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Synthesis and Characterization of a Polystyrene (Cork) Doped by Aluminium Oxide (Al_2O_3) to Improve Its Optical Properties Using the (UV-VIS) Techniques

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Abstract: Cork is considered one of the polymers of very low industrial value and is used only for secondary purposes such as packaging, and it is possible to have any other uses of high value by doping the cork with materials that can change its physical properties, this paper aimed to synthesize and characterize the optical properties of pure Polystyrene (200 grams) Cork, and Polystyrene (200 grams) Cork doped by Aluminum oxide in ratios (0.1 to 0.9) molar, for the preparation of Aluminum oxide, aluminum nitrate ($Al(NO_3)39H_2O$)) was used (as a source of Aluminum oxide, provided by (LOBA CHEMIE) company, with a molecular weight of 375.13 and a concentration of 98%, which is a white powder that is soluble in water, it was prepared at a temperature of (80) degrees Celsius for each Samples with different concentrations ranging from (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9) morality by adding N, N-Dimethylformamide for HPLC and Spectroscopy as an oxidizing agent and precipitant, then by Sol-Gel method at a temperature of 80°C for 60 minutes, samples of doped cork were deposited on glass slides. By using the ultraviolet technique (UV-VIS), the transmittance and absorption spectra were recorded within the wavelength range of (200-800) nm. The results showed that the transmittance decreased with increasing the cork doping percentage. The basic absorption peaks of the cork tends towards the low photon energy (red shift) when increasing the doping rates of Aluminum oxide, while it was tending towards the high energy (blue shift) photon at the cork before doping, and that is through the absorption coefficient values that were calculated from the absorbance spectrum, which is greater than Likewise, the optical parameters of reflectivity, extinction coefficient, and refractive index were calculated. The energy gap of the cork doped by Aluminum oxide is small compared to the energy gap of the pure polystyrene cork. It has been concluded that the Aluminum oxide ratios with different molar values confirm the cause of the energy gap shifts.

Keywords: Cork, Polystyrene, Optical Properties, Energy Gap, Aluminum Oxide

1. Introduction

Cork is one of the oldest substances known to mankind, a material that is based like a sponge and its origin is plant and is lightweight, and a insulating material also worse against water, sound, heat and electricity, it does not absorb water easily, and it is also characteristic of cork that it bears high pressure, and this substance appeared in the centuries BC where the barges were made of them, as well as to float fishing nets being a light material floating on the sea surface, and then used as pipe plugs [1]. It does not absorb water easily and can be compressed considerably, but returns to its first state after the pressure has subsided. Since the 4th century B. C., people have used corks and the Romans have worn cork sandals, and they have used cork to float shipyards and fishing nets [2, 3]. Cork plugs have been made since the 17th century. The cork is produced after obtaining the outer shell of the cork tree as it contains an outer layer of coarse sand which is brown, and is adjacent to the cork material and attached to the so-called tannic acid, the first step begins with the skimming of the outer layer, and the crust is placed in boiling water until the material becomes soft and the acid separates from it, after which it is easy to form a whole slab of cork, and the cork differs in quality and density and then is shipped to be used in industry [4, 5].

2. Optical Properties

The study of the optical properties of materials is of great importance because it gives a lot of Information about the type of electronic transitions that occur in the material, in addition to leaving the energy beams; it also describes the properties that determine the interaction of light with matter.

When the energy of the radiation absorbed by the semiconductor is greater or equal, it is approximately to a value the energy gap (Eg), as it causes an electron to move from the valence beam filled with electrons to The conduction beam is devoid of electrons, so the area of the spectrum of the incident rays is defined and where it starts P are electrons moving at the absorption edge, and the amount differs in the energy between the lowest point in the conduction beam and the energy of the highest point in the valence beam is called the optical energy gap [6].

