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## OPTICAL PROPERTIES FOR PREPARED POLYANILINE/GRAPHENE NANO COMPOSITES FILMS

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### ABSTRACT

In this research Polymer Polyaniline (PANI) was synthesized by the chemical oxidative polymerization method. Optical properties for pure PANI synthesized and PANI/GR nanocomposite films with different weight percentage of Graphene (1%, 3%, and 5%) were investigated using UV-visible double beam spectrophotometer within spectral region (300-900) nm for two cases before and after doping. The experimental results show that the optical properties such as absorbance, reflection, absorption coefficient, extinction coefficient, refractive coefficient, dielectric Constants and optical conductivity increased with an increasing of the concentration of Graphene (GR), as well as the results indicate that the values of transmittance and optical energy gap for direct allowed transition decreasing from 3.52 eV to 3.23 eV with increasing ratio of doping.

**Keywords:** *Polyaniline , Graphene , Doping , Nano films , Optical properties.*

### 1. INTRODUCTION

Polymer materials have a great potential in many scientific and technological researchers because their wide applications due to their unique properties such as low density, ability to form intricate shapes, versatile electric properties, good mechanical strength and low manu factoring cost. The wide range of polymer applications can be even more extended by incorporation of doping into polymer may enhance different physical properties of the host polymer. The electrical and optical characteristics of selected polymer can controllably modified owing to the type of the doped material used, its concentration and the way in

which it penetrates and interacts with the chains of the polymer[1,2]. The conducting polymers are a new group of synthetic polymers, at first these synthetic polymers were considered as insulators, with the development of the idea of doping this

concept has been entirely changed. Polyaniline (PANI) is the most widely studied conducting polymer because of its facile synthesis, low synthetic cost, good environmental and thermal stability [3]. PANI can be easily prepared either chemically or electrochemically from acidic aqueous solutions [4]. On the other hand Graphene (GR) is a leading light on the horizon of technology especially in

chemistry, physics and materials science. Regardless of its short history, has already made known a large amount of its potential applications including field emission, electronics, electrical properties energy and sensor [5]. Recently, the doped polymers have been the subjects of interest for both theoretical and experimental studies, according to their physical and chemical properties needed for specific application may be obtained by adding or doping with some dopant.

## 2. THE EXPERIMENTAL WORK

### 2.1 The Materials

The raw material used to prepare the samples were: Graphene Nanopowder which number of Layers 10-15 Layers, Diameter 10-15 micron and thickness 10-15 nm. On the other hand the chemicals materials used in this work were listed in Table 1.

*Table 1: listed the chemical materials used in the work.*

| Material              | State              | Weight        | Chemical formula   | company                                 | Purity  |
|-----------------------|--------------------|---------------|--------------------|-----------------------------------------|---------|
| Aniline hydrochloride | Solid-white        | 129.59 g/mol. | $(C_6H_5NH_2.HCl)$ | supplied by Hopkin and Williams company | 99.99 % |
| Ammonium persulphate  | Solid-white        | 228.2 g/mol.  | $(NH_4)_2S_2O_8$   | supplied by B.D.H company               | 99.5 %  |
| Hydrochloric Acid     | Liquid - Colorless | 36.46 g/mol.  | HCl                | supplied by B.D.H-England company       | 37%,    |
| Acetone               | Liquid - Colorless | 58.08 g/mol.  | $(CH_3)_2CO$       | Scharlau (Spanish)                      | 99.5 %  |
| Dimethyl formamide    | Liquid - Colorless | 78.13 g/mol.  | $CH_3SO.CH_3$      | Sigma-Aldrich, P ristine.               | 100 %   |
| Graphene              | Solid -Black       | 12.01 g/mol.  | GR.                | U.K.                                    | 98%     |

### 2.2 Synthesis (PANI) Polymer

PANI was prepared by chemical oxidative polymerization method, using a method similar to that reported [6]. Pure PANI was prepared by dissolving of (2.59 g) of aniline hydrochloride ( $C_6H_5NH_2.HCl$ ) in (50 mL) of distilled water. Then Take (5.71g) from ammonium peroxydisulfate ( $(NH_4)_2S_2O_8$ ) that dissolved in (50 mL) of distilled water, (2.59 g) and (5.71g) values corresponding to (0.2M) and (0.25M) respectively. Both solutions were kept each separately for 1 hour at room temperature ( $\sim 18-24^\circ C$ ). Then the two solutions were then mixed in a beaker and stirred with a magnetic stirring bar, briefly stirred. The color change from colorless to dark green indicates the formation of PANI, and left at rest to polymerize. Next day, the PANI precipitate was collected on a filter paper, washed with three 100-mL portions of (0.2M) Hydrochloric Acid (HCl), and similarly with acetone. Polymer leaves for a full day (24 hours) to dry in air and then in vacuum oven at  $60^\circ C$ , finally PANI powder combines.

