

Study the Optical Properties of Polyaniline-Multiwelled Carbon Nanotubes Nano Composite.

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Abstract

The study includes the recording of the spectrum of absorbance and transmittance for the blend solutions for polyanilin with carbon nanotube) and calculating the absorption coefficient and other optical constants. The samples have been prepared in different weight concentrations (0%,1%,3%,5%) (PANI- carbon nano tube). The values of absorbance, the refractive index values of pure polymer and its additives are increasing with the increase of the concentrations of these polymer, Noting that the increment of absorption coefficient values under the influence of addition caused by increasing density of the solutions as a result of the increased concentrations, that led to the increase of light absorbed because the interaction of the electromagnetic wave and the large molecules of the polymer increases with concentration, The results show that decreasing in the values of transmittance with all concentrations, the values of reflectance are increases with increasing concentration before and after the doping, the results showed decrease energy gap with increasing ratio of dopig.

Key words: Optical properties; Polyanilin; nanoThin films; Carbon nanotubes

الخلاصة:

هذه الدراسة تتضمن تسجيل طيف الامتصاصية والنفاذية لمزيج من محلول مركب من البولي انيلين مع انابيب الكربون النانويه المتعددة الأنابيب وتم حساب معامل الامتصاص والثوابت البصرية الأخرى. حضرت هذه العينات لعدة تراكيز مختلفة (0%,1%,3,5%) من بوليمر (PANI) كمحلول ثم إضافة أنابيب الكربون النانوية للتراكيز أعلاه على التوالي، وأيضاً العينات عدت بطريقة مزج السوائل قبل وبعد التشويب. تزداد قيم الامتصاصية و قيم معامل الانكسار للبوليمر النقي والمواد المضافة لها تزايد مع زيادة تركيز البوليمر، ونلاحظ زيادة في قيم معامل الامتصاص تحت تأثير إضافة الناجمة عن زيادة كثافة المحلول نتيجة لزيادة التركيز، والتي أدت إلى زيادة امتصاص الضوء لأن التفاعل بين الموجات الكهرومغناطيسية والجزيئات الكبيرة يزداد مع زيادة التركيز، وأظهرت النتائج انخفاض قيم النفاذية مع جميع التراكيز. إن قيم الانعكاسية تزداد مع زيادة التركيز قبل وبعد التشويب، وأظهرت الأشكال بان فجوة الطاقة للانتقال المباشر المسموح تقل مع زيادة نسبة التشويب.

الكلمات المفتاحية: الخواص البصرية , بولي انيلين , اغشية رقيقة نانوية , انابيب الكربون النانوية .

1-Introduction

The polymers are insulating materials electric , but this image has changed after the discovery made by each of the (Heeger) and (MacDiarmid) and (Shirakawa) who reached the possibility of modification of polymeric materials to become a good conducts electricity like metal material [Salaneck *et al.*, 1991]. The polymer (poly-aniline), one of conductive polymers which received much attention in recently because of its optical properties and electrically similar to the connectors [Elmansouri *et al.*, 2007]. The poiyaniline (PANI) exists in a variety of forms that differ in chemical and physical properties, The most common green protonated emeraldine has conductivity on a semiconductor level of the order of 10^0 S cm^{-1} , many orders of magnitude higher than that of common polymers ($<10^{-9} \text{ S cm}^{-1}$) but lower than that of typical metals ($>10^4 \text{ Scm}^{-1}$). Protonated PANI, (e.g., PANI

hydrochloride) converts to a nonconducting blue emeraldine base when treated with ammonium hydroxide,
 Figure. 1 [Stejskal and Gilbert, 2002].

