Effect Of Additive Al On the Optical Properties Of Polystyrene-Aluminum Composites

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Abstract

Additive aluminum powder to the polystyrene to prepare the composites Polystyrene–Aluminum.The samples were prepared by using mechanical compressed method at low pressure and a temperature 120°C.

Measurements of absorbance and reflectance spectra were carried out by UV-Visible spectrophotometer , the effect of additive aluminum on the optical band gap E_{op} and optical constants (refractive index n, extinction coefficient k ,dielectric constant ε and optical conductivity σ_{op}) were studied for the prepared composites .

Results showed a decrease in the E_{op} with increasing percent of aluminum from 4.1eV for pure polystyrene to about 3.12eV for the composite Ps+30%Al. Values of each of n and k show observable changes, these changes are associated with the increase in scattering, reflection, and optical absorption on the film surface with the increase of Al percentage. The dielectric constant of Ps-Al composites is greater for all Al concentrations and may be attributed to interfacial polarization in the heterogeneous media, it was observed that the optical conductivity increasing from $0.12\times10^{5}S.cm^{-1}$ for pure polystyrene to about $1.32\times10^{8}S.cm^{-1}$ for Ps+30%Al.

These results indicate that the optical properties of PS-Al composites can be controlled by the appropriate selection of Al concentration and the optical properties of the composites can be modified by the addition of impurities ,thus increase the industrial application for the composites.

Key words: polystyrene, polystyrene composites, optical properties.

Introduction

Composite of inorganic particles with polymers is an interesting research subject because of the important potential application in photo catalytic degradation of polymers, and in fields of adhesives, textiles, optics and electronics .A new class of organic polymers capable of conducting electricity has recently been developed [1, 2]. The concept of the conductive polymer was first present in 1950 [3], these polymers are attractive for electric and photo electronic devices because of their doping capability and advantages of facile processing and become conductive upon partial oxidation or reduction, a process commonly referred to as 'doping'. These composites consist of a polymer matrix in which a second phase, which is usually either a metal or carbon-based filler, is dispersed, usually by conventional methods of polymer processing [4].

Examples of the conducting polymers are poly (p-styrene, poly aniline, poly (p-phenylenevinylene)-- etc. These polymers can be fabricated to have a high degree of flexibility [5, 6].

Polystyrene is amorphous polymer with bulky side group, general properties are hard ,rigid ,and transparent at room temperature and possesses many of the properties desired for a sensor[7], furthermore ,it has a good charge storage capacity and dopant dependent optical properties, conductivity of the polystyrene can be controlled by the addition of a dopant, which results in a partly filled band and allows
it to be easily switched from the "off" to the "on" state. The conductivity of polystyrene composite makes it an ideal shield against static electricity [8].

Polystyrene composites based on Al particles are of great interest due to their ability to combine the inherent processibility of polymers with the electrical conductivity of metals and have been used in a number of applications such as electromagnetic frequency interference (EMI) shields ,and are being tested to use as protection against electromagnetic
Radiation, antistatic devices, and conducting coatings [9], because of the technological importance of these composites, their electrical properties have been widely studied [10].

In this paper, we focus on the modification of the optical properties of polystyrene- Al composites by studying the effect of additive Al particles on these properties and to study changes in the optical constants (absorption spectra, optical energy gap, refractive index, dielectric constant and optical conductivity) by using the optical method.

Experimental Part

Experiments on optical reflectivity and absorbency provide the way to determine the dielectric constant of the solid, which is related to the band structure and to the optical conductivity.

The starting materials for the preparation of composite samples were polystyrene powder and Aluminum powder (99.99%) supplied by (Merk, India). For preparing composite samples, a weighed quantity of aluminum powder was first thoroughly mixed with a measured weighed of polystyrene, and the resultant mixture was well mixed so as to obtain a uniform composition, the composite mixture thus obtained was compressed at low pressure 60mpa. and at a temperature of about 120°C, the pressure was maintained for about 3hours. Five samples of Ps-Al composites with Al- varying from (0, 5, 10, 20 and 30 wt%) were prepared in the form of circular disc of radius 10mm and thickness around 0.45±0.08mm measured by using digital vernier. The optical spectra of Polystyrenes-Al composite films were obtained using (Shamindza UV-Vis. Spectroscopy) in the wavelength range 200-1000nm.

