Optical Properties of Blend of PMMA:PVDF

Nadhim A. Abdullah and Fatima H. malk*

Department of Materials Sciences, Polymer Researches Centre, University of Basra, Basra, Iraq

*Fatima.hameed16@yahoo.com.

DOI: https://doi.org/10.47372/uajnas.2021.n1.a16

Abstract

In this study, thin films of PMMA Poly (methyl methacrylate)- Polyvinylidene fluoride(PMMA-PVDF), PMMA polymer and soluble PVDF polymer were prepared at (5%)Toluene and polymeric blends in 1:1 volume ratio of polymers and in different proportions of polymers. The studied films were prepared by the Spin coating method, and the optical parameters of the thin films were measured within a range (300-900)nm and the thickness of the films were constant (223 nm). Absorbance (A), linear absorption coefficient (α), refractive index (n), extinction coefficient(K), real and imaginary dielectric constant ($\in_r, \in_i$) and optical energy gap Eg were studied, as the best edge of optical absorption was 5% PVDF, And electronic transmission between levels was direct transmission.

Keyword: PMMA, PVDF, Spin coating, optical parameter.

Introduction

In the few past decades and according to the general industries, physical and chemical properties of polymers, such as easy and coast effective manufacturing methods, chemical resistance, nontoxic, flexibility, high transmission in the visible and near-infrared regions, large thermo-optics coefficients, dispersions and refractive coefficients also have focused on the optical properties of different polymers. These properties can be recognized by measuring and calculating some physical coefficients of polymers , such as absorbance, linear absorption coefficient, refractive index, extinction coefficient, dielectric constant and energy gap, to determine the ability to be useful in several areas. There are many advanced optical applications involved polymers as an active material that control on its efficiency in different technological fields. Two of these polymers are PMMA and PVDF [12,15].

The mixture is a simple and active method to improve its characteristics and to achieve a new material with a modulating properties on each of the mixed materials. PMMA has individual properties, such as simple synthesis process, electrical performance, high transparency, caused by its lower optical absorption in the visible region, low refractive index, rigidity, good mechanical properties and good thermal parameters. It has great interest and many advantages in variant modern applications as a result of these properties[11,14]. Also, PVDF has excellent mechanical properties, high dielectric constant, high chemical resistance, thermal stability and good compression coefficient, despite the distinctive properties of the PVDF polymer, it has a low surface energy and high cost, so it is mixed with polar polymers by deformation method to expand its application areas. These properties have led to several uses for it, whether it is pure or in other polymer composites, and PVDF is more compatible with PMMA[3,5].

PVDF:PMMA blends have been used in many studies as pure or mixed with other polymer or nano-materials, as a manufacture of battery with a long life and high energy density, as a results of the polymeric mixture which is highly ionic, PVDF:PMMA blends was used in solar cells with their efficiency which was 0.5 [1-4, **10**]. It is noted that PVDF crystallizes with PMMA and this crystalline depends on the proportions of the compounds and the type of solvent,[18].

In this work, we investigated the optical properties of thin films of Poly (methyl methacrylate):Polyvinylidene fluoride (PMMA-PVDF) blend by solutions mixing method.

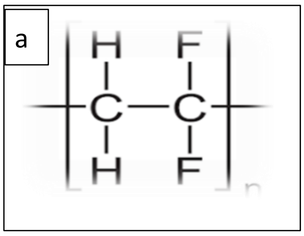
Materials and Method

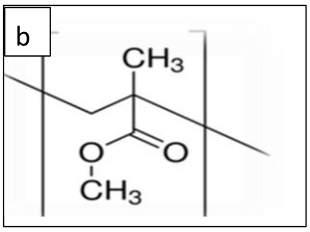
1. **Material**

Polyvinylidene fluoride (PVDF) is a polymer with specifications molecular formula $(C_2H_2F_2)_n$, mp:166-170℃, low density (1.78 g/cm^3). Polymethylmethacrylate (PMMA) with a molecular formula of $(C_5O_2H_8)_n$, Density (1.18 g/cm^3), Melting point of 160^{0}C (320^{0}F; 433^{0}K), all equipped by Sigma-Aldrich. The polymers have chemical structures shown in Figure (1: a and b).