2.1. Transmittance

Optical transmittance (T) is the ratio between the intensity of the radiation transmitted from the thin membrane (I_T) to the intensity of the fallen radiation (I_0) and expressed by the relation [7].

$$T = \frac{I_T}{I_0} \tag{1}$$

The semi-conductor material when exposed to a beam of radiation, part of the falling rays will be carried out and the transmittance of the rays depends on the fallen photons and the properties of the semiconductor material, as well as the thickness of the membranes and the temperature of the preparation and the percentage of addition of impurities

2.2. Absorbance

Optical absorption (A) is the ratio between the intensity of radiation absorbed by the membrane (I_A) to the intensity of the radiation falling on it (I_0), is known as absorption, as it represents the decrease in the energy of electromagnetic radiation when entering the membrane, it depends on the nature and the thickness of the semiconductor and expressed by the relation [8].

$$A = \frac{I_A}{I_0} \tag{2}$$

2.3. Reflexivity

The optical reflectance (R) the ratio between the intensity of the radiation falling, to the intensity of the radiation reflected at the limit between the two mediums, it is known as reflectivity. Reflexivity can be calculated according to the law of energy conservation and by knowing the value of both transmittance (T) and absorption (A) [8].

$$R + T + A = 1 \tag{3}$$

2.4. Absorption Coefficient

Absorption coefficient is the ratio of the decrease in the flux of radiation energy falling relative to the unit of distance towards the spread of the wave within the medium known as absorption coefficient, it depends on the properties of the semiconductor in terms of the energy gap and the type of electronic transmissions that occur between the energy band and the energy of the fallen photons through the relation [9-11].

$$E = h\upsilon \tag{4}$$

And finally we find that the absorption coefficient can be written in terms of the absorbance (A) by the following equation

$$\alpha = 2.303\frac{A}{t} \tag{5}$$

Where t denote the thickness of the layer

2.5. Refractive Index

Refractive index is the ratio between the speed of light in the vacuum (c) to its speed in the medium (v) which is called the refractive coefficient (n), and the refractive index depends on the type of material and its crystal structure and is expressed by the following equation [12].

$$n = \left[\left(\frac{1+R}{1-R}\right)^2 - \left(k_0^2 + 1\right)\right]^{\frac{1}{2}} + \frac{1+R}{1-R} \tag{6}$$

2.6. Extinction Coefficient

The extinction coefficient is the amount of energy absorbed in the thin membrane, and the energy absorbed by the material from the fallen photons, in other words, it represents the extinction or attenuation occurring in the electromagnetic wave inside the material [13].

$$K_0 = \frac{\alpha\lambda}{4\pi} \tag{7}$$

2.7. Energy Gap

Energy gap is an important visual constant, and is a function of temperature as its value changes slightly with the change of temperature where the energy gap increases in some semiconductors while in others, the energy gap for pure semiconductor is not completely empty where there are local levels resulting from synthetic defects. The energy gap for the direct electronic transmissions allowed can be calculated by plotting the relation between $(h\upsilon)$ and $(\alpha \upsilon h)^2$ by extending the best straight line that is a definite extension of the photon energy axis. The value of the energy gap is determined by the intersection point with the x axis at which $(\alpha \upsilon h)^2 = o$ [14].

3. Experimental

This part of the work includes a detailed description of the preparation of Aluminum Oxide (Al_2O_3), which is used to dope polystyrene (cork) dissolved in Benzene by the method of Sol-Gel method with volumetric ratios (0.1, to 0.9) mol with increasing step of 0.1 at a temperature Chamber by magnetic stirrer to obtain nine samples of doped polystyrene, and then studying the structural and optical properties of the samples by means of X-ray diffraction devices, a UV scale and an infrared device.

3.1. The Sol-Gel Method

The sol-gel system consists of several locally available tools through which polystyrene can be doped, these are:

