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Study the Optical Properties of Polyaniline-PEDOT Nano Composite

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Abstract

The study includes the recording the absorption and permeability spectra of a combination of polyaniline compound solution with poly(3,4-ethylenedioxythiophene) PEDOT and calculating the absorption factor and other optical constants. These samples were attended to different concentrations (0.01%,0.02%,0.03%) of PEDOT added to polyaniline. 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 doping.

***Keywords**: Optical properties; Polyaniline; Nano thin films; PEDOT*

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 polymer materials to become a good conducts electricity like metal material [1]. 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. 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^{10} S cm^{-1}) many orders of magnitude higher than that of common polymers ($<10^{-9}$ S cm^{-1}) but lower than that of typical metals ($>10^{4}$ S cm^{-1}). Protonated PANI, (e.g., PANI hydrochloride) converts to a nonconducting blue emeraldine base when treated with ammonium hydroxide, Figure(1) [4] .

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 also has the potential of many technological applications [2]. The poly-aniline enters in many applications, as shown in figure (2)[3].

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2. Poly (3,4-ethylenedioxythiophene)PEDOT

PEDOT, poly(3,4- ethylene dioxy thiophene) [1], is a conductive polymer [5] that can be used in many different applications such as antistatic coating of polymers and glass, high conductive coatings, organic LED-(OLED) displays [6], nano-fiber electrodes for cell stimulation [7], solar cells, cathode material in electrolytic capacitors, printing wiring boards [8], textile fibres with colour changing properties, transparent electrodes for thick-film electroluminescence, source gate and drain in the rapidly developing organic semi-conductors field[10].

2.1 Advantages of PEDOT

For PEDOT, there are many advantages besides the environmental-friendliness mentioned above. Since synthetic biodegradable sutures were first approved by the US Food and Drug Administration (FDA) in the 1960s, polymers prepared from lactic acid have been found useful in the medical industry,Secondly, PEDOT was reported to have better processibility than ot her biopolymers, and is therefore widely used as packing materials, Moreover, the production of PEDOT is also energy saving compared to petroleum-based polymers, Due to these unique properties, PEDOT plays a significant role in biodegradable polymers.[9]

3. Experimental Part

3.1 The materials used in the search

a Conductive polymer (polyanilin)
b. Slides of glass
c. PEDOT

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 (chloroform), 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 Clean samples, 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 Poly (lactic acid) to the solution to form the two percentages by weight (97%, 98%, 99%), where the ratio of PEDOT are added (0.01,0.02,0.03)% respectively, and that the films thickness is 75 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) [9].

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

The optical absorbance coefficient α_{op} of solution and film is given by the equation [5]:

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

where (d) represent a thickness of sample.

The ratio (I / I_o) called (Transmittance), (T_r) connected with absorbance by equation [6]:

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

5.2 Refractive Index (n)

The refractive index can be given by the equation [7]:

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

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

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 [8]:

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 [8]:

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

Reflectance also can be obtained from absorption and transmission spectrum in accordance to the law of conservation of energy by the relation.

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

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) [9].

5.4 Extinction Coefficient (K_n)

Extinction coefficient (k_o) given by following equation (8).

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

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 [10]:

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

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 [3]

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

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, A respectively 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 ($10^4 cm^{-3}$). 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}.cm $^{-}$3) [5], 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[1].

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.

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) 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 [7].

6.3 Refractive index

The measured values of refractive index of (PANI) before and after doping (are

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.

6.5 Direct energy gap

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

6.6 Extinction Coefficient

The measured values of extinction coefficient (K n) of (PANI) before and after doping are shown in figures (11,12).

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).

From the Figures (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).

