

# Preparation and study of the optical properties and dielectric properties of the Polyaniline doped Graphene and poly (vinyl alcohol)

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## Abstract: -

In this research, a poly-aniline polymer (PANI) was prepared using chemical oxidation polymerization method, and then it was doped with nano-graphene (GR) and poly (vinyl alcohol) (PVA), each separately with different weight ratios. The optical properties were studied through UV-vis (1800) Spectrophotometer within the range (300-900 nm) to measure the absorption, transmittance, reflection, refractive index, extinction coefficient, partial dielectric constant (real and imaginary), indirect energy gap, is estimated to be (3.02-3.60) eV. Used to determine X-ray diffraction the grain size and Interfacial distances of pure poly-aniline (PANI) samples, doped graphene (PANI / GR) and poly (vinyl alcohol) (PANI/PVA).

**Key words:** Poly -aniline, graphene, poly (vinyl alcohol) optical properties, dielectric parameters

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## I. Introduction

In general, each class of polymer has its own characteristics, and there is one feature that most of the polymers observed have in common being an electrical insulator. In contrast, the conductive polymers have the ability to conduct electricity, same as the metals such as copper, Aluminum, and iron [1,2]. A lot of conductive polymers have an array of potential applications in the optoelectronics devices and in the micro-electronics industry such as diodes, field-effect transistors [3], light-emitting diodes [4] photovoltaic Cells [5] electrical capacitance [6] as well as sensors [7-8] among these polymers is polyaniline, in the recent polyaniline has several compounds and blends as well as many derivatives which need to achieve the required conductivity for given applications. The most necessary domain applications of conductor blends is in static material conductors of antistatic applications, these blends must have electrical conductivity within the range ( $10^{-6}$  - $10^{-5}$ ) S/cm [9], It is considered one of the polymers that, depending on the degree of oxidation, changes its color, where the difference in the amount used can control its color, and the change in the difference in quantity helps convert the material from one oxidation state to a second oxidation state, and along the polymeric chain makes a change in the conjugation of double bonds as shown in Figure (1)

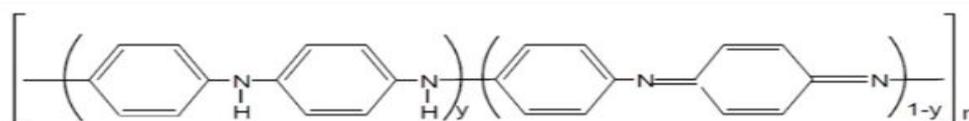


Figure (1) Polymer Poly-aniline (PANI)Form

The color of poly-aniline (PANI) changes according to the change in oxidation, at  $1-y=0$  called (LE) (Leucoemeraldine) almost colorless, blue in any half-oxidized shape at (Emeraldine base) (EB)  $1-y=0.5$  and blue Violet is completely and oxidized at  $1-y =1$  (PE) (pernigraniline) and is the most stable form of poly-aniline (PANI) EB [10].

## II. Experimental Work

Poly-aniline (PANI) is prepared in oxidized chemical polymerization by dissolving the chemical substance (0.2M) aniline hydrochloric ( $C_6H_5NH_2HCl$ ) and with weight (2.59mg) in the amount (50ml) of water distilled in the glass bottle. Also dissolving the chemical substance (0.25M) of ammonium persulfate ( $(NH_4)_2SO_8$ ) with weight (5.7mg) in the amount (50ml) in distilled water, which is considered an oxidized factor that separates each solution for a period of about one hour (1h) at laboratory temperature ( $18-24C^\circ$ ). Then the

two solutions are mixed and placed on the magnetic stirrer device for an hour (1h) after that it begins to change from colorless transparent to dark green, which leads to form a poly-aniline polymer (PANI). Then leaving it in state of polymerization for a period (24h) then the deposited poly-aniline (PANI) will be collected on the filtration sheet and rinsing it with (100ml) methanol and then rinsing it with (100ml) acetone after that deposit will be left on the filtration sheet for (24hrs) to dry or placed in an oven at temperature (60C°) Finally the polymer powder will be collected from the filtration sheet to be ready to use.

### III. Doped Process with graphene (GR), or Poly (vinyl Alcohol) (PVA)

#### 3-1-Preparation of Composite Films (PANI/GR)

The Composite films were prepared by dissolving PANI and graphene (GR) in (10ml) of solvent (NMP) in a typical procedure (0,1,3,5) Wt%.

The mixing process made using magnetic stirring device for (2) hrs in a temperature (50 C°).

