Effect of Poly (Methyl Methacrylate) Solute Concentration in Chlorobenzene on the Optical Properties of Films Prepared by Spin Coating

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DOI: https://doi.org/10.47372/jef.(2024)18.2.94

Abstract: This study addresses the effect of solute concentration on the optical properties of poly(methyl methacrylate) (PMMA) films prepared using the spin-coating technique. The films were fabricated at three concentrations (1.5%, 2% and 2.5%) and examined over a wavelength range (250-900. nm) .The results showed a significant decrease in transmittance with increasing solute concentration, reflecting its impact on absorption characteristics. Furthermore, the optical band gap was determined, showing a decrease from 3.91 eV at a concentration of 1.5% to 3.892 eV at a concentration of 2.5%, indicating a direct relationship between increased solute concentration and a narrowing of the band gap. Other optical constants, including the refractive index, were calculated using models such as the Wemple-DiDomenico and Drude-Lorentz models. These findings highlight the effect of solute concentration on the optical properties of PMMA films, suggesting their potential use in various optical applications.

Keywords: Poly (methyl methacrylate), Spin coating, Optical properties, Wemple-DiDomenico model, Drude-Lorentz model.

Introduction: Poly(methyl methacrylate) (PMMA) is a versatile polymer that has a wide range of optical and electronic applications due to its excellent transparency, low cost, and ease of fabrication [1]. PMMA thin films are commonly used in coatings, lenses, and optical devices[2]. The optical properties of PMMA films, such as transmittance and refractive index, are significantly influenced by various factors such as preparation method, solute concentration, and annealing conditions [3].

This study investigates the effect of solute concentration on the optical properties of PMMA films prepared using the spin-coating technique. Spin coating is a widely used method for producing uniform thin films, allowing precise control over film thickness and morphology [4]. By varying the concentration of PMMA in the solution, we aim to explore how optical properties, such as transmittance, refractive index, and energy gap, change with concentration.

2. Materials and Methods:

2.1 Materials: Poly(methyl methacrylate) (PMMA) was used as the primary material in this study and was obtained from Shanghai New Century Dental Materials Co., Ltd. in powdered form. Chlorobenzene with 99% purity was used as the solvent. Films were prepared at different PMMA concentrations (1.5%, 2%, and 2.5%).

2.2 Solution Preparation: Specific amounts of PMMA were dissolved in 20 mL of chlorobenzene (0.3 g, 0.4 g, and 0.5 g to achieve concentrations of 1.5%, 2%, and 2.5%, respectively). The solution was stirred using a magnetic stirrer for 60 minutes at 70°C to ensure complete dissolution. Subsequently, the solution was left to rest for 48 hours to guarantee homogeneity.

2.3 Spin Coating Process: The solution was applied to clean glass substrates using a spin-coating apparatus, where the rotation speed was set to 3000 rpm for 20 seconds to ensure uniform film thickness. No thermal annealing was applied to the films after deposition to maintain the solute concentration as the sole influencing factor.

2.4 Optical Measurements: The optical transmittance and absorbance of PMMA films were measured using a UV-Vis spectrophotometer in the wavelength range of 250-900 nm.

The refractive index and other optical parameters were calculated using appropriate equations from the Wemple-DiDomenico and Drude-Lorentz models, which involve various parameters beyond transmittance. The thickness of the films was determined using the gravimetric method, based on mass differences.

3. Results and Discussion:

3.1. Transmittance (T) and Absorbance (A):

Figure ($1_{a,b}$) display the transmittance and absorbance spectra as a function of wavelength for poly(methyl methacrylate) films prepared at different concentrations (1.5%, 2%, 2.5%). It is evident that the transmittance decreases with increasing polymer concentration, especially in the visible spectrum range (400-700 nm). This is attributed to the increased viscosity of the solution, the formation of aggregates on the film surface, and the subsequent increase in film thickness, leading to higher optical absorption and reduced transmittance.