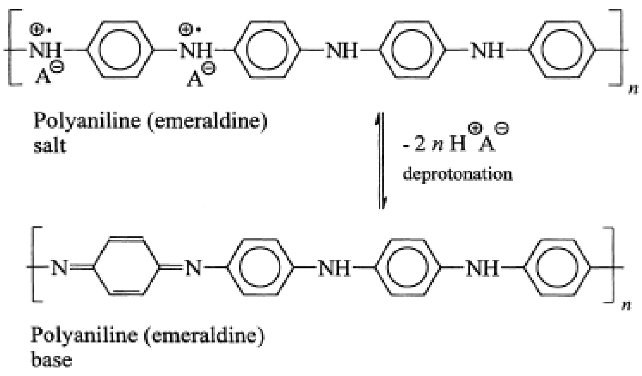

Figure 1: Polyaniline (emeraldine) salt is deprotonated in the alkaline medium to polyaniline (emeraldine) base. A– is an arbitrary anion, e.g., chloride[4]

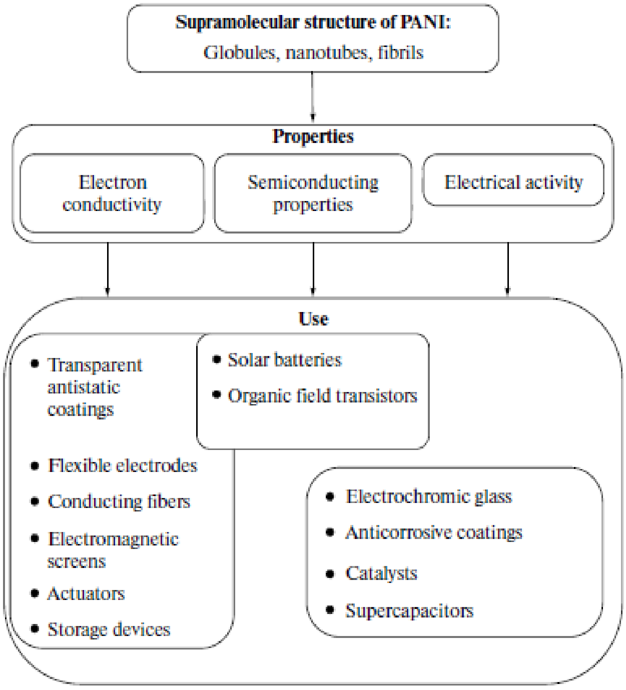

Figure 2: Application of poly-aniline)[3]

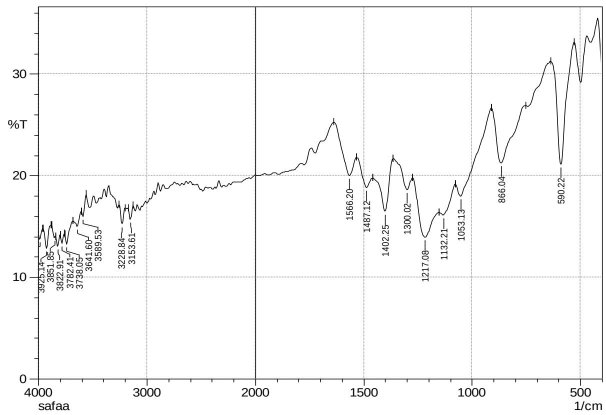

Figure 3: FT-IR spectra of (PANI)

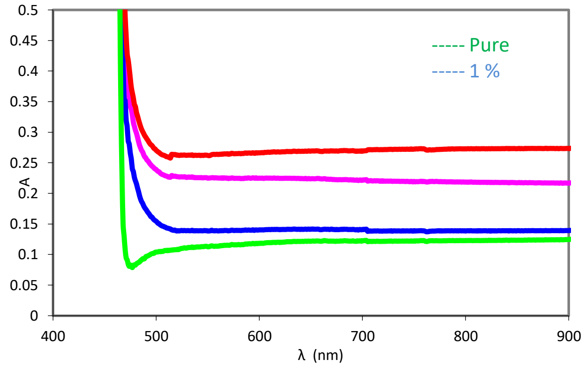

Figure 4: Absorbance with different wavelengths for (PANI + PEDOT)