#### 3-2-Preparation of Composite Films (PANI/PVA)

The Composite of PANI doped by PVA (1,3,5,7) Wt% weight ratios synthesized by the following these steps.

- 1) Powder of PVA dissolved with distilled water.
- 2) Pasty step is the step that the mixture of PVA and PANI turns to mold.
- 3) The mold (PANI and PVA) is Casting by hand on the glass slide.

## IV. Results and Discussion

### 4 - X- RAY Diffraction test

The X-ray diffraction pattern of the pure (PANI) powder shown in (Fig. 2) it shows two sharp peaks and this indicates that it possesses an amorphous layer, which can be attributed centered to the benzenoid and quinoid repeating rings in the PANI chains [11] However (Fig. 3) For the case of doping polyvinyl alcohol (PANI/PVA), a narrow very sharp peak appears. As for the case of graphene doping (PANI/PVA), the appearance of an expansion at the top leads to an increase in the crystallization of the polymer resulting from an increase in the percentage of graphene addition as shown in (Fig. 4). It can be noted through the X-ray spectrum that the wide peaks Evidence that the material of polyaniline films is (Amorphous), and the result of the X-ray diffraction spectrum for the rest of the films was similar regardless of the type of impurity, and this is consistent with what the researchers found [12] and Table (1) shows the diagnosis of X-ray diffraction for PANI pure doped (GR, PVA).

Table (1) X-ray diffraction (PANI) pure and doped

Sample	Pos. [°2Th.]	D (nm)	d-spacing [Å]	FWHM [°2Th.]
PANI pure	25.315	51.73	3.51823	0.1574
	29.001	51.13	3.0789	0.1574
PANI/GR5%	26.293	69.08	3.38953	0.1181
PANI PVA5%	23.329	103.08	3.81379	0.0787

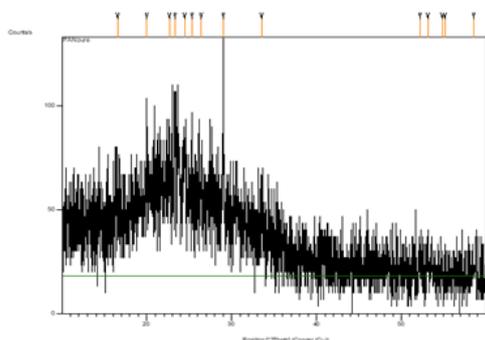


Figure (2) XRD pattern for the preparation of pure poly-aniline powder

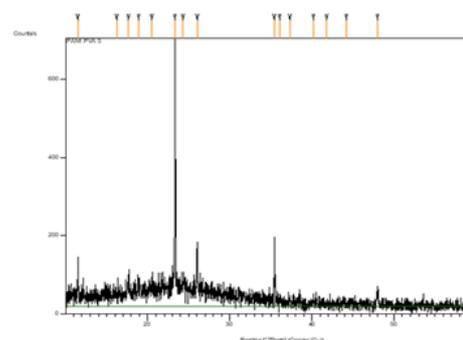


Figure (3) represents the XRD pattern of PANI/PVA

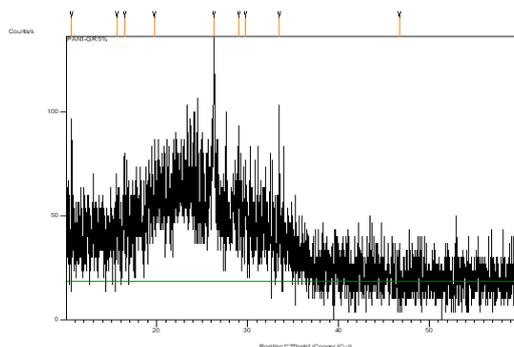


Figure (4) represents the XRD pattern of PANI/GR powder

### V. Absorbance (A)

According to the optical absorbance by using the relationship [13]

$$A = I/I_0 \quad (1)$$

where  $I$  is the intensity of the absorbed radiation,  $I_0$  the intensity of the incident radiation

The optical properties, including the absorbance ( $A$ ) were measured using (UV-Vis 1800) Spectrophotometers. Figure (5a,b) shows that the absorbance spectrum of all pure and impure (PANI/GR) and (PANI/PVA) films decreased with increasing length. The wavelength, while the absorbance increased with increasing concentration the ratio of doping with (GR and PVA), because the absorbance is proportional to the number of absorbed molecules directly, according to Beer-Lambert's law and through free electrons that absorb the energy of the incident light corresponds to [14,15], the absorption coefficient was also calculated ( $\alpha$ ) According to the relationship (2) depending on the absorbance values ( $A$ ) and ( $d$ ) the thickness of the film

$$\alpha = 2.303 (A/d) \quad (2)$$

By knowing the value of the absorption coefficient, the type of electronic transitions was determined [16] and it became clear that the values of the absorption coefficient ( $\alpha < 10^4 \text{ cm}^{-1}$ )

i.e., The transmission is indirect.