2.**Samples Preparation**

PMMA was dissolved in toluene solvent as (5 g / 100 mL) by stirring for five hours at 50°C, as well as, 5g of PVDF polymer that was dissolved in 100 mL of toluene solvent by stirring for six hours at a temperature of 70°C, then the solutions were filtered by a filter of 0.45 µm. The preparation of the polymeric blend done by applying 1:1 volume ratio of the polymers for solutions and stirred at 60°C for one hour to get a homogenous solution. The thin films were prepared by using the spin coating technique with constant rotation speed (1000 rpm), a glass substrates (with a distances of 2.5cmx2.5cm) was used. The samples have annealed at 60°C temperature for 30 minutes.[9]





Fig(1): Chemical Structure of (a) PVDF, (b),PMMA

Results and Discussion

It is worth noting that the optical UV-VIS measurements were done under the laboratory conditions of 25℃ by using the spectroscopy and the wavelengths Rang (300-1000)nm, and we have sought accuracy in obtaining approximately equal thicknesses (d) equal to (223nm) for the various models in the deformation ratios of the membranes by repositioning more than once to reach the required more closely.

1. Absorbance of thin films

Figure (2) shows the relationship between the optical absorbance and the wavelength of the prepared models, optical absorption edge is at 300 nm and remains stable within the wavelengths range of (320-1000) nm, as the absorption edge values for thin films of 5% for PMMA polymer dissolved with toluene are few, while the optical absorption edge increases to 0.2 (a.u) for the polymer mixture films PMMA:PVDF. The best absorbency is in thin films which are 0.3 (a.u) from 5% PVDF dissolved with toluene.

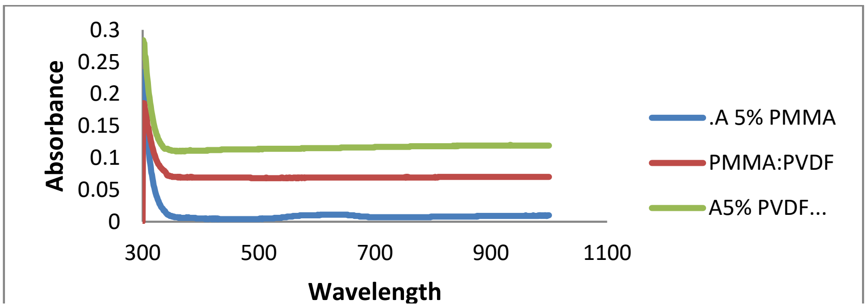


Fig (2): Relationship between absorbance and wavelength.

2. Absorption coefficient (α):

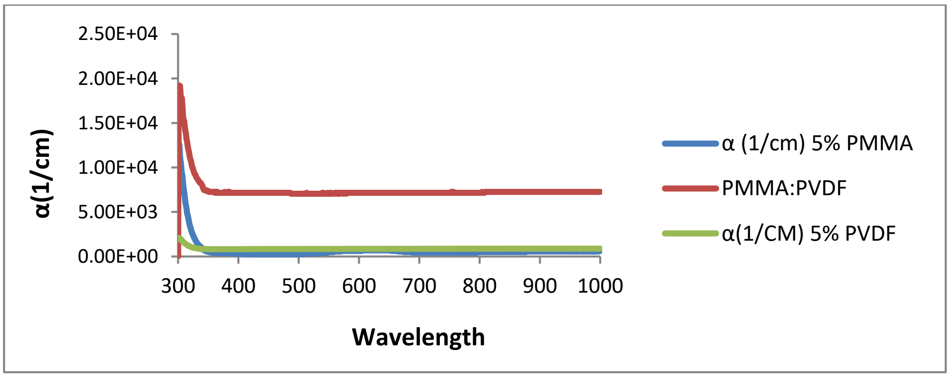
Linear absorption coefficient (α) was calculated using (11):

$$\alpha = \frac{2.303}{d} * a \dots\dots\dots..[1]$$

Where: d: Thickness of thin film and a: Absorbance.

The value of the absorption coefficient determines the type of electronic transfer that occurs within solid materials.

Fig (3) shows, the type of electronic transitions that they are direct transitions, since the values of the absorption coefficient (α) are greater than 10^4 cm^{-1}. As a result of these direct transitions that we obtained, it becomes clear that the change in the momentum value is zero (Δk = 0), meaning that the momentum and energy are preserved for all the prepared films **[13].**



Fig(3): Relationship between absorption coefficient and wavelength

3. Refractive index (n):

Refractive index is calculated from the following equation **(13) or [17]: -**

$$n = \frac{1+R}{1-R} + \sqrt{\frac{4R}{(1-R)^2} - K^2} \dots\dots\dots [2]$$

Where: R is Reflexivity and K is Extinction coefficient.

