (I_0) of a sample, [9]:

$$A = -\log T = \log\left(\frac{I_0}{I}\right) \quad \text{.................................} (1)$$

Where, I_0 is the intensity of incident light. I is the intensity of the absorbed light at distance (x).

The absorption coefficient (α) is defend as the ability of a material to absorb the light of a given wavelength can be expressed by Lambert Beer's law [10]:

$$\alpha = 2.3\frac{A}{x} = \frac{2.3}{x}\log\left(\frac{I_0}{I}\right) \quad \text{............................} (2)$$

where, (x) is sample thickness.

Dielectric constant is defined as the response of the material towards the incident electromagnetic field. The dielectric constant of compound is divided into to parts real and imaginary, and can be written as [11]:

$$\varepsilon^* = \varepsilon_r + i\varepsilon_i \quad \text{...} (3)$$

Result and Discussion

1. Optical characterization:

The Optical measurements of absorbance of (PMMA) and (PVA) blends in different concentration were carried out in the range (200-900) nm. As shown in Fig.(1) the intensity of absorption peak has increased by decreasing of PVA ratio. It can be observed that there is a sudden decrease in the absorption values in the visible region; the best absorption was for the 100% PMMA-0%PVA (pure PMMA). This may be attributed to the decreasing in the levels at the energy band by increasing the PVA consternation. These results are in good agreement with our previous results [12].

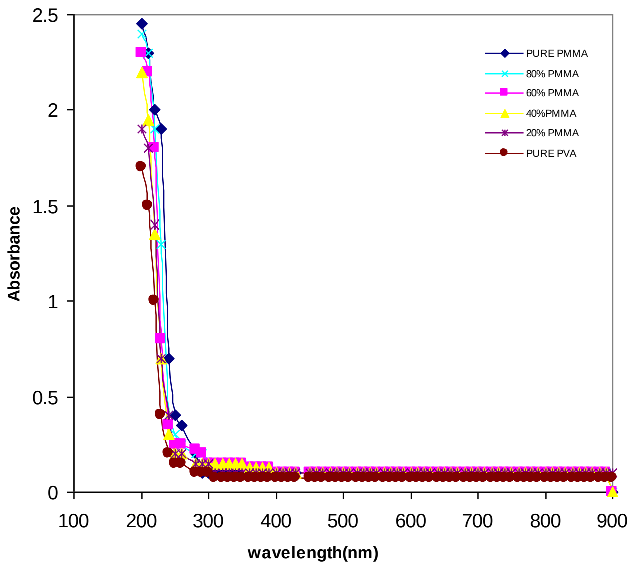

Fig.(1) Absorption spectra of films.

2. Refractive index dispersion:

Refractive index is one of the fundamental properties for an optical material because it is closely related to the electronic polarization of ions and the local field inside materials. The refractive index (n) of the prepared samples can be determined from the absolute values of the reflectance of the investigated films using the following formula [13]:

$$n = \left\{\left[\frac{4R}{(R-1)^2} - k^2\right]^{1/2} - \frac{R+1}{R-1}\right\} \quad \text{..............} ...(4)$$

Where k is the extinction coefficient and R is the optical reflectance. The extinction coefficient can be obtained from the relation $k = \alpha\lambda/4\pi$. Plots in Fig.(2) represent the dispersion in the refractive index for pure (0% PVA) and doped PMMA thin films in the investigated range of wavelengths. Inspection of the figure indicates that for all compositions that the refractive index decreases with increasing wavelength as well as it increases PVA content increases from (0–100)%. A more rapid variations in n(λ) values may be seen at the low wavelength range (200-300) nm. Towards higher values of wavelengths (300-500) nm, the refractive index reaches a nearly constant value.

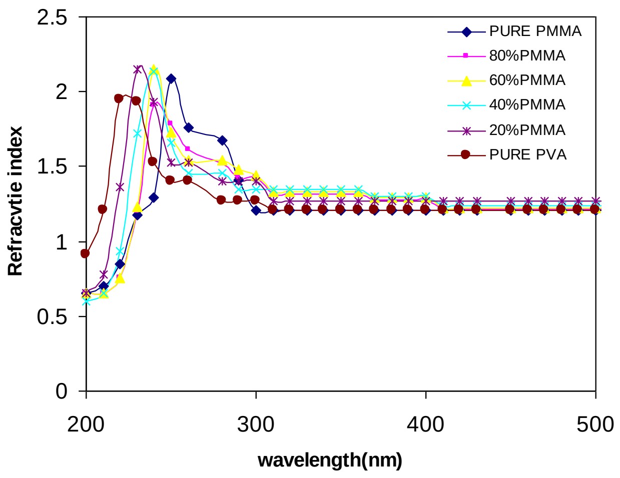

Fig.(2) Refractive index versus wavelength for films.