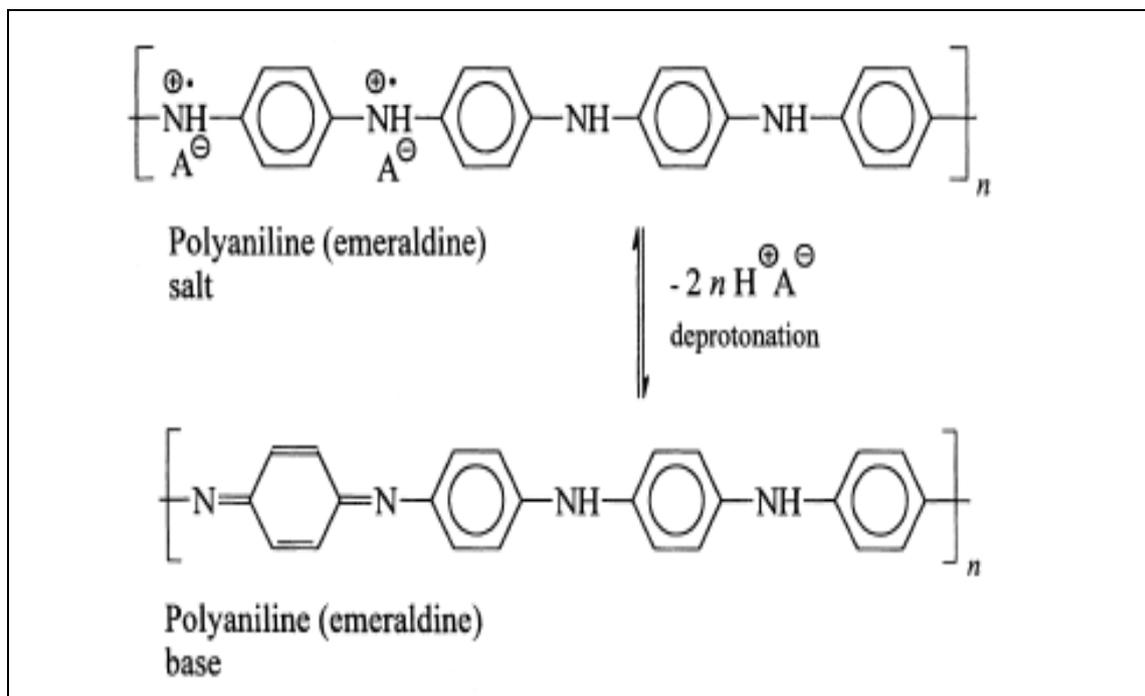


Figure. 1 Polyaniline (emeraldine) salt is deprotonated in the alkaline medium to polyaniline (emeraldine) base. A–is an arbitrary anion, e.g., chloride [Stejskal and Gilbert, 2002].

Polyanilin is one of the most investigated conducting polymers, due to its high chemical and thermal stability and the ease of polymerization, together with the relative low cost of production it alsohas the potential of many technological applications [Al-Mashhadani et al., 2014]. The poly-aniline enters in many applications, as shown in figure.2 [Abdulla and Abbo, 2012].

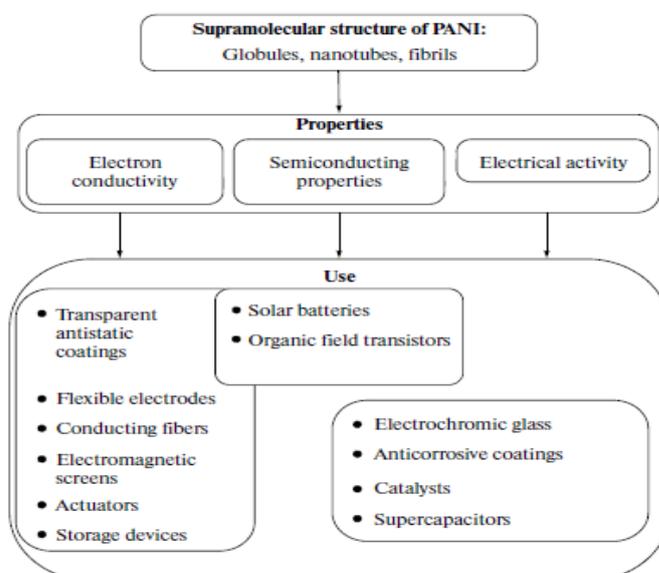


Figure 2: Application of poly-aniline.

2-Carbon nanotube

In which the atoms are connected in a three-way curved foils a vicious form cylinder is obtained Carbon arc with the change of energy in order to become a continuous stream rather than AC, and thus can be obtained the tubular structures in a sediment on the pole [Smalley, 2003]. These pipes consisting entirely of carbon, and has named nanotubes, due to the diameter of a few nanometers. There are many ways to produce nanotubes composed of carbon molecules, which are:

a- Action electrical analysis using electrodes Table Ravit in molten salts, b- Thermal catalyst for hydrocarbon analysis and c- Evaporation of graphite using a laser [Pantano, 2008]. In addition, depending on the working methods of the nanotubes, have different electronic properties, some are expected to be a metal while others are semiconductors. It turns out that these nanotubes are incredibly strong it Hundreds of times stronger than steel, and partly due to the geometric hexagon shape, which can distribute Forces and deformations due to the strength of the Commonwealth of carbon-carbon, as well as, consequently has the properties of electronic unusual [Pantano, 2008].

Carbon nanotubes have been used in many areas such as automotive fuel tanks industry, Tennis rackets, golf, skiing and sticks on the snow, and the coating of military materials that are not detected by radar. One of the new applications of nanotechnology, nano-carbon component of the ink tube is a ink was developed By Dr. Lee Jin Wong of the Korea Institute of Electrical Technology Research. The technique is highly developed It includes coating plastic surfaces so the ink to make a thin surface able to conduct electricity. It can be applied this technique on a variety of areas, including touch screens and displays foldable [Smalley, 2003].

3- Experimental Part

3.1- The materials used in the search

- a Conductive polymer (polyanilin)
- b. Slides of glass
- c. Carbon nano-tubes

3. 2- Prepare polymer

The polymer preparation in a way(polymer addition) has been dissolve (0.16) of the polymer in 50 ml of material (DMV), and then the solution is placed on the magnetic mixer and stir well to dissolve the article.

3. 3- Prepare thin films

Thin films were prepared by deposition of material on pieces of glass after Tndifaa well, and be a sedimentation process using a spin coating method.

3.4- Prepare the solution used for doped

To prepare the membranes are vestiges addition amount of carbon nano-tubes to the solution to form the two percentages by weight (1%, 3%, 5%), where the ratio of carbon nano-tubes are added (0.000016,0.000048,0.00008) respectively, and that the films thickness is 40 nm using electronic measuring device.

4- Optical measurements

The absorbance and transmittance for solutions were measured by using a device measuring the spectrum, made by (Shemadzo) company, Japan, type (Double-Beam Spectrophotometer (UV-1800)) where the range of wavelengths is (200-700) nm. A computer programmer make scanned for all wavelengths and gave the value of wavelength that occurs in it a greatest absorption.