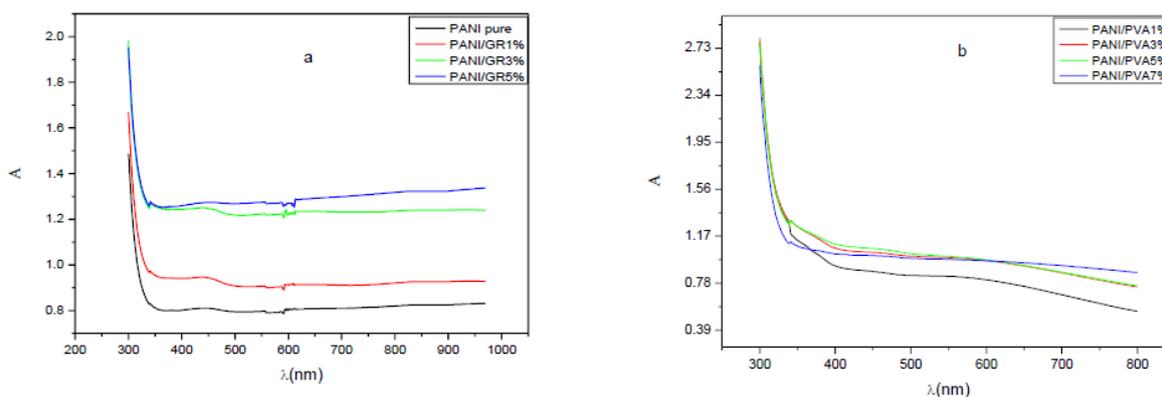


Figure5: Absorbance change with wavelengths (a) of pure polyaniline -doped (PANI/GR) and (b) (PANI/PVA)

### VI. Transmittance (T)

The transmittance ( $T$ ) of all the prepared films was calculated using the following relationship [17].

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

Where ( $I_T$ ) represents intensity of the transmitted radiation and ( $I_0$ ) represents intensity of the incident radiation, From Figure (6 a, b) it can be noted that the transmittance values increase with increasing wavelength, and with increasing concentration ratio (GR) as well as (PVA) with (PANI) the transmittance decreases, this behavior is due to the type of covalent bonds between the polymer chains with additives [18].

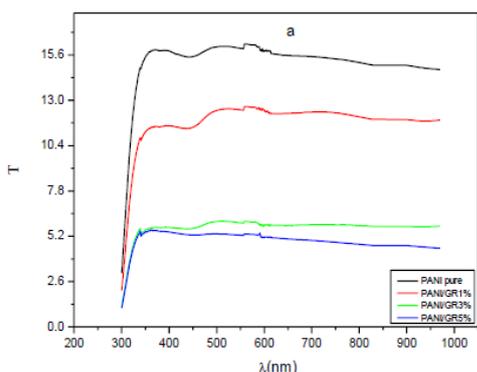


Figure 6a: Transmittance with  $\lambda$  for (PANI /GR)

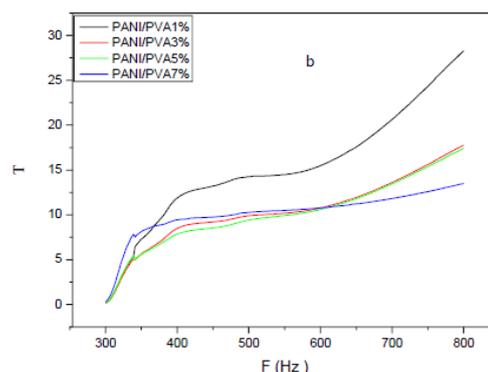


Figure 6b: Transmittance with  $\lambda$  for (PANI /PVA)

### VII. Reflectivity (R)

The reflectivity, absorbance and permeability can be linked through the relationship [19]

$$R = 1 - (A+T) \quad (4)$$

where (A) the absorbance and (T) the transmittance

Figure (7a) shows the reflectivity of PANI/GR. It can be seen from the figure that the reflectivity increased with the increase in the percentage of doping with graphene because the surface has a roughness average, grain size and crystal defects for all (PANI) films, both pure and doped, and this agrees with [20,21], while Figure (7b) depicted a decreasing with the increase in the percentage of doping in relation to (PVA)