3. Determination of the dielectric constant:

The real (ε_r) and imaginary (ε_i) parts of the dielectric constant were obtained using the formula $\varepsilon_r = n^2 - k^2$ and $\varepsilon_i = 2nk$ [14]. The variation in the real (ε_r) and imaginary (ε_i) parts of the dielectric constant for different samples are shown in Fig.(3) and (4). They indicate the same pattern curves but the values of real part are higher than those of the imaginary part.

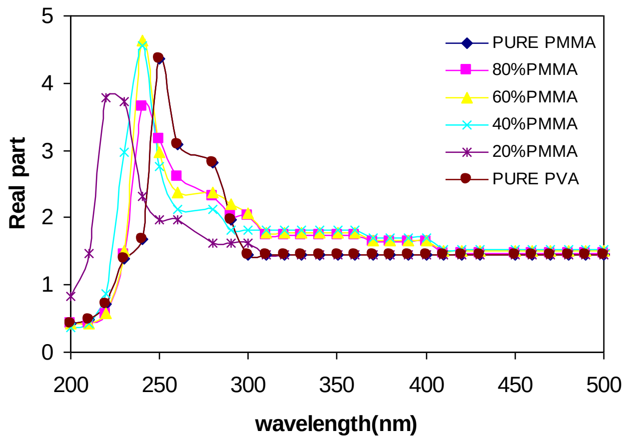

Fig.(3) Real part of dielectric constant versus wavelength.

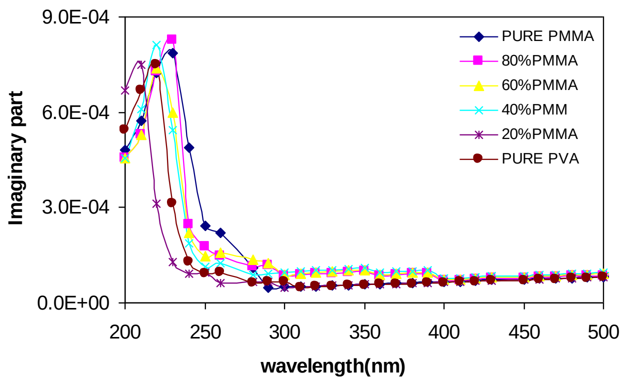

Fig.(4) Imaginary part of dielectric constant versus wavelength.

Analysis of the obtained data of refractive index can be used to obtain the high frequency dielectric constant through two procedures [15]: The first, describes the contribution of the free carriers and lattice vibration modes of the dispersion, while the second procedure is based upon the dispersion arising from the bound carriers in an empty lattice. However, both procedures were employed for the obtained value of lattice high frequency dielectric constant ε_∞.

The First Procedure

The following equation shows the relation between the optical dielectric constant (ε), wavelength λ and refractive index [16]:

$$\varepsilon = n^2 = \varepsilon_{\infty(1)} - \left(\frac{e}{4\pi c^2 \varepsilon_o}\right)\left(\frac{N}{m^*}\right)\lambda^2 \quad \text{.............} (5)$$

where c is the velocity of the light, ε_0 the permittivity of free space (8.854×10^{-12} F/m), N the free carrier concentration and m* the effective mass of the charge carriers. The nature of the dispersion of n^2 as a function of wavelength λ^2 for different samples is shown in Fig.(5). The refractive index is an anomalous dispersion in the region of the high frequency. Both the refractive index and absorption of electromagnetic radiation were found to be increased as frequency increases. Furthermore, the refractive index becomes large, when the frequency of the radiation crosses with the characteristic frequency of the electron. From Fig.(5), it can be seen that the dependence of n^2 is linear at longer wavelength, both the refractive index and absorption of electromagnetic radiation were found to be increased as frequency increase. The values of lattice high frequency dielectric constant $\varepsilon_{\infty(1)}$ is determined from the intersection of the straight line with $\lambda^2 = 0$. Table (1) shows the values of both $\varepsilon_{\infty(1)}$ and the ratio (N/m*), of the investigated films at different concentrations, which determined from the intercept and the slope of the line, respectively. In the same order, it is known that in the range of transparency, when the electron damping parameter $\gamma << \omega$, we have the relation [17]:

$$n^2 = \varepsilon_\infty - \frac{\omega_p}{\omega^2} \quad \text{.......} (6)$$

where ω_p is the plasma frequency with $\omega_p^2 = e^2 N / \varepsilon_0 m^*$, and ω is the incident light frequency, the values of ε_∞ and ω_p are listed in Table (1).

