

Preparation and Characterization of Poly-Aniline Hydrochloride (PANI-HCL) Nanocomposites by Radiation

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Abstract: The nano compound Poly-Aniline Hydrochloride (PANI-HCL) was prepared with different weight ratios before and after irradiation which was presented in the form of film using the casting method and irradiated using the Cobalt (^{60}Co) element which emits gamma radiation (1.2) MeV and for a period of 72 h. The polymer was diagnosed using Fourier Transfer Infrared Spectroscopy (FTIR). The topography of the film was studied through microscopic images and the optical properties including absorbance, transmittance, absorption coefficient, refractive index and energy gap were studied. The electrical properties included measuring the hall effect. The results showed that the irradiation resulted in an increase in absorbance values, absorption coefficient and refractive index while decreasing the values of energy gap and permeability. The measurements showed that the effect of polymerization before and after irradiation was n-type.

Key words: Poly-aniline hydrochloride, gamma radiation, transmittance, refractive index, polymerization, n-type

INTRODUCTION

Polymers are complex chemical compounds from a large number of atomic groups connected with each other by various chemical bonds such as ionic, covalent and mineral. They are used in various industrial fields such as crystalline alloys in membrane technology for the separation of gases such as oxygen and helium and in the manufacture of plastics, industrial rubber. In nuclear fields, polymeric membranes are used to separate radioactive isotopes, nuclear pollutants and nuclear doses such as cellulose reagents and poly-carbons (Kadhim *et al.*, 2017). The effect of radiation in polymers leads to increased damage to particles. The material that interact with them significantly for the particles that have the ability to ionize and break the bonds that link them and have a significant influence in the covalent bonds balance in the impact of other bonds as it is a little in the bonds of ionic and very little in the metal bonds (Sperling, 2005). The polymer exposure to a high dose of radiation for a period of a long lead to the loss of obedience and the strength of its composition to crumble and become a powder in the end, radiation leads to the process of tangled.

MATERIALS AND METHODS

Poly-Aniline Hydrochloride (PANI-HCL): The poly-aniline hydrochloride line series of numeric molecule (Oligomer), the poly aniline consider conduction polymers

the conductivity of it variance from (10^0 - 10^{10}) S/cm (Negi and Adhyapak, 2002). The method of oxidation and ionization for aniline ($\text{C}_6\text{H}_5\text{NH}_2$) in began nineteen century by the German scientific Willstter, the aniline can interact with acid chemical solution and based and result from this special compounds have important scientific applications. The general structural form to polymer show by the Fig. 1 (Barton and Ollis, 1979).

Poly Vinyl Alcohol (PVA): Main physical features of Poly Vinyl Alcohol (PVA) is water soluble, semi crystalline, nontoxic, biocompatible, eco-friendly, better film and fiber forming, good mechanical properties, excellent chemical resistance and biodegradable. The physical features of it produced by the Polymerization of Vinyl acetate to Poly Vinyl Acetate (PVAC) and then

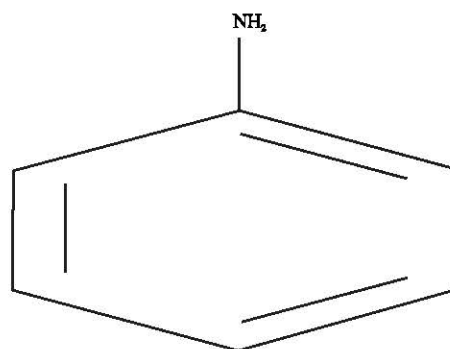


Fig. 1: Synthesis of Poly-Aniline (PANI)

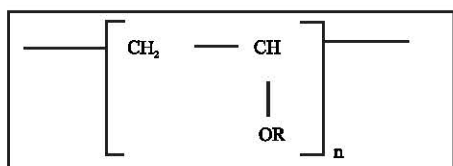


Fig. 2: Structure of polyvinyl alcohol

hydrolysis to obtain of PVA. Poly Vinyl Alcohol (PVA) is a hydrophilic polymer which is serving special in application in medicine due to excellent biocompatibility and biodegradable. Finally, important property of (PVA) is semicrystalline nature which is the existence of both amorphous and crystalline areas causing interfacial effects which increases the physical features. So, these unique characterizes of poly vinyl alcohol make it used in most commonly synthetic polymers (Stasko *et al.*, 2009; Peresin *et al.*, 2010).