Other factors, such as crystal defects and light scattering, also contribute to this reduction [5]. As for absorbance, the films show the highest absorbance at shorter wavelengths, which then decreases gradually within the visible range. The absorbance values reached (0.039, 0.042, 0.04) at concentrations of (1.5%, 2%, 2.5%), respectively.

Additionally, as the polymer concentration increases, absorbance rises, and the optical absorption edge shifts toward longer wavelengths. This shift in the optical absorption edge can be explained by the increase in film thickness, which affects the electronic transitions related to the energy gap, thereby influencing the film’s ability to absorb light at certain wavelengths [6].

3.2. Reflectivity: The reflectivity was calculated using equation [7]:

$$R = 1 - \sqrt{T * \exp(A)} \quad . \qquad (1)$$

Where: A: absorbance and T: transmittance.

Figure (2) shows the reflectivity as a function of the wavelength of the photon incident on the film. It is observed that the reflectivity curve for all films rises at shorter wavelengths, then begins to decrease when the photon energy reaches a value equivalent to the optical gap energy, leading to an increase in absorbance.

In the visible spectrum region, reflectivity values decrease due to the increase in transmittance. Generally, films prepared with higher concentrations exhibited the highest reflectivity values.

This is explained by the increase in film thickness as the amount of solute (PMMA) increases, and the reduction in porosity, which decreases with higher concentrations [8].

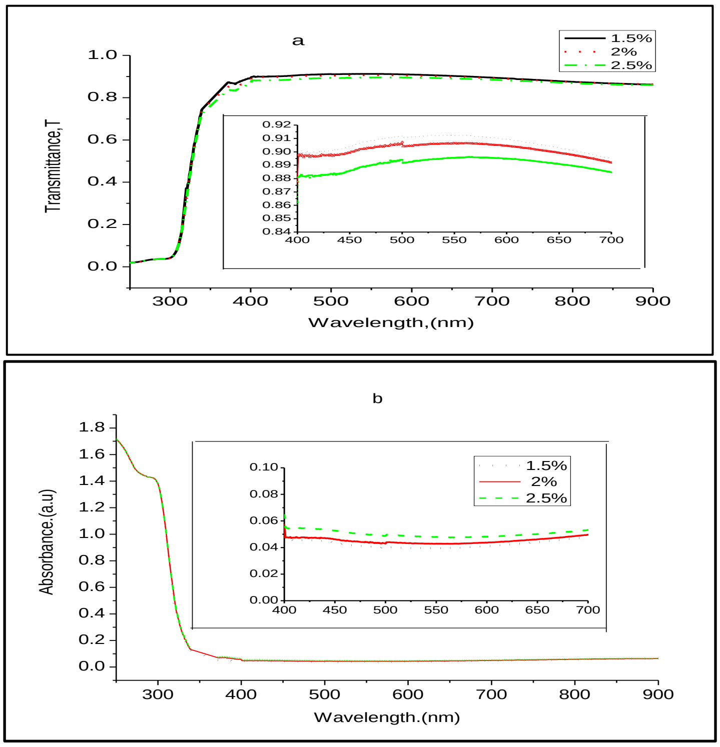


Figure (1): (UV-Vis),(a) transmittance and b) absorbance versus wavelength of PMMA films at, (1.5%,2%,2.5%)

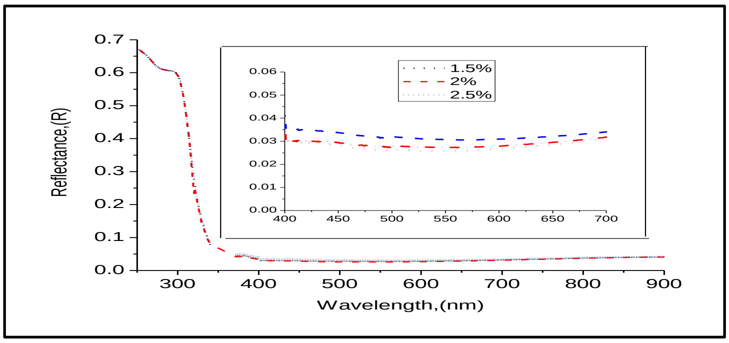


Figure (2) : Reflectivity versus wavelength of PMMA films at (1.5%,2%,2.5%)