Theoretical Part

Optical methods are very useful for the quantitative determination of the electronic band structure of solids. Complex dielectric constant ε is directly related to the optical properties and characterizes the optical properties of solid material. The complex index of refraction N of the medium *is* defined as [11]:

N □□□□□□ n □□k (1)

Where n is the usual refractive index and k is the extinction coefficient, in optical experiments one does not usually measure n and k directly, the measurable quantities are the reflectivity *R* and the absorption coefficient α. It can be shown that these quantities are related to n and k by the expressions [12]

$R=|(1-N/1+N)|^2=[(1-n)^2+k^2]/[(1+n)^2+k^2]$ (2)

$k=\alpha c/2\omega=\alpha\lambda/4\pi$ (3)

Where $\omega=2\pi\upsilon$ is the angular frequency of the incident photon & c is the velocity of light, from these expressions n and k can be determined. The dielectric constant is related to the optical conductivity σ_{op} by the relation:

$\boldsymbol{\varepsilon=\varepsilon_l+4\pi i\sigma_{op}}$ (4)

Where ε_l describes the "bound charges" and σ_{op} describes the free charge, in this representation the conduction electrons are considered as a part of the dielectric medium.

The real part of dielectric constant is:

$\boldsymbol{\varepsilon_r==n^2-k^2}$ (5)

and the imaginary part is:

$\boldsymbol{\varepsilon_{im}=2nk}$ (6)

Optical conductivity (σ_{op}) is a measure of the frequency response of the composite when irradiated with light and determined from the relation:

$\boldsymbol{\sigma_{op}=\alpha nc/4\pi}$ (7)

Results and Discussion

Figure(1) illustrates the change in the absorbance A &the reflectance R of polystyrene films under the influence of additive Al, it can be observed that small quantities of Al - impurities added 5% and 10% have no considerable effect on the absorption spectra. The enhanced absorption is observed at 20% and 30% Al content, this suggests the decrease in the band gap with the increase of Al particles, the small absorption peaks appear as an indication that some states have been created in the region between the conduction and the valance band, appearance of a fine absorption spectrum at 30% Al content is due to the presence of discrete energy levels.

The absorption coefficient (α) was found experimentally from the relation [13]:

$\boldsymbol{\alpha=2.303A/d}$ (8)

Where d is the thickness of the film, results showed that the values of α for polystyrene-Al composites are $>10^4$ /cm which indicate to the direct electronic transition. The optical absorption coefficient is exponentially dependent on the incident photon energy in the exponent edge, which is strongly related to the structural randomness of the system, and obeys the empirical Urbach rule [14]:

$\boldsymbol{\alpha=\alpha_o\exp(h\upsilon/\Delta E)}$ (9)

Where α_o is a constant & ΔE is the Urbach energy which is the width of the localized states and can be determined from plotting inα against $h\upsilon$ as shown in figure (2), the values of ΔE for the prepared composites decreased with the increase of Al- content, as given in table (1) this decrease in ΔE is attributed to the impurity levels localized (Al -donor levels) and this could give rise to the allowed states near the conduction band forbidden region, also these allowed states could well merge with the conduction band .

