

# Effect Of Adding The Nickel Complex To Leucine Derivative On Photophysical Characteristics Of Polyvinyl Alcohol

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**Abstract:** *The current research included a study of photocatalytic degradation of polyvinyl alcohol (PVA) films prepared by the pouring method after adding different weight ratios of nickel complex to a leucine derivative (0.4%, 0.2%, 0.1%, 0.05%, 0.025%) with thickness of  $75 \pm 5 \mu\text{m}$ . The effect of the additive ratio on the photocatalytic degradation speed of polymeric films relative to pure films before and after exposure to the source of ultraviolet was studied, which showed the highest absorption at the wavelength of 356 nm with irradiation times starting from 25-100 hrs. The photocatalytic degradation process has been monitored by using the UV-VIS spectrophotometer to calculate the degradation rate constant ( $K_d$ ), the infrared (FT-IR) device to calculate the growth coefficient of carbonyl ( $I_{CO}$ ) and hydroxyl ( $I_{OH}$ ) groups and the viscosity technique to follow the change in the viscosity-average molecular weight. It was found through FT-IR and UV-Vis that the degradation rate constant and growth coefficients of carbonyl and hydroxyl were inversely proportional with the concentration of the added nickel complex and the irradiation time. The results of viscosity measurements obtained from the calculation of the degradation degree and the numerical rate of chain (S) scission showed that increasing concentration S of the added nickel complex reduces the degradation of the polymer molecular weight. Thus it is considered a stabilizer for photocatalytic degradation.*

**Keywords:** *photocatalytic degradation, Ni complex for leucine derivative, PVA*

## I. INTRODUCTION

Polyvinyl alcohol (PVA) with the general formula  $[-\text{CH}_2\text{CH}(\text{OH})-]_n$  is considered a well-known polymer for many industrial, commercial, medical and food applications. It is a common synthetic polymer used for many end products, such as resins, sutures, and food packaging materials that often in contact with food (1,2). This polymer has exceptional physical and chemical properties (3-5) such as high transparency, good elasticity, non-toxicity, chemical resistance, solubility in water, biodegradability, and the similarities in physical properties with human tissues, which make it biocompatible. Hence, PVA films were widely developed for biomedical and biological applications (6).

PVA is a semi-polar polymer in the form of a White powdery, tasteless, odorless, non-toxic, water-soluble (7), its density is (1.19-1.31)  $\text{g}/\text{cm}^3$  and its melting point is 230 °C. It degrades rapidly over 200 °C, where it undergoes pyrolysis at high temperatures (8). Polyvinyl alcohol was prepared for the first time in 1924 by Haehner and Herrmann from polyvinyl acetate as a substrate (9). During the UV irradiation, the hydroxyl (OH) group oxidized and the free radicals produced with many other chemical reactions. The high water-adaptive hydroxyl (OH) group converts to the low water-adaptive carbonyl (C=O) group, and reduces the PVA

solubility after the fractionation process. Whereas the alpha and beta carbon atoms from the carbonyl group are broken off by reactions of Norrish type I and type II; the evidence is low molecular weight <sup>(10)</sup>.

The nickel complex of the leucine derivative is a bimetallic macrocyclic complex. Increasing the commercial value of the dithiocarbamate compounds and their complexes with the transitional elements as well as their broad biological efficacy, have attracted the interest of researchers towards studying their chemistry and identifying their characteristics <sup>(11, 12)</sup>.

Dithiocarbamate is similar to carbamate in that the oxygen atoms are replaced by sulfur atoms and are an interesting group from organic compounds that play a remarkable role in organic and inorganic chemistry <sup>(11)</sup>. These compounds are easily prepared as primary and secondary amines interact with carbon disulfide in the presence of a base such as KOH, NaOH, etc. These compounds have shown different applications in many aspects, including industry, agriculture, chemical drilling, biochemistry and analytic chemistry. It also can interact and form a stable compound with a wide range of transition and representative elements, making them distinct links in inorganic and biological chemistry. Ligand dithiocarbamate has the ability to stabilize the oxidation state of the central mineral and allow it to adopt its preferred geometry. Dithiocarbamate (dtc) ligand has the capability to stabilize the oxidation state of the central metals and allow adopting their preferred geometry.

This research aims to study the possibility of using chemicals that help improve the physical and optical properties of this polymer by adding chemicals that work to reduce the degradation of polymeric materials for permanent or external use (such as tanks, tubes and greenhouses) when exposed to ultraviolet radiation coming from the sun to reduce damages of environmental degradation caused by polymeric materials to a minimum.

## II. MATERIALS AND METHODS

### *Materials*

Leucine(96%),Methanol(99%),Nikle chloride (99%),DW,PVA(97%),were purchased from sigma, fluka and Aldrich

### *Preparation of a nickel complex of Leucine derivative*

About 0.05 g of ligand has been dissolved in absolute methanol (10 ml) in a circular flask equipped with a magnetic stirrer and a reflux condenser, then 0.098 g of metal nickel chloride NiCl<sub>2</sub> dissolved in 5 ml distilled water (D.W) has been added to it. The mixture has been heated and refluxed for an hour as the color of the solution turns from yellow to dark green, filtered, washed with methanol, and left to dry.

### *Preparation of polyvinyl alcohol*

Seven grams of polyvinyl alcohol polymer has been dissolved in a volume of 100 ml of D.W with continuous stirring in a circular flask-250 ml equipped with a magnetic stirrer to obtain a more homogeneous solution at 80 °C for 1 hr.

### *Preparation of polymeric films*

The polymeric films of PVA have been prepared by the following steps:

1. 3 ml of the pre-prepared PVA solution has been taken.
2. The nickel complex of leucine ligand (previously prepared) has been dissolved in D.W and took 1 ml of this solution with different weight ratios (0.4%, 0.2%, 0.1%, 0.05%, 0.025%).
3. Mixing the two volumes taken from the above two steps to get a more homogeneous mixture without bubbles.