5. Theoretical calculations

5.1- Absorbance

Absorbance defined as the ratio between absorbed light intensity (I_T) by material and the incident intensity of light (I_o) [Mwolfe *et al.*, 1989].

$$A = \log \frac{I_o}{I_T} \quad (1)$$

The optical absorbance coefficient (α_{op}) of solution and film is given by the equation [Abdulla and Abbo, 2012]:

$$\alpha_{op}=2.303A/d \quad (2)$$

where (d) represent a thickness of sample.

The ratio (I / I_o) called (Transmittance), (T_r) connected with absorbance by equation [Mwolfe, 1989]:

$$T_r = e^{-2.303A} \quad (3)$$

5.2-Refractive Index (n)

The refractive index can be given by the equation [Reddy, 2010]:

$$n = \frac{c}{v} \quad (4)$$

where defined as a ratio between the speed of light in a vacuum (c), to the speed of light in a medium (v) .

The values of refractive index were measured practically then applied in equation depending on the reflectance and the extinction coefficient (K_n) as shown in the following equations [Nahida, 2012; , Saeed and Suhail, 2012]:

Then, refractive index will be:

$$n = \sqrt{\frac{4R}{(1-R)^2} - K^2} + \frac{1+R}{1-R} \quad (5)$$

5.3 -Reflectance (R)

The reflectance can be represented depending on the value of refractive index by the equation [Nahida, 2012]:

$$R = \frac{(n-1)^2 + K_{n2}}{(n+1)^2 + K_{n2}} \quad (6)$$

Reflectance also can be obtained from absorption and transmission spectrum in accordance to the law of conservation of energy by the relation [Nahida, 2012]:

$$R + T + A = 1 \quad (7)$$

when light radiation passes from one medium into another having a different index of refraction, some of the light is scattered at the interface between the two media even if both are transparent.

Since the index of refraction of air is very nearly unity. Thus, higher index of refraction of the solid, greater is the reflectivity. For typical silicate glasses, the reflectivity is approximately (0.05). Just as the index of refraction of a solid depends on the wavelength of the incident light, so the reflectivity varies with wavelength. Reflection losses for lenses and other optical instruments are minimized significantly by coating the reflecting surface with very thin layers of dielectric materials such as magnesium fluoride (MgF_2) [Saeed and Suhail, 2012].

5. 4-Extinction Coefficient (K_n)

Extinction coefficient (k_o) given by following equation:

$$k_o = \alpha_{op} \lambda / 4\pi \quad (8)$$

where (λ) is the wavelength of incident photon.

It represents the imaginary part of complex refractive index (n^*): The extinction coefficient represents the amount of attenuation of an electromagnetic wave that is traveling in a material, where it values depend on the density of free electrons in the material and also on the structure nature [Tintu *et al.*, 2010]:

$$n^* = n - i k_o \quad (9)$$

where: n , the real part of refractive index. n^* : complex refractive index which depends on the material type, crystal structure (particle size), crystal defects and stress in the crystal.

5.5- Electronic Transitions

The optical data were analyzed from the classical relation for near optical absorption in semiconductor [Chopra, 1969]

$$\alpha = A[(hf - E_g)^r / hf] \quad (10)$$

where (f) is the frequency is plank constant and r is the ($1/2, 3/2, 2, 3$) for transition (direct allowed, direct forbidden, indirect allowed and indirect forbidden, respectively). A is a constant and E_g is defined as the optical energy band gap between the valence band (V.B) and the conductive band (C.B). The type of transition depends on the absorption coefficient value when α value is larger than (10^4cm^{-3}). The transition called (direct transition) where electron moves from V.B to C.B with the same wave vector (k), and momentum are conserved . while ,indirect transition occurs when the value of absorption coefficient is less than ($10^4 .\text{cm}^{-3}$) [Jamal *et al.*, 2008], where the electrons transferred from V.B to C.B at the same wave vector (k) .the momentum and energy must be conserved with phonon assistant [Abdulla and Abbo, 2012].

6. Results and Discussion

6.1 -FT-IR Test

The polymers were characterized by (FTIR) spectroscopy as a powder, the (FTIR) spectra were recorded. The figure 3, showed that the presence of the expected function groups, for example the band at (3134) related to stretching group of (NH) exist in compound, band at (3080) can be assigned to the stretching (C-H) Aromatic,

the emergence of several peaks between (1562 - 1490) related to bending group of (C=C) aromatic.

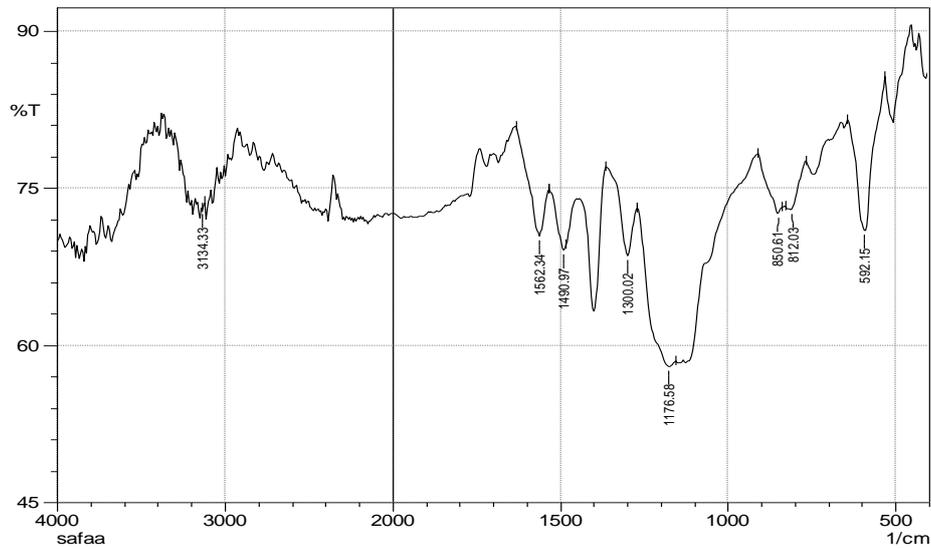


Figure 3: FT-IR spectra of (PANA)

6.2-Absorbance Spectrum

Absorbance measurements of (PANA) before and after doping, were plotted as a function of wavelength, as shown in figure 4. This figure shows that the absorbance of pure polymer and its additives are increasing with the increase of the concentrations of carbon nanotubes.