1. Magnetic stirrer and hot plate.
2. Holder.
3. Thermometer.
4. Beakers.
5. Sensitive balance.

3.2. Preparation of Aluminum Oxide

For the preparation of Aluminum oxide, aluminum nitrate ($Al(NO_3)_3 9H_2O$)) was used (as a source of Aluminum oxide, provided by (LOBA CHEMIE) company, with a molecular weight of 375.13 and a concentration of 98%, which is a white powder that is soluble in water, it was prepared at a temperature of (80) degrees Celsius for each Samples with different concentrations ranging from (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9) morality by adding N, N-Dimethylformamide for HPLC and Spectroscopy as an oxidizing agent and precipitant, and through the following equations:

$$AL(NO_3)_3\,9H_2O + H_2O \xrightarrow{\Delta} AL_2O_3 + H_2O$$

$$W_t = \frac{M_{wt} * V * M_O}{1000}$$

Where

(M_O) Denotes the molecular concentration

(W_t) Denotes the solution weight

(M_{wt}) Denotes the molecular weight

(V) Denotes the volume of distilled water in (mL)

A (773 mg) was dissolved in (69 mL) of distilled water and placed in the magnetic stirrer at a temperature of 80 C^O for 60 minutes, to obtain complete dissolution for the first sample, and then dissolve (740 mg) in (66.5 mL) of distilled water and placed in the magnetic stirrer at a temperature of 80 C^O for 60 minutes to get the second sample. Also, (804 mg) was dissolved in (75 mL) of distilled water and placed in the magnetic stirrer at a temperature of 80 for 60 minutes to get the third sample, (761 mg) was dissolved in (68.5 mL) of distilled water and placed in the magnetic stirrer at a temperature of 80 C^O for 60 minutes to obtain the fourth sample, then, (801 mg) was dissolved in (70 mL) of distilled water and placed in a magnetic stirrer at a temperature of 80 C^O for 60 minutes to obtain the fifth sample, and (845 mg) was dissolved in (79 mL) of distilled water and placed in the magnetic stirrer at a temperature of 80 C^O for 60 minutes to obtain the sixth sample, (744 mg) was dissolved in (66 mL) of distilled water and placed in a magnetic stirrer at a temperature of 80 C^O for 60 minutes to obtain the seventh sample, and finally a (969 mg) was dissolved in (87 mL) of distilled water and placed in a magnetic stirrer at a temperature of 80 C^O for 60 minutes to obtain the eighth sample, and (840 mg) was dissolved in (74 mL) of distilled water and placed in a magnetic stirrer at a temperature of 80 C^O for 60 minutes to obtain the ninth sample.

Meanwhile, ten samples of the synthetic white cork (polystyrene) that was obtained after use (the waste) was dissolved in laboratory Benzene with a weight of 200 grams for each sample to become a solution and ten samples were prepared, to prepare doped cork samples, each of the nine previously prepared samples was added to a sample of 200 grams of cork dissolved in benzene and placed in the magnetic stirrer for 60 minutes to obtain the nine samples of the gelatinous solution of the cork doped by Aluminum oxide, then the solutions were placed in the bakers with the magnetic stirrer for 60 minutes to complete mixing and that to obtain a gelatinous solution. Spread it on glass slides, then leave the samples for 24 hours to dry and ready for testing.

4. Results and Discussion

In this part of the paper, the main results that have been obtained from the experiments made of polystyrene (cork) doped by aluminum oxide in different rate of molar (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0) are presented, and the data characterized by the UV-visible device used to evaluate the band gap and optical properties.

Optical Results of Polystyrene (cork) doped by Aluminum Oxide (Al_2O_3)

1. Absorbance

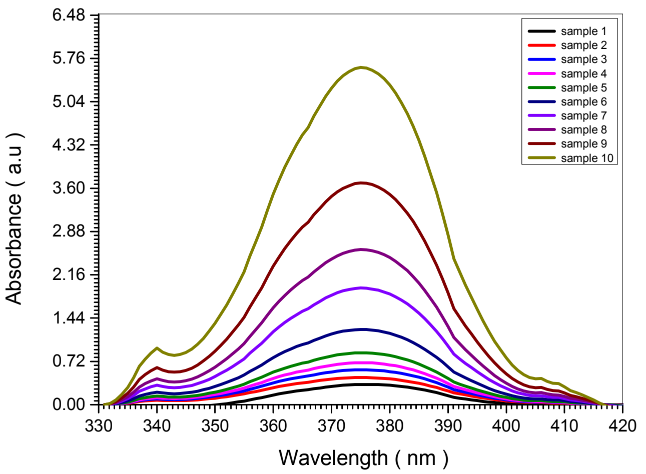

Figure 1. *Relation between absorbance and wavelengths of polystyrene (cork) doping by aluminum oxide in different rate of molar (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 08, 0.9 and 1.0).*