4. The mixture (4 ml) has been poured into glass templates previously prepared from glass slides fixed on a piece of glass placed on a horizontal surface that has been leveled with a leveling scale to ensure the uniform distribution of the solution in the template.
5. Leaving the mixture for 24 hrs to dry.
6. The polymeric films have been removed by a blade and the thickness has been measured by a micrometer, where the thickness of the polymeric films ranged between 70-75  $\mu\text{m}$ .
7. Polymeric films have been cut with dimensions ranged from 1.5-3.5 cm in proportion to spectroscopic measuring devices (FT-IR, and UV-vis).

#### *Irradiation technique*

The prepared samples have been irradiated using a fluorescent lamp with power (125 watts) equipped with a filter with a maximum intensity of wavelength at 356 nm for 100 hrs and several stages and periods (0, 25, 50, 75, 100) hrs at 37 °C and intensity light equal

$$I_0 = 1.5 \cdot 10^{-8} \text{ ein.dm}^{-3}\text{s}^{-1}$$

#### *Monitoring photocatalytic degradation of polymeric films*

The photocatalytic degradation of the prepared polymeric films was followed using an ultraviolet device to calculate the absorbance of the polymeric films at a wide range of wavelength between 200-700 nm, which enables us to calculate the degradation rate constant ( $K_d$ ) by the optical oxidation of polyvinyl alcohol films with the nickel complex according to the first level law as shown in Eq. 1:

$$\ln(a-x) = \ln a - K_d t \quad \dots\dots\dots (1) \text{ Where, } a: \text{ the concentration of the material before irradiation, } x: \text{ the concentration of the material after the time (sec) of irradiation, } t: \text{ irradiation time (sec).}$$

If ( $A_0$ ) represents the absorbance of the polymer film containing a limited concentration of the complex before the irradiation process, and ( $A_t$ ) represents the absorbance at the irradiation time ( $t$ ) of the same film, so ( $A_\infty$ ) can be considered as the absorbance of the polymer film at infinity of time. The relationship between the absorbance and concentration is as shown in the following Eqs. :

$$a = A_\infty - A_t$$

$$x = A_t - A_0$$

$$a-x = (A_\infty - A_0) - (A_t - A_0) = A_\infty - A_t \quad \dots\dots\dots (2)$$

After substituting the values of  $a$  and  $x$  into Eqs. 1 and 2 results:

$$\ln(A_\infty - A_t) = \ln(A_\infty - A_0) - K_d t \quad \dots\dots\dots (3)$$

We plot the relationship between  $\ln(A_\infty - A_t)$  with the irradiation time ( $t$ ) and obtain the straight-line equation indicating that the reaction is of the first level and its slope represents the degradation rate constant ( $-K_d$ ).

The photocatalytic degradation of the prepared polymeric films is also monitored using an FT-IR device (Bruker) with a range of 400-4000  $\text{cm}^{-1}$ .

The absorption site of the carbonyl group has been determined at 1730  $\text{cm}^{-1}$  in order to calculate the growth amount of the carbonyl group coefficient ( $I_{CO}$ ).

Also, the absorption site of the hydroxyl group has been determined at 3430  $\text{cm}^{-1}$  to calculate the growth amount of the hydroxyl group coefficient, which is a guide to monitor the degradation behavior of polyvinyl alcohol. By comparing the absorbance with the absorbance of the reference peak for PVA at 1224  $\text{cm}^{-1}$ , and by applying Eq. 4:

$$I_{(S)} = A_{(S)}/A_{(R)} \quad \dots\dots\dots (4)$$

Where:  $I_{(s)}$ : the growth coefficient of the group under study,  $A_{(s)}$ : Absorbance of the group under study,  $A_{(R)}$ : the absorbance of the reference peak.

By applying Beer-Lambert law, the transmittance (T%) is transformed to values of Absorbance by using Eq. 5:

$$A = 2 - \log (T\%) \dots\dots\dots(5)$$

#### *Determination of viscosity-average molecular weight*

The molecular weight of polymers is determined by calculation of the viscosity average using Eq. 6 (equation of Mark-Houwink):

$$[\eta] = K(MV)^a \dots\dots\dots(6)$$

Where:  $[\eta]$ : Intrinsic viscosity,  $a$  &  $K$ : constants depend on the polymer and solvent nature and temperature,  $M_v$ : viscosity-average molecular weight.

By using a Viscometer, the viscosity of polyvinyl alcohol in water has been measured by monitoring the flow time of the solvent ( $t_0$ ), the flow time of the pure polymer solution and the solution of the polymeric compound solution in the solvent after each irradiation time ( $t$ ).

The viscosity of the pure polymers and the polymeric compound (consisting of polyvinyl alcohol with 0.4% of the nickel-leucine complex) has been measured at each irradiation time.

The relative viscosity has been calculated using Eq. 9:

$$\eta_{rel} = \frac{t}{t_0} \dots\dots\dots(7)$$

$$\eta_{sp} = \eta_{rel} - 1 \dots\dots\dots(8)$$

$$[\eta] = \left( \frac{\eta_{sp}}{C} \right) \dots\dots\dots(9)$$

Where:

$C$ : the concentration of polymer solution ( $g/100cm^3$ ),  $\eta_{rel}$ : Relative viscosity.

However, by applying Eq. 9, the molecular weight of the degraded and non- degraded polymer can be calculated. The molecular weights of polyvinyl alcohol, with and without additives, were obtained from measurements of Intrinsic viscosity in the  $H_2O$  solution using the following Eq.:

$$[\eta] = 2.0 \times 10^{-4} M_v^{0.76}$$

The degree of degradation ( $\alpha$ ) has been calculated from Eq. 10:

$$\alpha = \frac{1}{P_t} - \frac{1}{P_0} \dots\dots\dots(10)$$

Where:  $p_0$ : the numerical average of the polymerization degree before irradiation,  $p_t$ : the numerical average of the polymerization degree at the time ( $t$ ) of irradiation.

The numerical average of main chain (S) scission has been calculated from Eq. 11:

$$S = \frac{M_{v,0}}{M_{v,t}} - 1 \dots\dots\dots(11)$$

Where:  $M_{v,0}$  and  $M_{v,t}$  are the initial viscosity-average molecular weights at the irradiation time (0) at the irradiation time ( $t$ ), respectively.

