



Preparation, Characterization, and Optical Properties of Modification Waste Polystyrene

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Abstract

In this work, a thin film of Modification Waste Polystyrene (MPS) with Sulfuric acid have been prepared by using spin coating method. The optical properties have been evaluated by means of transmittance and reflectance spectra, measured in the wavelength range of 300 to 900 nm. The thin films' optical constants, including refractive index (n) and extinction coefficient (k), were calculated. The studies on optical absorption spectra studies revealed that the indirect allowed transition is the absorption mechanism. The optical energy gap has been calculated to be 2.554 eV .

Keywords: Optical properties, Waste Polystyrene, Refractive index, optical energy gap

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التحضير والتوصيف والخصائص البصرية لتعديل نفايات البوليستيرين

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المستخلص

في هذا العمل، تم تحضير غشاء رقيق من نفايات البوليستيرين (MPS) مع حامض الكبريتيك باستخدام طريقة الطلاء الدوراني. فيما بعد تم تقييم الخصائص البصرية بواسطة أطيف النفاذية والانعكاس، والتي تم قياسها في مدى الطول الموجي من 300 إلى 900 نانومتر. ثم تم تحديد الثوابت البصرية مثل معامل الانكسار (n) ومعامل الخمود (k) للأغشية الرقيقة. كشفت الدراسات التي أجريت على دراسات أطيف الامتصاص البصري أن الانتقال غير المباشر المسموح به هو آلية الامتصاص، ولقد وجد أن قيمة فجوة الطاقة الضوئية Eg تساوي 2.554 eV.

الكلمات المفتاحية: الخصائص البصرية، نفايات البوليستيرين، معامل الانكسار، فجوة الطاقة الضوئية

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معلومات البحث

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Introduction

Investigations on the optical characteristics of polymers with different optical properties have recently received a lot of interest in the current research environment due to their use in optical devices [1]. The great increase in worldwide population together with the need of people to adopt improved living condition led to a dramatically increase of plastics consumption. Plastics are light, durable, hygienic and economical where they are useful for various applications encompassing food and product packaging, automobile production, agricultural products, and home furnishings [1-4]. Plastics recycling should be done to help reduce the amount of pollution created throughout the process, enhance process efficiency, and conserve energy. The 1990s saw the emergence of post-consumer recycled polymers for use in food packaging, which was motivated by the desire of business to reduce the problems with solid waste that were partly caused by plastic packaging. Recycled plastics have been used for food packaging for several years now, and this phenomenon may continue to rise. This is because of the high cost of crude oil, which is required to make the petrochemicals that are used to make plastics, in addition to the recent advancements in plastic recycling technologies that allow for enhanced quality and safety of post-consumer recycled plastics designed for food packaging applications [5-8].

Once, it has reached the end of its useful life, Modification Waste Polystyrene (MPS) can be recycled in a variety of ways. Technical, environmental, and economic factors all have a role in the method of recycling that is chosen [9,10]. Material recycling, chemical recycling, and

thermal recycling are the three ways to recycle discarded EPS. Prior to restoring PS as an ingot or pellet and reusing it as a raw material, everyday goods, and construction materials, the material recycling method first reduces the volume of EPS by heating, solvent, or friction. The goal of the chemical recycling process was to obtain the styrene monomer for future chemical application. Thermal recycling, in which used EPS can be burned to produce energy, is a useful technique for dealing with polluted waste MPS. [11-14].

2. Experimental

2.1 Materials

Modification Waste Polystyrene (MPS) was purchased from market and Sulfuric acid, Dichloromethane (DCM) of purity 99.998 used as solvent, Acetone, and Ethanol were supplied by Aldrich chemical company.

2.2 Measurements

The MPS thin film absorbance and transmittance spectra measurements were recorded in the wavelength range of 300 to 900 nm at room temperature by using double beam UV-visible spectrophotometer (CE-7200-Aquarius). The optical absorption (A) and reflectance spectra (R) were analyzed to determine the optical constants such as absorption coefficient (α), refractive index (n), and extinction coefficient (k). Analysis of the absorption coefficient was also carried out to determine the optical band gap and nature of the transitions. The prepared films thickness was measured ($\sim 0.5 \mu\text{m}$).