Poly Vinyl Alcohol (PVA) is commonly used in cosmetic, adhesive, food, paper, medicine and packaging industries. The chief functional uses of poly vinyl alcohol involve filtration, optics and catalysis. Several of the important properties of PVA are the result of its major cohesive energy because of polarity from group of hydroxyl that produce intra molecular of hydrogen bonding.

But the same features that provide PVA with unique performance and hydrophobicity make it susceptible to plasticization in humid environments (Peresin *et al.*, 2010). In addition, to the degree of swelling or rubbery in water or biological fluids is high (Bilmeyer, 1971). Polyvinyl alcohol has glass transition Temperature $T_g = 85^\circ\text{C}$ and melting point Temperature $T_m = 230^\circ\text{C}$ and density is of $1.3 \text{ (g/cm}^3\text{)}$. Figure 2 shows structure of Poly Vinyl Alcohol (PVA).

Experimental part 4: The materials used in the search:

- Poly-Aniline (PANI)
- Poly Vinyl Alcohol (PVA)
- Distilled water
- Slides of glass

Prepare polymer: The poly-aniline hydrochloride polymer was prepared by dissolving the polyvinyl alcohol powder 30 g in the distilled water (90) mL. The aniline hydrochloride was then added with different weight ratios (1-3) g to the 50 mL polyvinyl alcohol solution and mixed with the magnetic vibrator to obtain a homogeneous solution and prepared in a film form using the casting method for (24) h to dry and irradiate by

using the Cobalt Co^{60} element which is half the age of (5.2) years and sends a gama beam (1.2) MeV for a period of (72) h.

Optical measurements: The absorbance and transmittance for solutions were measured by using instrument measuring the spectrum, made by (Shemadzo) company, Japan, type (Double-Beam Spectrophotometer (UV-1800)) where the range of wavelengths is (300-1100) nm. A computer programmer make scanned for all wavelengths and gave the value of wavelength that occurs in it a greatest absorption.

Theoretical calculations

Optical properties 6-1

Absorbance (A): Absorbance defined as the ratio between absorbed light Intensity (I_r) by material and the incident Intensity of light (I_o) (Mwolfe *et al.*, 1989):

$$A = \log \frac{I_o}{I_r} \tag{1}$$

The optical absorbance coefficient of solution and film is given by the Eq. 2 (Mwolfe *et al.*, 1989):

$$\alpha_{op} = 2.303A/d \tag{2}$$

where, (d) represent a thickness of sample. The ratio (I/I_o) called (Transmittance), (T_r) connected with absorbance by Eq. 3 (Abdulla and Abbo, 2012):

$$T_r = e^{-2.303A} \tag{3}$$

Electronic transitions: The optical data were analyzed from the classical relation for near optical absorption in semiconductor (Chopra, 1969):

$$\alpha = A \left[(hf - E_g)^r / hf \right] \tag{4}$$

Where:

f = The frequency

h = The plank constant

r = The (1/2, 3/2, 2, 3) for transition (direct allowed, direct forbidden, indirect allowed and indirect forbidden, respectively)

A = The constant

E_g = The defined as the optical energy band gap between the Valence Band (VB) and the Conductive Band (CB)

The type of transition depends on the absorption coefficient value when α value is larger than (10^4 cm^{-1}). The transition called (direct transition) where electron moves from VB to CB with the same wave vector (k) and momentum are conserved. While, indirect transition occurs when the value of absorption coefficient is $<10^4 \text{ cm}^{-1}$ (Chopra, 1969; Rao *et al.*, 2011) where the electrons transferred from VB to CB at the same wave vector (k). The momentum and energy must be conserved with phonon assistant (Rao *et al.*, 2011).

