Published Online First: May, 2024
https://doi.org/10.21123/bsj.2024.7953
P-ISSN: 2078-8665 - E-ISSN: 2411-7986
Baghdad Science Journal

Preparation and Study of the Optical Properties of Recycled Materials of Polymethyl methacryalate Doped with Different Ratios of 4-(2- Pyridylazo) Resorcinol Monosodium Salt Hydrate

Zainab J. Sweah[1], ***Fatima H. Malk****[2], ***Muhsen Chelab Muhsen***[1], ***Baheya abdulbaqi***[2]

[1]Chemistry and Polymer Technology, Polymer Research Center, University of Basrah, Basrah, Iraq.
[2]Department of Physics and Material Science, Polymer Research Center, University of Basrah, Basrah, Iraq.

Received 15/10/2022, Revised 18/11/2023, Accepted 20/11/2023, Published Online First 20/05/2024

Abstract

This paper presents an incoming method of developing a novel optical sensor using polymethylmethacrylate was reused with the presence of the ethanol-derived resin from Frankincense (1:1) (wt:wt%-(2-Pyridylazo) Resorcinol Monosodium Salt Hydrate) (azo dye) by solution casting technique. The prepared samples were Scanning Electron Microscopes(SEM),and studied by UV-VIS spectrophotometer for wavelengths 400-800nm, the absorbance increased; however, when it exceeded 7%, the absorbance value decreased, and the behavior was identical to that of the transmittance. The absorption coefficient and Extinction coefficient and optical energy gap at 5% is the best value. were also computed. Based on the results obtained the study was reached about the possibility of using the prepared films to develop optical fiber sensors from recycled polymethylmethacrylate, with good specifications that are considered a good treatment of trash in the environment.

Keywords: Absorption, Azo dye, Salt, Sensors, optical properties, Waste polymethylmethacrylate.

Introduction

Polymer blends enable the development of new polymeric materials with tailored technological properties[1-4] .Conduction factors can help you achieve effective optimization. Interface active compounds based on macromolecules that can combine important polymeric material groups such as amorphous thermoplastics, crystalline thermoplastics, and elastomers are suitable coupling agents. Frankincense, an oleo gum resin derived from the trees of the Burseraceae family's genus Boswellia Roxb. ex Colebr, is widely used in traditional Arab, African, Ayurvedic, and Chinese medicines to treat a wide range of ailments including fever, pain, and swelling. Identifying biologically active compounds in Boswellia oleo gum resins would allow for more rational drug discovery. Frankincense trees are primarily found in the dry regions of East Africa, the Arabian Peninsula, and the Middle East[5].It uses waste poly (methyl methacrylate), PMMA, which is a brittle thermoplastic. The waste of Polymethyl Methacrylate and some other plastics has recently been reused to get rid of the pollution that occurs because of it, as the disposal of these materials requires a very long time, and by working on the reuse of these materials, there are serious ways to get rid of pollutants and contribute to preserving the environment. Polymethyl Methacrylate is one of the important polymers, which is used in various fields, whether it is a pure or reused polymer[6]. A (PMMA)-Polystyrene (PS) doped with nanoparticles was used for modern applications[7]. The potential of using it as a new filling material for bladder implantable medical devices was studied [8], as well as the linear and nonlinear photo response of the nickel-silica/PMMA core film for flexible optoelectronic applications [9]. A tunable solid-state laser based on PMMA doped with pyromethane dyes was also used [10]. Recycled Polymethyl Methacrylate (PMMA) was used to produce the optical fibre sensor systems[11]. To improve its optical properties, we used frankincense components dissolved in alcohol as additives to waste PMMA with organic azo dye (4-(2-Pyridylazo) Resorcinol Monosodium Salt Hydrate). Fig. 1, showed the chemical structure of the composition of the polymer blends prepared. This work aims to investigate the effect of (4-(2 Pyridylazo) Resorcinol Monosodium Salt Hydrate) dye and resins of Frankincense on the structural, and optical properties, of the waste PMMA.