Values of optical energy gap E_{op} for pure polystyrene & Ps-aluminum composite have been estimated from $(\alpha h\upsilon)^2$ versus $h\upsilon$ plots using the Mott and Davis model [15] and are shown in figure (3), it can be seen that E_{op} decrease with the increase of Al content, this trend may be explained as follows, when the aluminum content is low at 5% and 10%, the Al-particles are isolated that is, placed so far apart that there is no interaction between them, as the aluminum content is raised at 20% and 30%, clusters of metal particles are formed, a cluster may be considered as a region in the polymer matrix where metal particles are in physical contact or very close to each other, this means that the band gap is decreased as a result of changes in the molecular mobilities and redistribution of the structure. The variation of energy gap as a function of Al concentration is shown in figure (4), it can be seen that E_{op} decreased from 4.1eV for pure Polystyrenes to about 3.12eV for Ps+30% Al composite. Our results are in good accordance with the previously published results [16].

The inverse of the absorption coefficient is $\delta=2/\alpha$ and known as skin depth, [17], δ is a measure of the distance of penetration optical beam into the medium before the beam is dissipated. In practice, δ has a very small value indicating that an optical beam incident on a specimen penetrates only a short distance below the surface, values of δ at a certain wavelength are given in table (1).

Refractive index n is increased with the increase of Al concentration, it can be observed that (n) increases from 1.81 to about 6.42 when the Al-concentration increased from (0 to 30)%, the high values of n is attributed to some complicated polarization and structural defects in polystyrene with the increase of Al- concentration. Extinction coefficient values exhibits clear changes with the increase of Al content, these changes are associated with the increase in scattering, reflection, and optical absorption on the film surface with the increase of Al concentration. Values of refractive index and extinction coefficient at λ=500nm are given in table (1).

The behavior of real and imaginary part of dielectric constant with the photon energy is shown in figure (5), compared to pure polystyrene, the dielectric constant of Ps-Al composites is greater for all Al-concentrations and is attributed to interfacial polarization, a phenomenon that appears in heterogeneous media consisting of phases with different conductivity [18], that is, polystyrene-Al composites with aluminum particles dispersed in the polystyrene resin. Ps becomes more heterogeneous as more Al is added to it, because of the formation of accumulation of charges at the interfaces between the dispersed phase and the polystyrene matrix, the sudden change in the relationship between the real part of dielectric constant and Al-concentration at 20% and 30% is attributed to the formation of continuous chains of the conducting phase that spans throughout the polystyrene matrix. The range of variation of dielectric constant is in agreement with the observations of [2,19].

The single oscillator parameters were calculated in terms of the wimple – Didomenico model [20]. This model plays an important role in determining the behavior of the refractive index. The dispersion data of refractive index can be described by the relation:

$$\mathbf{n^2-1=E_d\text{-}E_o/[E_o^2-(h\upsilon)^2]} \qquad (10)$$

Where E_o is single oscillator energy and E_d is the dispersion energy which is a measure of the strength of interband optical transition ,by plotting $1/(n^2-1)$ versus $(h\upsilon)^2$ and fitting line shown in figure (6), E_o and E_d are determined directly from ,the gradient $(E_oE_d)^{-1}$ and the intercept (E_o/E_d) on the vertical axis, the values of E_o and E_d decrease with the increase of aluminum content as given in table (1), we found that E_o values is related empirically to the direct band gap by $E_o \approx 1.2E_{op}$, also the long wavelength refractive index n_∞ for the composite was determined from the interception of the vertical axis of figure (6). The values of n_∞ were found between 1.27 and 1.06, these values are in good agreement with others [5, 21] .

The behavior of optical conductivity σ_{op} with photon energy is shown in figure (7), it can be seen that, at low Al- concentration 5% and 10%, σ_{op} has low values which is due to interface scattering of discontinuous metal particles, Al-particles form small isolated islands embedded in polystyrene matrix, as the Al content increased and reaches a critical point, which represents the moment when there is enough conductive particles present to make a continuous network as the proportion of Al is increased, the islands grow and continuous Al-paths extending through polystyrene are established, the optical conductivity of the composite changing from 0.12×10^{5}S.cm^{-1} for pure polystyrene to 1.32×10^{8}S.cm^{-1} for Ps+30%Al composite, furthermore the σ_{op} vary slowly with the volume fraction of aluminum up to 10% and enhanced drastically until 30%, the fluctuation in the optical conductivity at 5% and 10% Al content may be attributed to the segmental mobility of the polymer molecules.