Refractive index (n): The refractive index can be given by Eq. 5 (Reddy *et al.*, 2010):

$$n = \frac{c}{v} \tag{5}$$

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 Eq. 6 (Saeed and Suhail, 2012). Then, refractive index will be:

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

Electrical properties

Hall effect: Hall effect known as the difference in the distribution of the current in the conductive or semi-conductive segment due to the magnetic field (AL-Jammal, 1990; Mohammed, 2016) which shed a magnetic field on a conductor carrying an electric current direction perpendicular to the direction of current flow generates a delinquency charge carriers aside and cause the generation of electric driving force over the connector direction perpendicular to the direction of both the current and the magnetic field. The hall effect in semiconductors measurements are given the following Eq. 7 (AL-Jammal, 1990):

$$R_H = -\left(\frac{1}{ne}\right) = \frac{V_H \cdot t}{I_x \cdot B_z} \tag{7}$$

Where:

- R_H = Hall coefficient
- n = The concentration of carriers
- e = Electron charge
- t = The thickness of the films
- I_x = Current flowing in the films
- B_z = The intensity of the magnetic field

And from this relationship the concentration of the majority carriers account, using the following relationship was hall mobility of these carriers account (Mohammed, 2016; Lindberg, 1952) Eq. 8:

$$\mu_H = |R_H| \sigma \tag{8}$$

Where:

- μ_H = The Hall mobility
- σ = The electrical conductivity

RESULTS AND DISCUSSION

FT-IR test: The infrared spectral measurements of the Poly-Aniline Hydrochloride (PANI-HCL) pre-irradiated polymerase showed the absorption bundles shown in Table 1. Figure 3 and 4 show the infrared absorption spectra which shows the chemical bonds in the polymer prepared before and after irradiation. Results showed that the polymer’s active groups were congruent with the chemical composition.

Optical images: The photovoltaic microscope of a Nikon type with a digital imaging microscope used a magnification force of 1000× to detect the changes in pre-and post-irradiated gates in Fig. 5 and 6 where dendritic branches appeared to indicate the formation of a polymorphic membrane during the polymerization process. Homogeneous and free of glare or holes. We note that the process of irradiation led to changes in the color of polymer due to the intensity of radiation falling on the polymer and this is due to the formation of double bonds (Ali, 2005) (Table 2).

Absorbance spectrum: The absorption was calculated in practice and for all polymer films recorded in the Poly-Aniline Hydrochloride (PANI-HCL) before and after

Table 1: Absorption Packs for Poly-Aniline-Hydro Chloride (PANI-HCL)

Absorption packs (1/cm)	Shaky group
3100	(NH ₂)
1475	(C = C)
1350	(C-N)
3150	(C-H)
3650	(OH)
2850	(C-H) alibatics

Table 2: Absorption values of the Polymer-prepared Poly-Aniline Hydro Chloride (PANI-HCL) before and after irradiation

A		
Ani-HCL+PVA	Non-radiated	Irradiated
1 g+50 mL	0.18850	0.27050
2 g+50 mL	0.20850	0.33375
3 g+50 mL	0.36875	0.38825