2.3 Synthesis

2.3.1 Sulfonation Reaction

The MPS reacted with Sulfuric acid by using 1:5 wt. ratios. The reaction was carried out in DCM as a solvent with stirrer at 80°C for 4 hours. Finally, it was filtered to separate the precipitate from the

mixture medium. The product was washed with distilled water (150 mL) to remove any acid remain with the product. The product was then dried in a vacuum oven at 85°C and weighted [15-20]. The scheme of the sulfonation reaction for PS is shown in Figure (1).

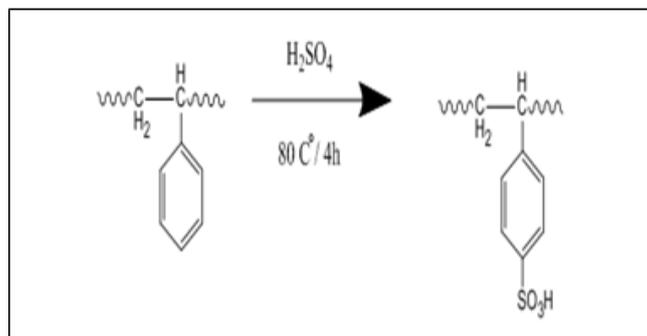


Figure (1): Scheme of the sulfonation reaction for PS

3. Results and Discussions

The crystalline nature of PS thin film was identified from the measured Fourier Transform Infrared (FTIR) spectrum as shown in Figure (2) below. The FT-IR spectra of PS, gave a peak at 3050 cm⁻¹ for carbon-to hydrogen C-H bond stretching of aromatic ring and two peaks at 2850 cm⁻¹ and 2975 cm⁻¹ for asymmetric and symmetric CH₂ respectively. There is a peak at

1600 cm⁻¹ for (double bonds) stretching C=C of aromatic ring and two peaks at 800 cm⁻¹ and 1000 cm⁻¹ for in plane bending C-H and out of plane bending C-H of aromatic ring respectively. The other two peaks, carbon-to-hydrogen bending stretching vibration, at 750 cm⁻¹ and 1450 cm⁻¹ for scissoring CH₂ and rocking CH₂ respectively. The peaks value for FTIR spectra of PS are shown in Table (1).