Conclusions

The effect of additive aluminum on optical properties of polystyrene -aluminum composites has been investigated, we can conclude the following points:

1-The overall absorbance and reflectance have been increased with the increase of Al-content.

2-Conductive was observed in the relationship between band gap energy and composition in the concentration range under study, which was ascribed to the existence of continuous network of aluminum in the polystyrene matrix.

3- Optical band gap of Ps- Al composites decreased with an increase in Al concentration, and the dielectric constant of Ps-Al composites is greater for all filler concentrations and is attributed to interfacial polarization.

4- The optical conductivity of such systems varies continuously as the composition is changed

5- Ps-Al composites are versatile, relatively inexpensive ,useful as light weight shielding for cabinets housing and it is an important material for the modulation of visible light .

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Table No.(1): Gives the values of some optical constants for Ps-Al composites

sample	ΔE eV	δ µm	Refractive index(n)	Extinction coefficient $k\times10^{-5}$	E_o eV	E_d eV
Pure Ps	0.491	225.4	1.81	5.8	4.84	0.72
Ps+5%Al	0.487	201.8	2	6.3	4.64	0.59
Ps+10%Al	0.473	198.7	3.23	6.9	4.52	0.5
Ps-20%Al	0.453	128.6	4.39	7.4	4.12	0.49
Ps+30%Al	0.422	110.7	6.42	9.34	3.61	0.32