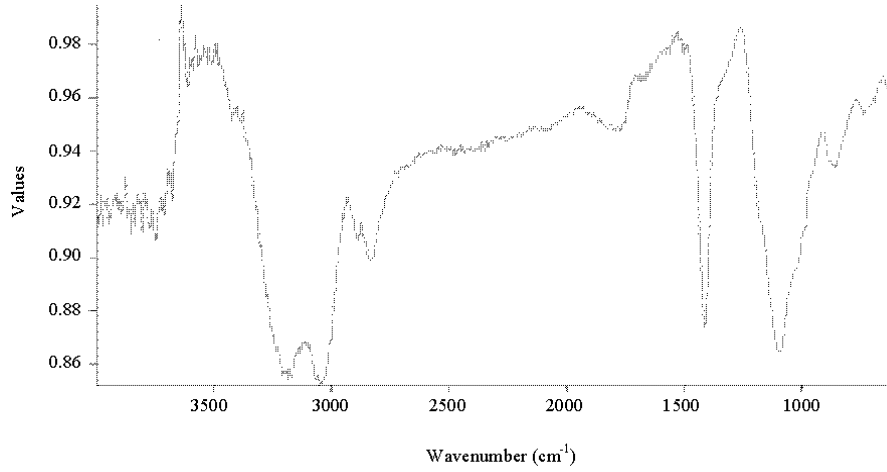


Fig. 3: The absorbance spectra of the polymer-prepared Poly-Aniline Hydrochloride (PANI-HCL) prior to irradiation

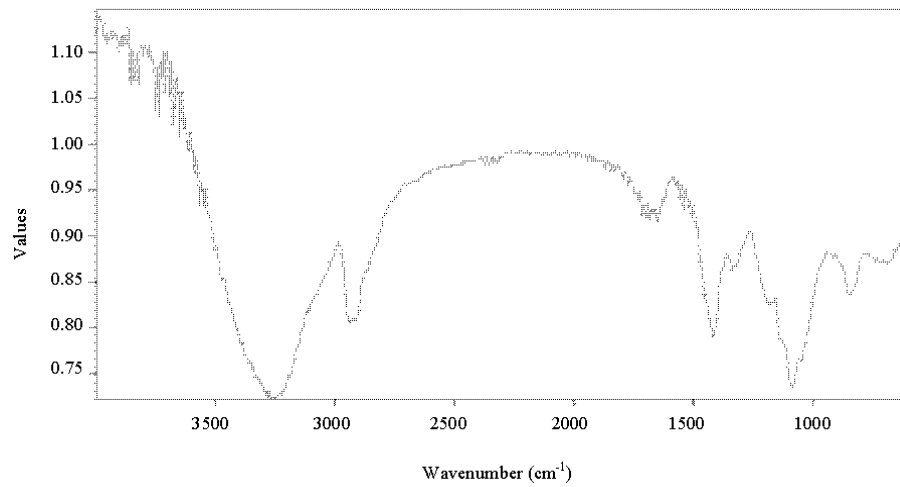


Fig. 4: The absorbance spectra of the polymer-prepared Poly-Aniline Hydrochloride (PANI-HCL) after irradiation

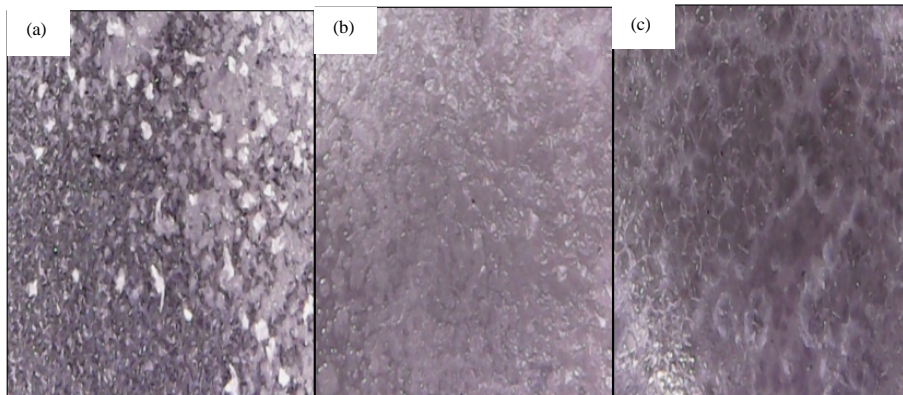


Fig. 5: Images of polymer films prepared by poly-aniline hydrochloride prior to irradiation: a) Ani-HCL+PV (1 g+50 mL); b) Ani-HCL+PV (2 g+50 mL) and c) Ani-HCL+PV (3 g+50 mL)