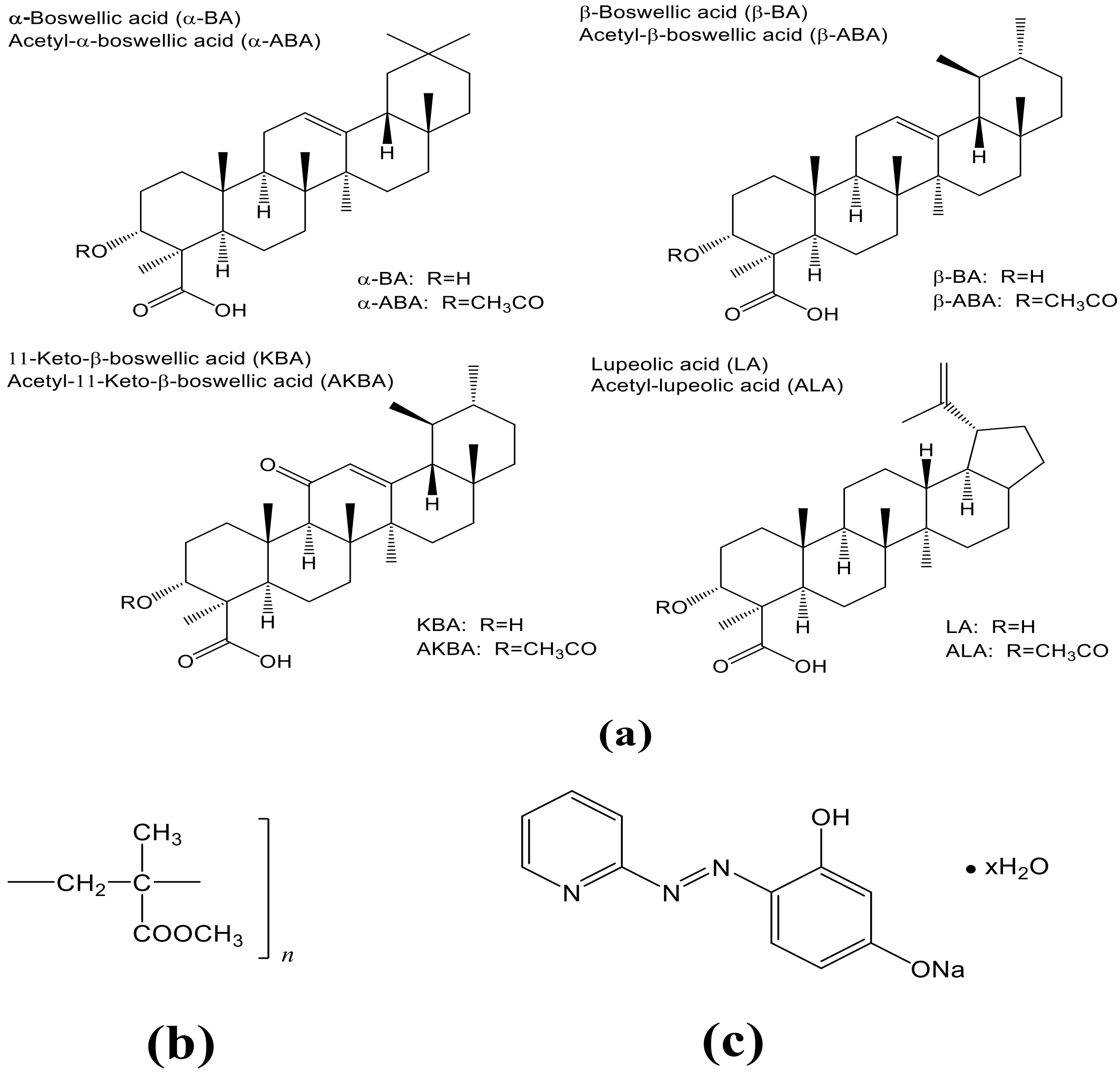


Figure 1. Chemical structure of the composition of a-Frankincense, b- polymethyl methacrylate, and c- 4-(2- Pyridylazo) Resorcinol Monosodium Salt Hydrate.

Materials and Methods

Frankincense (Oligoum resin from Boswellia Birdwood, Burseraceae was purchased from the local market for herbs and spices in Basrah/Iraq, waste of polymethylmethacrylate was collected from the used Residential and commercial aquariums which were collected and crashed and Sieved with (2.2) micrometer particle size, ethanol 97% was used as an extracted solvent and tetrahydrofuran was purchased from Merck company.

Extraction Procedure

The process of extracting the viscous resin containing Pentacyclic Triterpenic Acids (PTA) was carried out with absolute ethanol solution for frankincense (Oligoum), and the process of extracting was carried out at room temperature[12,13] three times to obtain the highest yield of final extracted materials.

Preparation of Samples

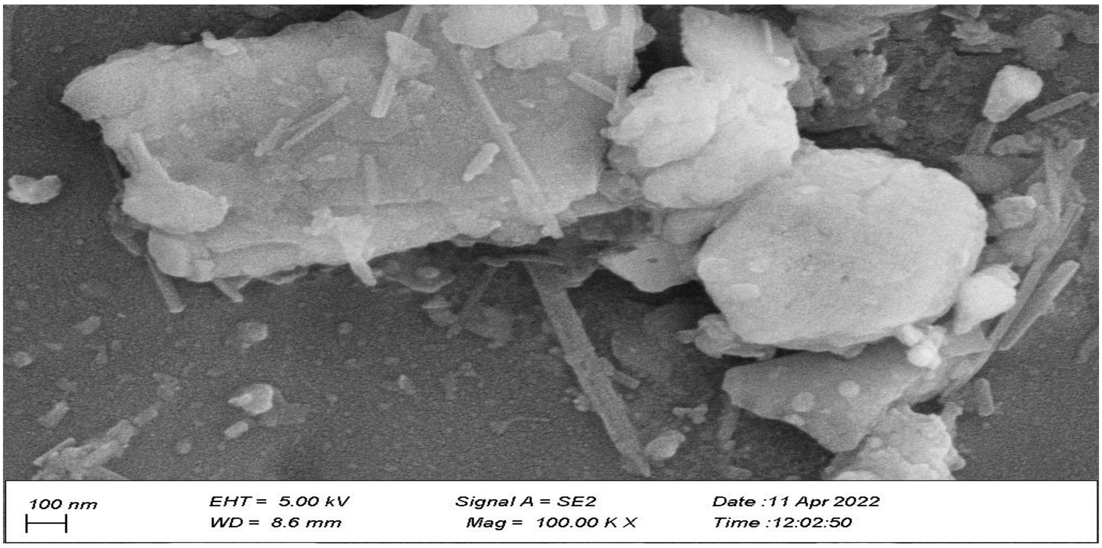
A set of embodiments was prepared from the reaction of 1% of completely dissolved polymethylmethacrylate waste in THF with 1% of frankincense extract dissolved in the same solvent, with different proportions of azo dye (0%, 1%, 3%, 5%,7% ,and 9%) were dissolved in tetrahydrofuran using a magnetic stirrer to prepare samples from (A . B. C. D. E and F), then the solution was poured into glass film with dimensions 2cmx 2cm by casting method. Table 1, showed the composition of the prepared samples. The absorption and transmittance spectra of wavelengths 400-900nm were recorded using a UV-Vis dual-beam spectrophotometer. The morphology of the polymer with and without dye was studied using a Philips ZEISS Scanning Electronic Microscope. The average diameter of the nanofibers was measured by the measurement software.

Table 1. showed the composition of the prepared samples.

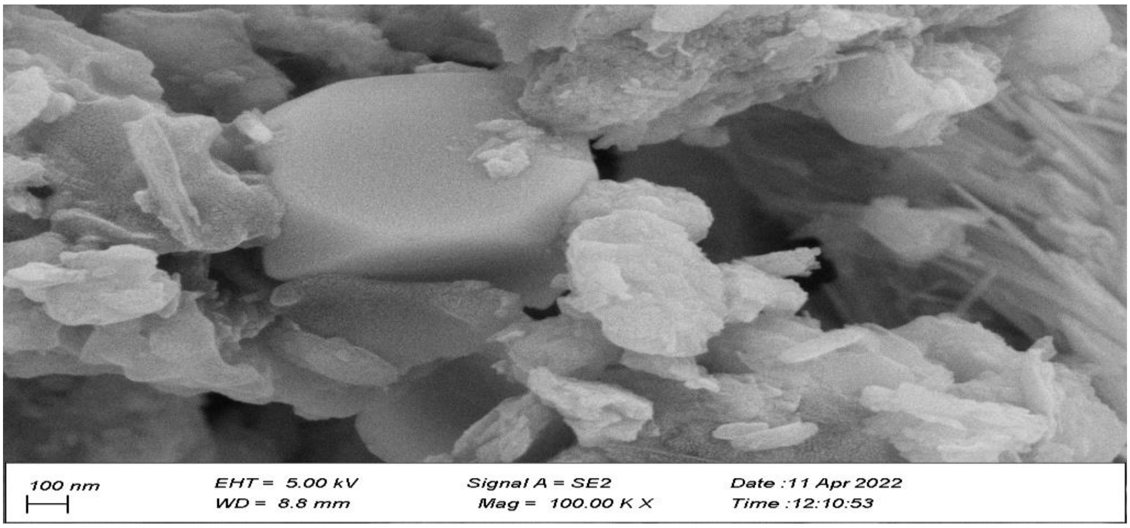
Symbol	Azo dye
A	0%
B	1%
C	3%
D	5%
E	7%
F	9%