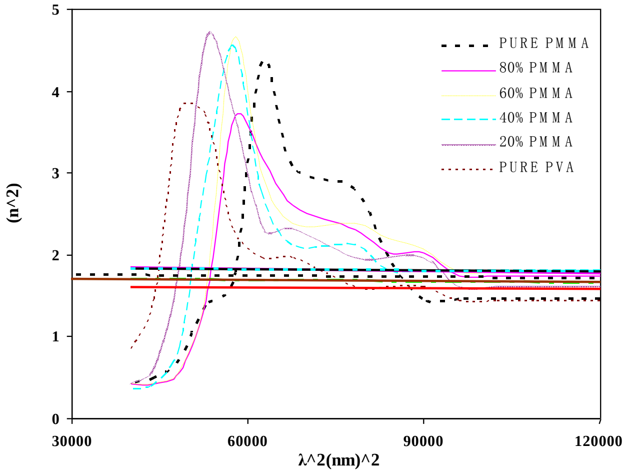

Fig.(5) Dependence of (n^2) on the wavelength (λ^2) for prepared films.

Table (1)
Optical parameters of PMMA thin films with different concentrations.

Film	$\varepsilon_{\infty(1)}$	$\varepsilon_{\infty(2)}$	$N/m^* \times 10^{44} (cm^{-3} g^{-1})$	$\omega_p \times 10^9 (Hz)$
a	1.61	1.38	6.31	1.35
b	1.71	1.41	6.72	1.39
c	1.76	1.42	6.94	1.40
d	1.87	1.31	7.35	1.46
e	1.85	1.51	7.25	1.44
f	1.72	1.37	6.76	1.39

The Second procedure

Determination of the dielectric constant could be defined by the dispersion relation of the incident photon. The refractive index was also fitted using a function for extrapolation towards shorter wavelength. The Moss model [18], which stated that: “the free carriers contribution to dispersion are relatively small”. This means that data corresponding to the wavelength range lying below the absorption edge of the material has to be used. The properties of the investigated samples could be treated as a single oscillator at wavelength λ_0 at high frequency. To find the high frequency dielectric constant ($\varepsilon_{\infty(2)}$), we have used the following equation [19]:

$$n^2 - 1 = \frac{S_0 \lambda_0^2}{1 - (\lambda_0/\lambda)^2} \quad \text{.......} (7)$$

where S_0 is the average oscillator strength, λ_0 is an average oscillator wavelength. Equation (7) can be written as follows:

$$\frac{n_\infty^2 - 1}{n^2 - 1} = 1 - \left(\frac{\lambda_0}{\lambda}\right)^2 \quad \text{.......} (8)$$

Where n_∞ is the refractive index at infinite wavelength λ_0. Table (2) shows the values of λ_0 and S_0, they were obtained from slope and intercept of $(n^2 - 1)^{-1}$ versus λ^{-2} curves at different concentrations. In Fig.(6), the intersection with $(n^2-1)^{-1}$ axis is $(n_\infty^2-1)^{-1}$ and hence n_∞^2 at λ_0 equal to $(\varepsilon_{\infty(2)})$.

The values of $(\varepsilon_{\infty(1)})$ and $(\varepsilon_{\infty(2)})$ are closed with each other and small difference between them may be due to the lattice vibrations and bounded carriers in an empty lattice which are in the transparent region [20]. This means that the lattice vibration and bounded carriers varies with different concentration of (PMMA/PVA) films.

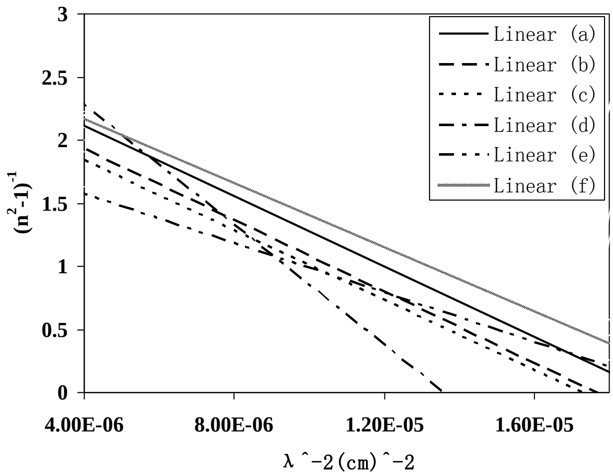

Fig.(6) Variation the $(n^2-1)^{-1}$as a function of λ^{-2}.