### III. RESULTS AND DISCUSSION

The results of the UV-visible spectrum for the polymer (PVA) induced by adding the nickel complex to the leucine derivative showed that the concentrations (0.4%, 0.2%, 0.1%, 0.05%, 0.025%) of the added complex reduced the speed of the light reaction with the polymer. It can be seen that through the absorbance values, as shown in Table 1. The absorbance values of PVA films decrease with increasing the concentration of the added complex for the same

irradiation time, as shown in Figures 2, 3, 4, 5, and 6. It has an absorbance less than the absorbance of the pure polymer, as shown in Figure 1. These results are consistent with the values of the degradation constant calculated from the slope of the straight-line equation in Figures 7, 8, 9, 10 and 11. It was observed that the degradation constant is inversely proportional to the concentration of the added complex. The addition ratio (0.025%) exhibited the highest percentage of the degradation constant, while the addition ratio (0.4%) exhibited the lowest value for the degradation constant, as shown in Table 2.

The infrared spectrum measurements showed that the absorption band decreased with the addition of the nickel complex to the two bands of carbonyl and hydroxyl at the wavelength number  $1730\text{ cm}^{-1}$  and  $3430\text{ cm}^{-1}$ , respectively, as shown in Figures 12,13 and 14. The infrared spectrum showed that the peaks of two bands of carbonyl and hydroxyl groups for the film containing the added complex are less than the pure film, meaning that the complex works on the photo stabilizing of polyvinyl alcohol, as shown in Table 3 for calculating the hydroxyl and carbonyl coefficient. This encourages the use of the current added complex as a good stabilizing agent.

Measurements of viscosity exhibited that the viscosity-average molecular weight is inversely proportional to the irradiation time due to the increase in the rate of polymer degradation, as shown in Tables 4 and 5. These tables exhibited that the added complex relatively large led to decrease values of the viscosity-average molecular weight at the beginning of the irradiation periods. In contrast, the rates of this decrease reduced with the increase of the irradiation periods due to the fact that the process of breaking bonds from weak bonds was extensive. This is considered evidence as in the straight-line equation of the chain scission and the degradation degree, as in Figures 15 and 16. The complex acts as a stabilizing material for the photocatalytic degradation of the polymer, and this is consistent with the previous results obtained from measurements of FT-IR and UV-visible spectroscopy.

#### IV. CONCLUSIONS

The photocatalytic degradation of polyvinyl alcohol (PVA) films has been studied after adding different weight ratios of nickel complex to the leucine derivative by using UV-visible and infrared spectroscopy as well as viscosity measurements for the purpose of calculating the viscosity-average molecular weight. From the obtained results, they were shown as follows:

A- The degradation rate constant ( $K_d$ ) and the growth coefficient of carbonyl ( $I_{CO}$ ) and hydroxyl ( $I_{OH}$ ) groups are inversely proportional to the added nickel complex and the irradiation time.

B- By calculating the degradation degree and the numerical rate of the S-chain scission, it was found that the presence of the nickel complex reduces the viscosity of the molecular weight degradation. Thus it is a stabilizer for the photocatalytic degradation process.

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Table 1. Absorbance values of pure PVA and which contained different concentrations of the added complex with thickness of  $75 \pm 5 \mu\text{m}$  at 276 nm (UV spectroscopy)

Absorbance $A_t$					Irradiation time (hr)
100	75	50	25	0.0	
<b>0.892</b>	<b>0.718</b>	<b>0.574</b>	<b>0.461</b>	<b>0.145</b>	<b>PVA</b>
<b>0.811</b>	<b>0.603</b>	<b>0.444</b>	<b>0.361</b>	<b>0.094</b>	<b>PVA + 0.025% Ni_leu</b>
<b>0.669</b>	<b>0.541</b>	<b>0.352</b>	<b>0.287</b>	<b>0.084</b>	<b>PVA + 0.05 % Ni_leu</b>
<b>0.568</b>	<b>0.446</b>	<b>0.305</b>	<b>0.223</b>	<b>0.076</b>	<b>PVA + 0.1 % Ni_leu</b>
<b>0.451</b>	<b>0.339</b>	<b>0.264</b>	<b>0.185</b>	<b>0.067</b>	<b>PVA + 0.2 % Ni_leu</b>
<b>0.339</b>	<b>0.254</b>	<b>0.191</b>	<b>0.157</b>	<b>0.058</b>	<b>PVA + 0.4 % Ni_leu</b>

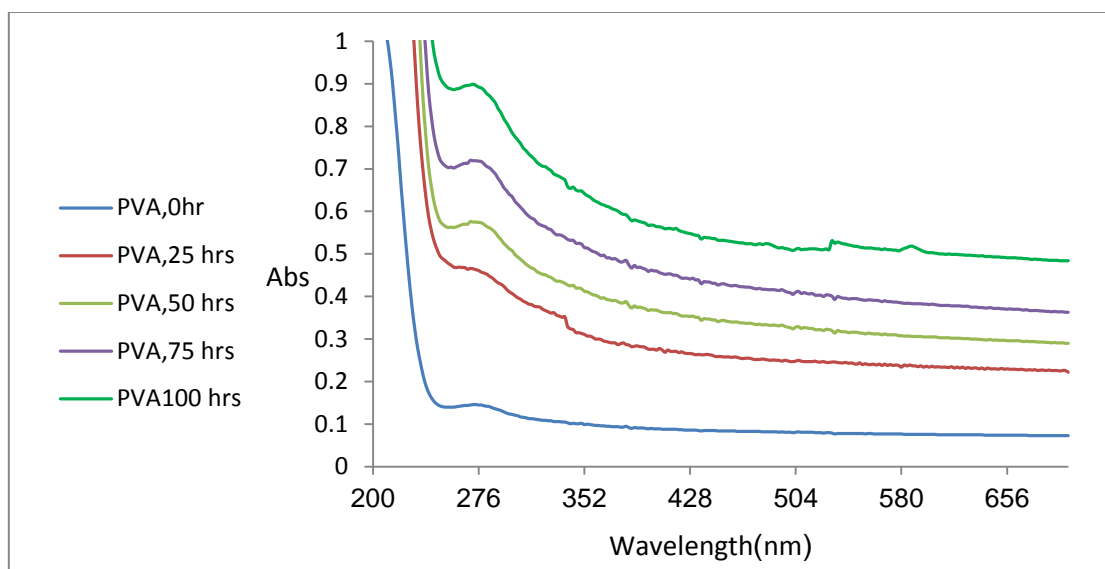


Figure 1. The change in the UV-visible spectrum of additive-free poly vinyl alcohol films with thickness of  $75 \pm 5 \mu\text{m}$  at different irradiation times