In the absorbance graph we found that the behavior of the curves is the same for the ten samples of polystyrene (cork) doped by aluminum oxide in different rate of molar (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 08, 0.9 and 1.0) studied. Using UV-VIS 1240 min spectrophotometer, showed all the results of absorbance in Figure 1. Figure 1 shows the relation between absorbance and wavelengths for polystyrene (cork) doped by aluminum oxide in different rate of molar which gives gradually increasing in the a absorption up to the wavelengths 375 nm at which crosponding to the photon energy 3.31 eV, and that is directly proportional to the doping rate of the (aluminum oxidemolar).

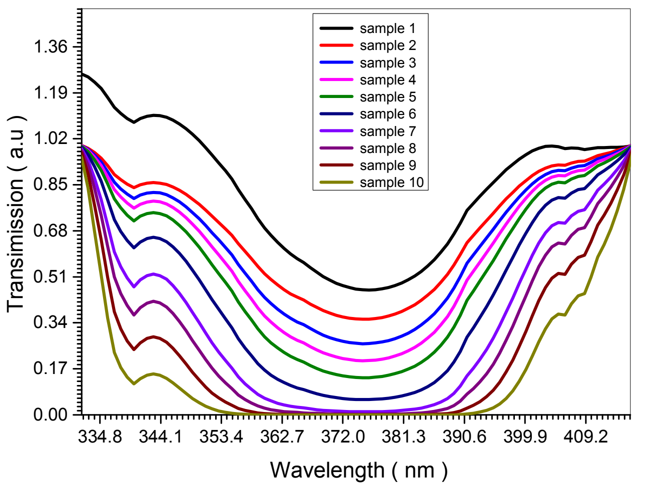

Figure 2. *Relation between transsimitance and wavelengths of polystyrene (cork) doped by aluminum oxide in different rate of molar (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 08, 0.9 and 1.0).*

In the transmittance graph we found the that the behavior of curves is the same for polystyrene (cork) doped by aluminum oxide in different rate of molar (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 08, 0.9 and 1.0) samples, Figure 2 shows the efficet of doping on the transmittance and it clarifyed an inverse proportional between the doping rate and the transmittance value.

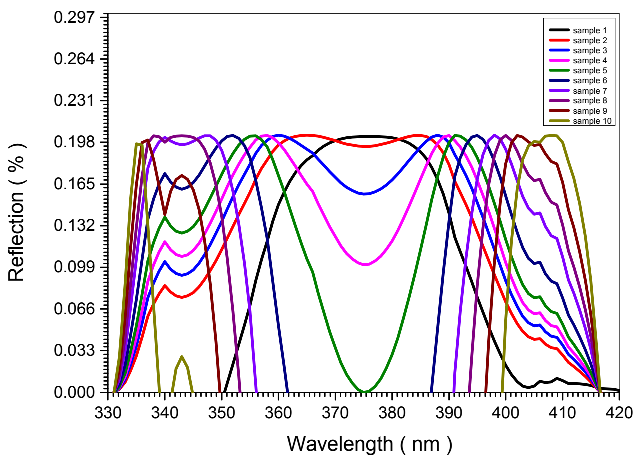

Figure 3. *Relation between reflection and wavelengths of polystyrene (cork) doped by aluminum oxide in different rate of molar (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 08, 0.9 and 1.0).*

The reflection graph for all samples of polystyrene (cork) doped by aluminum oxide in different rate of molar (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 08, 0.9 and 1.0) is presented in Figure 3, which shows that the reflection for all samples of polystyrene (cork) doped by aluminum oxide in different rate of molar has a maximum value of 0.1972% in the wave length range (335 to 410) nm, at this range the reflection becomes completely a mirror. The efficet of doping on the refelection increases the transission by increasing the dopping rate, and the graph shefted towards the red spectrum after the wave length value of 375 nm and plue sheft befor 375 nm.