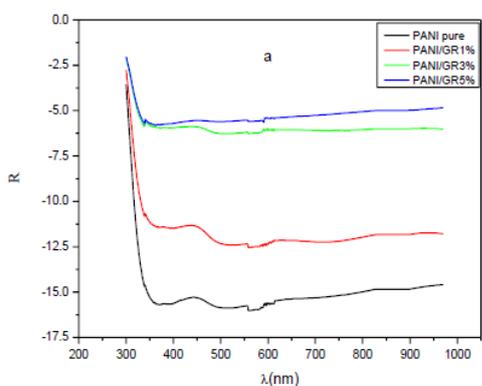


Figure 7a: Reflectivity VS as a function of  $\lambda$  of PANI before and after GR doping

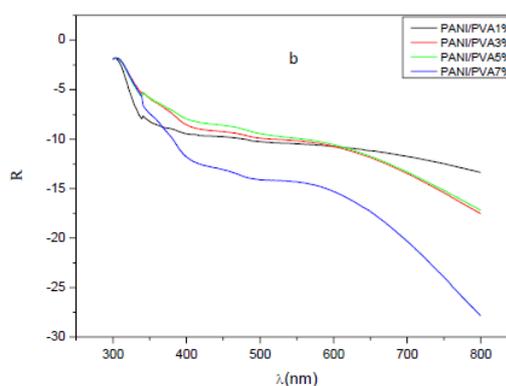


Figure 7b: Reflectivity VS as a function of  $\lambda$  of PANI before PVA doping

### VIII. Extinction Coefficient (K)

Figure (8 a, b) depicted an increase in the extinction Coefficient (K) with the increase in the rate of doping at the wavelength range (350 - 900) nm. This is attributed to the large absorption coefficient that leads to an increase in the absorption of part of the incident light, and this agrees with [22] , and in Figure (8a) the best doping ratio (5%) for (GR) while (7%) the best distortion ratio relative to (PVA) as indicated in Figure (8b) .

The Extinction coefficient (K) were determined from the use of the relationship [23].

$$k = \alpha\lambda/4\pi \quad (5)$$

where ( $\lambda$ ) is the wavelength, ( $\alpha$ ) represents the absorption coefficient

To calculate the refractive index (n) from knowing the coefficient of refraction (K) and reflectivity (R), according to the following relationship [24]

$$n = \sqrt{\{(4R/1-R)^2 - (K^2)\} + (1+R)/(1-R)} \quad (6)$$

Figure (9a), for in ducted the determination of refractive index for PANI/GR and it can be noticed an increase in the refractive index (n) with an increase in the percentage of doping with graphene. Figure (9b), can be seen with an increase in the percentage of doping (PVA) and the reason is due to the dependence of the refractive index on the reflectivity and the extinction Coefficient

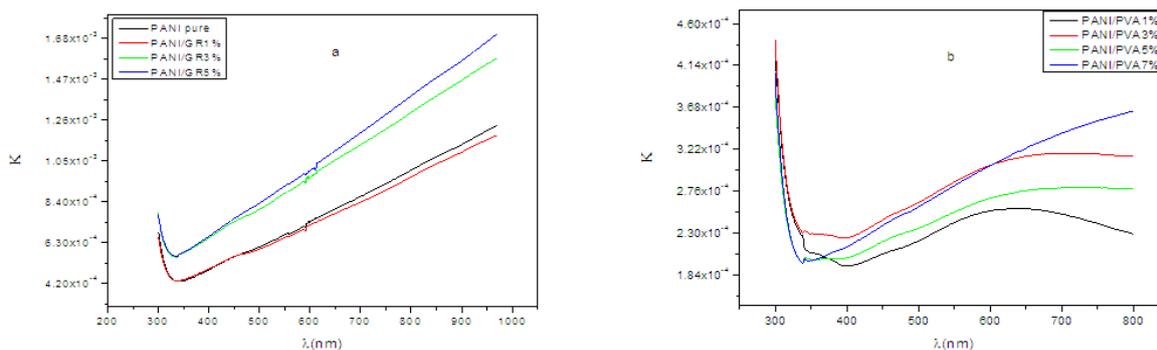


Figure (8a, b): Extinction Coefficient as a function of ( $\lambda$ ) of PANI after and before (GR, PVA) doping