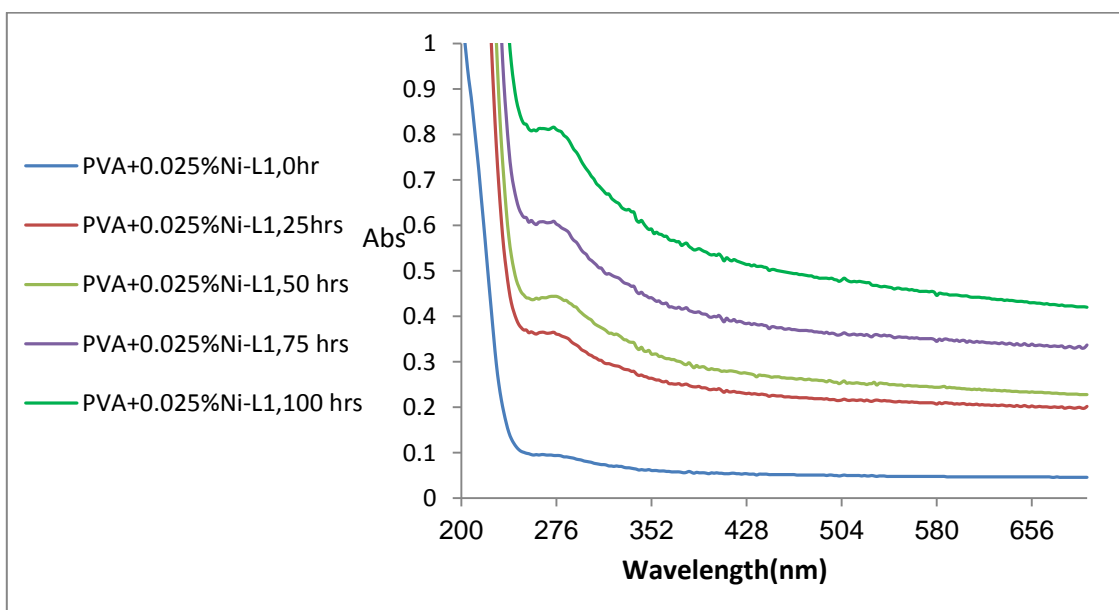


Figure 2. The change in the UV-visible spectrum of poly vinyl alcohol films containing 0.025% Ni-Leu complex with thickness of  $75 \pm 5 \mu\text{m}$  at different irradiation times

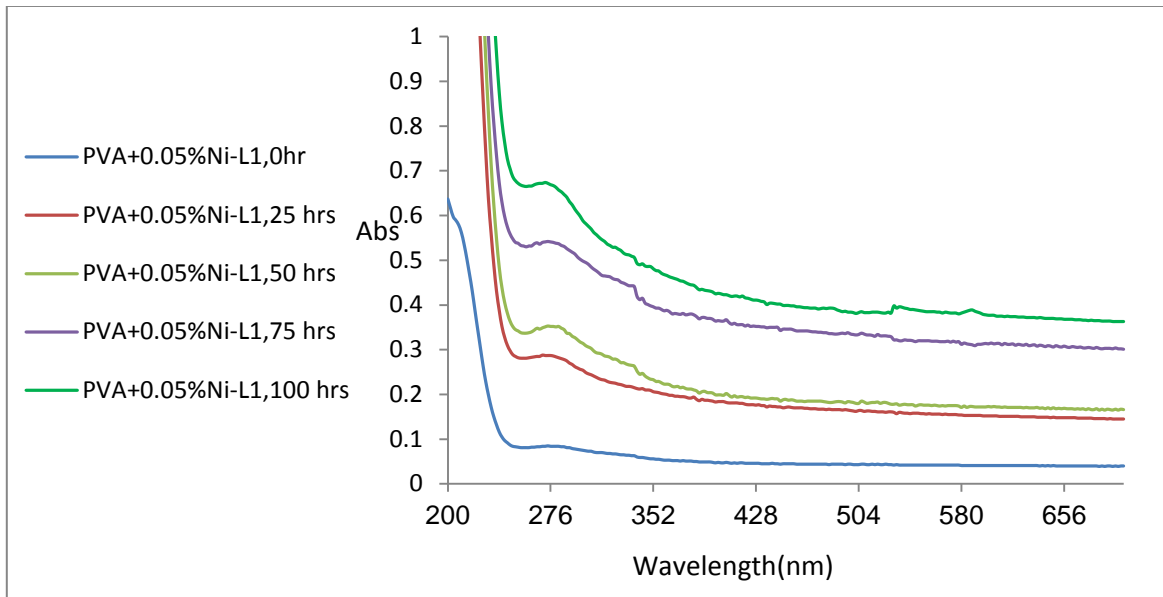


Figure 3. The change in the UV-visible spectrum of poly vinyl alcohol films containing 0.05% Ni-Leu complex with thickness of  $75 \pm 5 \mu\text{m}$  at different irradiation times