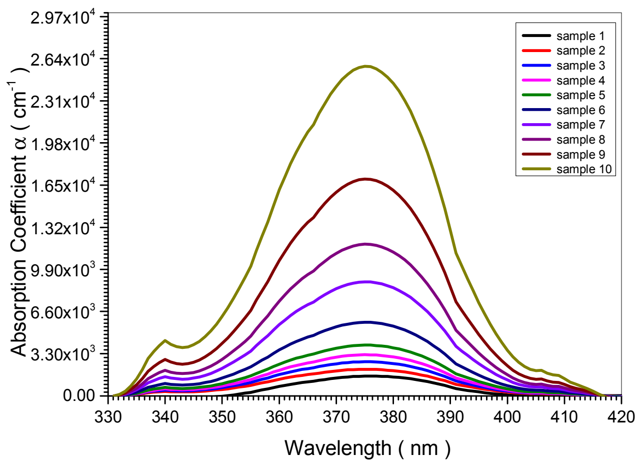

Figure 4. *The relation between absorption coefficient and wavelengths of polystyrene (cork) doped by aluminum oxide in different rate of molar (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 08, 0.9 and 1.0).*

The absorption coefficient (α) of all polystyrene (cork) doped by aluminum oxide in different rate of molar (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 08, 0.9 and 1.0) was found from equation (5). Figure 4 shows the plot of (α) vrs wavelength (λ) of polystyrene (cork) doped by aluminum oxide in different rate of molar, and obtained that the value of $\alpha = 1.55x10^3\ cm^{-1}$ for sample 1 in the U. V region (375 nm) but for sample 10 it equal $2.58x10^4\ cm^{-1}$ at the same wavelength, that means the transition must corresponds to a direct electronic transition, and the properties of this state are important since they are responsible of the electrical conductivity. Also, Figure 4 shows that the value of (α) for the all polystyrene (cork) doped by aluminum oxide in different rate of molar increases while doing rate increases in a direct proportionality.

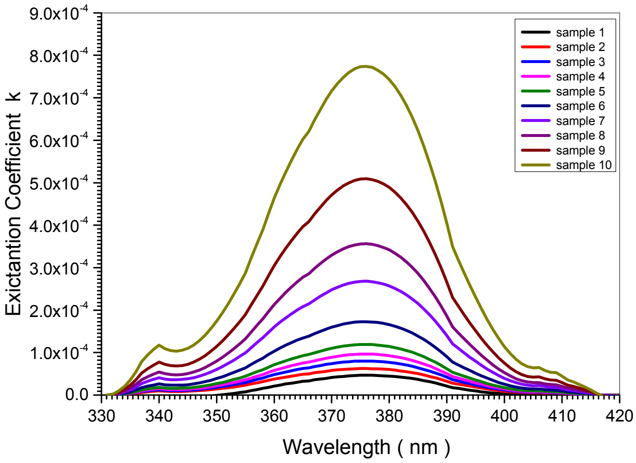

Figure 5. *The relation between extinction coefficient and wavelengths of polystyrene (cork) doped by aluminum oxide in different rate of molar (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0).*

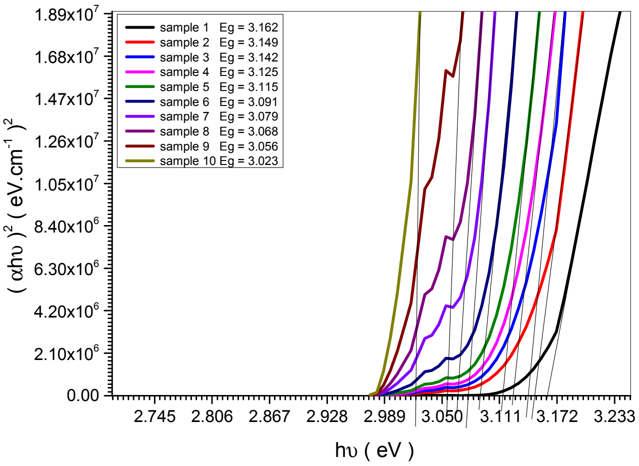

Figure 6. *The relation between the optical energy band gap of all polystyrene (cork) doped by aluminum oxide in different rate of molar (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 08, 0.9 and 1.0).*