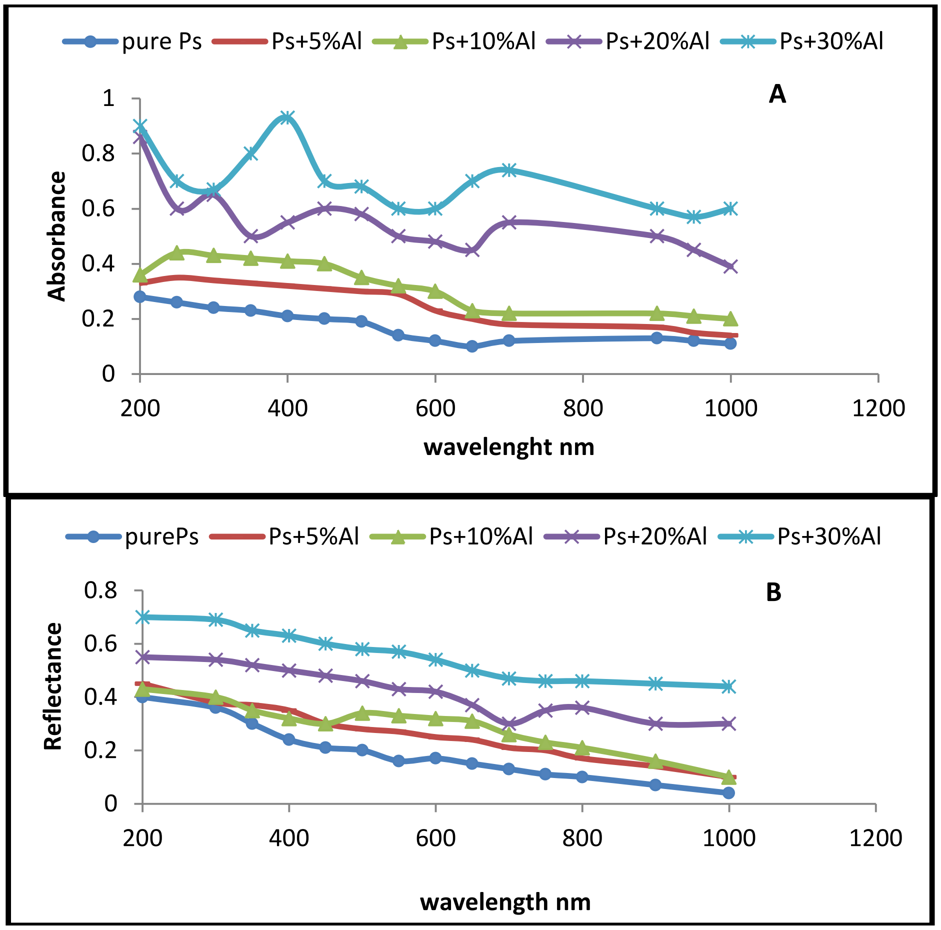

Figure No.(1): The variation of (A) Absorbance (B) Reflectance with the wavelength for Ps-Al composites.

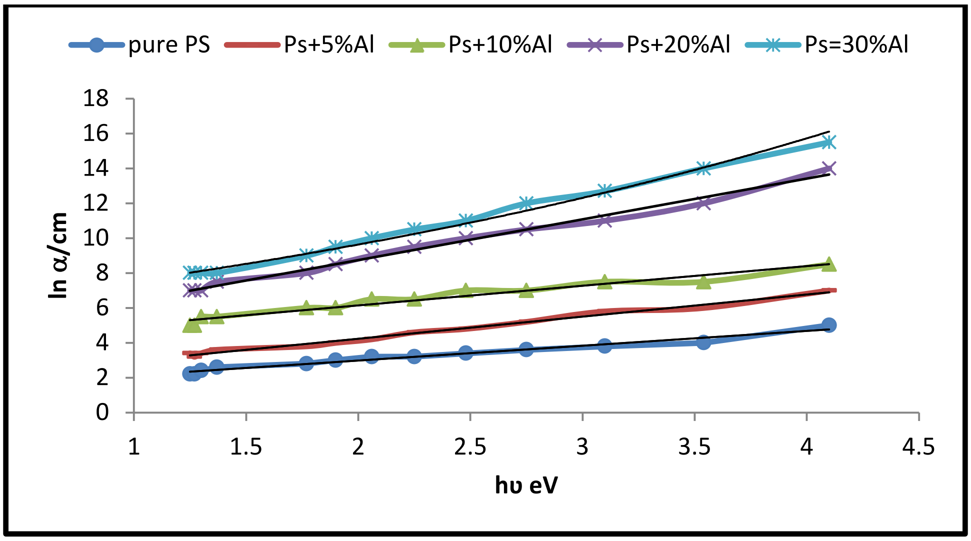

Figure No. (2): The relation between lnα and photon energy.

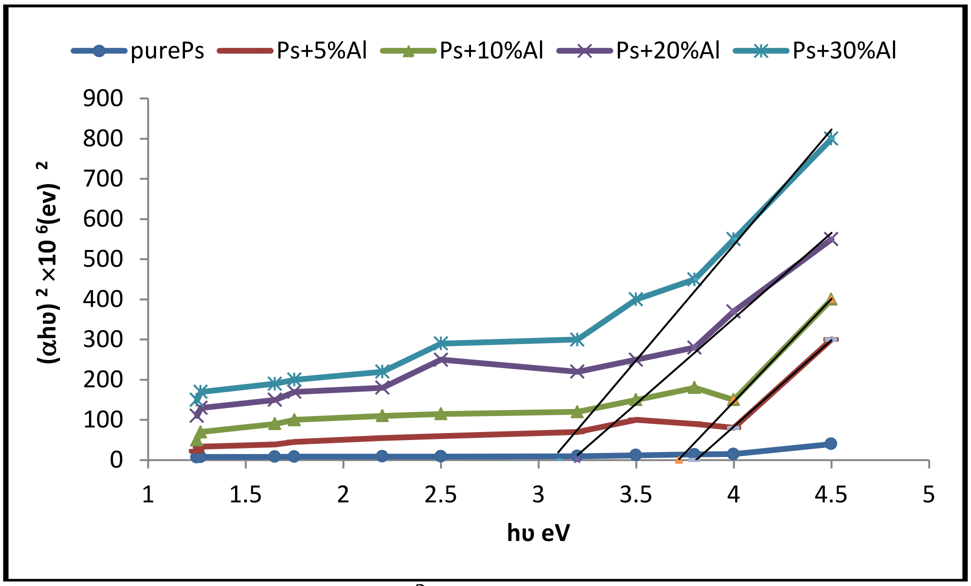

Figure No. (3): Variation of $(\alpha h\upsilon)^2$ versus photon energy for Ps-Al composites.