### 2.3 Synthesis The Solution used for Doped

After prepared Pure PANI solution as shown in section 2.2, prepared doped PANI solution with different doping ratio of GR (1%, 3% and 5%). GR solution was prepared by adding weight ratios of GR Powder ( 0.0017 , 0.005 and 0.0085 gm) and dissolved in 10ml of (DMF) solvent separately, and then solutions is placed on magnetic stirring for 2 hours. After allowing those to dissolve completely, the solutions were mixed of pure PANI solution and GR and they were prepared separately by using magnetic stirrer for 5 hours, the blend solution was kept into a clean glass bakery. We using the following equation to Calculate the Percentages for doping in the mixture [7].

$$W_t \% = \frac{W_{td}}{W_{td} + W} \times 100\% \quad (1)$$

Where,  $W_t$  % is Percentages for doping,  $W_{td}$  weight of GR Powder which taken in this work equaled to 0.0017 , 0.005 and 0.0085 g<sub>m</sub> and  $W$  weight of PANI Powder which taken in this work equaled to 0.16 g<sub>m</sub>

## 2.4 Synthesis Nano Films

Nano films were prepared by deposition of material on pieces of glass after Clean samples, and be a sedimentation process using a spin coating method. The nano film thicknesses which are prepared for this study are (67,45,43 and 40 nm) with spinning speed is (3000, 3500 ,4000 and 4500 rpm ) for pure PANI and doped PANI by ratios (1%, 3% and 5%) of GR respectively, while the spinning time is 30 seconds. Heat treatment include the prepared nano films were keeping at room temperature (R.T) about 24 hours to dry. However, there are several methods used for measuring thickness of the film, such as weight, optical, electrical and other methods. In our work the thickness of the nano films was measured by optical method and using electronic measuring device is called optical thin film measurement. This method is done by using Lambda (LIMF-10), this measurement system is easy to set up and the software is used friendly. It is suitable for both on-line manufacturing and desktop measuring with the ability to connect to your microscope to reduce the spot size or to dismantle for sole spectroscopic use. The color of PANI solution is green (acidic solution) without GR, the color of the solution changed from green to dark green with adding GR.

## 2.5 Optical Properties Evaluations

Optical parameters of the nano films deposited on glass slides were evaluated by using (shimadzu) company double-beam Spectrophotometer (UV-1800) in the wavelength range (300-900) nm. The spectroscopic behavior of materials is utilized to estimate their optical constants such as refractive index ( $n$ ), extinction Coefficient( $k$ ), real and imaginary of dielectric constants ( $\epsilon_r, \epsilon_i$ ). Several methods were proposed to estimate these optical constants, they involve evaluation:

### 2.5.1 Absorbance (A)

The absorbance ( $A$ ) is defined as the logarithm of the ratio between absorbed light intensity ( $I$ ) by material and the incident intensity of light ( $I_0$ ). ( $A$ ) can be determined from the following relation [8].

$$A = -\log T = \log \left( \frac{I_0}{I} \right) \quad (2)$$

Where, ( $I_0$ ) is the incident intensity of light. ( $I$ ) is intensity of the absorbed light at distance ( $x$ ).

### 2.5.2 Transmittance (T)

Transmittance( $T$ ) is given by the ratio of the intensity of the transmitting rays ( $I_T$ ) through the material to the intensity of the incident rays ( $I_0$ ) on it as follows[9].

$$T = I_T / I_0 \quad (3)$$

We can find ( $T$ ) as a function of wavelength through the exponential relationship for both absorbance and transmittance which [10].

$$A = \log(1/T) \quad (4)$$

$$T = 10^{-A} \quad (5)$$

### 2.5.3 Reflectance (R)

The reflectance (R) can be represented depending on the value of refractive index by the equation [11].

$$R = (n-1)^2 + k^2 / (n+1)^2 + k^2 \quad (6)$$

(R) also can be obtained from absorption and transmission spectrum in accordance to the law of conservation of energy by the relation [12].

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

### 2.5.4 Absorption Coefficient ( $\alpha$ )

The absorption coefficient ( $\alpha$ ) is defined as the ability of material to absorb the light of a given wavelength can be expressed by Lambert-Beer's law through the relation [13].

$$I = I_0 \exp(-\alpha t) \quad (8)$$

$$\alpha = (2.303/t) \exp(I_0/I) = (2.303/t) A \quad (9)$$

Where ( $I_0$ ) and ( $I$ ) are the intensities of incident and transmitted radiation respectively, ( $t$ ) is the thickness of the sample.

### 2.5.5 Extinction Coefficient (k)

The extinction Coefficient ( $k$ ) represents the imaginary part of complex refractive index ( $n^*$ ) [14].

$$N^* = n - ik \quad (10)$$

Where ( $n$ ) the real part of refractive index,  $N^*$ : complex refractive index which depends on the material type, crystal structure (grain size), crystal defects and stress in the crystal and ( $k$ ) Extinction coefficient, is given by following equation [14].

$$k = \alpha \lambda / 4\pi. \quad (11)$$

Where  $\lambda$  is the wavelength of incident photon rays. ( $\alpha$ ) Absorption coefficient.

### 2.5.6 Refractive Index (n)

Refractive Index ( $n$ ) is the ratio of light speed in vacuum  $C$  to its speed in a

medium  $V$ , The refractive index can be given by the equation [15].

$$n = c/v \quad (12)$$

The values of refractive index were measured practically then applied in equation depending on the reflectance and the extinction coefficient  $k$  as shown in the following equations. Then, refractive index will be [16].

$$n = \sqrt{\frac{4R}{(1-R)^2} - K^2} + \frac{1+R}{1-R} \quad (13)$$

### 2.5.7 Dielectric Constants ( $\epsilon_r, \epsilon_i$ )

Dielectric constant is defined as the response of the material towards the incident electromagnetic field. The dielectric constant of compound divided into two parts real and imaginary, and can be written as [17].

$$\epsilon = \epsilon_r + i\epsilon_i \quad (14)$$

Where  $\epsilon_r$  is the real part of the complex

dielectric constant,  $\epsilon_i$  is the imaginary part of it. For the estimation of the dielectric constant involve two parts, one can use the following expressions [18].