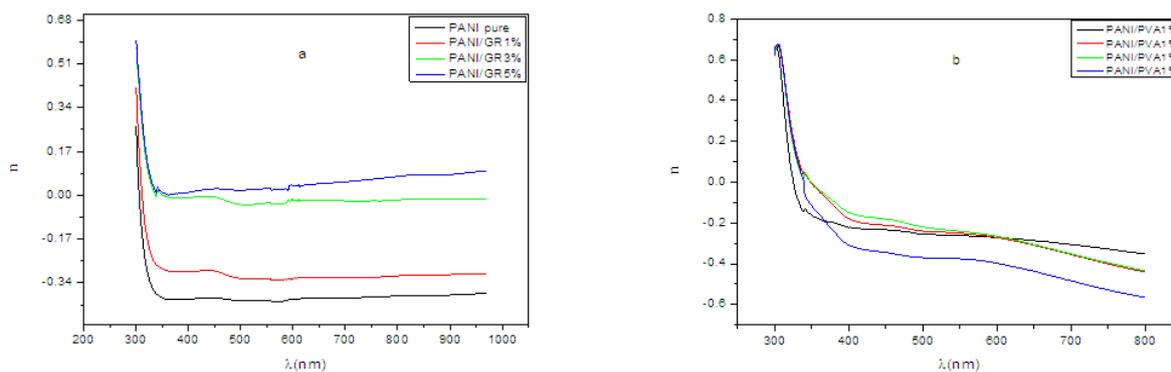


Figure (9 a, b): Refractive index with ( $\lambda$ ) of PANI before and after as per doping ratios with (a) GR (0,1,3, and 5) and (b) PVA (1,3,5 and 7)

### IX. The Optical Conductivity( $\sigma_{opt}$ )

Optical conductivity is calculated used the following relationship [25]

$$\sigma_{opt} = nc\epsilon_0\alpha \quad (7)$$

where (c) is the speed of light in a vacuum ( $\square$  ) permittivity in a vacuum

The curves show an increase in the optical conductivity value with an increase in the percentage of doping, and the highest conductivity value is Figure (10a) at the ratio PANI/GR doping (5%) and also Figure (10b) and at the ratios PANI/PVA doping (7%) due to its dependence on the absorption coefficient ( $\alpha$ ) and the refractive index (n).

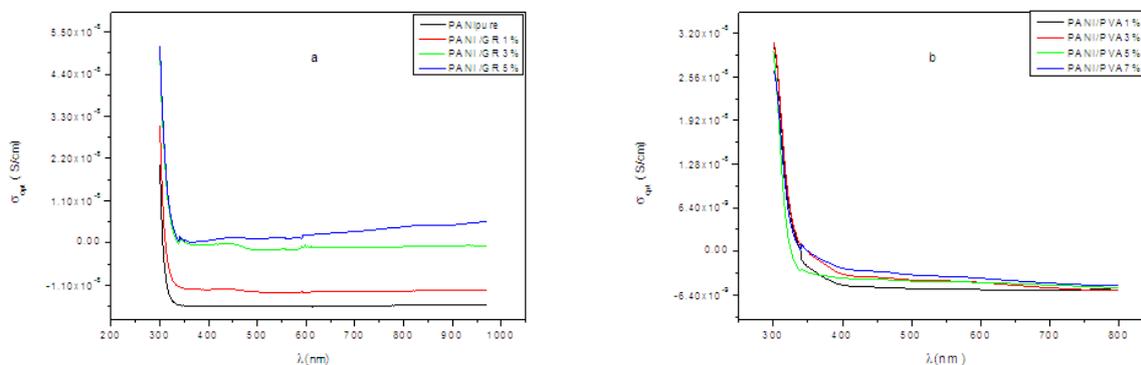


Figure 10: Relationship between optical conductivity and wavelength of polyaniline and doped with (a) GR according to ratios (0, 1, 3, 5) and (b) PVA according to ratios (1, 3, 5 and 7)

### X. Energy Gap ( $E_g$ )

By knowing the values of the absorption coefficient, the type of indirect electronic transitions was determined and the energy gap of the prepared films was calculated from the intersection of the photon energy axis ( $E = h\nu$ ) with the straight part of the curve. Figure (11a,b) shows the decrease in the energy gap values in

PANI polymer due to the increase of the doping ratio with PANI/GR as well as PANI/PVA, which leads to an increase in the conductivity that leads to a decrease in the energy gap when the electrons move to the lowest occupied energy level in The conductive band (CB) for the highest occupied energy level in the valence band (VB) and this corresponds to [26,27] energy gap values shown in Table (2) represents the energy gap with the doping ratios.