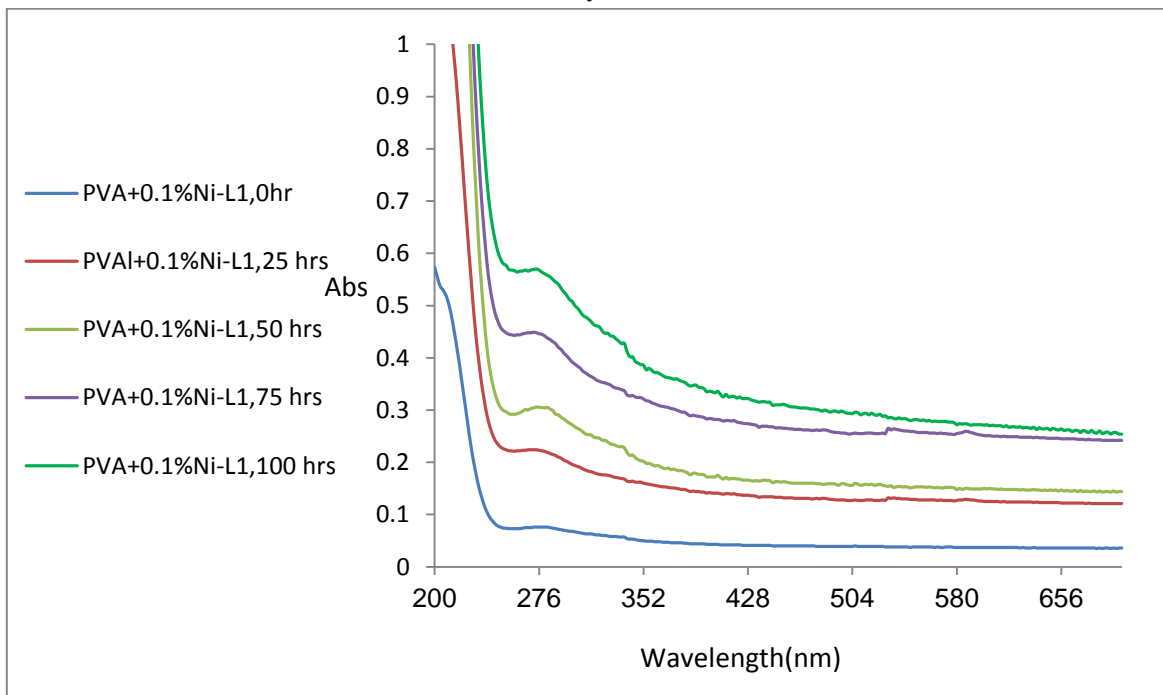


Figure 4. The change in the UV-visible spectrum of poly vinyl alcohol films containing 0.1% Ni-Leu complex with thickness of  $75 \pm 5 \mu\text{m}$  at different irradiation times



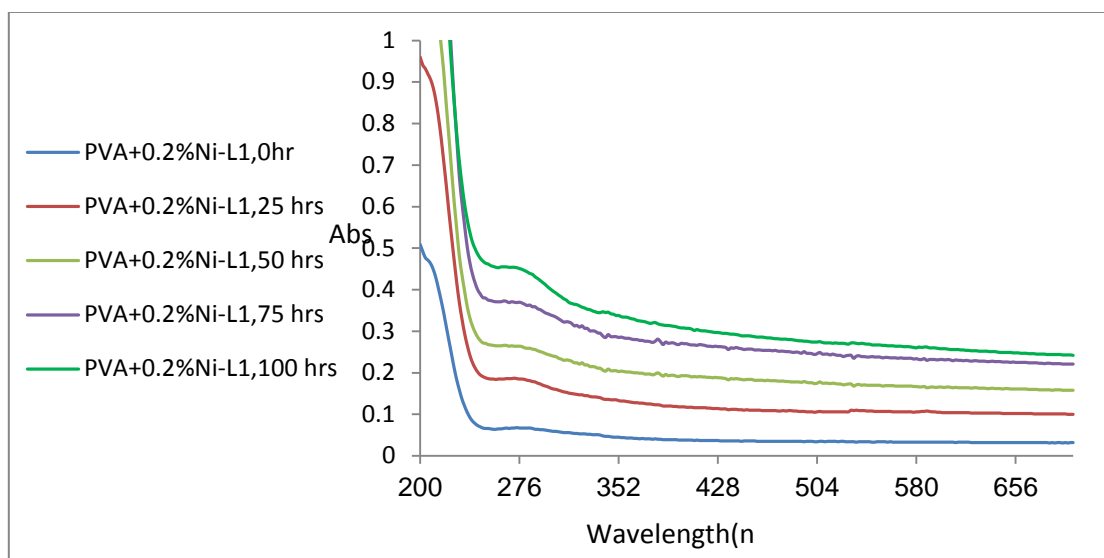


Figure 5. The change in the UV-visible spectrum of poly vinyl alcohol films containing 0.2% Ni-Leu complex with thickness of  $75 \pm 5 \mu\text{m}$  at different irradiation times