Results and discussion

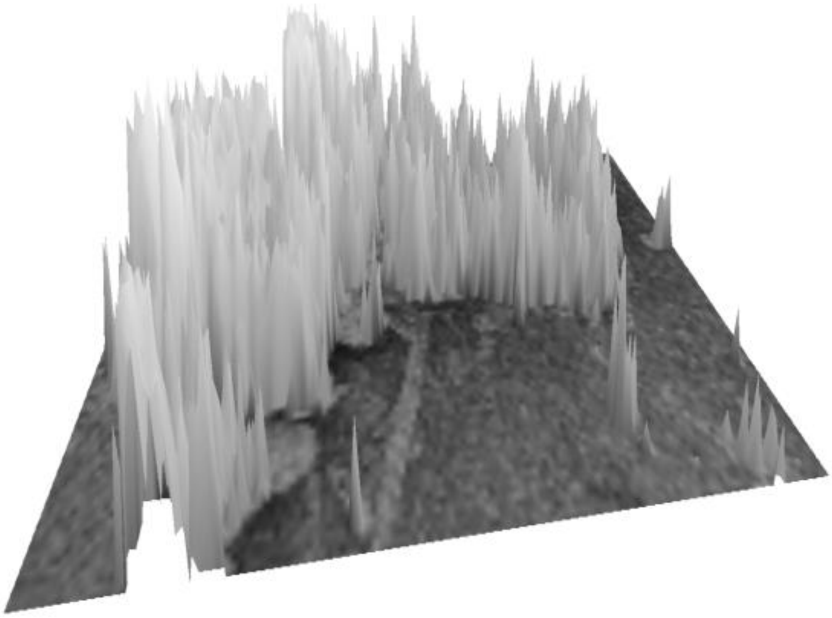
SEM micrographs Fig. 2, revealed that the dye had influenced the microstructure of the polymers, Where we noticed the change in the distribution of grains too wide distribution when adding dye to the samples (A and D) with and without the dye when the magnification was 100.00KX. SEM images clearly show the surface morphology of the PMMA with organic Dye. This morphology confirms the complete amorphous nature of PMMA polymer and complete doping of the dye. The images show the profile of the SEM image of a sample and that the gray value distribution with distance is all that is required is two SEM images showing the same area on a sample. The main difference between the two images is the degree of inclination of the sample between the sample surface normal and the electron beam.