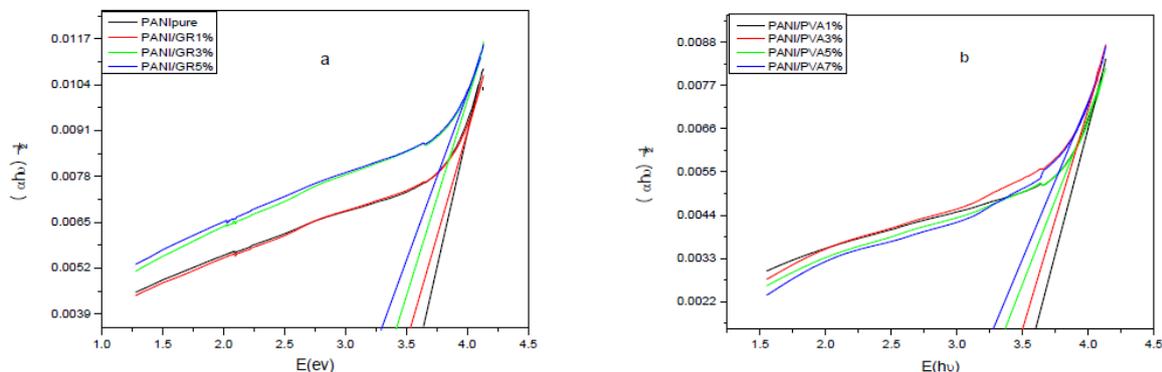


Figure 11: The relation between  $(\alpha h\nu)^{1/2}$  versus photon energy (a) pure polyaniline doped with graphene (b) polyaniline with polyvinyl alcohol

Table (2) The Value of the energy gap for pure (PANI) and doped with graphene and polyvinyl alcohol

Sample	Doping ratio	Eg(ev)
PANI pure	0%	3.58
PANI /GR	1%	3.46
	3%	3.32
	5%	3.28
PANI /PVA	1%	3.55
	3%	3.4
	5%	3.35
	7%	3.29

### XI. Dielectric constant

The dielectric constant can be calculated in terms of real and imaginary parts through the following two relationships (8,9) respectively

$$\epsilon' = (n^2 - K^2) \quad (8)$$

$$\epsilon'' = (2 n K) \quad (9)$$

where  $(\epsilon')$  the real constant,  $(\epsilon'')$  the imaginary constant (n) represents refractive index and (k) represents extinction Coefficient [28].

Figure (12 a, b,c,d) represents the real and imaginary dielectric constant or pure (PANI) and doping, ratios for GR and PVA their behavior it can be seen that their is acted in somewhat different in the visible light region, if the method of changing the real dielectric constant is not similar to the method of changing the refractive index as shown as Figure (12 a ,b), but the behavior of the imaginary dielectric constant is similar to the behavior of the extinction Coefficient due to the energy attenuation in it the middle Figure (12 c, d).

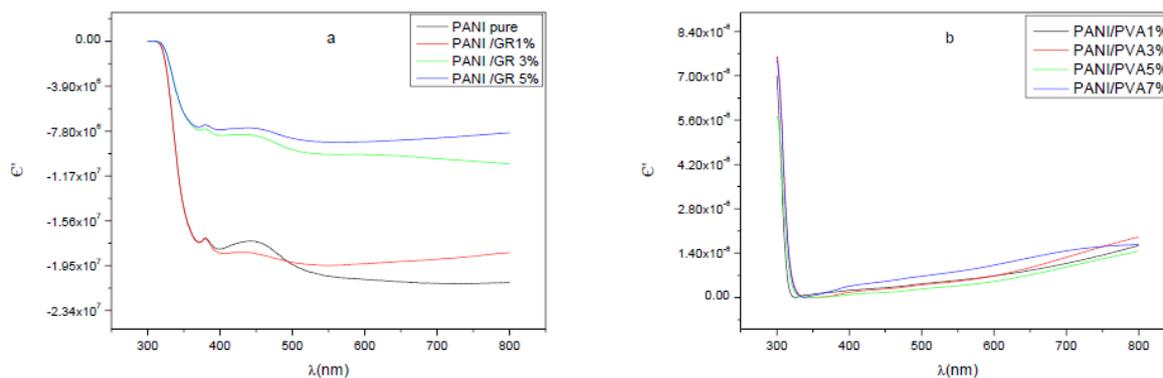


Figure (12 a, b): The real dielectric constant as a function of wavelength for PANI before and after doping with (a) GR (b) PVA