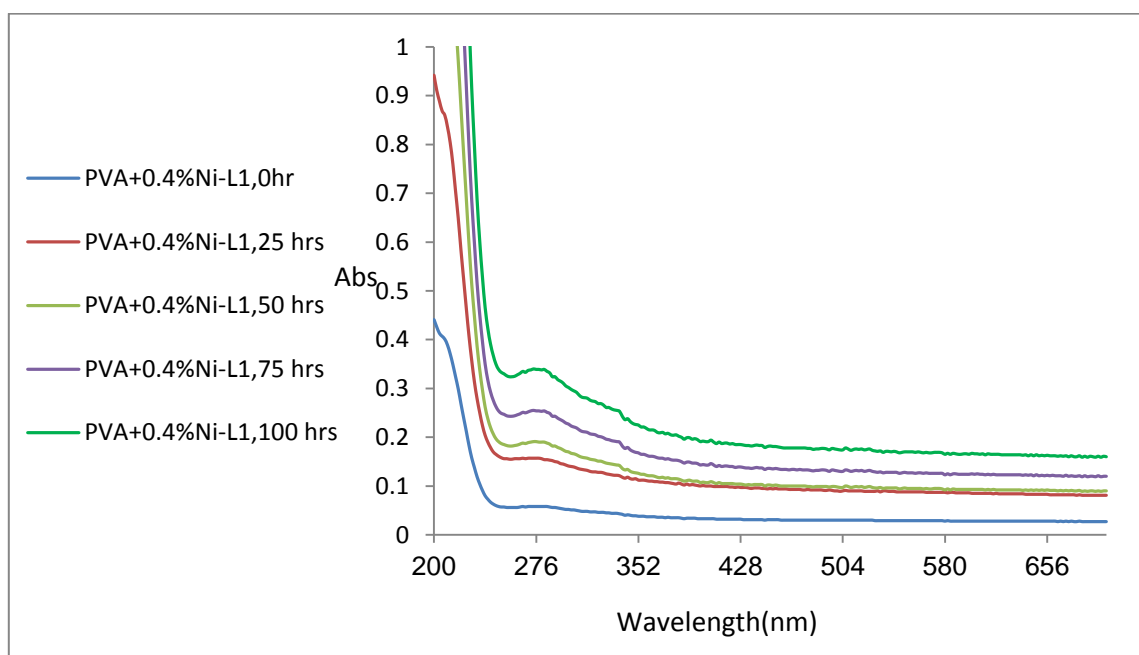


Figure 6. The change in the UV-visible spectrum of poly vinyl alcohol films containing 0.4% Ni-Leu complex with thickness of  $75 \pm 5 \mu\text{m}$  at different irradiation times

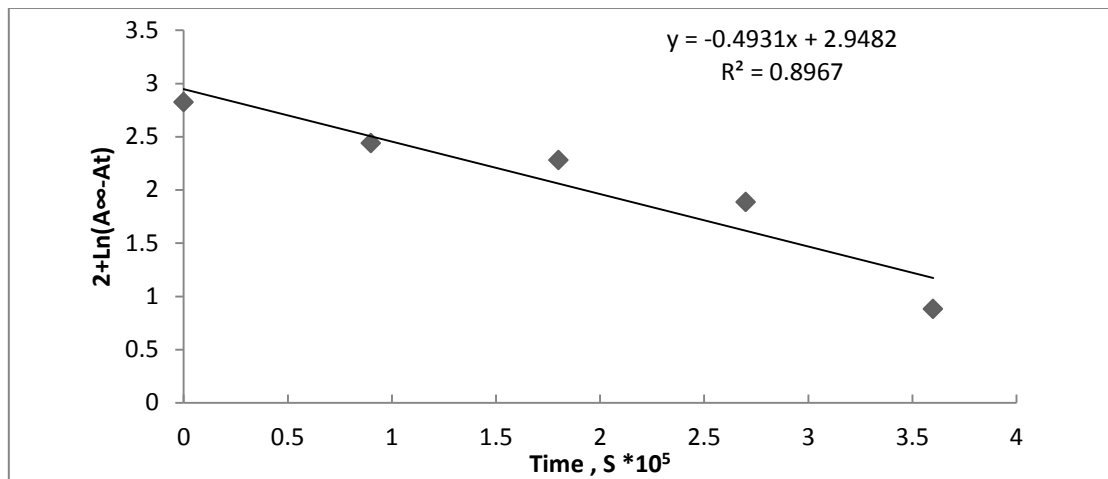


Figure 7. The relationship between the natural logarithm of absorption of a Ni-Leu complex at the concentration of 0.025% in PVA films with thickness  $75 \pm 5 \mu\text{m}$  and the irradiation time

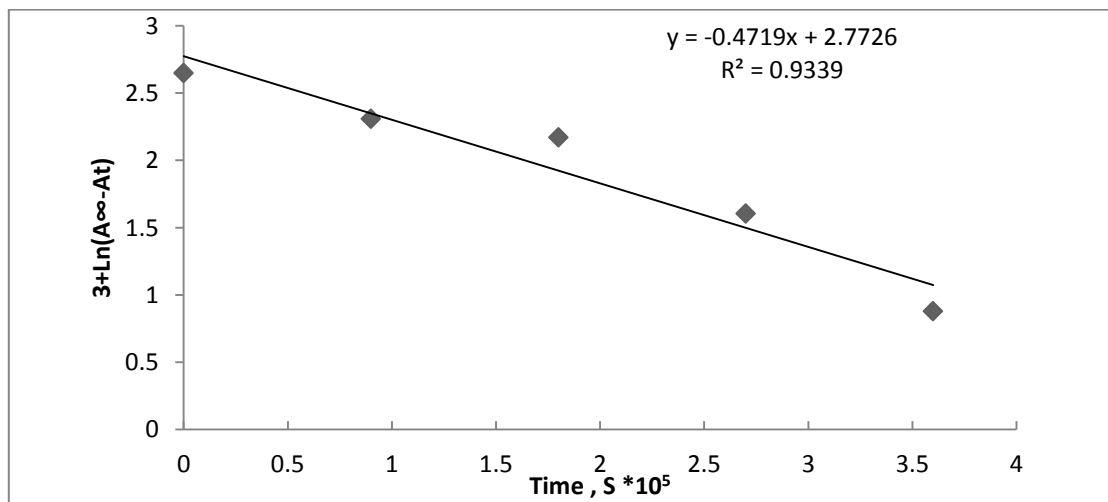


Figure 8. The relationship between the natural logarithm of absorption of a Ni-Leu complex at the concentration of 0.05% in PVA films with thickness  $75 \pm 5 \mu\text{m}$  and the irradiation time

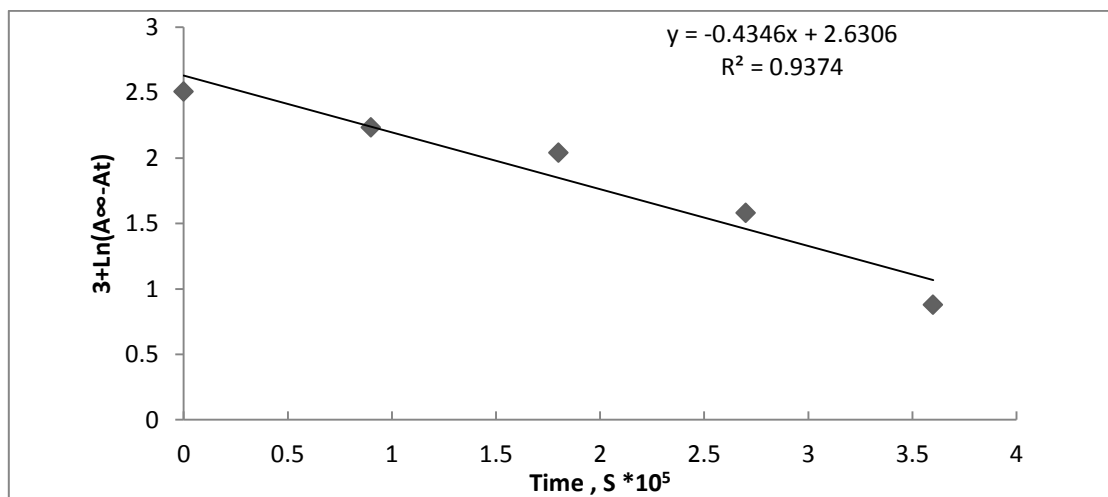


Figure 9. The relationship between the natural logarithm of absorption of a Ni-Leu complex at the concentration of 0.1% in PVA films with thickness  $75\pm 5 \mu\text{m}$  and the irradiation time