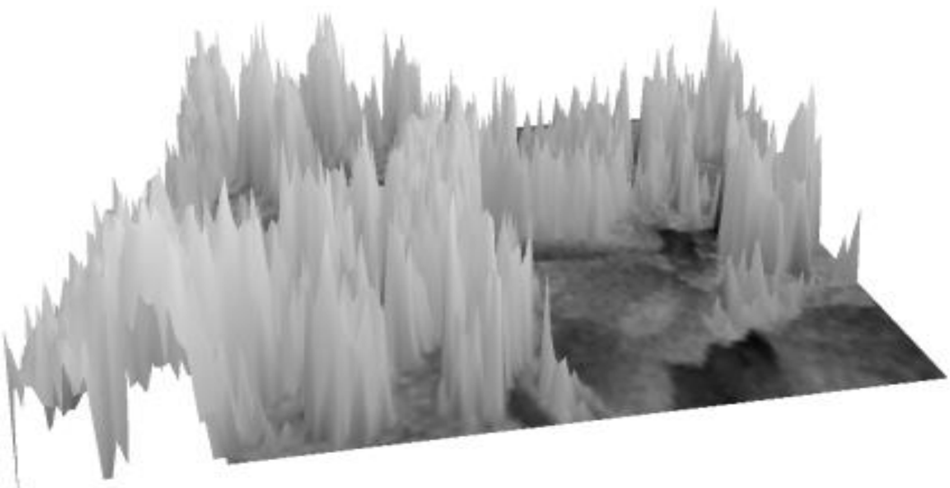
a_1-SEM image of A sample



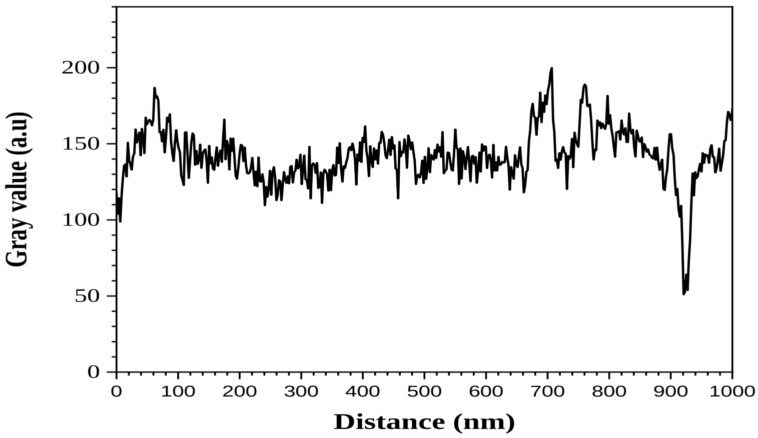
b_1-SEM image of D sample



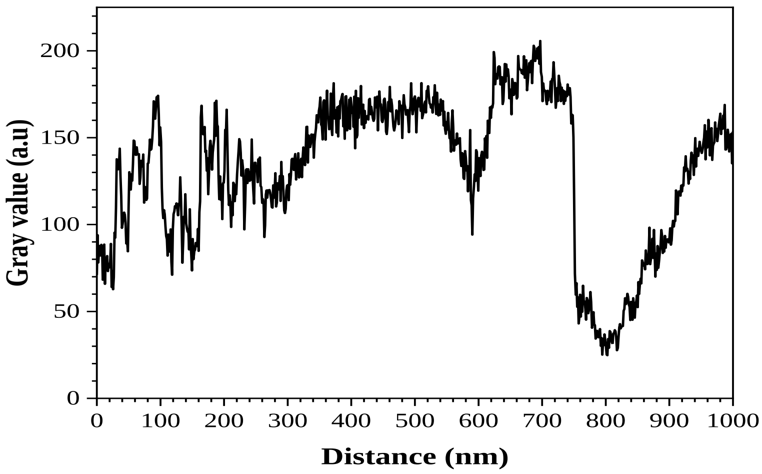
a_2-the surface profile of A.



b_2- the surface profile of D.



a_3- the distribution of gray value with the distance of A.



b_3- the distribution of gray value with the distance of D.

Figure 2. Topography of surface morphology and surface profile A and D can use image features from scanning electron microscope images.

Optical Properties

The measurements of the absorption of the prepared thin films were made under laboratory conditions at a temperature of 25°C and using a spectrophotometer for wavelengths (400-900nm), and its specificity in obtaining fairly similar thicknesses. For different models in the doping ratios of the films by re-deposition more than once and reaching the desired thickness more closely[14]. Fig. 3, indicate, wavelength-dependent absorbance values it appears that the absorbance curves operate within the wavelengths from 400-800 nm and the absorbance begins to increase with the increase in the concentration of the azo dye. the samples have the broadest absorbance range and a broad absorption peak within 400-680 nm for samples A, and C. The absorbance of samples E and F can be explained by saturation. The transmittance measurements were taken for all of the prepared thin films under the same absorbance measurement conditions (room temperature $25C^0$ and within the wavelength range 400-900nm), and it appears from Fig. 4. that the transmittance spectrum of the doped and undoped films reaches 90% percent transmittance. The shape of the transmittance curve is the expected behavior for it, as the transmittance is the opposite of the absorbance.

Published Online First: May, 2024
https://doi.org/10.21123/bsj.2024.7953
P-ISSN: 2078-8665 - E-ISSN: 2411-7986
Baghdad Science Journal

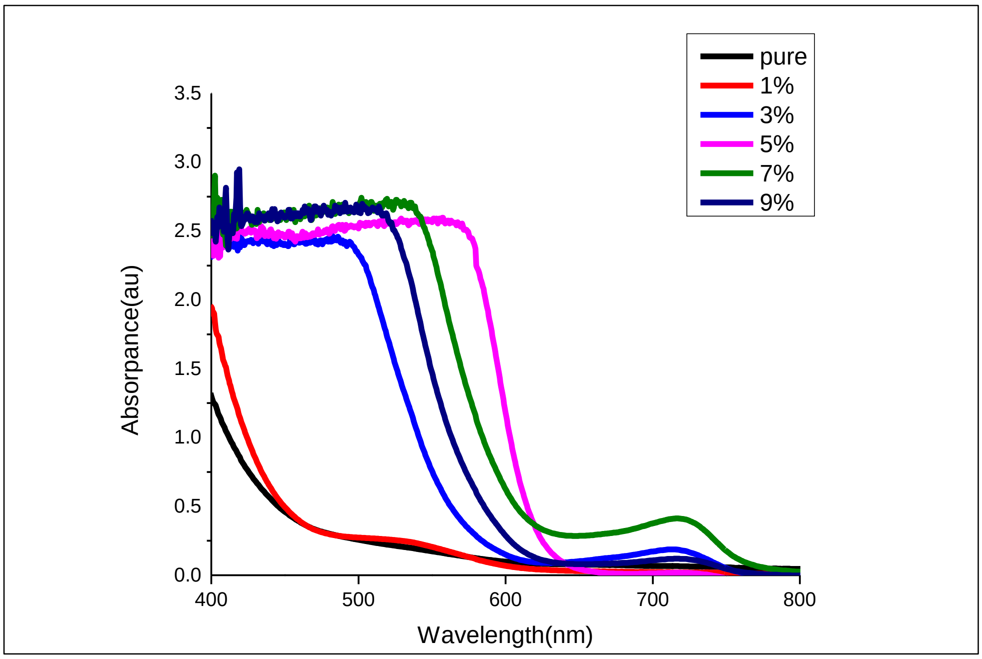


Figure 3. Wavelength-dependent absorbance values of pure and doping by dye (1%, 3%, 5%, 7%, 9%).

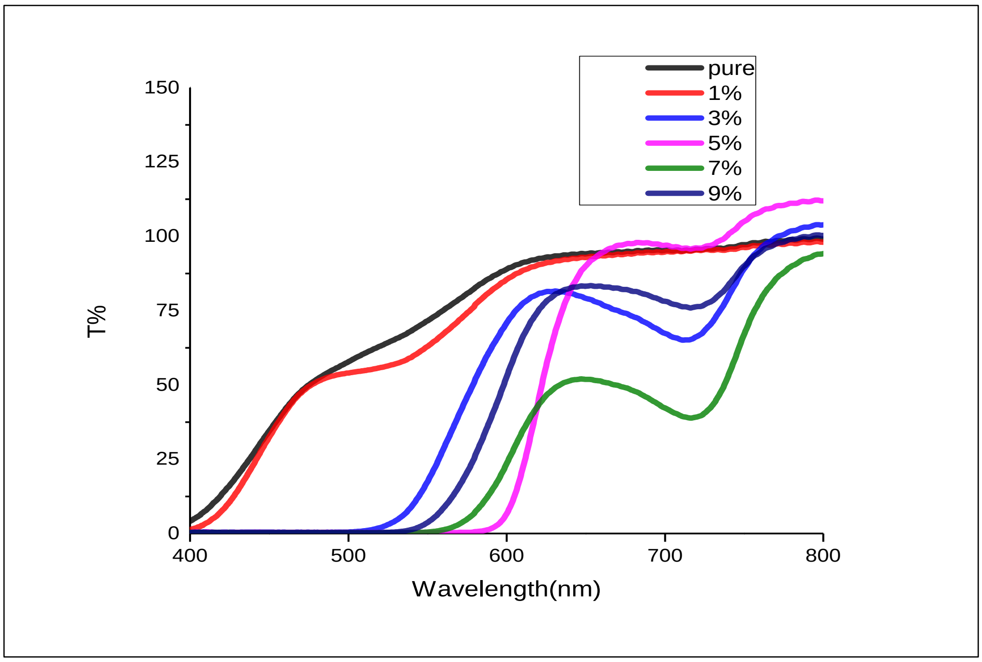


Figure 4. Wavelength-dependent Transmittance pure and doping by dye (1%, 3%,5%,7%,9%)