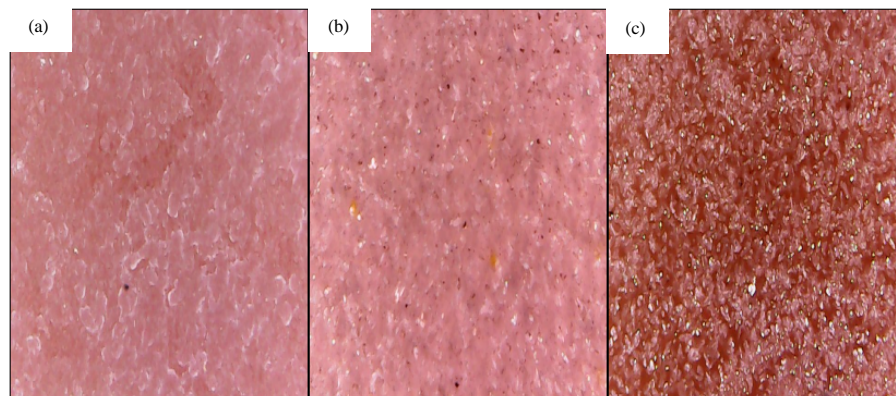


Fig. 6: Images of polymeric films prepared by poly-aniline hydrochloride after irradiation: a) Ani-HCL+PV (1 g+50 mL); b) Ani-HCL+PV (2 g+50 mL) and c) Ani-HCL+PV (3 g+50 mL)

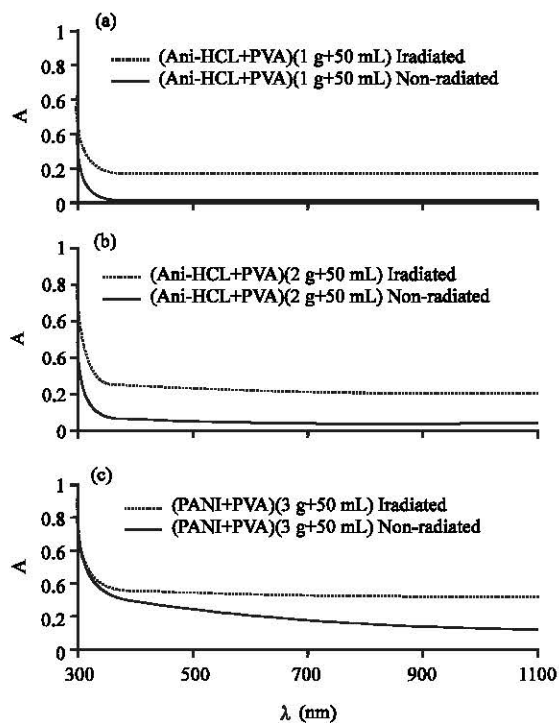


Fig. 7: a-c) Absorption as a function of the wavelength of the recorded polymer

irradiation. Figure 7a-c shows the absorbance as a function of the wavelength. We can observe the absorption change with the pre-irradiation rate of the polymer before the irradiation. The process of irradiation led to an increase in absorption because the irradiation process leads to crystalline defects (Ibrahim *et al.*, 2012). Table 2 shows the absorption values based on Eq. 1 at the mean wavelength 324 nm before irradiation and at the wavelength rate 335 nm after irradiation.