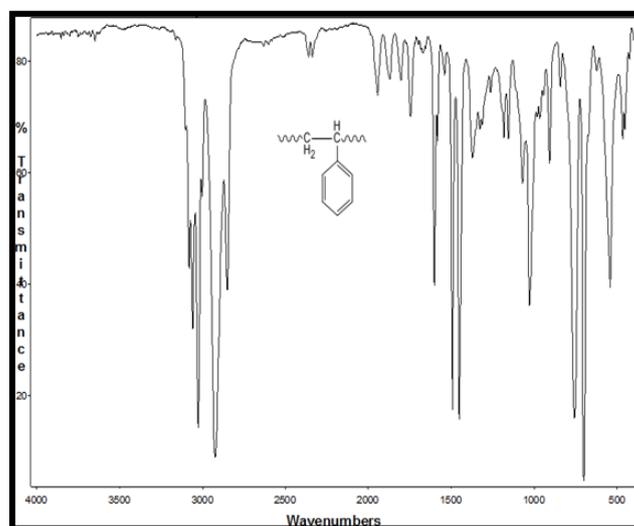


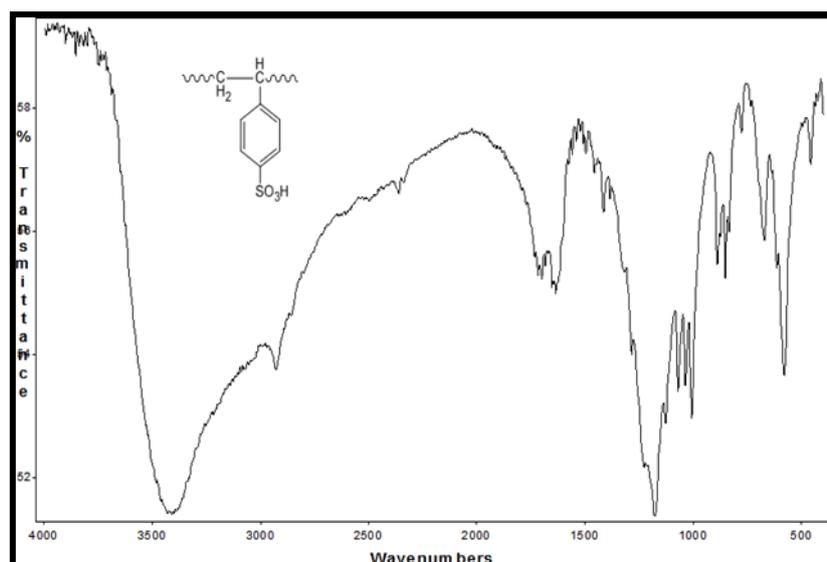
Figure (2): state the FTIR spectrum of PS

Table (1): State the Important Characteristics FTIR Bands and their Location for (PS)

Functional groups	Ar-H stre	CH ₂ Asy	CH ₂ sy	C=C Stre	C-H In plane	C-H Out of plane	C-H Sciss	CH ₂ Rock
Vibrations(cm ⁻¹)	3050	2925	2850	1600	1000	800	1450	725

The FTIR spectra of MPS is shown in Figure (3) below. As can be seen in the figure, there is a peak at 3390 cm⁻¹ for stretching OH of sulfonic group

and a peak at 1000 cm⁻¹ for stretching S=O. There is a peak at 1165cm⁻¹ for stretching SO₂ and the other peaks are shown in Table (2).

**Figure (3): State FTIR spectrum of MPS****Table (2): State the Important Characteristics FTIR Bands and their Location for (MPS)**

Functional groups	S-OH Stre	Ar-H stre	CH ₂ asy	CH ₂ sy	C=C Stre	C-H In plane	C-H Out of plane	C-H Sciss	CH ₂ Rock
Vibrations(cm ⁻¹)	3390	3025	1900	1830	1850	830	666	1000	1165

The HNMR- Spectroscopy was used to characterize PS by using Chloroform (sigma – Aldrich, 99.9% atom D) as a solvent. As shown in Figure (4), the PS gave the peaks at 1.4 and 1.9 ppm for methylene (d) and (c) respectively. The peaks at 6.6 and 7.2 ppm for proton (a) and (b) of aromatic ring respectively. The peak at 7.4 ppm

for solvent. After modification of waste polystyrene, the MPS was characterized by using DMSO (sigma–Aldrich, 99.9 % atom D) as a solvent. As shown in Figure (5) below, the MPS gave a new singlet peak at 10.4 ppm for OH group (a) and a peak at 2.5 ppm for solvent.