Figure (4) shows the relationship between the refractive index and the wavelength, as its value is equal to the correct one for the thin films of 5% PMMA and as its value is equal to 1.5 when the thin films of PMMA:PVDF with 5% PVDF, and this indicates the transparency of the material used.

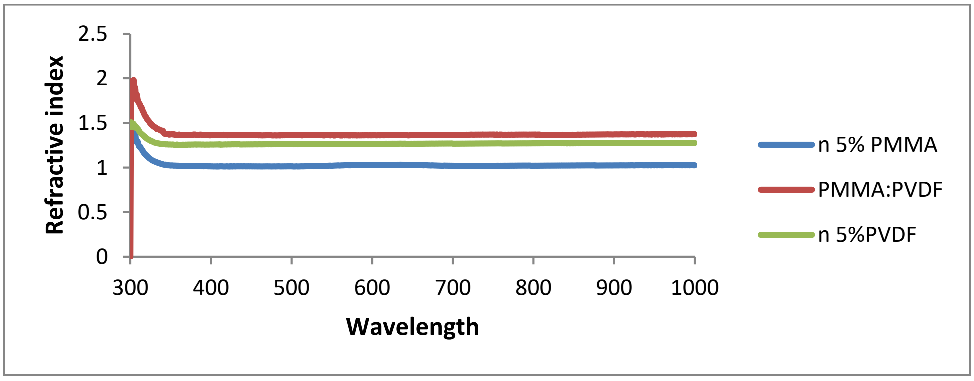


Figure (4): Relationship between the refractive index and the wavelength

4. Extinction coefficient (K):

The extinction coefficient is a measure of the portion of the lost light due to the dispersion and absorption of the distance unit from the penetration of the medium and can be estimated from the values of the absorption coefficient and wavelength λ using the following relationship (13):-

$$K = \frac{\alpha \lambda}{4\pi} \ldots \ldots \ldots [3]$$

Figure (5) shows the relationship between the Extinction coefficient and the wavelength, We observed that the effect of homogenous configuration of the blend thin film to increase the extinction coefficient the with the increase of wavelength, which achieved by the improvement of absorption where high absorption of the thin film occurs in the high values at UV local of extinction coefficient. Also, the increase in extinction coefficient with wavelength at visible and close IR region cause of the increase in absorption coefficient at visible and near infrared area, as in equation [3].