$$\epsilon_r = n^2 - k^2 \quad (15)$$

$$\epsilon_i = 2nk^2 \quad (16)$$

### 2.5.8 Optical Conductivity ( $\sigma_{op}$ )

The optical response of material is mainly studied in terms of the optical conductivity ( $\sigma_{op}$ ), which means the electrical conductivity results from the movement of the charge carriers due to alternating electric field of the incident electromagnetic waves. ( $\sigma_{op}$ ) can be expressed by the following equation [19].

$$\sigma_{op} = \alpha nc / 4\pi \quad (17)$$

### 2.5.9 Electrons Transitions

The photon absorption in many amorphous materials is found to obey the Tauc's relation [20].

$$\alpha h\nu = B(h\nu - E_g)^r \quad (18)$$

where  $E_g$  the optical band gap,  $\alpha$  the absorption coefficient,  $B$  is a constant proportion with the inverse of amorphousity, also is a constant known as the disorder parameter which is nearly independent of photon energy parameter,  $h$  is plank constant,  $\nu$  is the frequency of radiation,  $h\nu$  the energy of the incident photon, While index  $r$  is the order of the optical transition depending on the nature of electronic transition. The transition is called direct where electron moves from valence band (V.B) to conduction band (C.B) with the same wave vector ( $k$ ) i.e ( $\Delta k=0$ ), and momentum are conserved. While the transition is called indirect where the electrons transferred from V.B to C.B at the same wave vector ( $k$ ) but ( $\Delta k \neq 0$ ), the momentum and energy must be conserved with phonon assistant. The value of  $r$  may be discrete values such as  $1/2, 2, 3/2$  and  $3$  or higher corresponding to the allowed direct, allowed indirect, forbidden direct and forbidden indirect transition respectively. As well as  $\alpha$  help to know the nature of electron transition. If the values of absorption coefficient are high ( $\alpha > 10^4 \text{ cm}^{-1}$ ) lead to transition of electron are direct, and when the values of absorption coefficient are low ( $\alpha < 10^4 \text{ cm}^{-1}$ ) lead to transition of electrons are indirect [21].

samples were run in the wavelength range between  $4000 - 400 \text{ cm}^{-1}$ . The FT-IR spectra of synthesized pure PANI and PANI / GR nano films at different concentrations of GR ( 1% , 3% and 5% ) are presented in **figures 1(a,b,c and d)** respectively. **Figure 1(a)** represents FT-IR spectra of synthesized pure PANI. The characteristics peaks of PANI including broad peaks range  $3016.67 - 3417.86 \text{ cm}^{-1}$  corresponding to ( N-H stretching vibrations of secondary amine) and sharp peak at  $1560.41 \text{ cm}^{-1}$  (C=C stretching of quinoid ring (N=Q=N)),  $1413.82$  and  $1475.54 \text{ cm}^{-1}$  ((C=C stretching vibration of benzenoid ring (N-B-N)),  $1244.09$  ,  $1298.09$  (C - N stretching of secondary aromatic ring),  $1130.29 \text{ cm}^{-1}$  (Aromatic C-H in-plane bending vibrations ) ,  $611.43$ ,  $719.45$  and  $804.32 \text{ cm}^{-1}$  are attributed to (Aromatic C-H out-of-plane bending vibrations). The function groups at PANI agreement with [22,23]. The FT-IR spectrum, after added PANI with GR (PANI/GR) nanocomposites at different doping ratio (1% , 3% and 5% ) are shown in figures 1(b, c and d). From this figures that the intensity of emission is changed as it can be observed from the changed this is corresponding to each bond, while not noticed any change in the position of the bonds. The spectra information of PANI/ GR(1%, 3% and 5%) are presented in Tables below 2., 3. and 4.