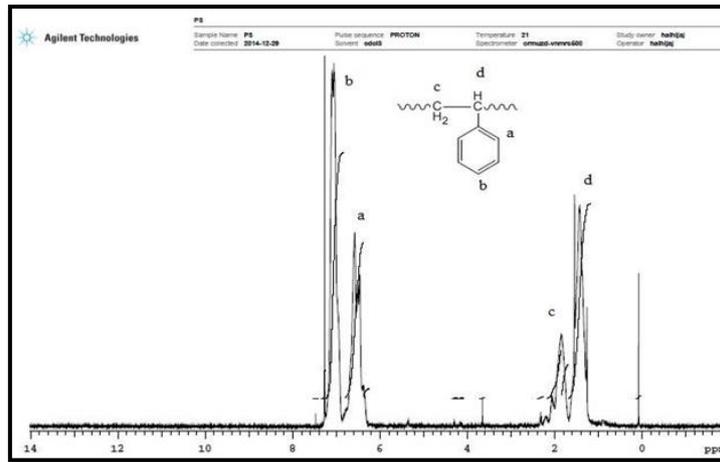


Figure (4) : State the HNMR-Spectroscopy for PS

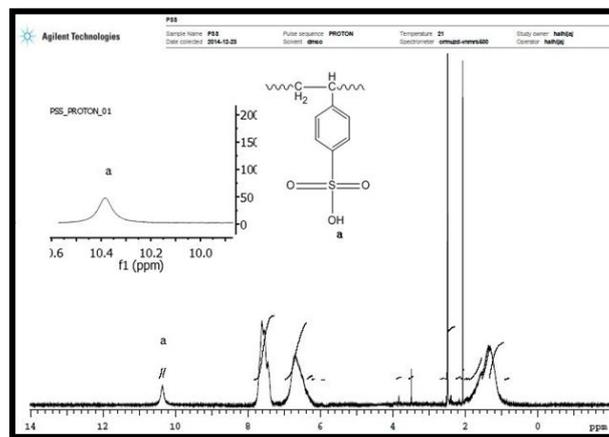


Figure (5): State the HNMR-Spectroscopy of MPS

To describe various aspects of band structure and energy gap in study of materials is through optical absorption. Figure (6) displays the MPS thin film's

absorbance in arbitrary units as a function of wavelength between 300 and 900 nm.

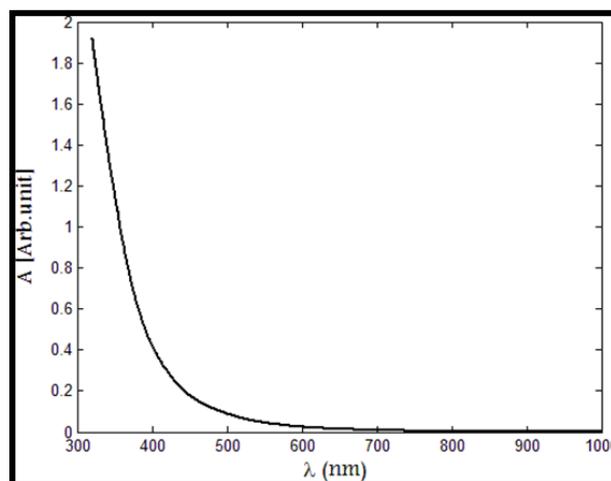


Figure (6): State the Absorbance as a Function of Wavelength for MPS thin Film

From the observed absorbance data, the absorption coefficient (α) can be calculated using the formula in Equation (1):

$$\alpha = 1/d (\ln I/I_0) \quad (1)$$

Where I_0 is the intensities of the incident and I_t is the transmitted beams, corrected for any reflection at the first surface while, d is the thickness of the film. The refractive index (n) as discussed by [9] can be determined by using Equation (2):

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

Where, R and k are the reflectivity and the extinction coefficient, respectively. The extinction coefficient could be determined from

the relation ($k = \alpha\lambda / 4\pi$), with λ is defined as the wavelength of incident light on films. The reflection (R) could be obtained by using the relation in Equation (3):

$$(1-R)^2 e^{-\alpha d} T = 1 - R^2 e^{-2\alpha d} \quad (3)$$

As shown in Figure (7), the dependence of reflection (R) and optical transmission (T) on wavelength. The transmittance is continuously increased with the incident wavelength. Since the absorption coefficient is related to optical transmission and reflection as defined in Equation (3), the data from transmission and reflection spectrum can be used to determine the absorption coefficient.

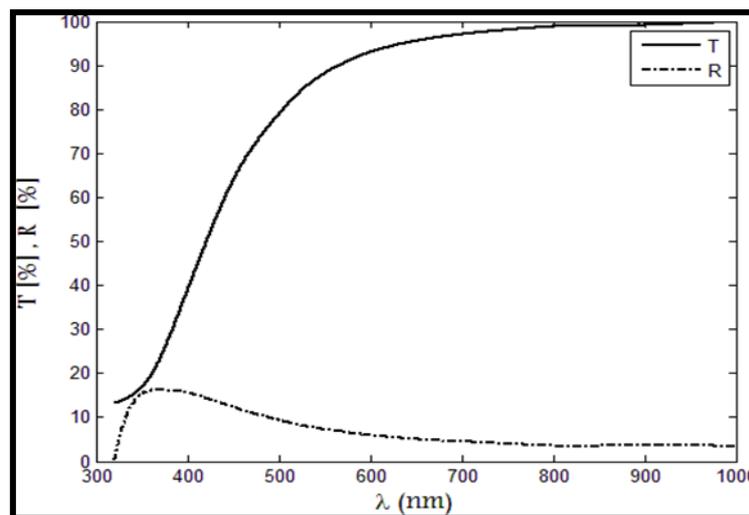


Figure (7) State Optical Transmittance and Reflectance Spectra as a Function of Wavelength for MPS thin film