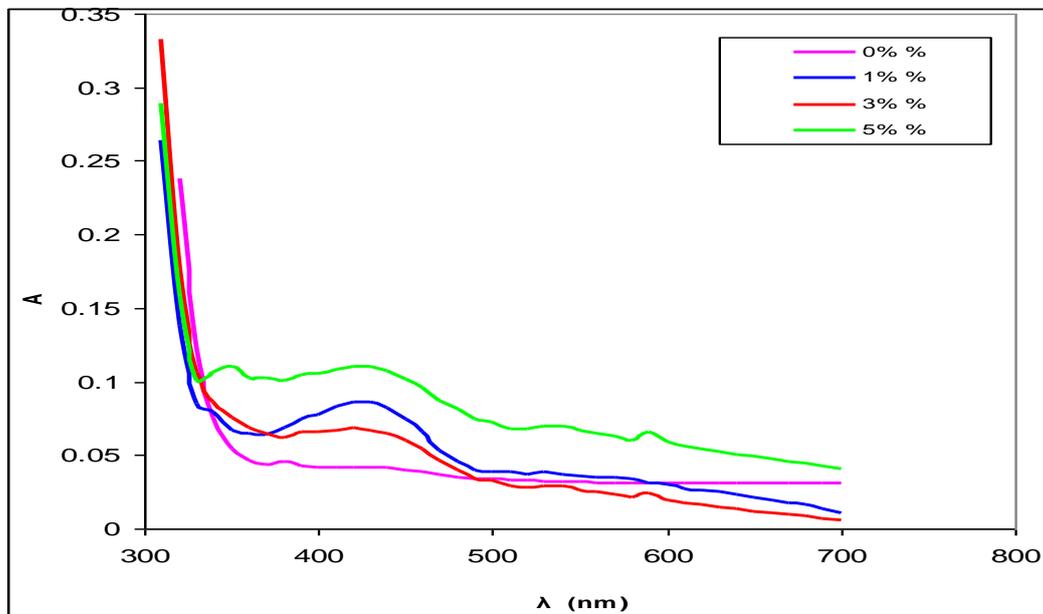


Figure 4: Absorbance VS with different wavelengths for (PANI + CNT).

Figure (4) represent the relation between the absorbance with wavelengths for pure PANI and doped for different ratio of doping. We can note from this figure, the values of absorbance increase when concentration increase, because the absorbance is

directly proportional with concentration according to the Lambert-Beer law, this is because the addition led to increase the values of concentration in same volume, then increase the number of particles that absorb the energy of incident light according to the Lambert-Beer law, this is agreement with [Nahida and Mohammed, 2015] .

6.3-Refractive Index

The measured values of refractive index of (PANI) before and after doping (are shown in figures (5 and 6).

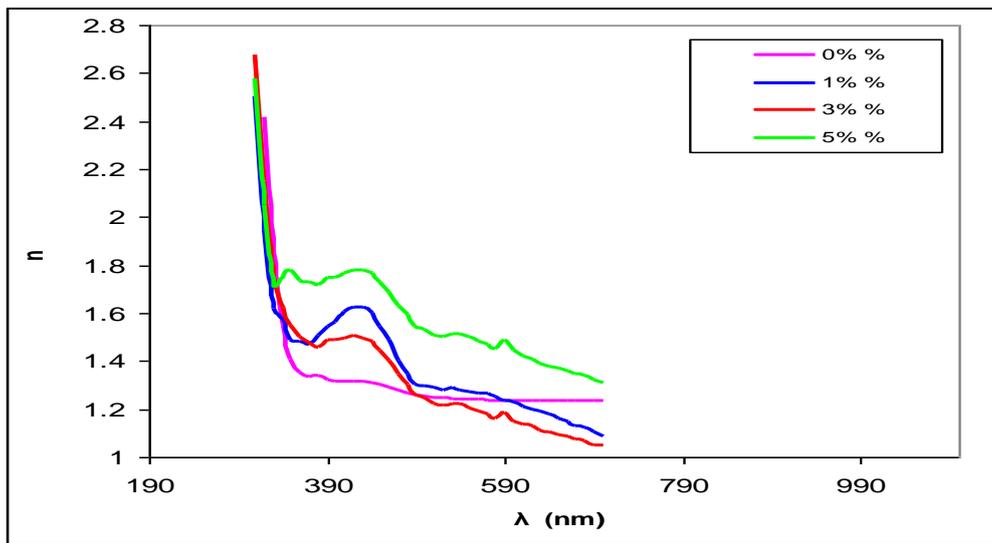


Figure 5: Refractive index VS as a function of wavelengths of (PANI) before and after CNT doping