## 3 RESULTS AND DISCUSSION

### 3.1 Fourier Transformer-Infra Red spectroscopy (FT-IR)

The new prepared PANI / GR nano films were identified by IR spectroscopy. The

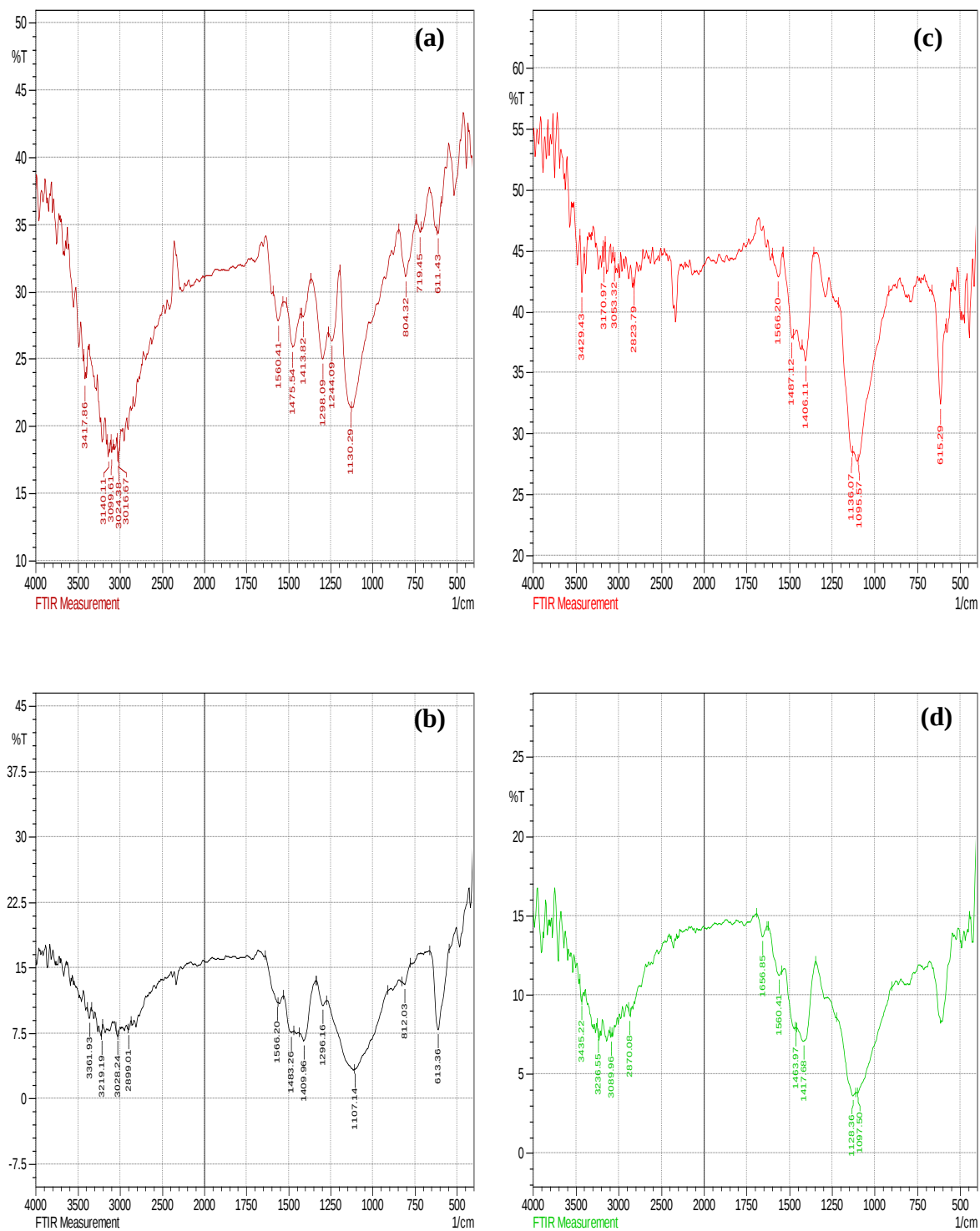


Figure 1(a, b, c and d): FTIR spectra of synthesized pure Polymer PANI and PANI/GR.

**Table 3: FT-IR Spectral data for PANI/GR(3%)**

| Vibration Bond range (cm <sup>-1</sup> ) | Observed Postion(cm <sup>-1</sup> ) | Expected vibrations                                    |
|------------------------------------------|-------------------------------------|--------------------------------------------------------|
| 600-900                                  | 615.29                              | Aromatic C–H out-of-plane bending vibrations           |
| 1000 – 1180                              | 1095.57 , 1136.07                   | Aromatic C–H in-plane bending vibrations               |
| 1400 -1480                               | 1406.11 , 1487.12                   | C=C stretching vibration of benzenoid (B) ring (N-B-N) |
| 1500-1600                                | 1566.20                             | C=C stretching of quinoid (Q) ring(N=Q=N)              |
| 2000-2900                                | 2823.79                             | C-H Vibration of CH <sub>2</sub>                       |
| 3000-3500                                | 3053.32 , 3170.97 , 3429.43         | N–H stretching vibrations of secondary amine           |

**Table 2: FT-IR Spectral data for PANI/GR(1%)**

| Vibration Bond range (cm <sup>-1</sup> ) | Observed Postion(cm <sup>-1</sup> ) | Expected vibrations                                    |
|------------------------------------------|-------------------------------------|--------------------------------------------------------|
| 600-900                                  | 613.36 , 812.03                     | Aromatic C–H out-of-plane bending vibrations           |
| 1000 – 1180                              | 1107.14                             | Aromatic C–H in-plane bending vibrations               |
| 1200 – 1300                              | 1296.16                             | C – N stretching of secondary aromatic ring.           |
| 1400 -1480                               | 1409.96 , 1483.26                   | C=C stretching vibration of benzenoid (B) ring (N-B-N) |
| 1500-1600                                | 1566.20                             | C=C stretching of quinoid (Q) ring(N=Q=N)              |
| 2000-2900                                | 2899.01                             | C-H Vibration of CH <sub>2</sub>                       |
| 3000-3500                                | 3028.24, 3219.19 , 3361.93          | N–H stretching vibrations of secondary amine           |

**Table 4: FT-IR Spectral data for PANI/GR(5%)**

| Vibration<br>Bond range<br>(cm <sup>-1</sup> ) | Observed<br>Postion(cm <sup>-1</sup> ) | Expected<br>vibrations                                          |
|------------------------------------------------|----------------------------------------|-----------------------------------------------------------------|
| 1000 – 1180                                    | 1097.50 ,<br>1128.36                   | Aromatic C–H<br>in-plane<br>bending<br>vibrations               |
| 1400 -1480                                     | 1417.68 ,<br>1463.97                   | C=C stretching<br>vibration of<br>benzenoid (B)<br>ring (N-B-N) |
| 1500-1600                                      | 1560.41 ,<br>1656.85                   | C=C stretching<br>of quinoid (Q)<br>ring(N=Q=N)                 |
| 2000-2900                                      | 2870.08                                | C-H Vibration<br>of CH <sub>2</sub>                             |
| 3000-3500                                      | 3089.96 ,<br>3236.55 ,<br>3435.22      | N–H stretching<br>vibrations of<br>secondary<br>amine           |