Optical constants

Absorption coefficient (α)

The absorption coefficient describes the attenuation of light intensity as it passes through a substance. It is defined as the sum of a substance's absorption cross-sections per unit volume during an optical process[15,16]. The higher the value, the shorter the length of light that can enter a substance before being absorbed. Light absorption by the dye. According to the results we obtained and displayed in Fig. 5, the type of electronic transitions is direct transitions because the values of the absorption coefficient (α) are greater than 10^4 cm^{-1}. As a result, in the absorption band, the absorption coefficient becomes extremely critical. Determine the type of electronic transfer that occurs in the electronic

Published Online First: May, 2024
https://doi.org/10.21123/bsj.2024.7953
P-ISSN: 2078-8665 - E-ISSN: 2411-7986
Baghdad Science Journal

structure of the material. For this purpose, the absorption coefficient was calculated as follows [17]:

$$\alpha = \left(\frac{2.303}{d}\right) A \qquad \ldots\ldots..1$$

Where; (α) is the Absorption coefficient,

(d) Thickness of films,

(A), Absorbance

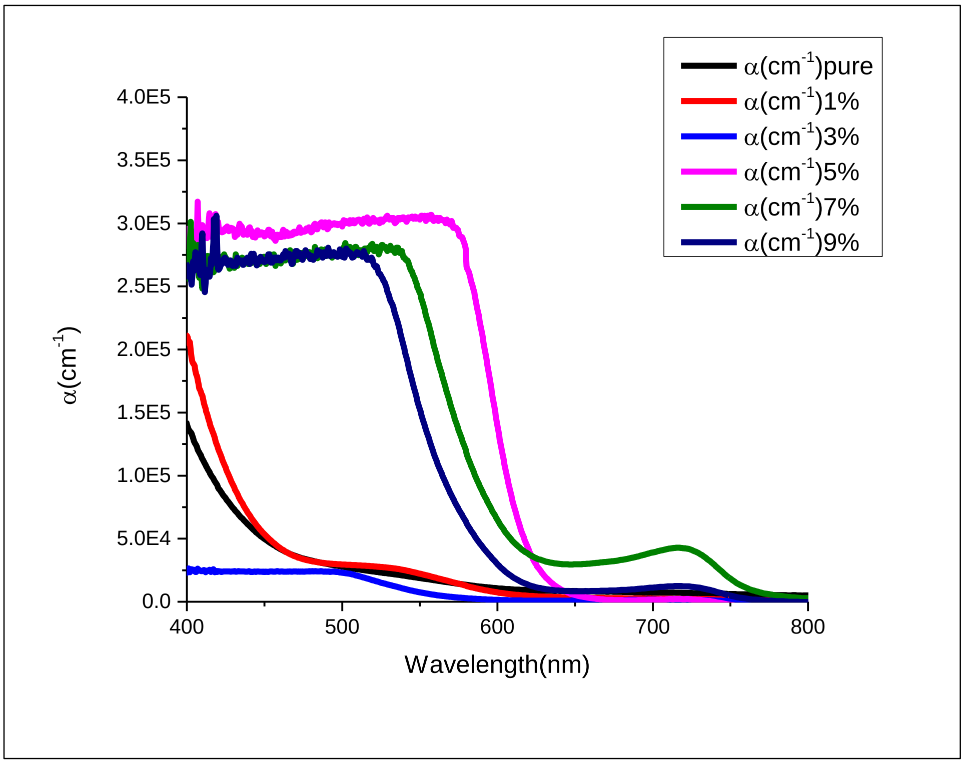


Figure 5. Wavelength-dependent absorption coefficient of pure and doping by dye (1%, 3%, 5%, 7%, 9%)

Extinction coefficient calculation

Beer's Law asserts that for a certain substance dissolved in a specific liquid solution and measured at a given wavelength, molar absorptivity is constant (and absorbance is proportional to concentration)[18]. As a result, molar absorptivity is also referred to as molar absorption coefficients or molar extinction coefficients. Because transmittance and absorbance have Molar absorptivity must cancel with concentration and light path units of measure[19,20]. The extinction coefficient as a function of wavelength is depicted in Fig. 6. It depicts the charge curve for Sample A (Pure) at 0.6, which begins to decrease as the wavelength increases. B(1%) The decay energy has a value between 0.9 and 1and starts to drop with increasing wavelength, Also, the Extinction coefficient in Samples (A and D) is less than one, whereas the driving energy in Samples(E (7%)and F (9%) is greater than one, and this behaviour is identical to the absorbance behaviour Fig. 7,The losses in the produced electromagnetic wave are caused by photon absorption and the occurrence of the process of electron transfer between the - double bond, Which, Extinction Coefficient K is, a measure of the fraction of light lost due to dispersion and absorption of the unit of distance from the center's penetration, and it can be estimated from the values of and using the following relationship by [21].

$$K = \frac{\alpha \lambda}{4\pi} \qquad \ldots.2$$

Published Online First: May, 2024
https://doi.org/10.21123/bsj.2024.7953
P-ISSN: 2078-8665 - E-ISSN: 2411-7986