3.3. Optical Absorption: The absorption coefficient was calculated using equation [9]:

$$\alpha = \frac{\mathrm{Ln}(\frac{1}{T})}{d} \quad . \qquad (2)$$

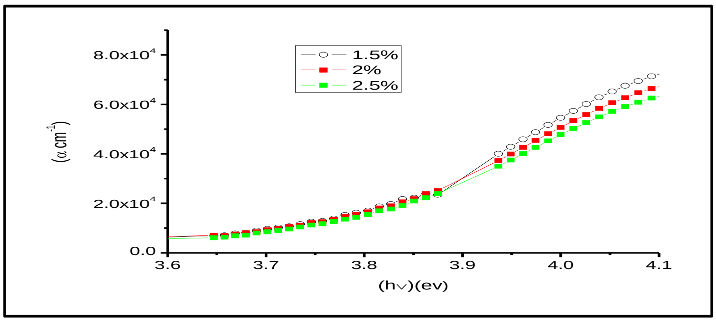
Where: d: Thickness of thin film and T: transmittance.

In Figure (3), the curve demonstrates low values at low photon energies, indicating Urbach tails, while it increases at higher energies due to direct electronic transitions. Increasing the solute concentration decreases the absorption coefficient due to higher film density and crystalline defects, which enhance light scattering [10].

3.4. Extinction Coefficient: The extinction coefficient was calculated using the absorption coefficient values according to the following relationship [11]:

$$K_{ex} = \frac{\alpha\lambda}{4\pi} \quad . \qquad (3)$$

Figure (4) shows the extinction coefficient as a function of the wavelength, it is clear that the extinction index values are the greatest possible in The high absorption region is at the energies corresponding to the basic absorption edge, that is, at short positive lengths due to its dependence on the optical absorption coefficient, and then it decreases over a long range of wavelengths in the visible region with increasing wavelength and weak attenuation of the electromagnetic wave occurs starting from the wavelength,(630-900 nm).The amount of this attenuation increases with increasing concentration for all prepared films[12].



Figure(3): Absorption Coefficient versus wavelength of PMMA films at (1.5%,2%,2.5%)

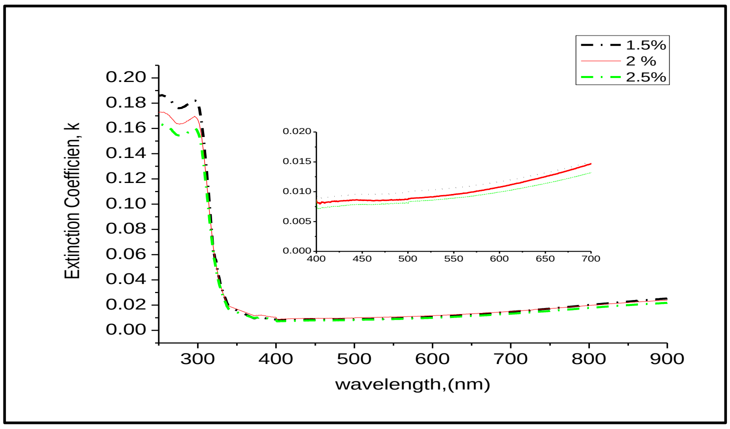


Figure (4): Extinction Coefficient versus wavelength of PMMA films at (1.5%,2%,2.5%)