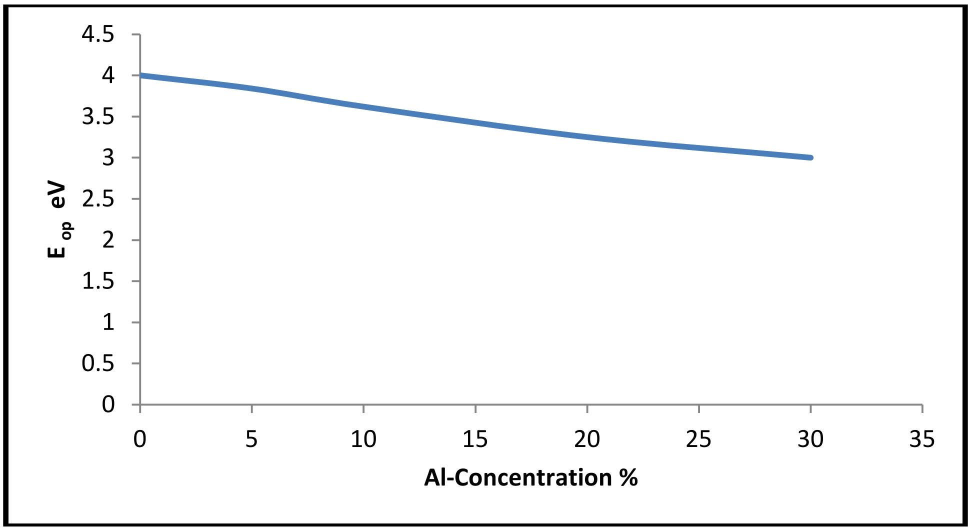

Figure No. (4): The dependence of the optical energy gap on the Al- concentration.