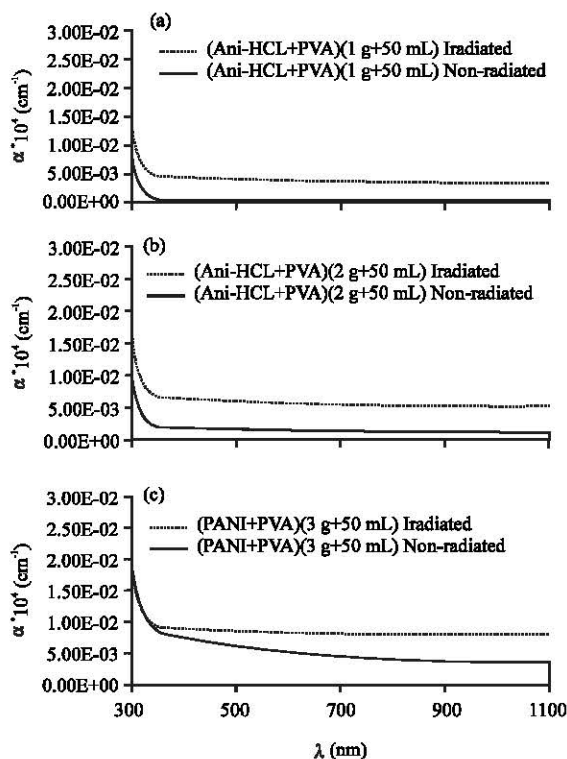


Fig. 8: a-c) Absorption coefficient as a function of the wavelength of the recorded polymer

Absorption coefficients: According to the absorption coefficient of the pre-irradiated and pre-irradiated polymer films in the primary absorbance area of the absorbance spectrometer, measured using a spectrometer using Eq. 2, Figure 8a-c shows the absorption coefficient as a function of the pre-irradiated and pre-irradiated polymer wavelength. The coefficient of absorption is $<10^4 \text{ cm}^{-1}$. This indicates that the transfer of

Table 3: The values of the absorbance coefficients of the Polythene Hydro Chloride (PANI-HCL) polymerase before and after irradiation

α		
Ani-HCL+PVA	Non-irradiated	Irradiated
1 g+50 mL	44.75417526	60.42
2 g+50 mL	49.50262887	79.23981959
3 g+50 mL	87.54961340	92.17935567

Table 4: Values of transmittance of the Poly-Aniline Hydro Chloride polymer (PANI-HCL) before and after irradiation

T		
Ani-HCL+PVA	Non-irradiated	Irradiated
1 g+50 mL	0.647888095	0.536413871
2 g+50 mL	0.618728328	0.463713778
3 g+50 mL	0.427809082	0.409025138

Table 5: The values of the energy gap of the recorded polymer (PANI-HCL)

E_g		
Ani-HCL+PVA	Non-irradiated	Irradiated
1 g+50 mL	4	3.850931677
2 g+50 mL	3.936507937	3.757575758
3 g+50 mL	3.604651163	3.532763533

Table 6: Refractive index values for polymer poly-aniline hydrochloride record before and after irradiation

n		
Ani-HCL+PVA	Non-irradiated	Irradiated
1 g+50 mL	2.173703260	2.435737851
2 g+50 mL	2.253136538	2.523852735
3 g+50 mL	2.532398001	2.525632941

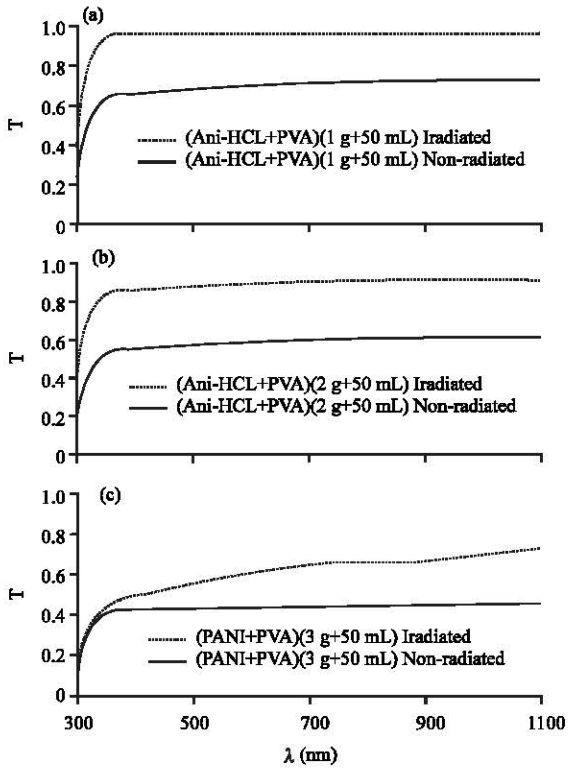


Fig. 9: a-c) Transmittance as a function of the wavelength of the recorded polymer (PANI-HCL)

indirect type and the irradiation process led to an increase in the values of the absorption coefficient. The reason is that the radiation led to increasing the local levels within the energy gap which led to an increase in the absorption factor values.