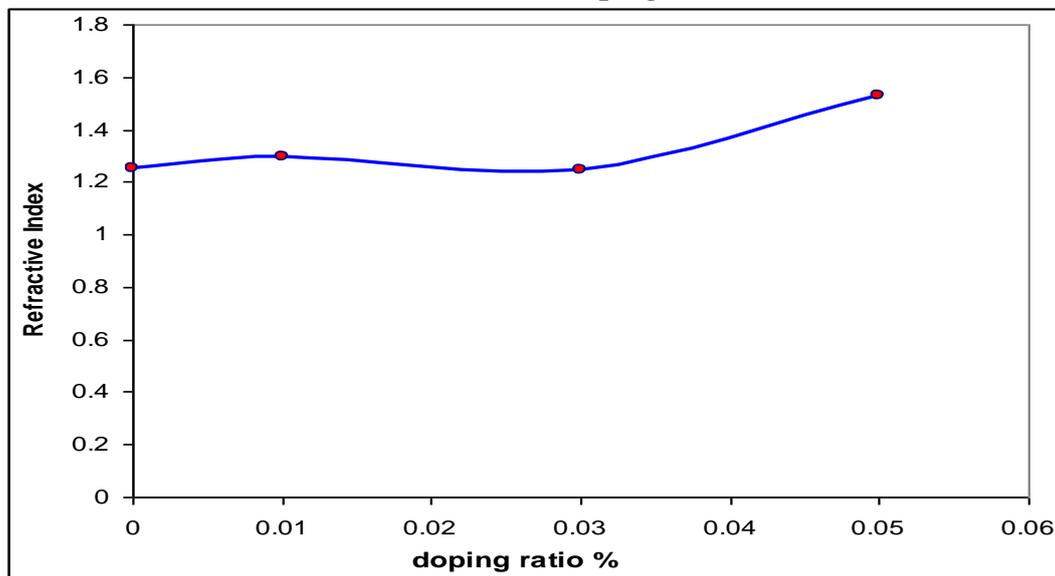


Figure 6: Represent the relation between the Refractive index VS with doping ratio.

The figure shows that the refractive index values of pure polymer and its doping are increasing linearly with the increase of the concentrations of doping ratio.

6.4- Absorption Coefficients

The values of α for all thin films are found to be greater than 10^4 cm^{-1} in the visible region, which means that the films have a direct optical energy gap[18]. The variation of the absorption coefficient (α) of (PANI)films is shown in Figures (7 and 8) as a function of wavelength.

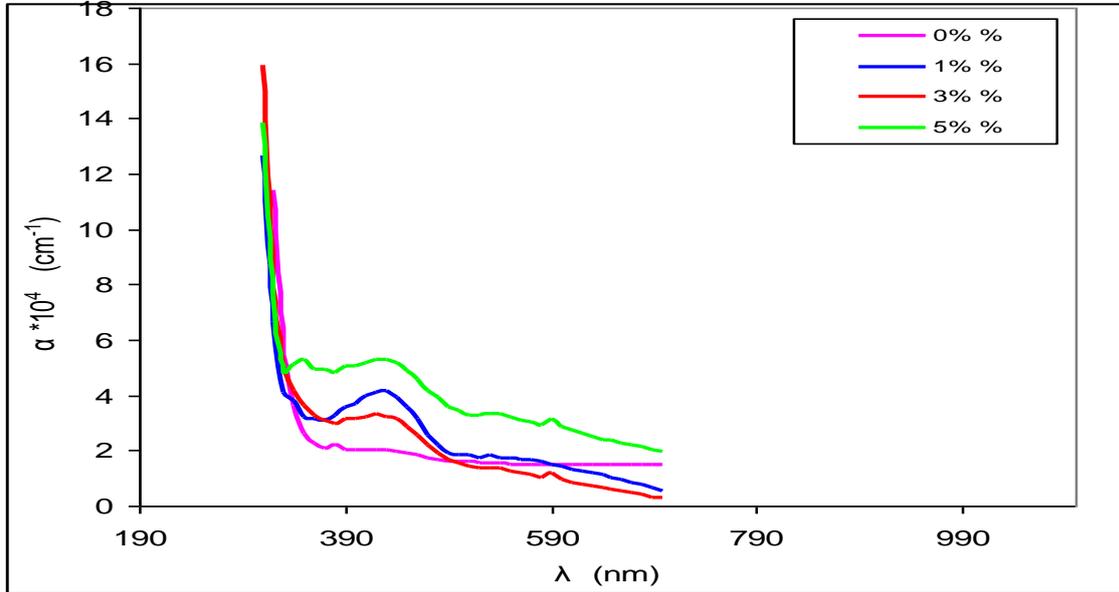


Figure 7: Absorption Coefficients as a function of wavelength for (PANI) before and after CNT doping