Extinction coefficient (K) was calculated using the equation $K = \frac{\alpha\lambda}{4\pi}$. The variation at the (K) values as a function of (λ) is shown in Figure 5 for all polystyrene (cork) doped by aluminum oxide in different rate of molar (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0) samples and it is observed that the spectrum shape of (K) is the same as that of (α). The Extinction coefficient (K) for all polystyrene (cork) doped by aluminum oxide in different rate of molar samples showed the value of (K) at (375 nm) wavelength, depending on the samples treatment method, where the value of (K) at 250 nm for sample 1 equal 4.45×10^{-5} while for sample 10 at the same wavelength equal 7.75×10^{-4}. The effect of aluminum oxide in different rate of molar occurs as a direct proportional, in other words, increasing the aluminum oxide doping rate causes increasing the Extinction coefficient (k) value.

The optical energy gap (Eg) has been calculated via equation $(\alpha h\upsilon)^2 = C(h\upsilon - Eg)$ where (C) is constant. Plotting $(\alpha h\upsilon)^2$ vrs photon energy $h\upsilon$ is shown in figure 6 for all polystyrene (cork) doped by aluminum oxide in different rate of molar (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 08, 0.9 and 1.0) samples. And by extra polating the straight thin tangant of the curve to intercept the energy axis, the value of the energy gap has been calculated for sample (1) and found to be equal (3.162) eV while for sample (10) is equal to (3.023) eV. The value of (Eg) was decreased from (3.162) eV to (3.023) eV, the decreasing of (Eg) related to increasing of aluminum oxide dopping rate of the samples. It was observed that the different aluminum oxide rate of molar confirmed the reason for the band gap shifts. Comparing this to the work [15] which entended that the electrical properties show that cork can be used as an antistatic packaging it is clear that cork can be a good material with conducting or semi-conducting properties.

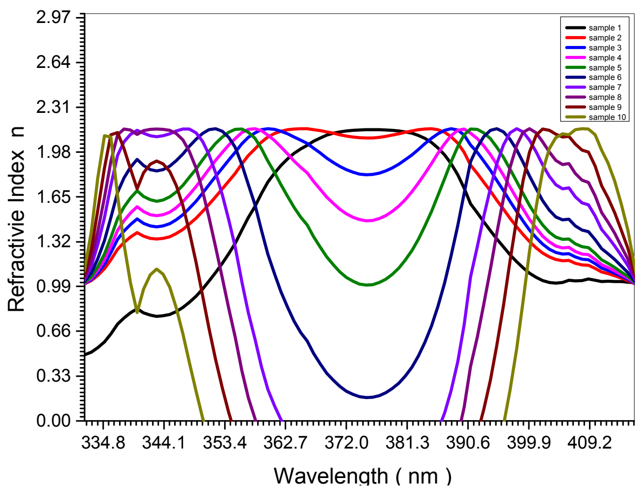

Figure 7. *The relation between refactivie index and wavelengths of polystyrene (cork) doped by aluminum oxide in different rate of molar (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 08, 0.9 and 1.0).*

The refractive index (n) is the relative between speed of light in vacuum to its speed in material which does not absorb this light. The value of n was calculated from the equation $n = \left[\left(\frac{1+R}{1-R}\right)^2 - \left(k_0^2 + 1\right)\right]^{\frac{1}{2}} + \frac{1+R}{1-R}$, Where (R) is the reflectivity. The variation of (n) vrs (λ) for all polystyrene (cork) doped by aluminum oxide in different rate of molar (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 08, 0.9 and 1.0) is shown in Figure 7. Figure 7 shows the plot of the refractive index (n) spectra of all polystyrene (cork) doped by aluminum oxide in different rate of molar, which indicates that the maximum value of (n) is (2.145) for all samples at wavelength ranged (335 to 410) nm, which is agree with the red shift that take place for aluminum oxide doping rate byond the wavelength 375 nm, and blue the shifty befor the wavelength 375 nm on the spectrum