Table 3 shows the values of the absorbance factor of the polymer poly-aniline hydrochloride at the rate of 324 nm wavelength before irradiation and at the wavelength of 335 nm after irradiation.

Transmittance: Transmittance was calculated for all polymer films recorded before and after irradiation from the absorbance spectrometry according to Eq. 3. Figure 9a-c shows the change in Transmittance as a function of the pre-irradiated polymer wavelength before irradiation. In surface topography during the irradiation process.

Table 4 shows the Transmittance values of the polymer poly-aniline hydrochloride at the 324 nm wavelength before irradiation and at the 335 nm wavelength after irradiation.

Energy gap: The energy gap values for indirect transitions for all polymer films recorded before and after irradiation were calculated using Eq. 4 by plotting the relationship between $(\alpha h\nu)^2$ and the projected photon energy and extending the straight part of the curve to cut the photon energy axis at point $\alpha h\nu = 0$, Fig. 10a-c shows that the irradiation process resulted in a decrease in the energy gap values. This is due to the fact that the irradiation process increased the absorption coefficient and thus, increased the energy gap due to the generation of extra levels within the vector between the coupling and the valence pack due to the displacement of the atoms from their positions (Jassim, 2005). Table 5 shows the values of the energy gap of the polymer and the pre-irradiated poly-aniline hydrochloride.

Refractive index: The refractive index of all polymer films recorded before and after irradiation was calculated by Eq. 6. Figure 11a-c shows the refractive index as a function of the wavelength where we observe a change in the refractive index with the increase of the weight ratio of both cases before and after irradiation. In refractive index values due to increased solution density (Fowles, 1975).

Table 6 shows the refractive index values of the recorded polymer at the rate of 324 nm wavelength before irradiation and at the wavelength of 335 nm after irradiation.

Table 7: Results of hall effect of the poly-aniline hydrochloride polymer prior to irradiation

Ani-HCL+PVA	R_H (cm ³ /C)	n_H (1/cm ³)	ρ (Ω .cm)	μ_H (cm ² /V.s)	$(\sigma_{D.C})_{RT}$ (Ω .cm) ⁻¹
1 g+50 mL	-3.22×10 ⁷	-1.939×10 ¹¹	3.686×10 ⁵	8.735×10 ¹	2.713×10 ⁶
2 g+50 mL	-7.584×10 ⁷	-8.23×10 ¹⁰	5.53×10 ⁷	1.369×10 ¹	1.805×10 ⁻⁸
3 g+50 mL	-5.548×10 ⁷	-1.125×10 ¹¹	3.903×10 ⁵	1.512×10 ¹	2.562×10 ⁻⁶

Table 8: Results of hall effect of the poly-aniline hydrochloride polymer after irradiation

Ani-HCL+PVA	R_H (cm ³ /C)	n_H (1/cm ³)	ρ (Ω .cm)	μ_H (cm ² /V.s)	$(\sigma_{D.C})_{RT}$ (Ω .cm) ⁻¹
1 g+50 mL	-1.57×10 ⁸	-3.95×10 ¹⁰	9.24×10 ⁴	1.70×10 ³	1.08×10 ⁻⁵
2 g+50 mL	-3.88×10 ⁸	-1.60×10 ¹⁰	2.02×10 ⁵	1.91×10 ³	4.93×10 ⁻⁶
3 g+50 mL	-6.09×10 ⁷	-1.02×10 ¹¹	2.89×10 ⁵	9.10×10 ²	3.44×10 ⁻⁶