3.5. Optical Energy and Urbach Energy: The optical energy gap for allowed direct transitions in PMMA films prepared at various concentrations was calculated based on the absorption coefficient values. This was achieved using the equation [13]:

$$\alpha h\nu = B(h\nu - Eg)^{r} \quad . \qquad (4)$$

In this equation , α represents the absorption coefficient, hν is photon energy, B,is a constant, $E_{g,}$ is the optical energy gap, r. is typically equal to ½ for direct transitions. By plotting the linear relationship between $(\alpha h\nu)^2$ and the photon energy (hν). The best-fit line intersects the energy axis at (αhν) = 0, indicating the optical energy gap. As shown in Figure ($5_{a,b,c}$), there is a decrease in the energy gap with solute concentration increased. This decrease in the energy gap with increasing concentration can be attributed to the formation of larger polymer aggregates and increased film thickness, which affect the molecular structure and lead to a reduction in the band gap energy. These structural changes result in localized states within the band gap that facilitate electronic transitions at lower energies, thereby reducing the optical energy gap[14].

Urbach energy was calculated using the regression from the logarithmic curve of the absorption coefficient using relation [15]:

$$\alpha = \alpha_0 \exp(h\vartheta / E_e) \quad . \qquad (5)$$

In this equation, E_u denotes the Urbach energy, α_0 constant.

Figure (6) shows the change of (Ln) as a function of the photon energy. By determining the slope of these curves, the width of the Urbach tails can be calculated. The results showed that Urbach energy values for all films were very close to those in Table (1), with these values