Figure 8 shows the variation of the real dielectric constant (ε_1) with the wavelength of all samples prepared by polystyrene (cork) doped by aluminum oxide in different rate of molar, which calculatedfrom the relation $\varepsilon_1 = n^2 - k^2$ Where the real the dielectric constant (ε_1) is the normal dielectric constant. From Figure 8 the variation of (ε_1) followed the refractive index, where at wavelength ranged (335 to 410) nm for all samples of polystyrene (cork) doped by aluminum oxide in different rate of molar, the absorption of the samples at these wavelength is small, but the polarization increased, and the maximum value of (ε1) equal to (4.63) at wavelength 375 nm. The effect of the treatment by aluminum oxide in different rate of molar of the samples on the (ε1) is shifted towards the red spectrum befor 375 nm and shifted towards the blue spectrum after 375 nm.

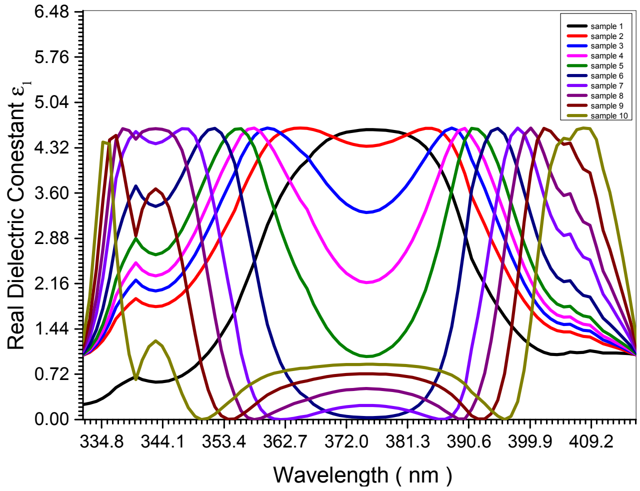

Figure 8. *The relation between the real dielectric constant and wavelengths of polystyrene (cork) doped by aluminum oxide in different rate of molar (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 08, 0.9 and 1.0).*

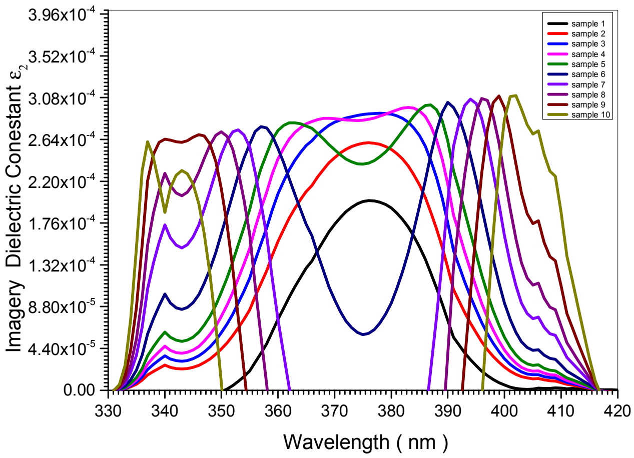

Figure 9. *The relation between imaginary dielectric conestant and wavelengths of polystyrene (cork) doped by aluminum oxide in different rate of molar (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 08, 0.9 and 1.0).*

Figure 9 shows the variation of the Imagery dielectric constant (ε_2) with wavelength of all samples prepared by polystyrene (cork) doped by aluminum oxide in different rate of molar, which calculated from the relation $\varepsilon_2 = 2nk$ Where the imaginary dielectric constant (ε_2) is the up-normal dielectric constant. From Figure 9 the variation of (ε_2) is follows the refractive index, where at wavelength ranged (335 to 410) nm for all samples of polystyrene (cork) doped by aluminum oxide in different rate of molar the maximum value of (ε_2) equal to (2.91×10^{-4}) at wavelength 375 nm, and the effect of the treatment by aluminum oxide in different rate of molar of the samples on the (ε_2) is shifted towards the red spectrum befor 375 nm and shifted towards the blue spectrum after 375 nm