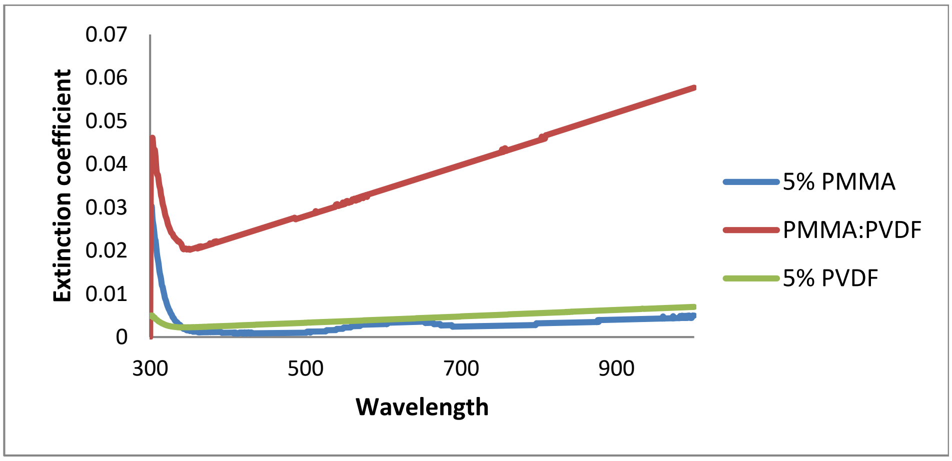


Fig (5): Relationship between Extinction coefficient and the wavelength

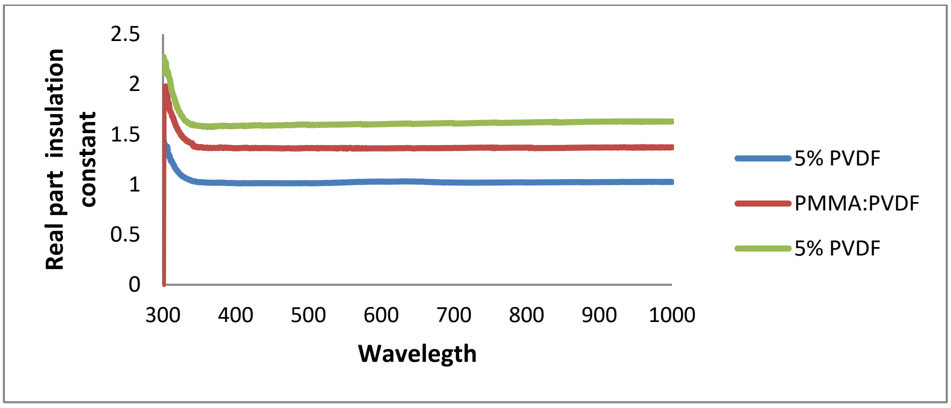
5. Dielectric Constant.

A real part of the dielectric represents the amount of deceleration of the speed of light in the medium, while the fictional part represents how the dielectric (medium) absorbs energy from the electric field by the influence of the motion of the polar diodes **(13) . or [17]**

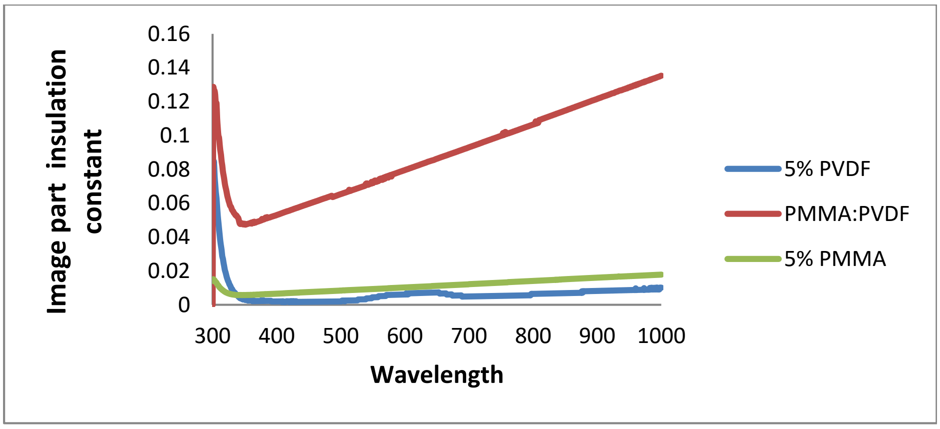
$$\epsilon_r = n^2 - K^2 \ldots \ldots [4]$$

$$\epsilon_i = 2nk \ldots \ldots [5]$$

Figure (6) shows the relationship between real part insulation constant and wavelength, it shows that the real dielectric curves remain stable within (320-1000) nm wavelengths, similar to the optical absorbance behavior, While the imaginary dielectric constant curves are similar to the damping coefficient curves, i.e. the highest level of energy absorbed by a dipole effect, they are at PMMA:PVDF blend shown in Fig (7).



Fig(6): Relationship between the real part of dielectric constant and the wavelength



Fig(7) : Relationship between the image part of dielectric constant and the wavelength

6. Optical Energy Gap (Eg)

Determine the energy gap for the prepared membranes and for the transitions to be direct, the equation was used to calculate the energy gap **(10)** is:-

$$\alpha hv = B(hv - E_g)^2 \ldots \ldots .. [6]$$

Fig(8):If the relationship is drawn between $(\alpha hv)^2$ against the energy of the photons (hv), then a straight line is drawn along the region where a rapid increase in the amount of $(\alpha hv)^2$, by cutting the amount of photons energy and the intersection point represents the energy gap value. Table (1) shows the optical energy gap for the prepared thin films.

Table (1) shows the optical energy gap for the prepared thin films.