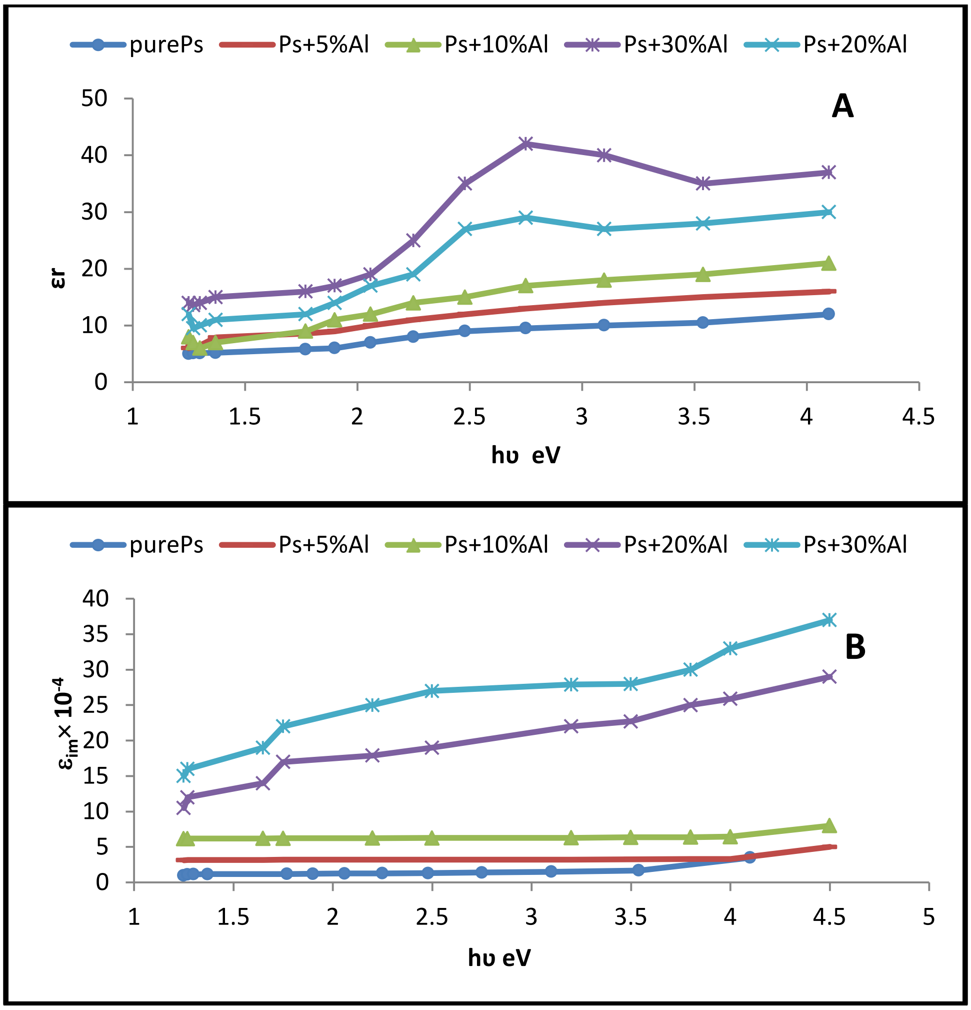

Figure No. (5): Real & imaginary part of dielectric constant (A & B) respectively against photon energy.

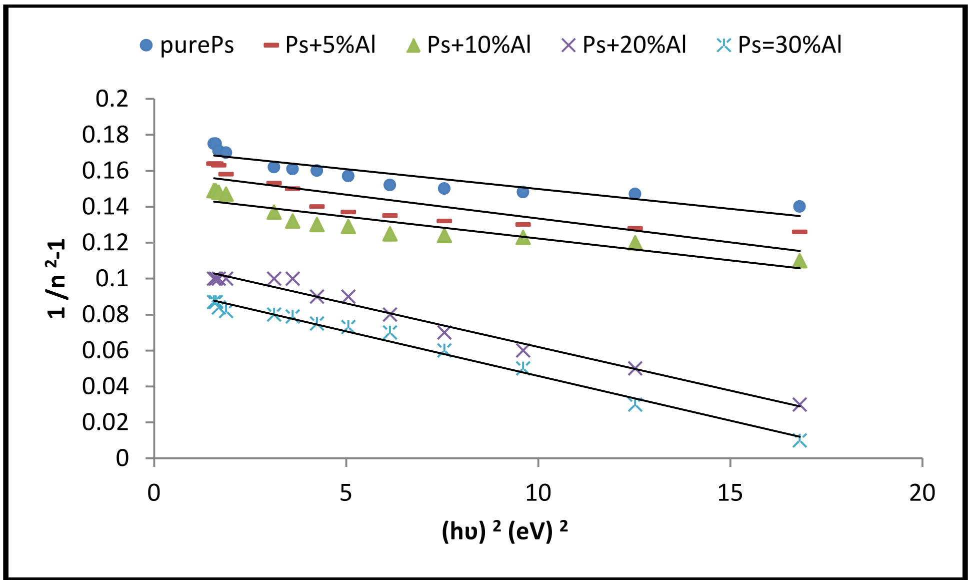

Figure No. (6): The variation of ($1/n^2$-1) with $(h\upsilon)^2$ of pure and doped Polystyrene film.