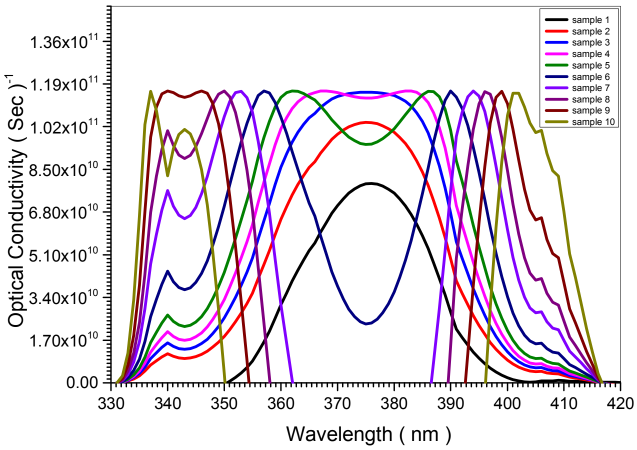

Figure 10. *The relation between optical conductivity and wavelengths of polystyrene (cork) doping by aluminum oxide in different rate of molar (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 08, 0.9 and 1.0).*

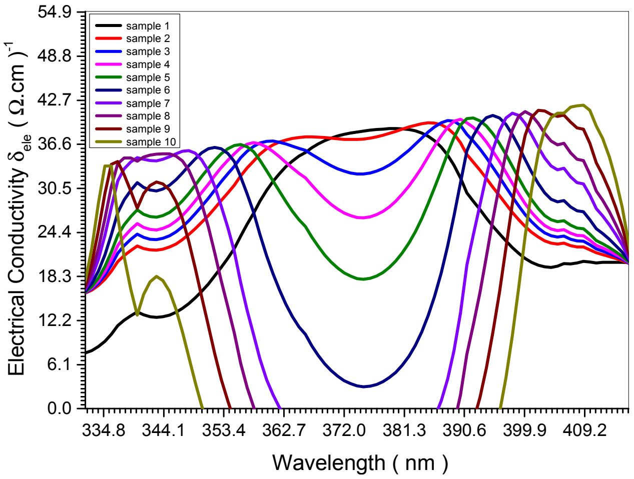

Figure 11. *The relation between electrical conductivity and wavelengths of polystyrene (cork) doping by aluminum oxide in different rate of molar (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 08, 0.9 and 1.0).*

Electrical and Optical Conductivity: The optical conductivity is a measure of frequency response of the material when irradiated with light which is determined using the following relation, $\delta_{opt} = \frac{\alpha n c}{4\pi}$ Where (c) is the light velocity. The electrical conductivity can be estimated using the following relation $\delta_{ele} = \frac{2\lambda\delta_{opt}}{\alpha}$. The high magnitude of optical conductivity (1.66×10^{11} sec^{-1}) confirms the presence of a very high photon response of the all polystyrene (cork) doped by aluminum oxide in different rate of molar. The increasing of optical conductivity at high photon energies is due to the high absorbance of polystyrene (cork) doped by aluminum oxide in different rate of molar, and may be due to electron excitation by photon energy as it is shown in Figures 10 and 11.

5. Conclusion

This study concluded that the polystyrene (Cork) as an insulating material that can be transformed into a semiconductor by doping it with Aluminum oxide, and since it is considered a cheap industrial and commercial waste and can be obtained easily, it can be a good addition in the field of manufacturing electronic devices such as diodes, transistor and integrated circuits. As well as the possibility of using it in solar cells.

6. Recommendations

1. Conducting the same study taking into account the change in the measurement of the thickness of samples in the Nano-scale boundaries by a fixed amount and noting the extent of this effect
2. Conducting the same study, taking into account the determination of the amount of solvent (benzene) for the cork material, and it shall be fixed for all samples.
3. Study the possibility of deforming the cork with a material other than metal oxides and see if it is possible to obtain a semiconductor from.

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