Sample	Eg(eV)
5% PMMA (Tluene)	4
PMMA:PVDF	3.8
5% PVDF (Tluene)	4.1

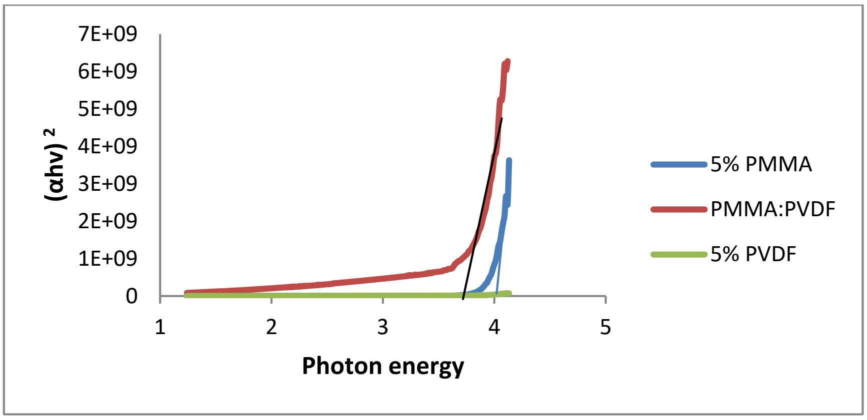


Fig (8): Relationship between $(\alpha hv)^2$ and photon energy

Conclusion:

The results of the absorption edge values for thin films of PMMA are few, while the absorbency of PVDF thin films are 0.3 (a.u), that make the optical absorption edge increases to 0.2 (a.u) for the blend films PMMA:PVDF, due to the effect of adding of PVDF to PMMA decreasing the transmittance and increasing absorbance of the blend thin film, while the results of the absorbance illustrated that the type of electronic transitions that they are direct transitions, since the values of the absorption coefficient (α) are greater than 10^4 cm^{-1}, these are the direct transitions that we obtained. It becomes clear that the change in the momentum value is zero ($\Delta k = 0$), meaning that the momentum and energy are preserved for all the prepared films.

It is observed that the blend of PVDF with PMMA can make the refractive index become higher with short wavelength and the change was clear at shorter wavelengths demonstrating the regular state of a scattering curve. It should be fixed that the estimations of the refractive index of blend repose in the middle of homopolymers. Additionally, the refractive index of the specimen improved the blend thin file increased.

The high significant magnitudes of the refractive index might be due to an increase in the intensity of valence charge carriers.

We observed that the effect of homogenous configuration of the blend thin film to increase the extinction coefficient with the increase of wavelength, which is achieved by the improvement of absorption where high absorption of the thin film occurs in the high values at UV local of extinction coefficient. Also, the increasing in extinction coefficient with wavelength at visible and close IR region causes the increase in absorption coefficient at visible and near infrared area.

The real dielectric curves remain stable within (320-1000) nm wavelengths, similar to the optical absorbance behavior, While the imaginary dielectric constant curves are similar to the damping coefficient curves, however the highest level of energy absorbed by a dipole effect for PMMA:PVDF blend. The energy gap values are determined for the prepared membranes (4, 4.1, 3.8) eV for PMMA, PVDF and PMMA:PVDF blend respectively, and the transitions are found to be direct.

References:

1. Aid,S. Anissa E, Sofiane Khelladi, Zaida Ortega, Sana Chaabani, (2019),On the miscibility of PVDF/PMMA polymer blends: Thermodynamics, experimental and numerical investigations, Polymer Testing, (73), 222-231.
2. AMUDHA, S. Austin S. J. MARUTHAMUTHU, P. (2013) A Novel Solid State Dye-Sensitized Solar Cell Containing PMMA/PVDF- Type Blended Polymer Electrolyte, Chem Sci Trans, 2(3), 955-963.