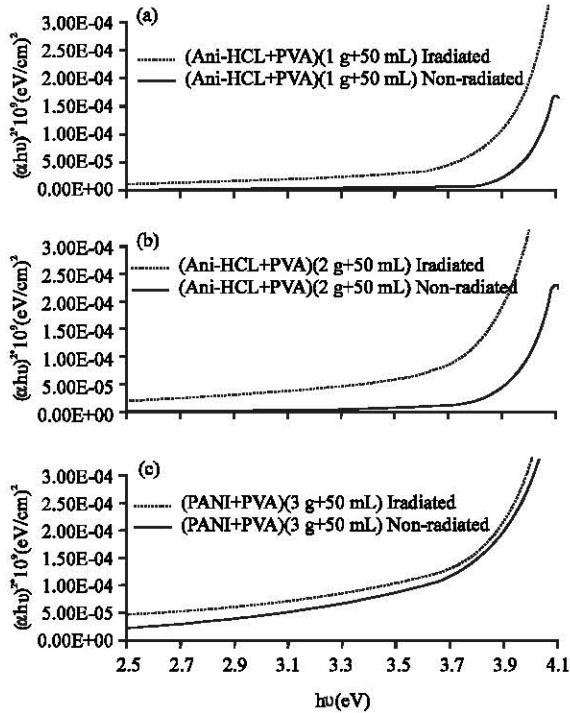


Fig. 10: a-c) The relation between $(\alpha h\nu)^2$ versus photon energy

Hall effect measurements: The hall effect measurements for the polymer films were obtained to obtain the value of the hall coefficient and the electrical conductivity and polymer mobility at room temperature. Hall effect measurements were made to determine the hall factor on the recorded films to determine the hall factor and the concentration of the carriers and the movement using hall effect measurement system type HMS 3000 manufactured by ECOPIA Taiwanese and using a magnetic field of magnitude ($B = 0.55$ tesla).

The results showed that the films of polymer (n-type) poly-aniline due to the bonds of Π which leads to the improvement of electrical properties through the increase in the concentration of carriers and electrical conductivity (Bai and Shi, 2007) (Table 7 and 8).

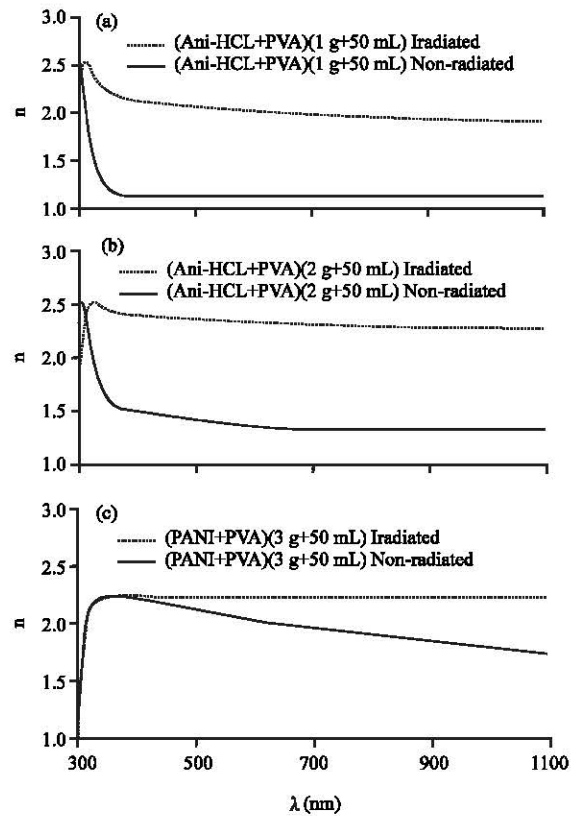


Fig. 11: a-c) The refractive index as a function of the wavelength of the recorded polymer

CONCLUSION

After studying and obtaining the results were concluded that:

- The energy gap is affected by radiation which is less after irradiation, absorption and coefficient increases after irradiation
- Irradiation affects the nature of the surface of recorded films, resulting in a decrease in permeability
- Irradiation process led to change the color of the polymer

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