Figure (8) depicts the refractive index (n) fluctuation with wavelength (λ) for MPS thin film. It is evident that as wavelength increases, refractive index drops. The value of refractive index (n) decreased due to the interaction between photons and electrons. With the changing of the

incident light beam's wavelength, this interaction caused changes in refractive index. As an illustration, consider the optical loss brought on by absorption and scattering, which reduces the amplitudes of oscillations in transmission intensity at shorter wavelengths. However, given that MPS

thin film is so clear, it can be disregarded in this paper. The primary loss in calculating the refractive indices for the MPS thin film results from transmission measuring processes, such as slight variations in the light of spot sizes and apertures.

The extinction coefficient (k) measures how much an electromagnetic wave is attenuated when passing through a material. Its value relies on the

quantity of free electrons in material as well as the type of structure. The extinction coefficient values and the absorption of light are intimately connected. According to the observations, the extinction coefficient drops as the wavelength increases. Figure (9), which depicts the (k) for MPS thin film as a function of wavelength in the 300–900 nm region.

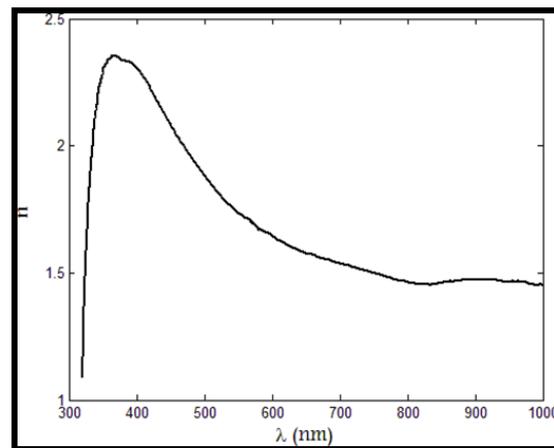


Figure (8): State the Variation of the Refractive Index (n) vs. Photon energy for MPS thin Film

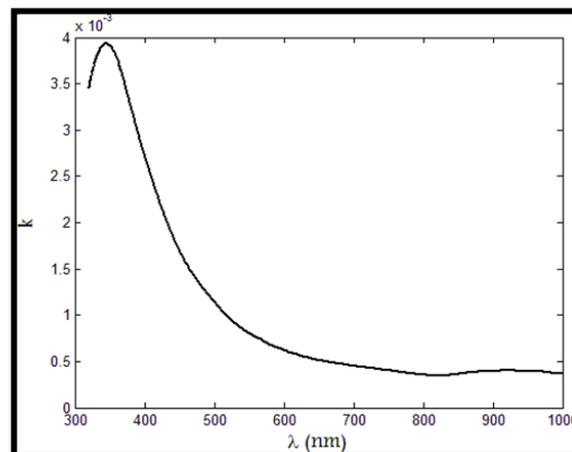


Figure (9): State the Variation of the Extinction Coefficient (k) as a Function of Wavelength for MPS thin Film

As shown in Figure (10), the fluctuation of absorption coefficient as a function of wavelength of the light in the range of 300 to 900 nm. It is clearly demonstrated that as the

wavelength increases, the absorption coefficient (α) decrease. This is brought on by a rise in permeability class in the wavelength range.