3. Benhabiles ,O , Francesco G, Tiziana M,, Hacene M, Hakim L, and Albert of(2019),Preparation and Characterization of TiO2-PVDF/PMMA Blend Membranes Using an Alternative Non-Toxic Solvent for UF/MF and Photocatalytic Application, Molecules, 24, 724; doi:10.3390/molecules24040724.
4. Choi ,S. W. Kim,J. R. Ahn,Y. R. Seong, Mu Jo, and Cairns, E. J. (2007) .High ionic conductive PVDF-based fibrous electrolytes, J Solid State ElectrocheS ,DOI 10.1007/s10008-008-0540-4, Stephan AM, Nahm K S Polymer 47:5952.
5. Danno ,T. Matsumoto, H. Nasir, Minagawa ,M. Horibe,H. Tanioka Tanioka,A. (2009). Tanioka, PVDF/PMMA Composite Nanofiber Fabricated by Electrospray Deposition: Crystallization of PVDF Induced by Solvent Extraction of PMMA Component, Journal of Applied Polymer Science, Vol. 112, 1868–1872 .
6. Huiliang, Z. Jianbin, S. Jianxun, L.Wenbin, Y.Lihong Chen,1 Yumei Zhong,1 Changcheng Ma1(2014,), PVDF/PMMA/Basalt Fiber Composites: Morphology, Melting and Crystallization, Structure, Mechanical Properties,and Heat Resistance, J. APPL. POLYM. SCI. DOI: 10.1002/APP.40494.
7. Kang JJ ,Wang XJ, Zhang HP, (2006) J Solid State Electrochem.
8. Kaneko M, Nakayama M, Wakihara M (2007) J Solid State Electrochem 11:1071.
9. Maya, Sh. Sharma ,Ke. and Suryasarathi Bo. (2013), Segmental Relaxations and Crystallization-Induced Phase Separation in PVDF/PMMA Blends in the Presence of Surface-Functionalized Multiwall Carbon Nanotubes, J. Phys. Chem. B117, 8589−8602.
10. Mahant, Y.P. Kondawar,S.B. Bhute, M. and Nandanwar, D.V. (2015), Electrospun poly (vinylidene fluoride)/poly (methyl methacrylate) composite nanofibers polymer electrolyte for batteries, Procedia Materials Science, 10, 595 – 602.
11. Ochoa, N.A, Masuelli, M. Marchese, J. (2003), Effect of hydrophilicity on fouling of an emulsified oil, wastewater with PVDF/PMMA membranes, Journal of Membrane Science 226 203–211.
12. Piao ,J.W.D , ,Yuan L.X. Cao Y.L (2005) J Solid State Electrochem, 9:183.
13. Singh, J. (2006)." Optical Properties of Condensed Matter and Applications". John Wiley and Sons, Ltd. ISBN: 0-470-02192-6.
14. Sultanova, N. Kasarova ,S. and Nikolov, I. (2016). Advanced Applications of Optical Polymers, Bulg. J. Phys. 43, 243–250.
15. Shan ,D. Gerhard ,E. Zhang, C, J. Tierney, W, D. Xie, Z. Liu and J. Yang, (2018), Polymeric biomaterials for biophotonic applications, Bioactive Materials 3, 434–445,
16. Shan, F. , Yang ,J. Zhiming Li ,Jiangong W. , ,Xinling W. (2008),. PVDF/PMMA brushes membrane for lithium-ion rechargeable batteries prepared via preirradiation grafting technique, Journal of Polymer Science: Part B: Polymer Physics, Vol. 46, 751–758.
17. Tamemy, F. H., (2016) Study of the optical and electrical properties of poly(3-Hioxy Thiophene ,2-5 dily) (P3HT) and the effect of Orange G on the properties and its application in fabrication of its.
18. Youssef ,A. EL-Nagar, I. El-Torky, A. and Abd El-Hakim, A. , (2019). Preparation and Characterization of PMMA Nanocomposites Based on ZnO-NPs for Antibacterial Packaging Applications, Proceedings of the 5th world nongress on new technologies, Lisbon, Paper No. ICNFA 105, 18-20.

دراسة الخواص البصرية للخليط (PMMA:PVDF)

ناظم عبد الجليل عبدالله وفاطمة حميد مالك*
قسم علوم المواد، مركز أبحاث البوليمر، جامعة البصرة، العراق
DOI: https://doi.org/10.47372/uajnas.2021.n1.a16

الملخص

تم في هذه الدراسة تصنيع أغشية رقيقة من البوليمرين بولي ميثايل ميثاكريلات (PMMA) وبولي فلوريد البوليفينيليدين (PMMA-PVDF) والمذابة بنسبة (5٪) في التولوين، وخلطت بنسبة حجمية 1:1 من البوليمرين. تم تحضير الأغشية بطريقة الطلاء البرمي، وبنسب مختلفة من البوليمرات، وتم قياس المعاملات البصرية للأغشية الرقيقة ضمن نطاق (300-900) نانومتر وسمك من الأفلام ثابت 223 نانومتر، تمت دراسة الامتصاص (A)، معامل الامتصاص الخطي (α)، معامل الانكسار (n)، معامل الانقراض (K)، ثابت العزل الحقيقي والخيالي (ϵ_r، ϵ_i)، وفجوة الطاقة الضوئية، حيث كانت أفضل حافة للامتصاص البصري هي 5٪ PVDF، والانتقال الإلكتروني بين مستويات الطاقة انتقالاً مباشر.

الكلمات المفتاحية:- ميثيل ميثاكريلات، فلوريد البوليفينيليدين، الطلاء البرمي، المعاملات البصرية.