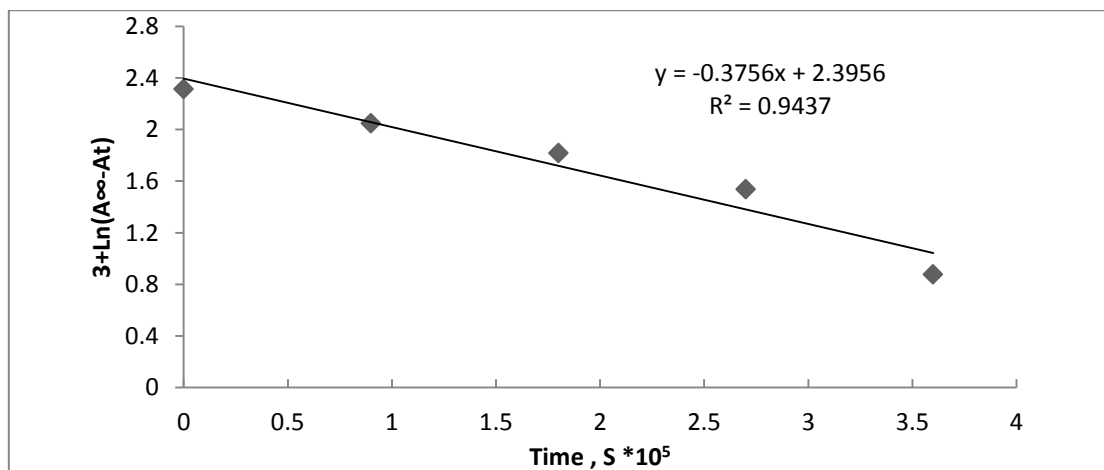


Figure 10. The relationship between the natural logarithm of absorption of a Ni-Leu complex at the concentration of 0.2% in PVA films with thickness  $75\pm 5 \mu\text{m}$  and the irradiation time

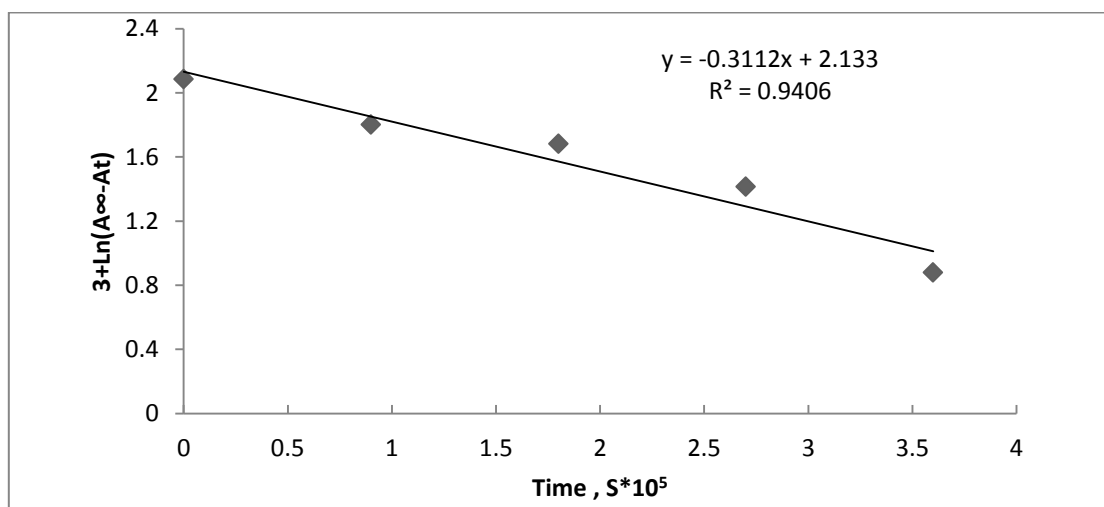


Figure 11. The relationship between the natural logarithm of absorption of a Ni-Leu complex at the concentration of 0.4% in PVA films with thickness  $75\pm 5 \mu\text{m}$  and the irradiation time

Table 2. Values of degradation rate constant ( $K_d$ ) for Ni-Leu complex in PVA films

The concentration (%)	Degradation rate constant $K_d (\text{Sec.})^{-1} \times 10^{-5}$
0.025	0.493
0.05	0.471
0.1	0.434
0.2	0.375

<b>0.4</b>	<b>0.311</b>
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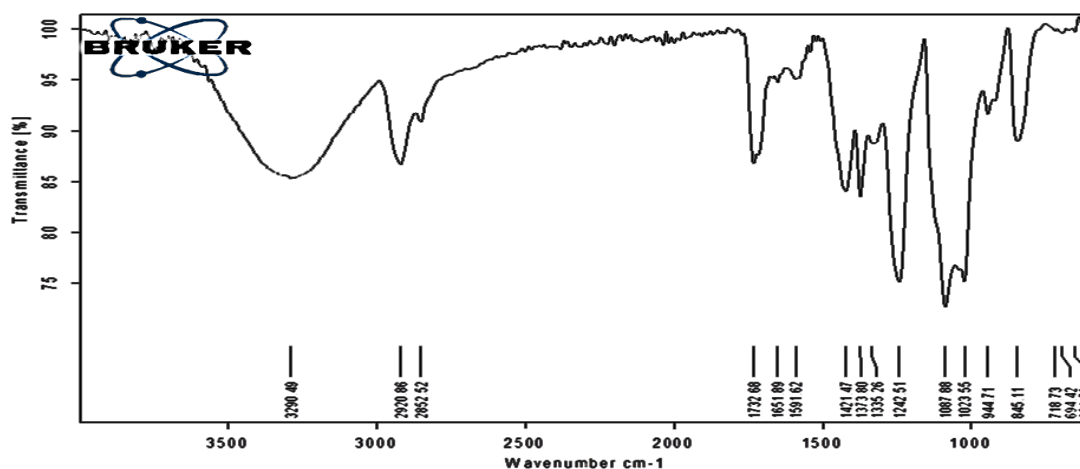