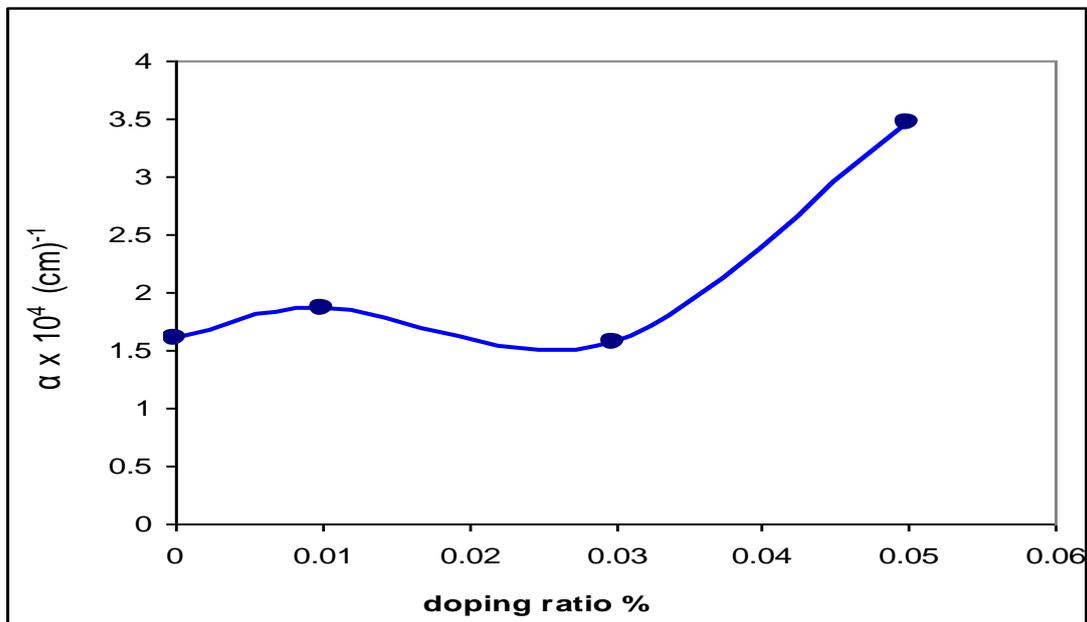


Figure 8: Represents the relation between the Absorption Coefficients (α) with doping ratio

6.5- Direct energy gap

According to equation (14) the optical band gap determined from the plot of $(\alpha hf)^2$ versus photon energy is shown in figure (9 and 10).

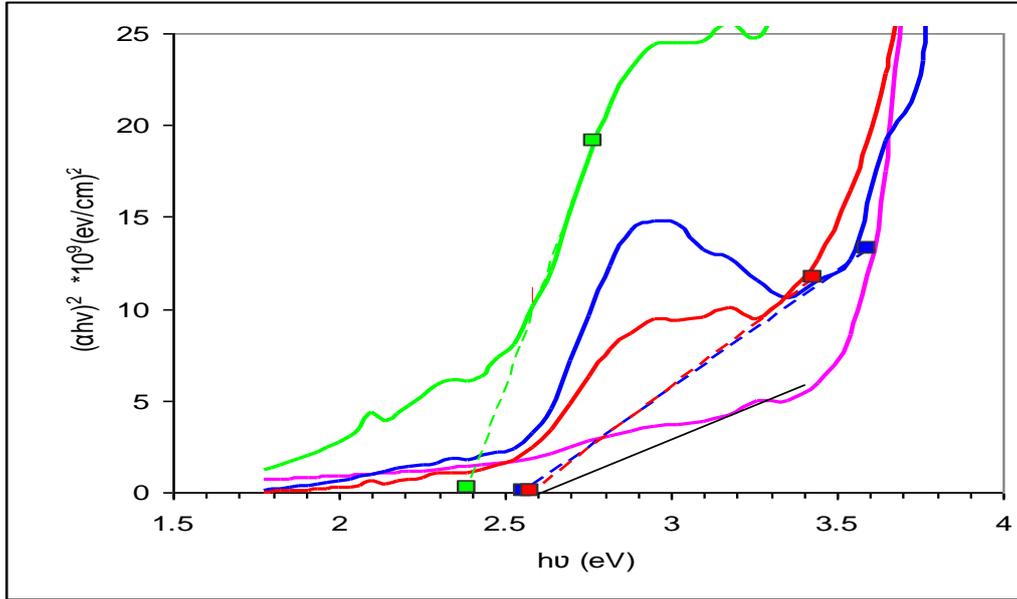


Figure 9: The relation between $(\alpha hf)^2$ versus photon energy

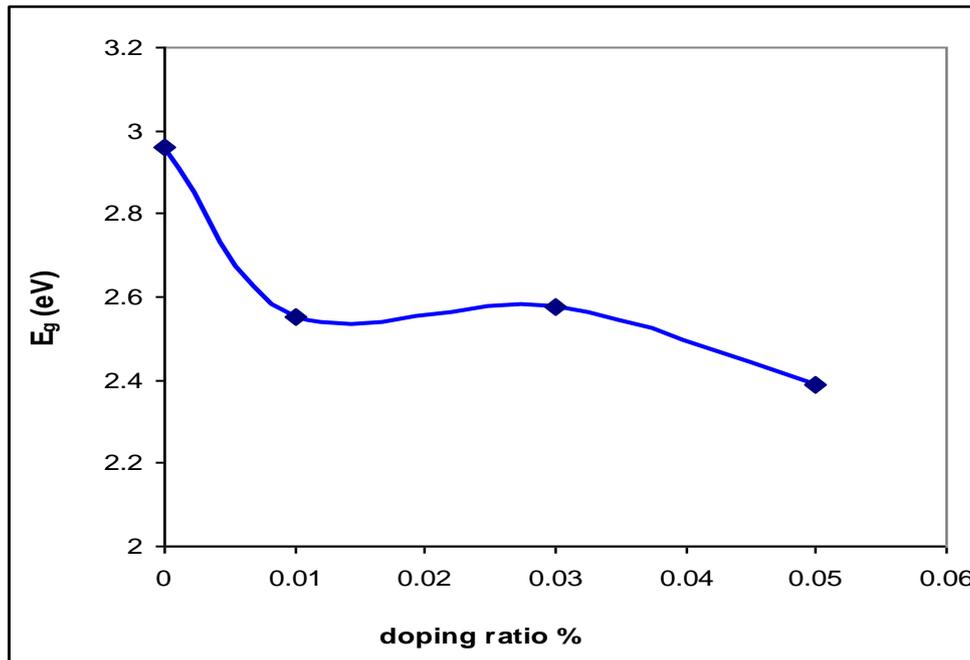


Figure 10: The relation between E_g and doping ratio

6.6 – Extinction Coefficient:

The measured values of Extinction Coefficient (K_n) of (PANI) before and after doping are shown in figures (11,12).