3. Dispersion Energy Parameters of Thin Films

The dispersion energy plays an important role in the research for optical materials because it is a significant factor in optical communication and in designing devices for spectral dispersion. The dispersion of refractive index of the thin films was analyzed using the concept of the single oscillator and can be expressed by Wemple and DiDomenco relationship, [21]:

$$n^2-1=\frac{E_d E_0}{E_0^2-E^2} \quad \text{...} (9)$$

Where E, E_0 and E_d are the photon energy, the oscillator energy and the dispersion energy, respectively. The parameter E_d, which is the measure of the intensity of the inter-band optical transition, does not depend significantly on the band gap. A plot of $(n^2-1)^{-1}$ versus E^2 of PMMA/PVA films for different concentrations is shown in Fig. (7)

The values of E_d and E_0 presented in Table (2) were obtained from the slope and the intercept, respectively, resulting from the extrapolation of the lines**.** It is clear that, the effect of the different concentrations on the refractive index and dispersion profiles were exhibited a linear displacement in the shape of the dispersion profile with decreasing refractive index. The refractive index declines towards long wavelengths, this is due to the influence of lattice absorption.

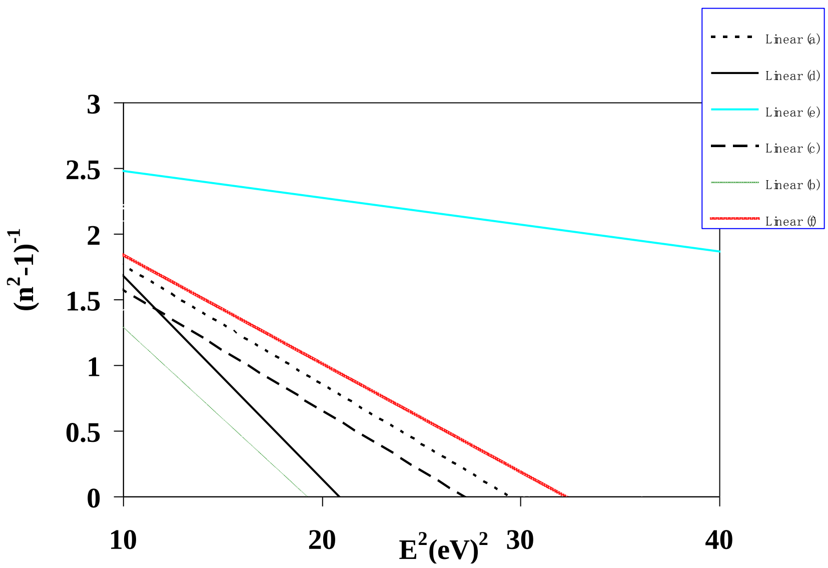

Fig. (7) Variation the $(n^2-1)^{-1}$ as a function of E^2.

Table (2)
Other Optical parameters of PMMA thin films with different concentrations.

film	$S_o.10^{14}(m^{-2})$	$\lambda_o(nm)$	ε	$E_o\,(eV)$	$E_d\,(eV)$
a	7.1830	52192	1.3748	5.4292	2.0352
b	7.0803	56670	1.3918	10.20	3.999
c	7.2313	57800	1.4010	5.2089	2.089
d	4.2080	73650	1.3090	4.569	1.416
e	0.0123	49700	1.3730	11.46	4.274
f	7.856	47000	1.3720	5.683	2.125

Conclusions

In this work, the refractive index behavior of PMMA/PVA thin films was studied using spectroscopic measurements, which covers a UV/VIS spectral ranges, This technique permit the detection of small changes in optical constants. The effect of PMMA concentration on the refractive index was obtained, we can conclude the followings:

1- The real and imaginary parts of the dielectric constant (ε_r) and (ε_i) indicated the same pattern and the values of the real part are higher than the values of the imaginary part.

2- The values of high frequency dielectric constant $\varepsilon_{\infty(1)}$ and $\varepsilon_{\infty(2)}$ are close with each other and the difference between them is very small.

3- Dispersion energy E_d, single oscillator energy E_0 and average oscillator wavelength λ_0 are determined, and found to be consist with the results of others like the results of references [19,20,21].

4- Ratio carrier concentration to the effective mass (N/m*) have been evaluated, and we can't compare it with other works because non of the references we have used found similar values.

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الخلاصة

تم في هذا البحث دراسة الخصائص البصرية لاغشية بولي مثيل ميثكرلايت (PMMA) وبولي فنيل الكحول (PVA) بنسب مختلفة(١٠٠/٠و٨٠/٢٠و٦٠/٤٠و٢٠/٨٠و٠/١٠٠) بعد تحضيرها بسمك ثابت باستخدام طريقة الصب. حدد معاملي الانكسار والخمود وثابت العزل بجزئيه الحقيقي والخيالي للاغشية. تم حساب بعض الثوابت البصرية المهمة مثل طاقة التذبذب وطاقة التشتت ومعدل قيمة قوة المتذبذب والطول الموجي للمتذبذب المنفرد و نسبة بين تركيزالحاملات الحرة والكتلة الفعالة.سجلت قيم ثابت العزل للترددات العالية من خلال طريقتين وتتراوح قيمتها بين (٦,٣١-٧،٣٥) للتراكيزالمختلفة للاغشية المحضرة.