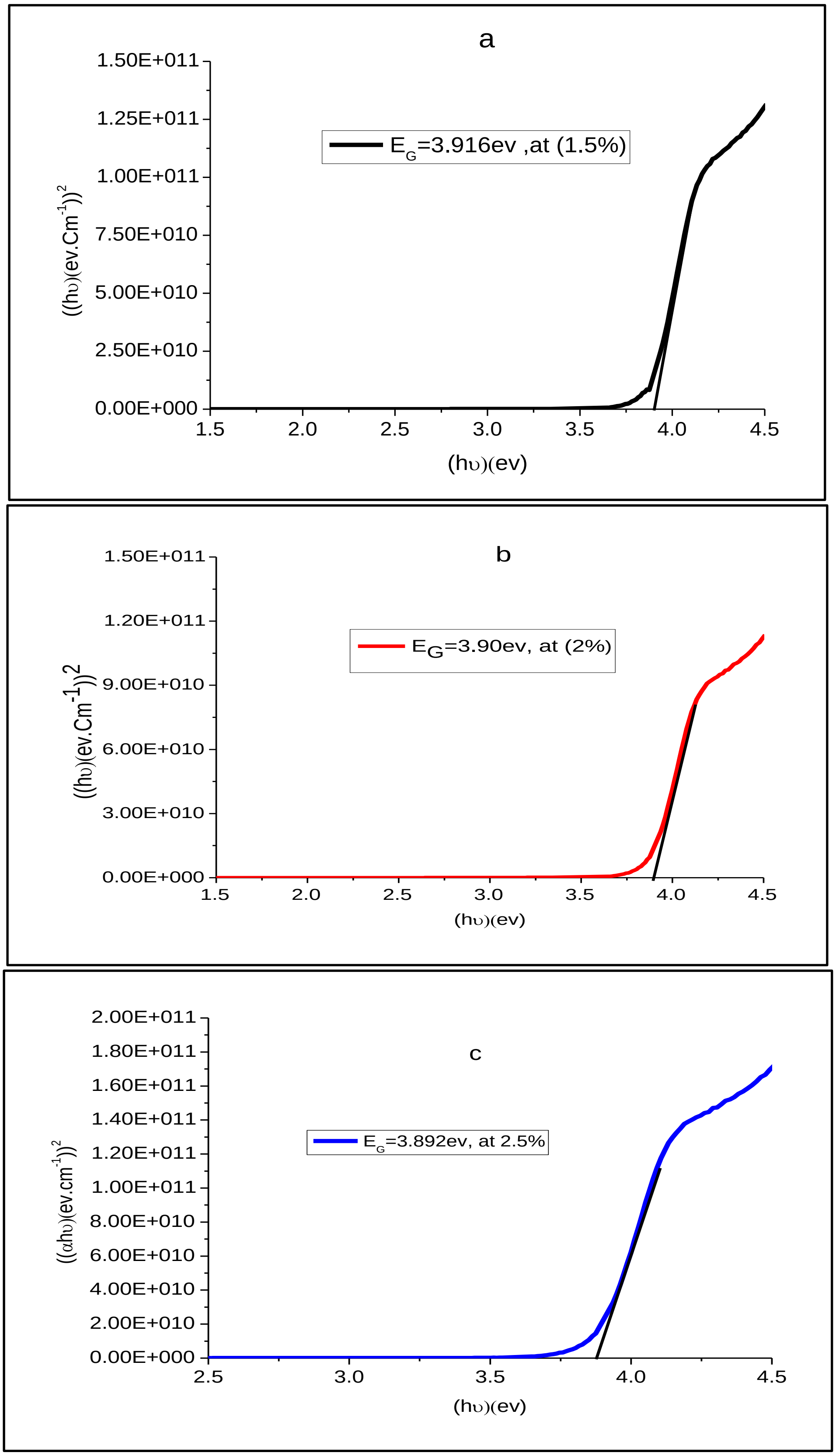


Figure (5): Plot of $(\alpha h\nu)^2$ vs. (hν) for PMMA thin films: a) 1.5% ,b) 2% ,c) 2.5%.

The slight increase in Urbach energy values within a narrow range (0.157–0.175 eV) as solute concentration increased from 1.5% to 2.5% may indicate that no significant changes occurred in structural disorder or defects within this concentration range [14].

Table 1: Values of optical band gap (E_g) and Urbach energy (E_u) for PMMA at different concentration.

Concentration%	band gap (E_g ev)	Urbach energy E_u (ev)	Thickness,(nm)
1.5	3.913	0.167	422
2	3.90	0.168	455
2.5	3.892	0.175	482

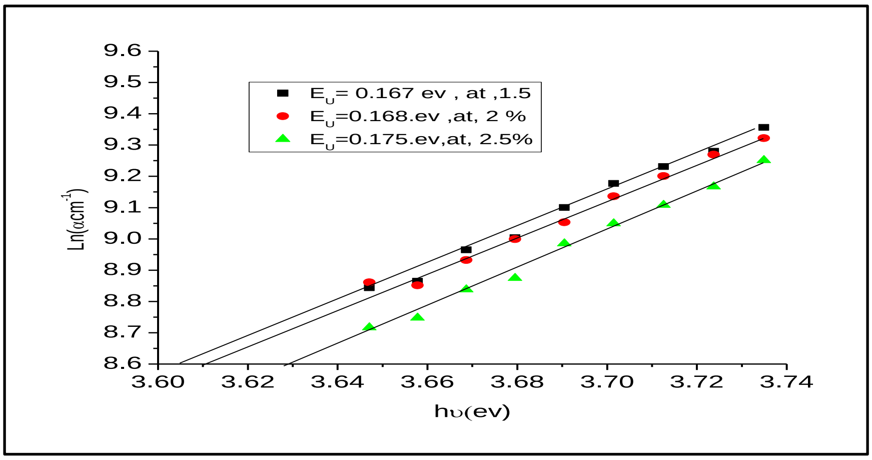


Figure (6): Plots of Ln(α) vs. (hν) for PMMA thin films at (1.5%,2%,2.5%)

3.5. Refractive Index: The refractive index of the prepared films was calculated using the following equation [16]:

$$n = \frac{(1+R)}{(1-R)} + \sqrt{\left[\left(\frac{1+R}{1-R}\right)^2 - (1+K^2)\right]} \quad . \qquad (6)$$

Where: R is Reflexivity and K is extinction coefficient.

Figure (7) shows that the refractive index gradually increases with the increase in PMMA concentration. This rise is attributed to the increased material density and the reduction of voids between polymer chains, which contributes to enhancing the material's ability to bend light within it[17].

The highest refractive index value was recorded at a 2.5% concentration, reaching 1.50.