### 3.2 Absorption(A) , Transmittance(T) and Reflection(R) Spectra of Pure PANI and PANI/GR Blend Nano Composite Films.

The UV-VIS absorbance spectra for pure PANI synthesized and PANI/GR nano composite films samples at different doping ratios of GR ( 1% , 3% and 5%) are shown in figure (2-a).UV-Visible spectrum of pure PANI synthesized nano film shows two prominent peaks, the first a weaker absorption peak at 384 nm is attributed to the transition of electron from

the valance band(V.B) or highest occupied molecular orbital (HOMO) to conduction band (C.B) or lowest unoccupied molecular orbital (LUMO) which is related to  $\pi$  band  $\rightarrow \pi^*$  band electronic transition of benzenoid ring of PANI, while the second a broad absorption peak at 452 nm is attributed to polaron band  $\rightarrow \pi^*$  band transition of benzenoid ring to quinoid ring. These peaks have been assigned to transition from (V.B) to (C.B) and charge transfer between benzenoid and quinonoid rings due to free nonbonding electrons that can absorb relatively low energy radiation. The absorption bands that have been obtained from the UV-Visible spectra are in good agreement with that reported in the literature [24,25]. In UV-Visible spectrums for PANI/GR nano composite films at different concentrations of GR ( 1% , 3% and 5% ) are similar to those of PANI, no remarkable difference was observed compare with UV-Visible spectrum of synthesized pure PANI nano film except the shift in the absorption peaks for PANI/GR towards higher wavelength side (red shift) may be due to the increasing concentration of GR , the interaction between PANI molecules and GR and presence of the hydrogen ions in the doped PANI (protonation by the dopant) which may cause the shifting of the peak this indicate decrease in optical band gap for the doped films, this is agreement with [26, 27]. It is clear from the figure that the absorption spectra for all pure PANI synthesized and PANI/GR nano composite films decreased with the increasing of wavelength, while the absorption increased with increasing GR concentration ,because the absorption is directly proportional to the number of absorbing molecules, when increase doping ratio increasing number of particle which absorbed the energy of incident light by free electrons according to the Beer – Lambert law and coincides with the literature as well [28,29].The optical transmission spectra of the pure

PANI and PANI/GR nano composite films with different concentrations of GR are shown in figure (2-b). This figure shows that the transmittance intensity increases with the increasing of the wavelength, and as the concentration of GR increases, the transmittance decreases. This behavior is because of the form of covalent bonds between polymer chains and additives that decrease the transmitting of the incident light especially at the shortest wavelengths. The electrons in the outer orbits have travelled to the higher energy levels and have occupied vacant positions of energy bands. Thus, part of incident light does not penetrate through it. As well as The decreasing in transmittance with increasing the concentration of GR in blend, leads to a decrease in light scattering losses, the relationship between the reflectance and wavelength is shown in figure (2-c). The reflectance increases with increasing the GR concentration because the surface roughness average, grain size and crystalline defects for all nano film for synthesized pure PANI and doped PANI increased with increasing doping ratio, this is agreement with [30, 31].

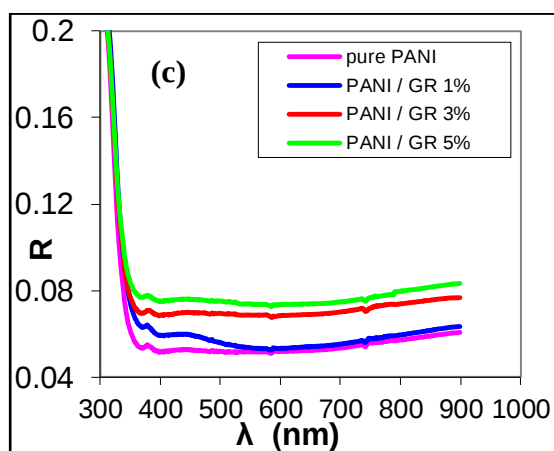
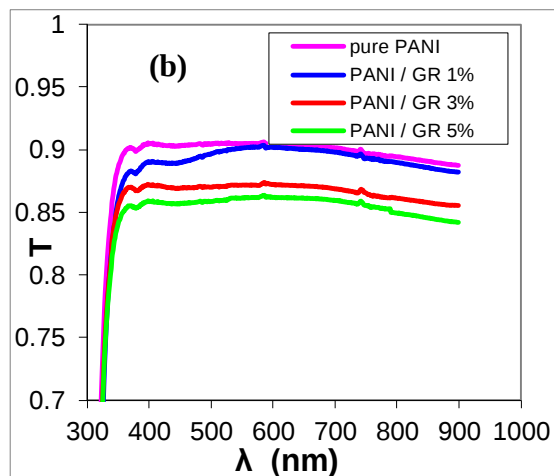
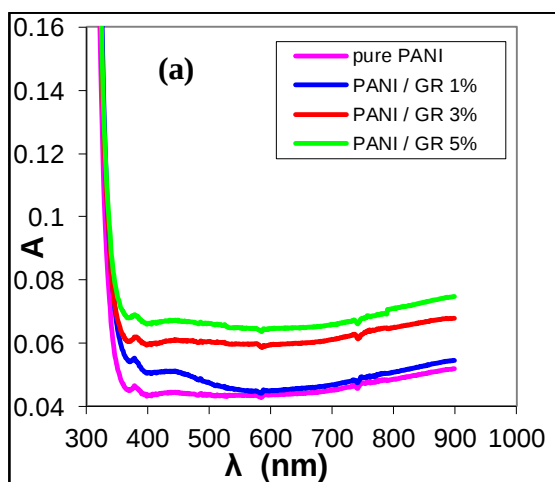


Figure 2: (a) Absorption, (b) transmittance and (c) reflectance spectra as a function of wave length for pure PANI and PANI/GR Nano composite films.