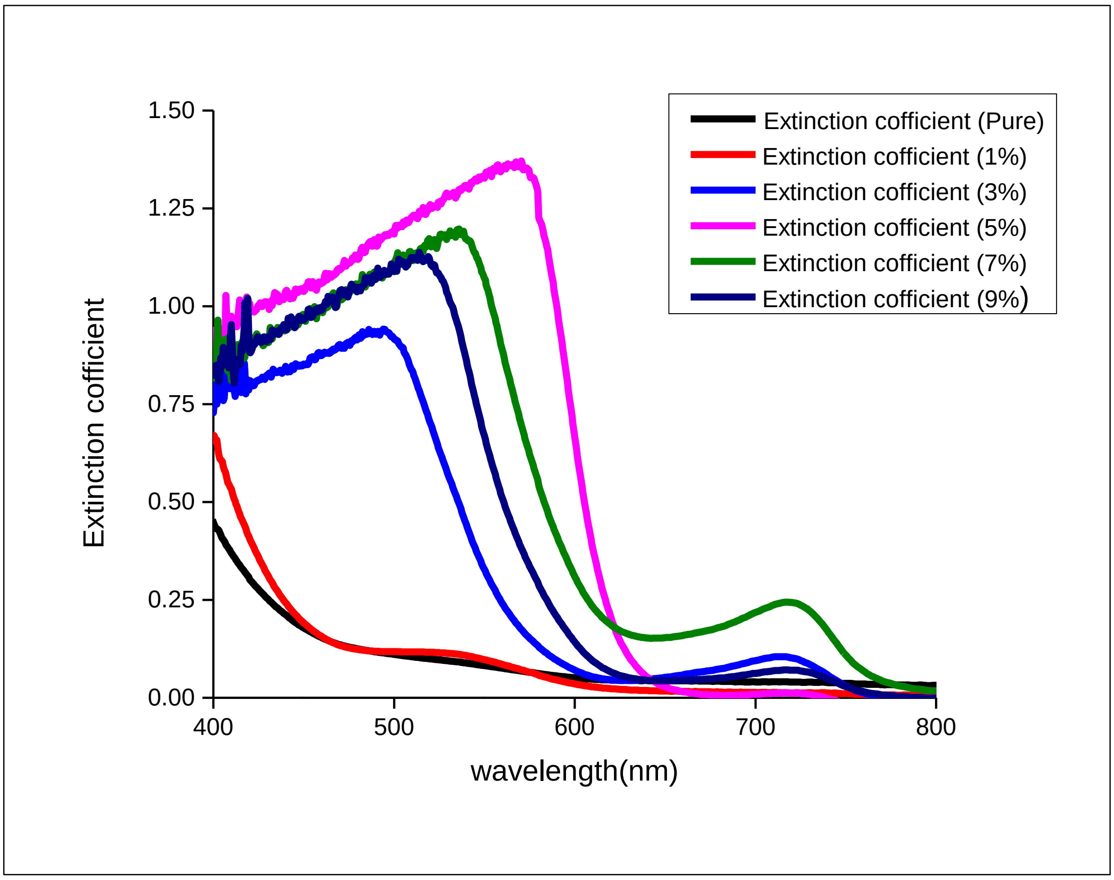


Figure 6. Wavelength-dependent Extinction coefficient of pure and doping by dye (1%, 3%, 5%,7%, 9%)

Optical Energy Gap

Eq. 3 was used to calculate the energy gap for the prepared films and direct transitions. The relationship between $(\alpha h\nu)^2$ was drawn against the energy of photons $(h\nu)$, and then a straight line was drawn along the region in which a rapid increase in the amount of $h\nu^2$occurs, so that it cuts the energy of the photons, and the point of intersection represents the value of the energy gap[22] .

$$\alpha = \frac{(h\nu - E)^r}{h\nu} \ldots \ldots \ldots 3$$

r, denotes the density distribution of the state index, which varies depending on the point of transition: direct (1/2 and 3/2 for allowed and forbidden, respectively) or indirect (2 and 3 for permitted and prohibited) [23]. Figs. 7 and 8 depict this, as well, Table 2 the energy gap's values.

Table 2. The energy gap's values.

Symbol	Eg (eV)
A	2.78
B	2.70
C	2.30
D	2.05
E	2.13
F	2.20

Published Online First: May, 2024
https://doi.org/10.21123/bsj.2024.7953
P-ISSN: 2078-8665 - E-ISSN: 2411-7986

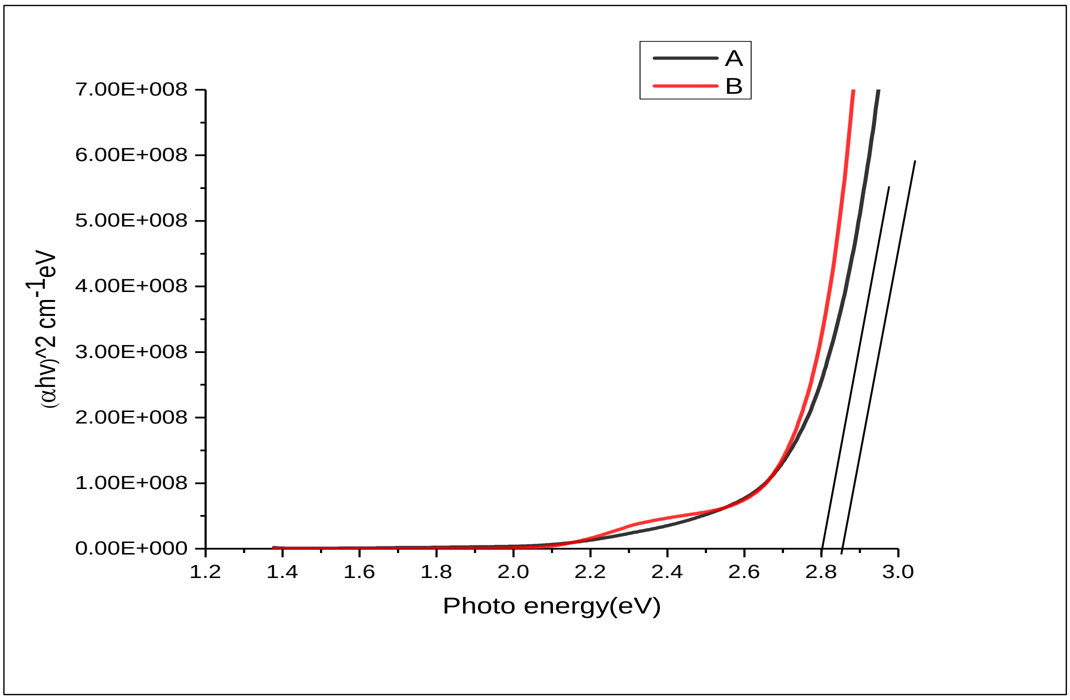


Figure7. Energy band gap of pure and doping by dye (1%)