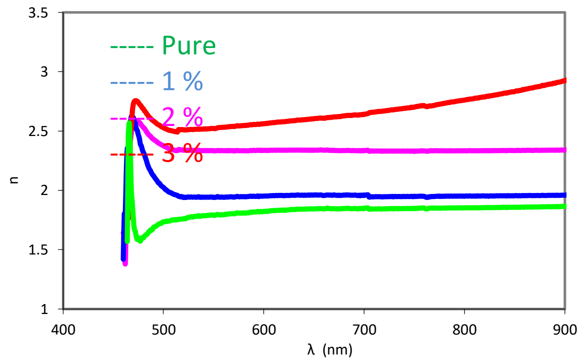

Figure 5: Refractive index as a function of wavelengths of (PANI) before and after PEDOT doping

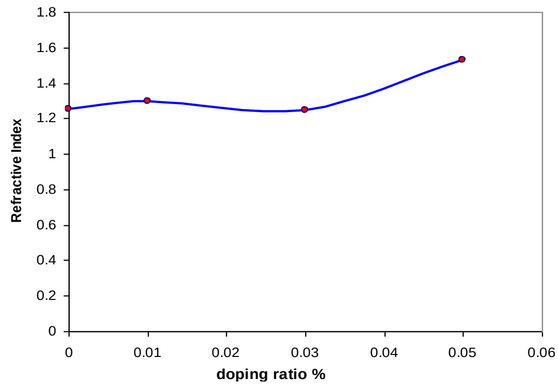

Figure 6: Represent the relation between the refractive index with doping ratio

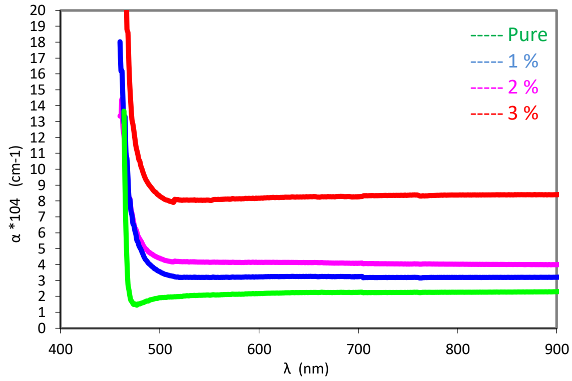

Figure 7: Absorption Coefficients as a function of wavelength for (PANI) before and after PEDOT do ping

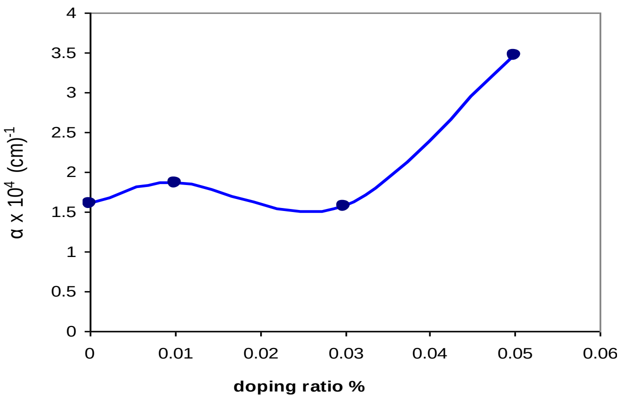

Figure 8: Represents the relation between the absorption coefficients (α) with doping ratio