### 3.3 Absorption Coefficient Spectra of Pure PANI and PANI/GR Nano Films.

The absorption coefficient  $\alpha(\text{cm}^{-1})$  is calculated by using equation (9) Figure (3) shows  $\alpha(\text{cm}^{-1})$  as a function of wavelength for the prepared all nano composite films. The obtained results showed that the values of  $\alpha$  for pur PANI and PANI/ GR all nano composite films are found to be greater than  $10^4 \text{ cm}^{-1}$  in the visible region , which means that all the nano composite films have allowed direct optical energy gap, so that the value of  $r$  in equation ( 18 ) is equal to  $\frac{1}{2}$  ,similar results are reported in literature [32, 33].

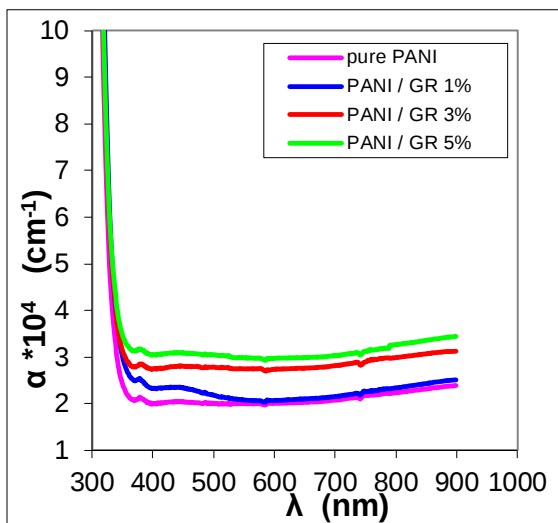


Figure 3: The variation of absorption coefficient versus wavelength for pure PANI and PANI/GR Nano composite films.

### 3.4 Extinction Coefficient Spectra of Pure PANI and PANI/GR Nano Films.

The extinction coefficient ( $k$ ) is determined by using equation (11). The relationship between ( $k$ ) and wavelength of the nanocomposite films are shown in figure (4). It can be clearly seen that ( $k$ ) increase as the doping percentage of GR increased, this may be attributed to high absorption coefficient and increase of absorb part of the incident light, this is agreement with [34].

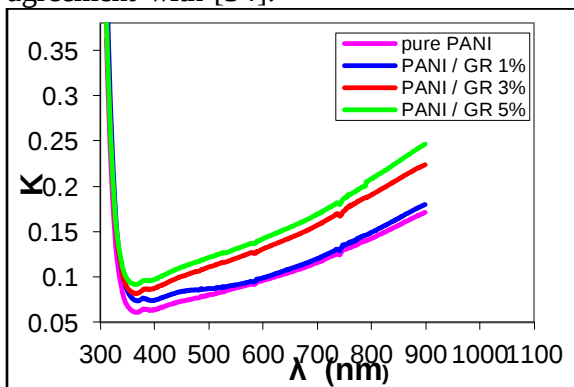


Figure 4: The variation of extinction coefficient versus wavelength for pure PANI and PANI/GR Nano composite films.

### 3.5 Refractive Coefficient Spectra of Pure PANI and PANI/GR Nano Composite Films.

Figure(5) illustrates the values of refractive coefficient ( $n$ ) as a function of the wavelength ( $\lambda$ ) for pure PANI and PANI/GR nanocomposite films. It is found that the values of ( $n$ ) decreasing with increasing wavelength as well as the values of ( $n$ ) for all nano composite films increasing with increase of the concentrations of doping ratio, this behavior can be explained on the basis of that increasing GR which in turn increase propagation velocity of light through them, in general,  $n$  increases by increasing the C – H bonds, similar results are reported in literature [35, 36].

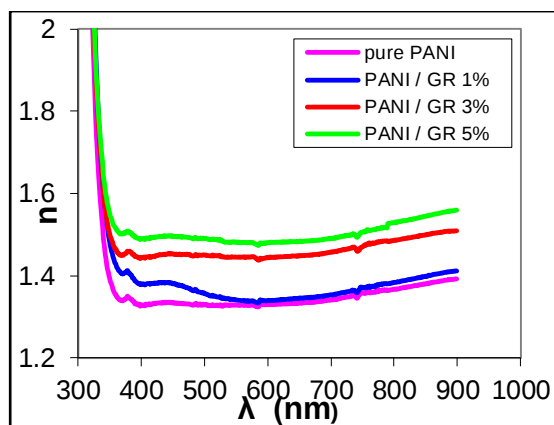


Figure 5: The variation of refractive coefficient versus wavelength for pure PANI and PANI/GR Nano composite films.

### 4.6 Dielectric Constants of Pure PANI and PANI/GR Nano Composite Films.

The real  $\epsilon_r$  and imaginary  $\epsilon_i$ . Parts of the dielectric constant as a function of wavelength are shown in figure 6 (a and b) for pure PANI and PANI/GR nano composite films at different concentration of GR. The variation of ( $\epsilon_r$ ,  $\epsilon_i$ ) with the wavelength of the incident radiation is due to the change of reflectance and

absorbance.  $\epsilon_r$  is calculated by using equation (15). It is clear that the variation of  $\epsilon_r$  mainly depends on the values of reactive index ( $n^2$ ) as a result of small values of extinction coefficient ( $k^2$ ) in comparison with ( $n^2$ ) and because the effect of extinction coefficient is very small may be canceling, while the imaginary part of dielectric  $\epsilon_i$  is calculated by using equation (16), because the refractive index is very small. It can observe that the variation of  $\epsilon_i$ . Mainly depends on the variation of ( $k$ ) values which are related to the variation of absorption coefficient  $\alpha$ . Pure PANI nano film sample values is very few change up to 300 nm to 900 nm. After adding GR impurity for samples 1%, 3%, and 5%, the imaginary part increases for all wavelengths up to 300 nm to 900 nm and with increasing GR concentration percentage. That result was agreement with [37, 38].