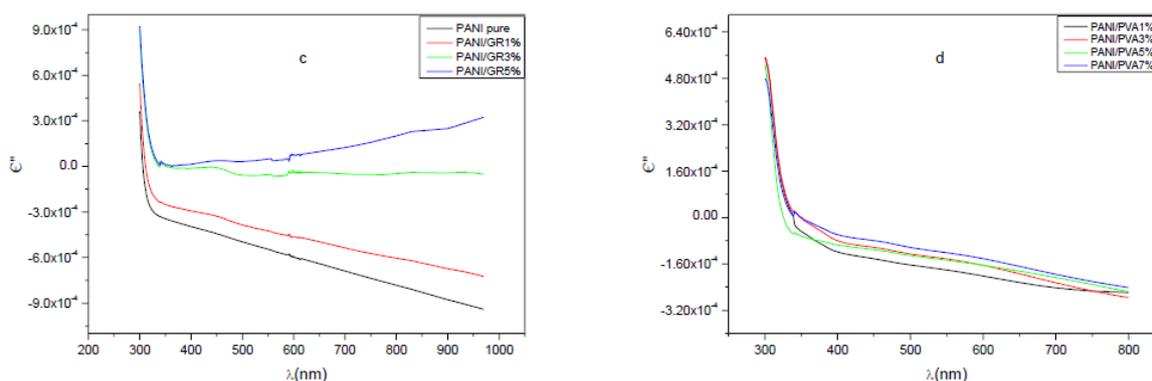


Figure (12 c, d): The imaginary dielectric constant as a function of wavelength for PANI before and after doping (c) GR (d) PVA

## XII. Conclusion

From the above results it can be concluded the following points: -

- 1 -The method of preparing the polymer PANI as a powder by chemical oxidation and the polymerization at room temperature was effective by aniline hydrochloride as a monomer and ammonium persulfate as an oxidizing agent and can be deposited as a thin film on the glass.
- 2 -By measuring the absorption coefficient ( $\alpha$ ), it is clear that the type of electronic transitions are indirect transitions that are allowed
- 3 -The highest value of the pure optical energy gap (PANI) is about (3.58ev) and it starts decreasing gradually with the increase in the percentage of doping with graphene (GR) between (3.46-3.28) ev the rate of doping 5%), as well as for poly (vinyl alcohol (PVA) between (3.55 - 3.29) ev 7% impurity.
- 4- It can be noted that the doping ratio affects the arrangement of the curves with respect to the optical constants of absorbance, transmittance, refractive index, attenuation coefficient, optical conductivity, dielectric constant in real and imaginary parts, and absorption coefficient.
- 5-The absorbance of polymers for X-rays is low, because mostly the characteristic of the transmittance and the passage of the rays through the prepared membrane, the appearance of a wide peak indicative of defects in the polymer, to obtain high crystallization, the polymer must be of high viscosity and low transmittance.

## References

- [1]. K I Ajeel and QS Kareem "synthesis and characteristics of polyaniline (PANI) Filled by Graphene (GR) nano-Films Journal of physics, lop conf. series 1234 (2019)
- [2]. G.P. Crawford Flexible flatc display john Wiely and Sons. NY (2005)
- [3]. S.S. Kim, Y.S Choi, K. Kim, J. H. Kim and S. Lm Appi. Phys. Lett. 82, 639 (2003)
- [4]. J-paloheima, E. Punkka, P. Kuivalain, H. Stubb and P. Lahti, EL.64 Acta Polytechnica a Scan dinavica Elec. Eng. Series. J Shkohen, 64, 178 (1989).
- [5]. K. Kaneto, T. ShiKaishi and K. Yoshino, gapan. J. Appl. Phys 44 ,107 (1985).
- [6]. J. Kido "Organic Display Physics World "27 -30 (1999).
- [7]. J.H. Burroughes, R. H. Friend and P.C. Allens, J. Phys. D. 22, 956 (1989).
- [8]. V. Jousseume, M. Mmorsli, A. Bonnet and S. Lefrant, "Synthetic Metals 101, 813 -814 (1999).