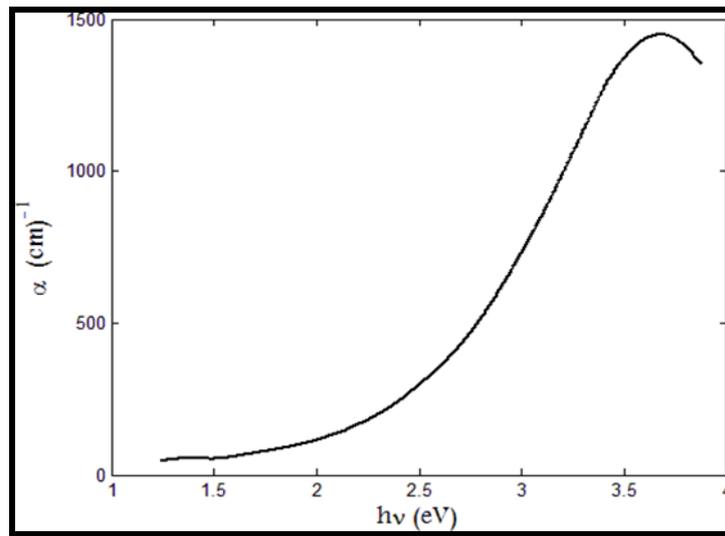


Figure (10): State the Explanation of the Absorption Coefficient (α) against the Photon Energy for MPS thin Film.

For most amorphous and semiconductors, the absorption edge for non-direct and direct transitions, can be obtained in view of the models proposed by Tauc et al. The following relationship, as in Equation (4), describes the relationship between the absorption coefficient (α) and optical band gap E_g .

$$\alpha = B (h\nu - E_g)^r / h\nu \quad (4)$$

Where B is an energy-independent constant, $(h\nu)$ is the photon energy and E_g is the optical energy band gap of the material (Tauc gap) and r determine the type of transition. According to Tauc law, the type of the optical transition is determined from the relation between $(\alpha h\nu)^{1/r}$ and photon energy $(h\nu)$ for the different value of the parameter r .

Depending on the nature of the electronic transition responsible for the absorption, parameter $r = 1/2, 3/2, 2,$ and $1/3$ is for allowed direct transition, forbidden direct transition, forbidden indirect transition, and indirect allowed transitions respectively.

The film crystal structure, the positioning and distribution of atoms inside the crystal lattice, as well as crystal regularity, all affect the energy gap values in general. Figure (11)'s plot of $(\alpha h\nu)^{1/2}$ versus photon energy $(h\nu)$ and its straight line extrapolation are used to determine the optical energy gap (E_g) value. According to investigations of optical absorption spectra, the absorption process is an indirect permitted transition. According to calculations, the optical energy gap, or E_g , has a value of 2.554 eV.

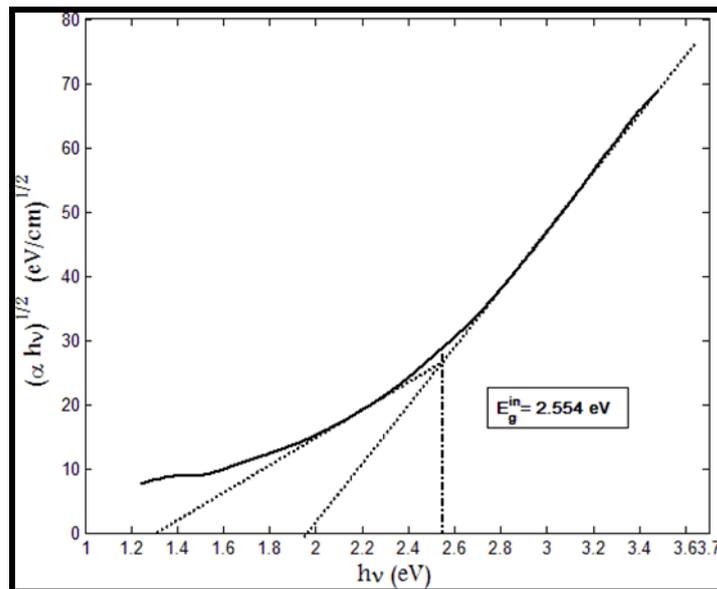


Figure (11): State the Plot of $(\alpha h\nu)^2$ versus Photon Energy ($h\nu$) for MPS thin Film.

4. Conclusions

The results reported in this research are obtained by using Optical absorption spectrum in order to calculate the optical properties for MPS thin film in range of 300 to 900 nm. It has been mentioned how the optical gap and absorption coefficient vary. Utilizing transmittance and reflectance spectra, the optical constants, refractive index, and extinction coefficient of these films were determined and analyzed. For MPS thin film, the indirect optical band gap values were calculated to be around 2.554eV with an absorption coefficient around 10^4 cm^{-1} .

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