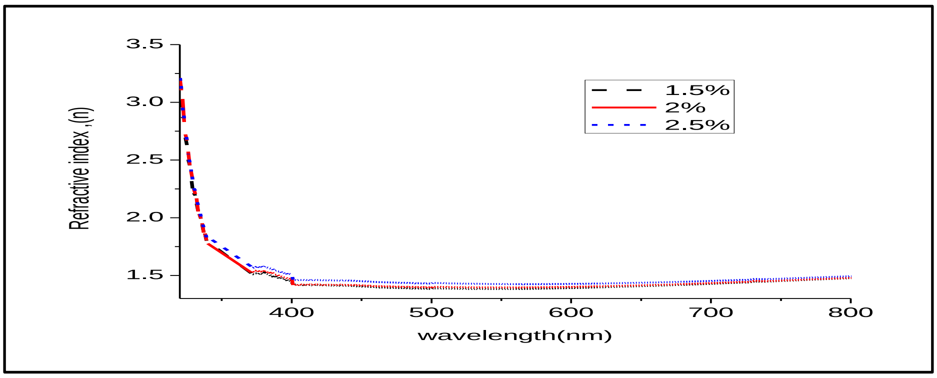


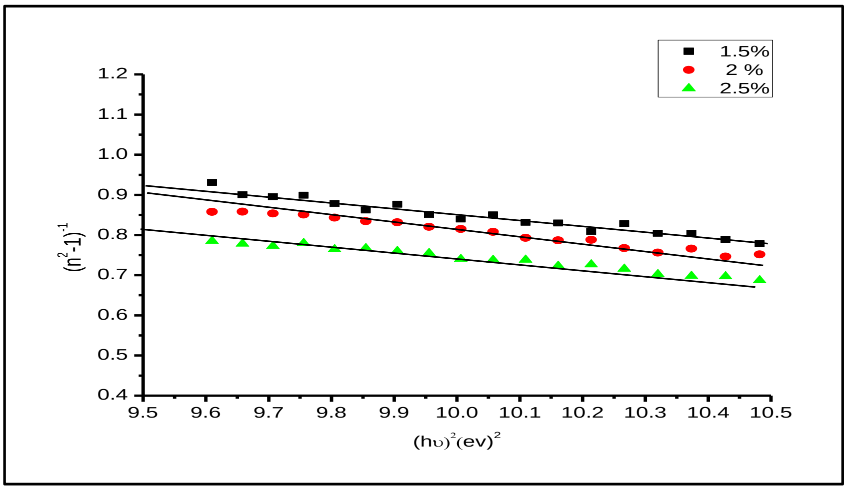
Figure (7): The refractive index versus wavelength of PMMA films at,(1.5%,2%,2.5%)

3.6.Refractive Index and Dispersion Parameters:

i) Wemple–DiDomenico (WDD) model: Using the Wemple–DiDomenico model and previously obtained refractive index data, the optical parameters as oscillator energy (E_0), dispersion energy (E_d), zero dielectric constant (ε_0), zero refractive index (n_0),were calculated using the relationship [18]:

$$n^2 = 1 + \left(\frac{E_0 E_d}{E_0^2 + h\vartheta^2}\right) \quad . \qquad (7)$$

As illustrated in Figure (8), the relationship between $(n^2-1)^{-1}$ and $(h\nu)^2$ yields straight lines, where the slope represents the ratio $(1/E_0E_d)$ and the intercept on the vertical axis represents the ratio (E_d/E_0). It is straightforward to calculate the values of E_0 and E_d for films prepared at different concentrations, as presented in Table (2). It is evident that the dispersion energy values E_d slightly increase from 7.08 to 7.10 eV. This suggests that increasing the solute concentration from 1.5% to 2.5% slightly affects the energy required for light dispersion within the film material, while the oscillator energy values trend oppositely to dispersion energy values, showing a decrease with increasing solute concentration. This decrease may indicate that the increase in concentration affects the oscillatory properties of light, reducing the energy required for oscillation [18].