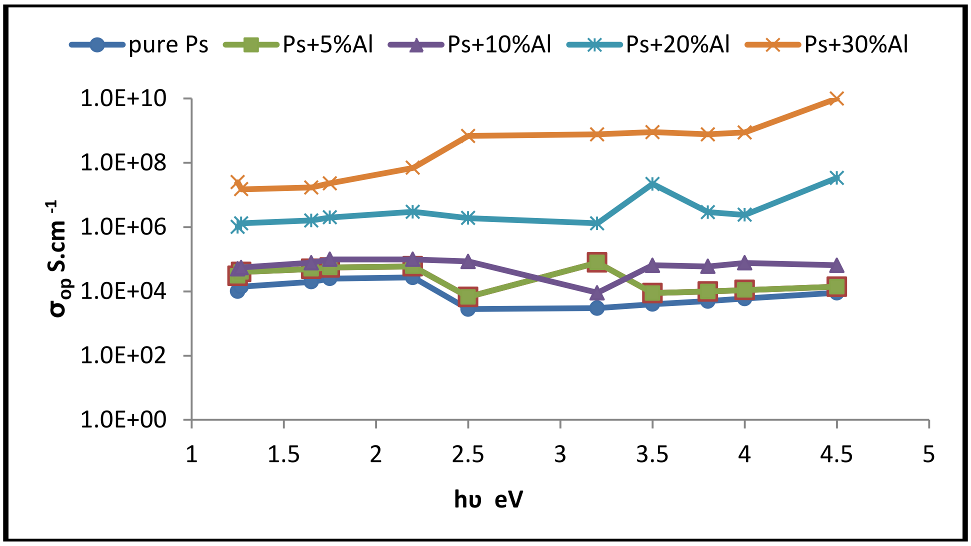

Figure No (7): Optical conductivity as a function of photon energy for pure polystyrene & Ps-Al composites

تأثيرإضافة الالمنيوم على الخواص البصرية لمركبات بولي ستايرين-ألمنيوم

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الخلاصة

أُضيف مسحوق الألمنيوم إلى البولي ستايرين لتحضير مركب بولي ستايرين-ألمنيوم بطريقة الكبس الميكانيكي عند ضغط منخفض ودرجة حرارة 120ºC. أجريت قياسات الامتصاصية والانعكاسية باستعمال المطياف الضوئي UV- Visible Spectrophotometer .

تمت دراسة تأثير إضافة الألمنيوم في فجوة الطاقة البصرية E_{op} وعلى الثوابت البصرية (معامل الانكسار n، وعامل الخمود k، وثابت العزل ε، والتوصيلية البصريةσ_{op}) للمركبات المحضرة.

أظهرت النتائج انخفاض قيمة فجوة الطاقة البصرية E_{op} مع زيادة نسبة الألمنيوم في المركب إذ انخفضت قيمتها من 4.1eV للبولي ستايرين النقي إلى حوالي3.12eV للمركب(Ps+30%Al)، وتبين أن قيم كل من n وk تتغير تغيرا ملحوظا وهذا التغير مصاحب للزيادة في التشتت، الانعكاسية والامتصاص البصري لسطح الأغشية مع زيادة نسبة الألمنيوم وكانت قيم ثابت العزل ε عالية لجميع نسب الألمنيوم وهذا قد يعود إلى الاستقطاب البيني في الأوساط المختلطة heterogeneous. ولوحظ ان قيم التوصيلية البصرية قد ازدادت من$0.12\times10^{5}S.cm^{-1}$ للبولي ستايرين النقي إلى حوالي $1.32\times10^{8}S.cm^{-1}$للمركب Ps+30%Al .

ان هذه النتائج تدل على انه يمكن التحكم في الخواص البصرية لمركب بولي ستايرين –ألمنيوم باختيار الكمية الصحيحة من الشوائب، ويمكن تغيير الثوابت البصرية بإضافة كمية محددة من الشوائب وبهذا يمكن زيادة التطبيقات الصناعية لهذه المركبات.

الكلمات المفتاحية: بولي ستايرين، مركبات البولي ستايرين، الخواص البصرية.