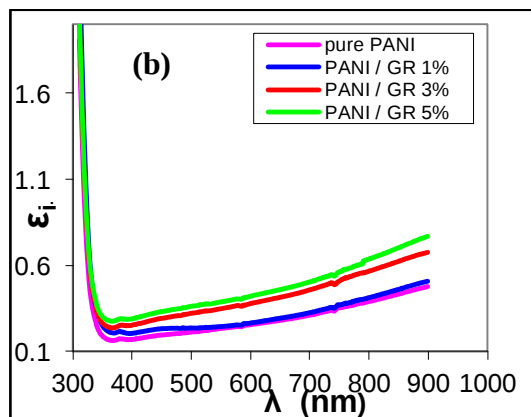
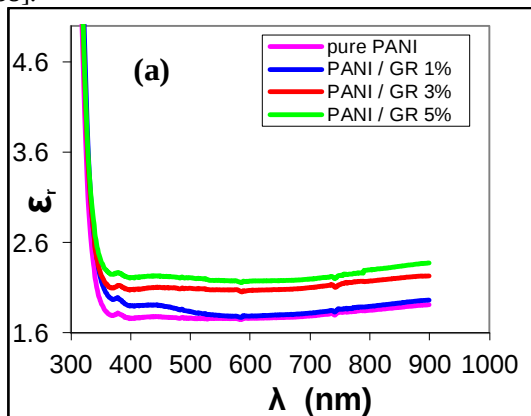


Figure 6: (a)  $\epsilon_r$  real dielectric constant (b)  $\epsilon_i$  imaginary dielectric constant. As a function of wave length for pure PANI and PANI/GR Nano composite films.

### 3.7 Optical Conductivity of Pure PANI and PANI/GR Nano Films.

The optical conductivity ( $\sigma_{op.}$ ) is determined by using equation (17). An increase was observed in optical conductivity as increasing in doping percentages of GR as shown in Figure (7). This may be due to increase the contribution of electron transitions between the valence and conduction bands, which lead to reduction of energy gap as a result of sit level generation. Similar results are reported in literature [39, 40].

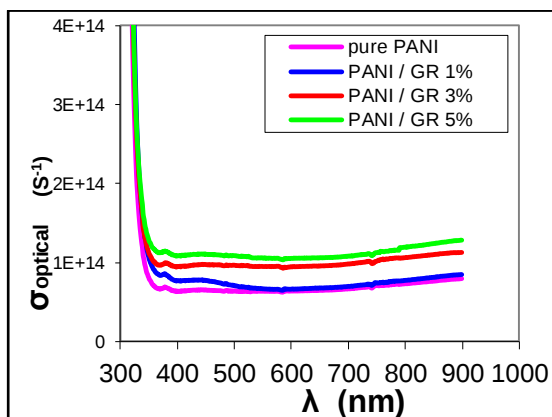


Figure 7: The variation of optical conductivity versus wavelength for pure PANI and PANI/GR Nano composite films.

### 3.8 Optical Energy Gap

The direct optical energy gap ( $E_g$ ) was calculated by using the relation (18) with  $r = 1/2$ . The experimental results to calculate the energy gap  $E_g$  according to Tauc relation, where  $(\alpha h\nu)^2$  is plotted against the photon energy ( $h\nu$ ), then  $E_g$  has been extracted by extrapolating the straight portion of the graph on  $h\nu$  axis at the value  $(\alpha h\nu)^2 = 0$ . Nano films prepared found that it has allowed direct energy gap, and from the Figure 8 (a,b,c and d), the values of  $E_g$  the pure PANI synthesized and

PANI/GR(1%,3% ,5%) nano composites films are listed in Table 5 respectively. Figure(9) shows allowed direct energy gap as a function of different weight ratio of GR. The curve show that the energy gap decrease with increasing the weight rate of doping (GR) which means a rising in conductivity, because the doping create polaron states (new levels) in band gap and that is increase with increase doping, which lead to smooth the transition of electrons from (the valence band (VB)-highest occupied energy level) to these local levels to the (conduction band(CB)-lowest occupied energy level), thus the band gap decrease. That result was agreement with[ 41,42 ].