Figure(8):The$(n^2-1)^{-1}$versus $(h\nu)^2$, of PMMA thin films at concentration(1.5%,2%,2.5)%

Using the values of E_0 and E_d, the zero refractive index (n_0) and zero dielectric constant (ε_0) can be calculated from the equation (7) by setting $(h\nu=0)$,becomes:

$$n_0^2 = \varepsilon_0 = \left(1 + \frac{E_0}{E_d}\right) \quad . \qquad (8)$$

The values of (n_0) and (ε_0) are given in Table (2) as (1.91, 2.14, 2.23) and (1.38, 1.39, 1.43) at concentrations (1.5%, 2%, 2.5%) respectively. The increase in the zero refractive index with increasing concentration indicates that the film material becomes denser with higher solute concentration. Additionally, the increase in the zero dielectric constant reflects an enhancement in the film material's ability to store electrical charges.

ii) Drude-Lorentz model : Using the Drude-Lorentz model, and from the obtained values of the refractive index, the high-frequency dielectric constant ε_∞ and the ratio of effective charge carriers to effective mass were calculated according to the equation [19]:

$$n^2 = \boldsymbol{\varepsilon}_\infty - \frac{1}{4\pi^2\varepsilon_0}\left(\frac{e^2}{c^2}\right)\left(\frac{N}{m^*}\right)\lambda^2 \quad . \qquad (9)$$

where ε_∞ is the high-frequency dielectric constant, c is the speed of light, ε_0 is the dielectric constant in free space, and N/m* is the ratio of free carrier concentration (N) to effective mass (m*). By plotting n^2 versus λ^2, the slopes and intercepts of the straight lines in Figure (9) allow for the determination of N/m*, ε_∞, and plasma frequency $(\omega_p = Ne^2/c)$. For all prepared films, the obtained values are recorded in the Table (2). It is clear that the high-frequency dielectric constant values increase, indicating that the material responds to high-frequency electric fields with increasing solute concentration. Furthermore, the charge carrier to effective mass ratio and plasma frequency increase significantly, suggesting an improvement in the mobility of free charge carriers within the film with the increase in solute concentration [20].

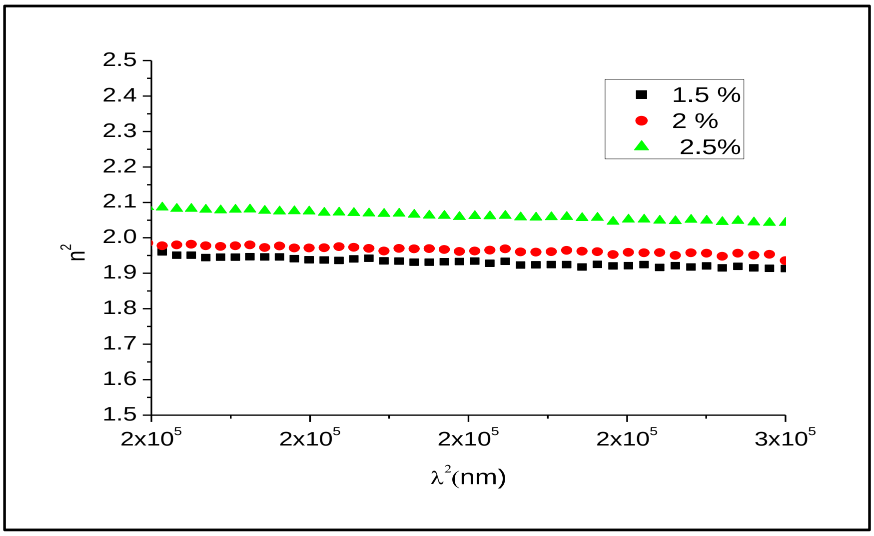


Figure (9): The (n^2) versus λ^2, of PMMA thin films at concentration(1.5%,2%,2.5%)

Table 2: The Optical parameters for pure PMMA thin films at different concentration.