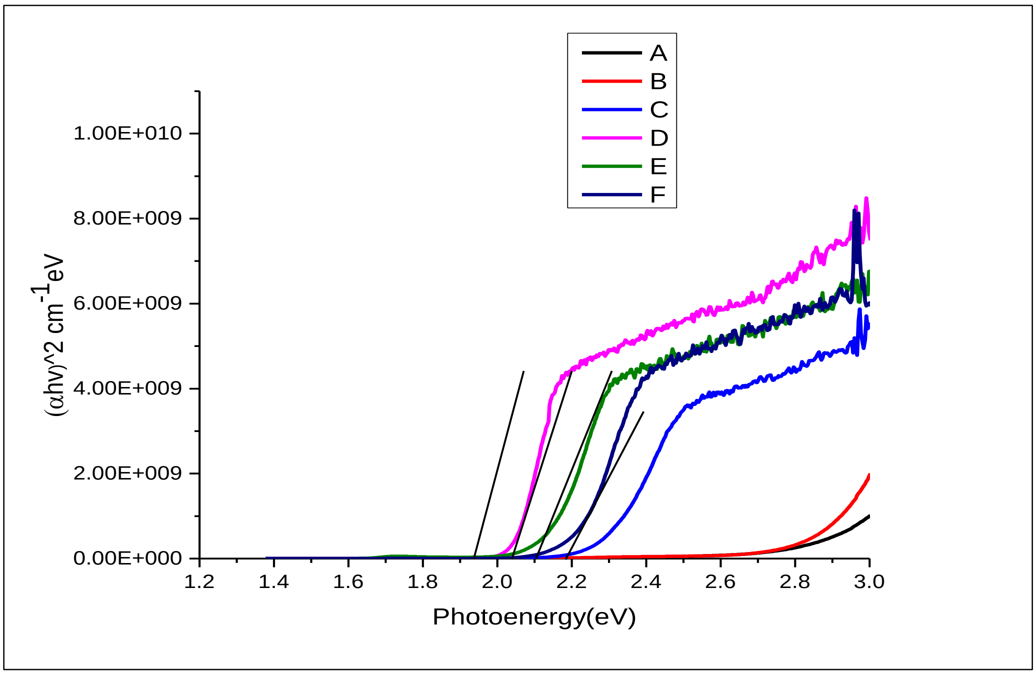


Figure 8. Energy band gap of pure and doping by dye (1%, 3%,5%,7%,9%)

Conclusion

This study makes it possible to use PMMA waste as an optical fiber composite with the alcoholic extract of Frankincense and different percent of azo dye. The prepared samples can be good candidates for preparing optical fiber sensors. and, Through this research, we were able to convert polymethyl methacrylate waste from an insulating material and not useful but harmful to the environment to a semiconductor material by doping with some available additives and it is possible to use the resulting material with this characterization as optical sensors, for example, and it could be used in spheroids by particular polymers or as a layer of solar cells. It has the potential to enhance the environment.

Author's Declaration

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are ours. Furthermore, any Figures and images, that are not ours, have been included with the necessary permission for re-publication, which is attached to the manuscript.
- No animal studies are present in the manuscript.
- No human studies are present in the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee at University of Basrah.

Author's Contribution

This work was carried out in cooperation with all researchers, collecting and weighing samples and preparing solutions. The work of B. A., diagnosing the samples prepared by M. G., writing, editing and analyzing data for research, was Z. J.S. and F. H. The researchers read and agreed on the final reference.

References

1. Hassan T Jaafar, Balqees M D Aldabbagh and Hanaa J Kadhim. Investigation of Super hydrophobic/Hydrophobic Materials Properties Using Electro spinning Technique. Baghdad Sci J. 2019 September; 16(3): 632-638. https://doi.org/10.21123/bsj.2019.16.3.0632
2. Helyati Abu H Shaari, Muhammad M Ramli, Mohd N Mohtar, Norizah Abdul R and A Ahmad. Synthesis and Conductivity Studies of Poly(Methyl Methacrylate) (PMMA) by Co-Polymerization and Blending with Polyaniline (PANi). Polym. 2021; 13(12): 1939. https://doi.org/10.3390/polym13121939
3. Zaynab NR. Water Temperature Effect on Hardness and Flexural Strength of (PMMA/TiO_2 NPs) for Dental Applications. Baghdad Sci J. 2022 January ; 19(4): 922-931. https://doi.org/10.21123/bsj.2022.19.4.0922
4. Mohammed M AlShehri , Zeid A ALOthman , Ahmed Y B H Ahmed , Taieb A . New Method Based on Direct Analysis in Real-Time Coupled with Time-of-Flight Mass Spectrometry (DART-ToF-MS) for Investigation of the Miscibility of Polymer Blends. Polym. 2022 Apr; 19; 14(9): 1644. https://doi.org/10.3390/polym14091644
5. Luay Ra , Alan Wh, Manon Ha , Nicolas F , Parag D , Ian E Cock . Chemical Composition, Antibacterial Activity and Antibiotic Potentiation of Boswellia sacra Flueck. Oleoresin Extracts from the Dhofar Region of Oman Evid.-based Complement. Altern. Med. 2021May; 1-23. https://doi.org/10.1155/2021/9918935
6. Mohith S K, Panduranga R . Synthesis and characterization of PMMA functional microspheres. React Funct Polym. 2000 November; 46(1): 29-37. https://doi.org/10.1016/S1381-5148(00)00033-X
7. Ahmed H, Basim A. Recent review on poly-methyl methacrylate (PMMA)-polystyrene (PS) blend doped with nanoparticles for modern applications. Res J Agric Biol Sci. 2019; 14(3): 6-12. https://doi.org/10.22587/rjabs.2019.14.3.2
8. Muhammad SZ. Prosthodontic Applications of Polymethyl Methacrylate (PMMA) an Update. Polym. 2020 Oct; 12(10): 2299. https://doi:10.3390/polym12102299
9. Carmelo C, Giulia N, Antonio S, Enza F . Acrylate and Methacrylate Polymers' Applications: Second Life with Inexpensive and Sustainable Recycling Approaches. Mater. 2022 Jan; 15(1): 282. https://doi.org/10.3390/ma15010282
10. Abomostafa HM , Abulyazied DE. Linear and nonlinear optical response of nickel core-shell @ Silica/PMMA nanocomposite film for flexible optoelectronic applications. J Inorg Organomet Polym. 2021 January ;31: 2902–2914. https://doi.org/10.1007/s10904-021-01883-9
11. Pen Y Ang , Marko C , Frederike L , Christian H , Dinara , Sebastian R, et al.. Organic Dye-Doped PMMA Lasing. Polym. 2021 October; 13: 3566. https://doi.org/10.3390/polym13203566
12. Prado AR, Leal-Junior AG, Marques C, Leite S, de Sena GL, Machado LC, et al. Polymethyl methacrylate (PMMA) recycling for the production of optical fiber sensor systems. Opt Express. 2017 Nov 27; 25(24): 30051-30060. https://doi.org/10.1364/OE.25.030051
13. Schmiech M, Lang SJ, Werner K, Rashan LJ, Syrovets T, Simmet T. Comparative Analysis of Pentacyclic Triterpenic Acid Compositions in