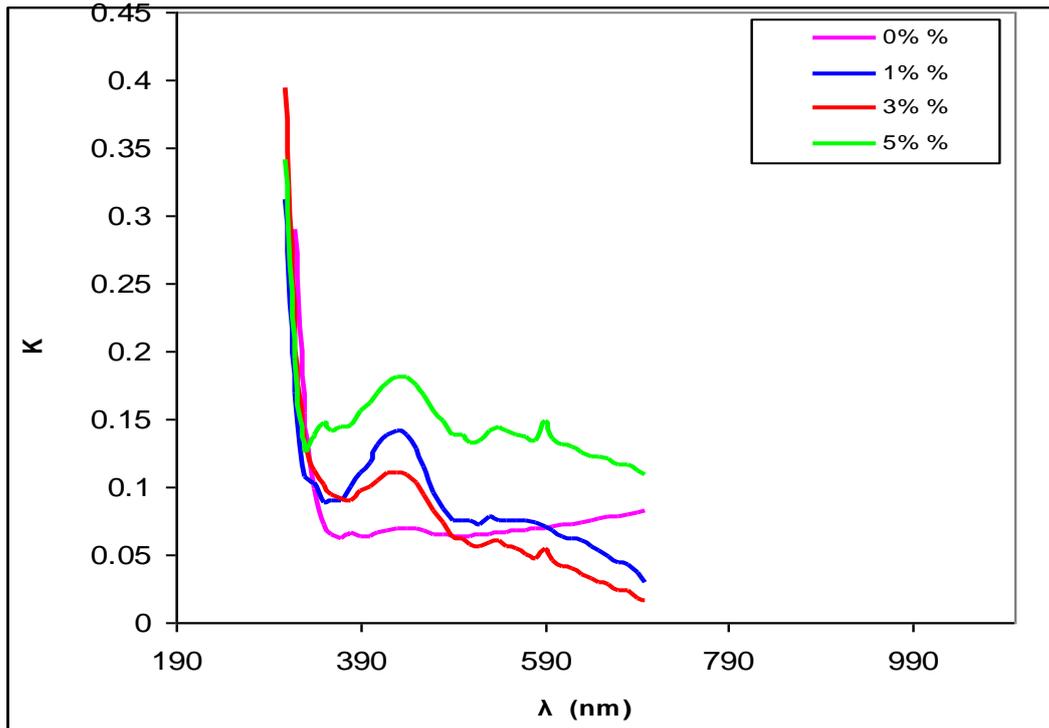


Figure 11: Extinction Coefficients as a function of wavelength for (PANI) before and after(CNT) doping.

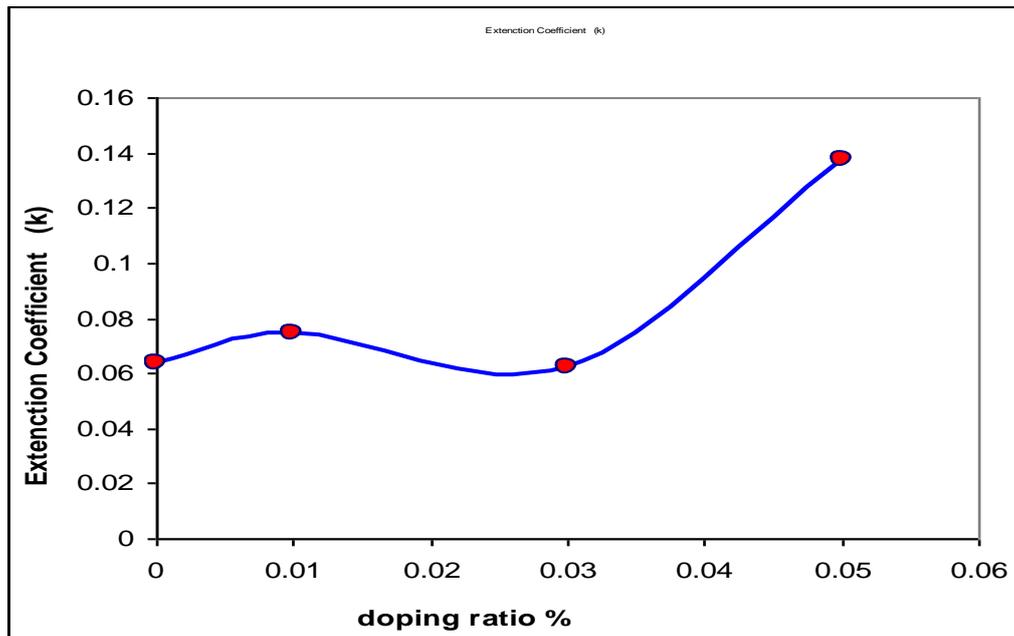


Figure 12: Represents the relation between the Extinction Coefficients (K n) with doping ratio.

The figure shows that the Extinction Coefficients values of pure polymer and its doping are increasing linearly with the increase of the concentrations of doping ratio.