Concentration %	E_d	E_0	ε_0	n_0	ε_∞	$\omega_P \times 10^{14} S^{-1}$	$(N/m^*)*10^{+58}$ (m^3*Kg^{-1})
1.5	7.08	7.72	1.91	1.38	2.02	5.4	2.20
2	7.09	6.38	2.14	1.39	2.05	5.36	2.40
2.5	7.10	5.75	2.23	1.43	2.14	7.39	4.76

Conclusion: The research addresses the effect of polymer concentration on the optical properties of methyl methacrylate (PMMA) polymer films prepared using the spin-coating technique. The findings indicate that transmittance decreases with increasing polymer concentration, particularly in the visible spectrum (400-700 nm),which was attributed to higher solution viscosity, the formation of aggregates on the film surface, and increased film thickness, leading to greater optical absorption. Conversely, the highest absorption values were observed at shorter wavelengths, suggesting increased light absorption with higher polymer concentration. It was also noted that reflectance increases at shorter wavelengths and decreases as photon energy reaches a value equal to the optical band gap energy. Generally, films prepared at higher concentrations exhibited higher reflectance values, indicating greater film thickness and reduced porosity.

The absorption coefficient showed variation with photon energy, with lower values at lower energies and higher values at higher energies due to direct electronic transitions. The film density and crystal defects increased with higher polymer concentration, resulting in enhanced light scattering. High values of the extinction coefficient were observed in the high absorption range, beginning to decrease in the visible spectrum with increasing wavelength. These values increased with higher polymer concentration, suggesting that the materials weaken the scattering of electromagnetic waves. The optical band gap was calculated from the absorption coefficient values, showing a decrease in band gap energy with increasing polymer concentration. The Urbach energy values were similar, indicating no significant changes in structural defects within the studied concentration range.

Results demonstrated an increase in the refractive index with increasing polymer concentration, with the highest concentration being 2.5%. This increase is attributed to higher material density and reduced spacing between polymer chains. Optical parameters were calculated using various models, including the Wemple-DiDomenico model and the Drude-Lorentz model. The results indicated an increase in effective charge density and refractive index with higher concentration, demonstrating improved material responsiveness to high-frequency electric fields.

Overall, the findings confirm that polymer concentration significantly influences the optical properties of PMMA films, enhancing understanding of how to improve the optical performance of polymer materials.

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تأثير تركيز البولي ميثيل ميثاكريلات (PMMA) المذاب في الكلوروبنزين على الخواص البصرية للأفلام المحضرة بتقنية الطلاء الدوراني

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الملخص: تتناول هذه الدراسة تأثير تركيز المذاب على الخصائص البصرية لأفلام البولي ميثيل ميثاكريلات (PMMA) المحضرة باستخدام تقنية الطلاء بالتدوير. تم تصنيع الأفلام بثلاثة تركيزات (1.5%، 2%، و2.5%) وقياسها ضمن مدى أطوال موجية يتراوح بين 250-900 نانومتر. أظهرت النتائج انخفاضاً ملحوظاً في النفاذية مع زيادة تركيز المذاب، مما يعكس تأثيره على خصائص الامتصاص. بالإضافة إلى ذلك، تم تحديد فجوة الطاقة البصرية، حيث لوحظ انخفاضها من 3.91 (إ.ف) عند تركيز 1.5% إلى 3.892 (إ.ف) عند تركيز 2.5%، مما يدل على وجود علاقة مباشرة بين زيادة تركيز المذاب وتضييق فجوة الطاقة. كما تم حساب الثوابت البصرية الأخرى، بما في ذلك معامل الانكسار، باستخدام نماذج مثل نموذج ويمبل-دي دومينيكو ونموذج درود-لورينتز. تبرز هذه النتائج تأثير تركيز المذاب على الخصائص البصرية لأفلام PMMA، مما يشير إلى إمكانيات استخدامها في تطبيقات بصرية متعددة.

الكلمات المفتاحية: بولي (ميثيل ميثاكريلات)- الطلاء الدوراني - الخصائص البصرية - نموذج ويمبل- دي دومينيكو - نموذج درود- لورنتز.