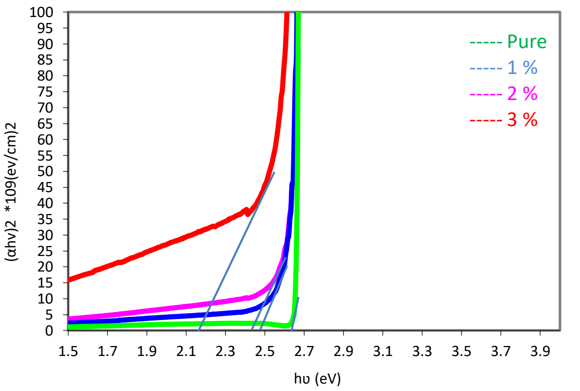

Figure 9: The relation between (αhf)^{2}versus photon energy

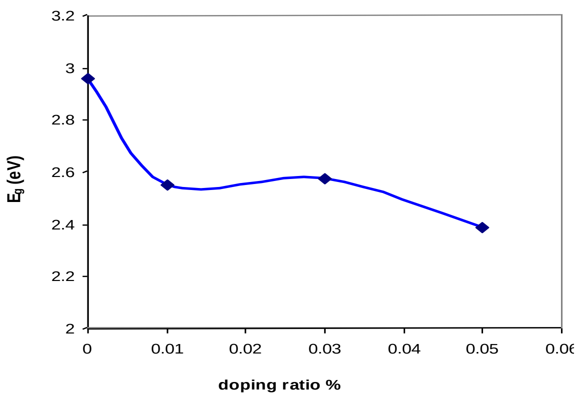

Figure 10: The relation between E_g and doping ratio

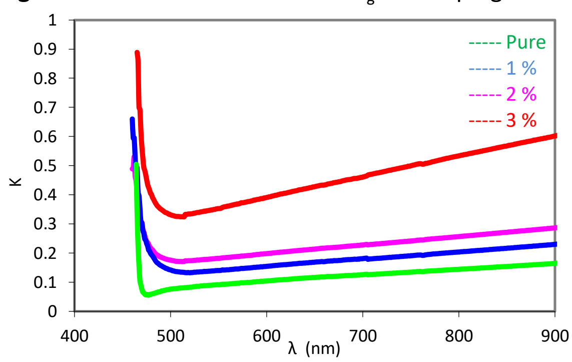

Figure 11: Extinction Coefficients as a function of wavelength for (PANI) before and after (PEDOT) doping

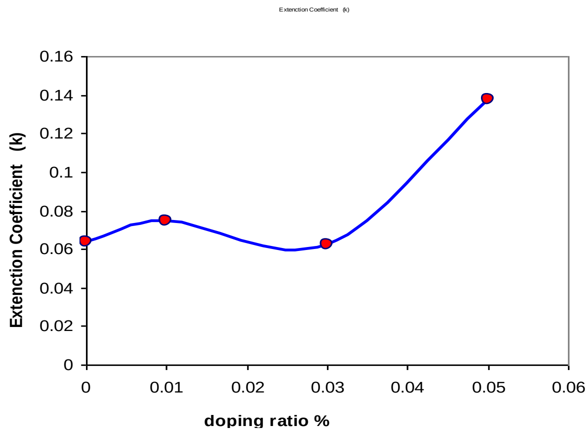

Figure 12: Represents the relation between the extinction coefficients (K n) with doping ratio

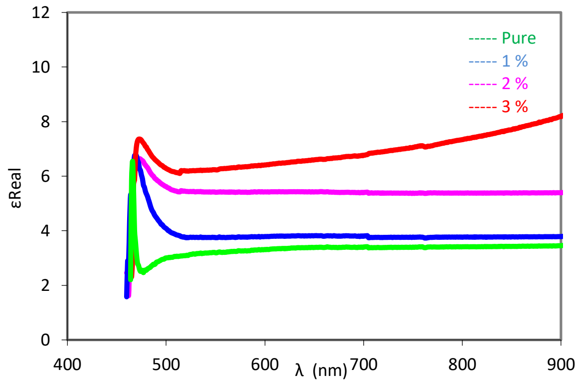

Figure 13: The real dielectric constant as a function of wavelength for (PANI) before and after doping

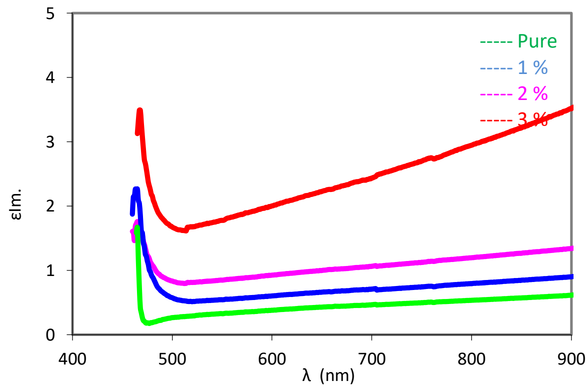

Figure 14: The imaginary dielectric constant as a function of wavelength for (PANI) before and after doping

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 PEDOT to the polymer

2. The addition, poly(3,4-ethylene dioxythiophene) to (PANI) led to the improvement optical properties.

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