6.7- Real and Imaginary Parts of Dielectric constant:

The real and imaginary of Dielectric Constant of (PANI) before and after doping (are shown in figures (13 and 14)).

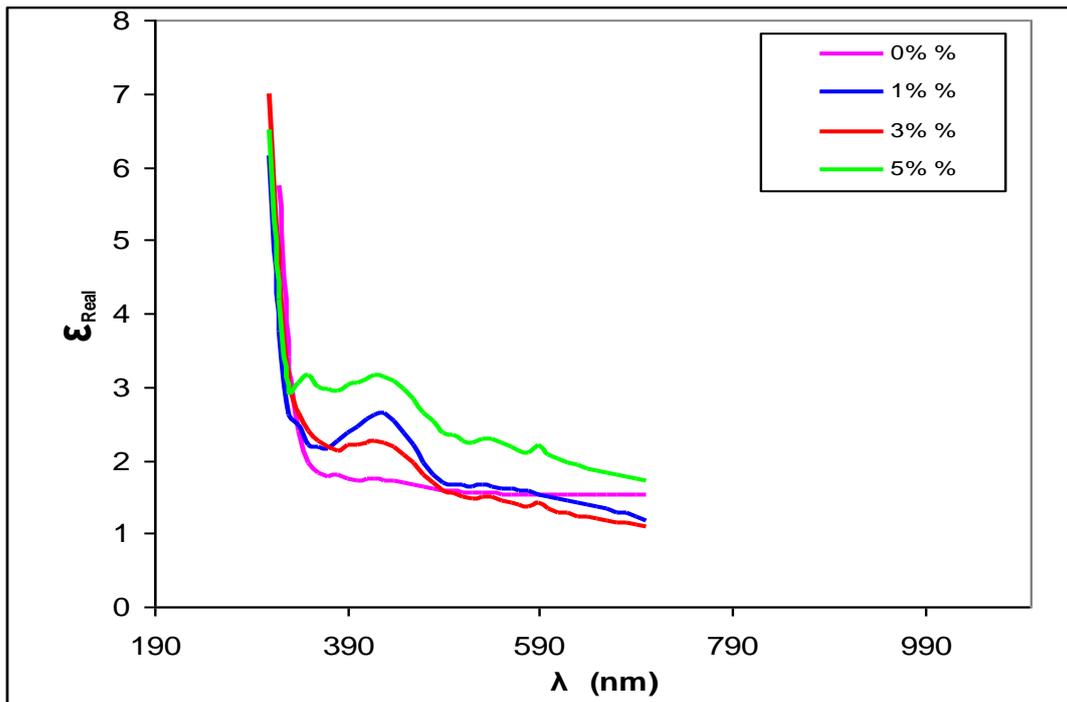


Figure 13: The real dielectric constant as a function of wavelength for (PANI) before and after doping

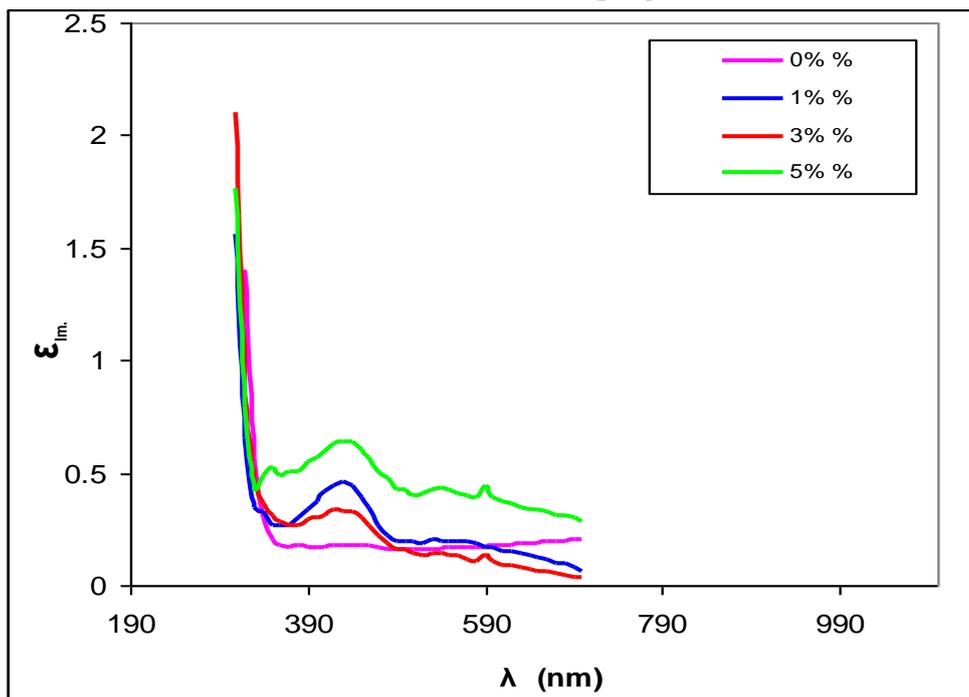


Figure 14: The imaginary dielectric constant as a function of wavelength for (PANI) before and after doping.

From the Figure (13,14) note that the real part of the dielectric constant changes are similar to the refractive index change and the imaginary part is dependent on (k_n) .

7. Conclusions

The summarized results from this work are the following:

1. It is found through the study that these polymers appear a continuous change in the optical properties as a result of adding (carbon nanotube) to the polymer
2. The addition of carbon nanotube to (PANI) led to the improvement optical properties.

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