- [9]. A. J. H. Almaliky, Hussein F Hussein and Khalid I Ajeel "The Synthesis and study of the electrical properties of composites (FeAl<sub>2</sub>O<sub>3</sub>) with paraffin wax and determination of the mechanism of electrical conductivity" Iop Conf. series. Materials Science and Engineering 987 (2020).
- [10]. K. M. Molapo, Peter M. Ndagili, Rachel F. Ajayi, Gcineka Mbambisa, Stephen M. Mailu, Njagi Njomo, Milua Masikini, Priscilla Baker and Emmanuel I. Iwuoha . Electronics of Conjugated Polymers (I): Polyaniline. Int. J. Electrochem. Sci., 7 (2012) 11859 – 11875.
- [11]. Biotechnology Research Lab., Faculty of Chemical Engineering, S. Pei and H. Cheng, CARBON ,55, (2011) 3040 –3059.
- [12]. R. A. Talab, Satar J. Qasim, " The optical properties of polyaniline (PANI) prepared by chemical method", Journal of Kufa – Physics Vol.1, No.2, pp.1-11, (2009).
- [13]. M. A. Omar, "Elementary Solid State Physics Principle and Applications", P.35-578, (1985).
- [14]. Z. H. Esfahani, M. Ghanipour and D. Dorrani "Effect of dye concentration on the optical properties of red-BS dyedoped PVA film". Theor Appl Phys (2014).
- [15]. A. Mehto, V.R Mehto, J . Chauhan, I. Singh and R. Pandey, "Preparation and Characterization of Polyaniline/ZnO Composite Sensor". Journal of Nanomedicine Research, Vol. 5, NO. 1 (2017).
- [16]. R. Kadum, Munf S. Majeed, Kareem K. Mohmmad, Hussain Ali badran Khalid I. Ajeel" Spectroscopic ellipsometry Study and Variability of optical porameters for blend polymer (PVA:POT) thin films proceeding of 1st int. and the 3rd scientific conf. college of science university of Tikrit 17-18 dec (2018) p4.
- [17]. J.I. Pankove, "Optical Processes in Semiconductors" , by Prentice Hall, Inc., (1971).
- [18]. Q. S. Kareem, K. I. Ajeel "OPTICAL PROPERTIES FOR PREPARED POLYANILINE/GRAPHENE NANO COMPOSITES FILMS" Journal of Basrah Researches ((Sciences)) Vol. (45). No. 2 (2019).
- [19]. W.D. Callister" Fundamentals of Materials Science and Engineering" Book, (2001)
- [20]. C. M. H. AL-humairi "Study the Optical and Electrical Properties of (PVA/Ag) and (PVA- TiO<sub>2</sub>) Nanocomposites". M.Sc. Thesis, University of Babylon, College of Education for Pure Sciences (2013).
- [21]. K.M. Ziadan, "The Electronic transitions of polyaniline doped with p-toluene Sulfonic acid". The First Scientific Conference the College of Sciences, Department of Physics, College of Science, University of Basrah (2013).
- [22]. B. H. Rabee, "Study of Optical and Mechanical Properties for (PVA/Ag/CO<sub>3</sub>) Composites". European Journal of Scientific Research, Vol.57, No.4, PP. 191- 209 (2012).
- [23]. R. K. Fakher Alfahed, Ahmed S. AL-asidy, Hussain Ali Badran , Khalid I. Ajeel . "Structural morphological and Z-scan technique for a temperature Controllable chemical reaction synthesis of zinc sulfide nanoparticles " Applied physics B 125 : 48 (2019)
- [24]. A.A Al- Ghamdi, W.E. Mahmoud, S, J. Yaghmour and, F. M. Al -Marzouk "Structure and optical properties of nanocrystalline Nio thin film synthesized by Sol- gel spin coating method ", Journal of Alloys and Compounds 486-9-13, (2009).
- [25]. S. O. Kasap "principle of electric material and devise "third edition MC Grow Hill, Boston (2005)
- [26]. A. G. Baker, "The Study of Optical Energy Gap, Refractive Index, and Dielectric Constant of Pure and Doped Polyaniline with HCl and H<sub>2</sub>SO<sub>4</sub> Acids". <http://dx.doi.org/10.14500/aro.10483>. Vol 7, No 1 (2019).
- [27]. S. A.S, Asaad A.K, Maysam A.R, "Preparation and Study of Some Optical Properties of (PVA-FeCl<sub>3</sub>) Composites Films". Journal of Chemical, Biological and Physical Sciences, Vol. 6, No. 4, PP. 1270-1280 (2016).
- [28]. K. K. Pohatgi - Mulkherjee, "Fundamentals of Photochemistry" , Wiley Eastern Limited ,(1978)

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