Oleogum Resins of Different *Boswellia* Species and Their In Vitro Cytotoxicity against Treatment-Resistant Human Breast Cancer Cells. Molecules. 2019 Jun 7; 24(11): 2153. https://doi.org/10.3390/molecules24112153

14. Al-Harrasi A, Rehman NU, Khan AL, Al-Broumi M, Al-Amri I, Hussain J, et al. Chemical, molecular and structural studies of Boswellia species: β-Boswellic Aldehyde and 3-epi-11β-Dihydroxy BA as precursors in biosynthesis of boswellic acids. PLoS One. 2018 Jun; 13(6): e0198666. https://doi.org/10.1371/journal.pone.0198666
15. Veenavee N K , Assa A S Devi , Johannes N , Matti A , Bernardo B , Tao H N, et al. First Principles Calculations of the Optical Response of $LiNiO_2$. Condens. Matter. 2022 September ; 7: 54. https://doi.org/10.3390/condmat7040054
16. Valentino P, Osman B , Jincan Z, Sachin M S , Adil M , Andrea C Ferrari, et.al. Mapping the complex refractive index of single layer graphene on semiconductor or polymeric substrates at terahertz frequencies. 2D Mater. 2022 March; 9: 025018 https://doi.org/10.1088/2053-1583/ac57c9
17. Singh N, Madhav H, Yadav S, Jaiswar G. Impact of vanadium-sulfur-and dysprosium-doped zinc oxide nanoparticles on various properties of PVDF/functionalized-PMMA blend nanocomposites: Structural, optical, and morphological studies. J Appl Polym .2019 March ; 136(9): 47116. https://doi.org/10.1002/app.47116
18. S. B. Aziz, Omed Gh. Abdullah, M. Brza, A. K. Azawy, D. Tahir.Effect of carbon nano-dots (CNDs) on structural and optical properties of PMMA polymer composite. Results Phys . 2019 October; 15: :102776. https://doi.org/10.1016/j.rinp.2019.102776
19. Nadhim AA, Fatima HM. Optical Properties of Blend of PMMA: PVDF. Univ. Aden J Nat Appl Sc. 2021 April; 25(1): 189-196. https://doi.org/10.47372/uajnas.2021.n1.a16
20. Zainab JS, Fatima HM, Waleed AH. Determination of the optical parameter from chitosan doping with nicotine. AIP Conf Proc. 2020 MARCH; 2213: 020065. https://doi.org/10.1063/5.0000090
21. Patrycja M, Michał P, Wojciech M. How to Correctly Determine the Band Gap Energy of Modified Semiconductor Photocatalysts Based on UV–Vis Spectrum. J Phys Chem Lett. 2018 Dec 6; 9 (23): 6814-6817. https://doi.org/10.1021/acs.jpclett.8b02892
22. Tahseen A, Mohammed T O, Fatima H M, Baheya A D. Optical characteristics of Portulaca grandiflora-doped Cellulose using the spray pyrolysis technique. Opto-Electronics Review. 2023 July; 31: 46553. https://doi.org/10.24425/opelre.2023.146553

تحضير ودراسة الخواص البصرية للمواد المعاد تدويرها من البولي ميثيل ميثاكريالات المشوب بنسب مختلفة من 4- (2- بيريديلازو) ريسورسينول ملح أحادي الصوديوم هيدرات

زينب جمعة صويح [1]، فاطمة حميد مالك[2]، محسن جالب محسن[1]، بهية عبد الباقي ضاحي[2]

[1]قسم الكيمياء وتكنولوجيا البوليمرات، مركز أبحاث البوليمرات، جامعة البصرة، البصرة، العراق.
[2]قسم الفيزياء وعلوم المواد، مركز أبحاث البوليمرات، جامعة البصرة، البصرة، العراق.

الخلاصة

يقدم هذا البحث طريقة لتطوير متحسس بصري جديد باستخدام بولي ميثيل ميثاكريلات المعاد استخدامه من النفايات مع الراتنج المشتق من اللبان بمحلول الإيثانول وبنسبة (1: 1) (وزن : وزن ٪ مع (2-بيريديلازو) ريسورسينول أحادي الصوديوم هيدرات) (صبغة الازو) بتقنية صب المحلول .ودرست العينات المحضرة باستخدام المجهر الالكتروني الضوئي(SEM) وكذلك درست الخواص البصرية (UV-VIS)باستخدام المطيافية البصرية للاطوال الموجية (400-800) نانو متر و تزداد الامتصاصية البصرية ماعدا النسبة 7% تقل قيمة الامتصاصية وكان هذا السلوك للنفاذية ايضا .ومنها تم حساب معامل الامتصاص ومعامل الخمود وفجوة الطاقة البصرية وكانت افضل قيمة للفجوة عند النسبة 5% ،ومن هذه النتائج تم التوصل في هذه الدراسة الى إمكانية استخدام الأغشية المحضرة في هذه الدراسة لتطوير مجسات الألياف الضوئية من البولي ميثيل ميثاكريلات المعاد تدويره ، بمواصفات جيدة والتي تعتبر معالجة جيدة للنفايات في البيئة..

الكلمات المفتاحية: معامل الامتصاص ، صبغات الازو ، ملح ،متحسس خواص بصرية، مخلفات من بولي ميثيل ميثاكريالات.