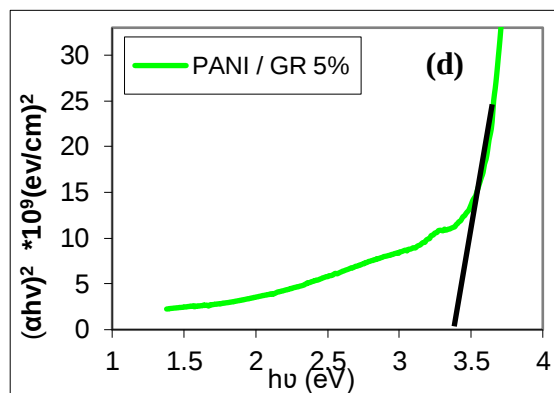
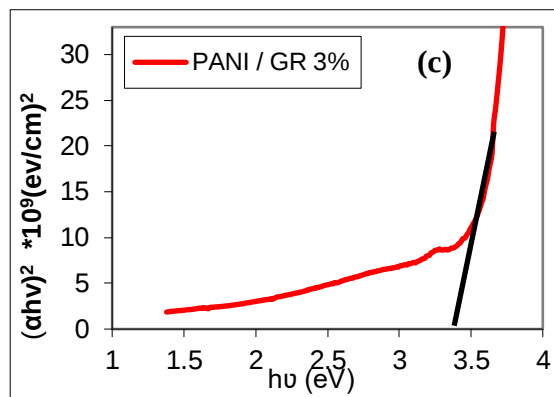
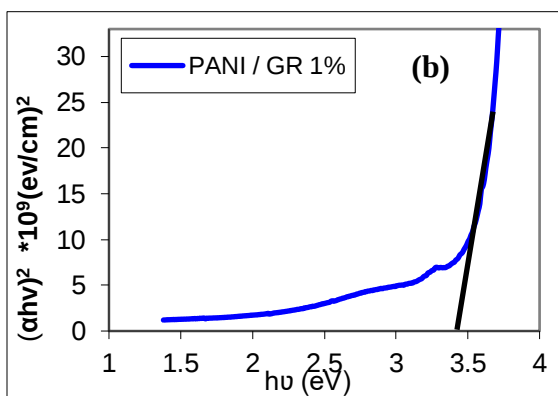
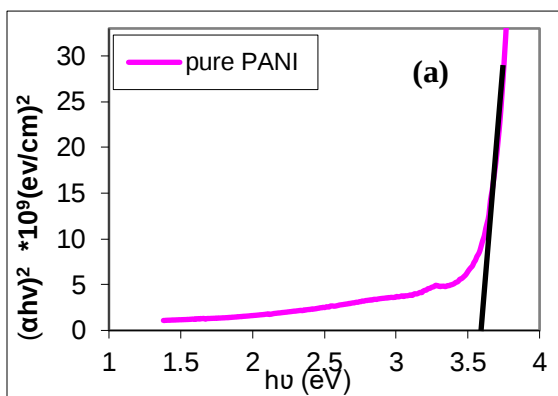


Figure 8: (a, b, c and d) respectively show the variation of  $(\alpha h\nu)^2$  as a function of  $h\nu$  for pure PANI synthesized and PANI/GR Nano composites films.

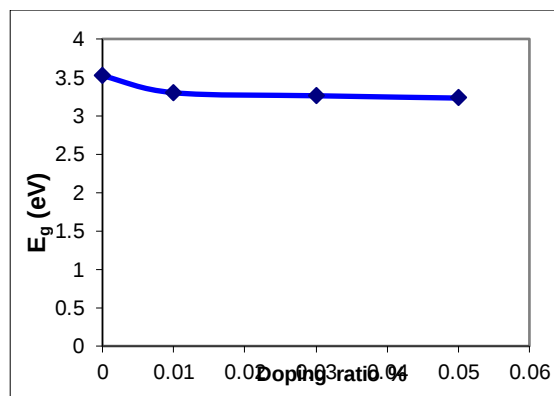


Figure 9: The variation of  $E_g$ (eV) versus doping ratio of GR for pure PANI and PANI/GR.

**Table 5:  $E_g(e_v)$  values for pure PANI synthesized and PANI/GR Nano composites films.**

| Compound  | $E_g (e_v)$ |
|-----------|-------------|
| Pure PANI | 3.52        |
| PANI/GR1% | 3.30        |
| PANI/GR3% | 3.26        |
| PANI/GR5% | 3.23        |

#### 4. CONCLUSION

The summarized results from this work are the following:

1-It is found through the study that this polymer appear a continuous change in their physical properties (optical) as a result of adding GR. to PANI polymer.

2- The optical band gap of pure PANI synthesized is higher than that of (PANI/GR) nano composite.

3- Measurement of optical energy gap and optical parameters such as refractive index and dielectric constants are strongly depending on the light wavelength and different doping ratios of GR.

4-The electronic transition in pure PANI synthesized and PANI/GR nano composites indicated direct allowed transition, All samples have allowed direct optical energy gap.

5- The maximum optical energy gap value is about 3.52 eV for pure PANI synthesized nano film and decreasing within range (3.52 – 3.23 ) eV when concentration of GR increased in nano composite samples.

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#### الخصائص البصرية للأغشية النانوية المحضرة لمركبات البوليانيلين/كرافين

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#### الخلاصة

في هذا البحث تم تحضير بوليمير بولي انيلين (PANI) بطريقة البلمرة بالاكسدة الكيميائية . الخواص البصرية للأغشية النانوية المحضرة النقية PANI و المشوبة بالكرافين (PANI/GR) مع نسب وزنية مختلفة من الكرافين (1%, 3%, and 5%) تم تشخيصها باستخدام مطياف الحزمة المزدوجة UV-visible ضمن المنطقة المرئية nm (300-900) لحالتين قبل وبعد التشويب. النتائج العملية وضحت بان الخواص البصرية على سبيل المثال الامتصاصية ، الانعكاسية ، معامل الامتصاص ، معامل الخمود ، معامل الانكسار ، ثوابت العزل والتوصيلية البصرية تزداد مع زيادة تركيز الكرافين (GR) ، كذلك النتائج اشارت بأن قيمة النفاذية وفجوة الطاقة البصرية للانتقال المباشر المسموح تقل من 3.52 الكترون فولط الى 3.23 الكترون فولط مع زيادة نسبة التشويب.

**الكلمات المفتاحية:** بولي انيلين ، الكرافين ، التشويب ، الاغشية النانوية ، الخصائص البصرية.