Figure 12. The infrared spectrum of additive-free PVA with thickness of  $75 \pm 5 \mu\text{m}$  before irradiation

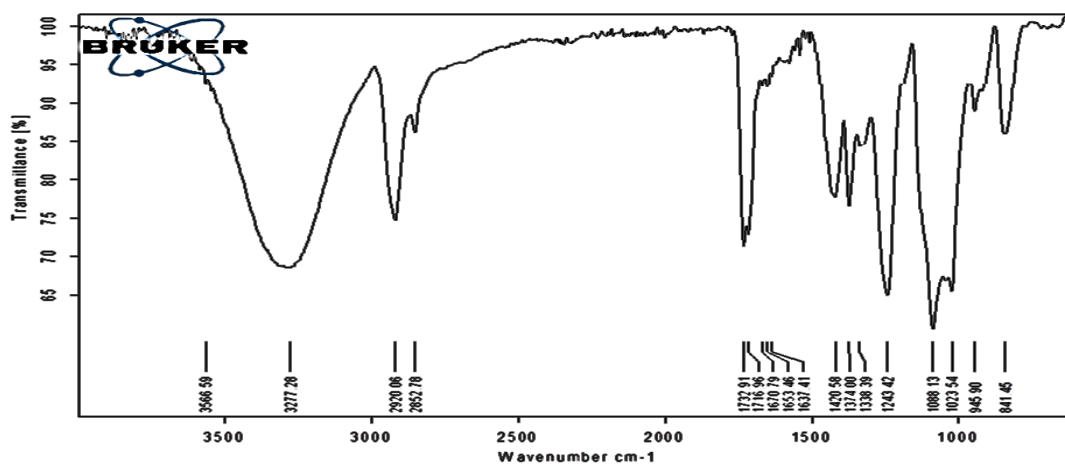


Figure 13. The infrared spectrum of additive-free PVA with thickness of  $75 \pm 5 \mu\text{m}$  after irradiation time of 75 hours

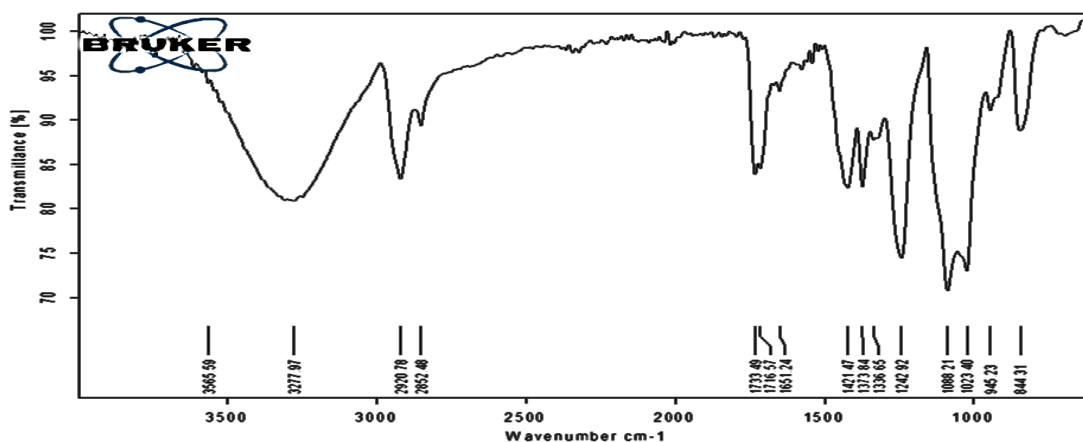


Figure 14. The infrared spectrum of additive-free PVA containing 0.4% Ni-L1 complex with thickness of  $75 \pm 5 \mu\text{m}$  after irradiation time of 75 hours

Table 3. The coefficient of carbonyl  $I_{CO}$  and hydroxyl  $I_{OH}$  groups values of PVA with and without 0.4% Ni-Leu complex after irradiation time of 75 hours

No.	Additives	$I_{CO}$	$I_{OH}$
1	PVA before irradiation	0.622	0.581
2	PVA after irradiation time of 75 hours	1.408	1.510
3	PVA containing 0.4% Ni-L1 complex after irradiation time of 75 hours	0.775	0.795

Table 4. The calculated values of viscosity molecular weight measurements for pure PVA films

Average of chain (S) scission	Degradation degree $\alpha \times 10^{-3}$	$\frac{1}{P} \times 10^{-4}$	Polymerization degree P	$(M_v) \times 10^3$	Irradiation time (hr)
0.0	0.0	7.658	1305.750	57.453	0
0.227	0.174	9.398	1064.000	46.816	25
0.492	0.377	11.433	874.659	38.485	50
0.800	0.612	13.787	725.272	31.912	75
1.054	0.807	15.734	635.545	27.964	100

Table 5. The calculated values for viscosity molecular weight measurements of PVA containing 0.4% of the complex Ni-Leu

Average of chain (S) scission	Degradation degree $\alpha \times 10^{-3}$	$\frac{1}{P} \times 10^{-4}$	Polymerization degree P	$(M_v) \times 10^3$	Irradiation time (hr)
0.0	0.0	7.658	1305.750	57.453	0
0.141	0.108	8.738	1144.318	50.350	25
0.300	0.230	9.962	1003.727	44.164	50
0.432	0.331	10.968	911.681	40.114	75

0.564	0.432	11.983	834.454	36.716	100
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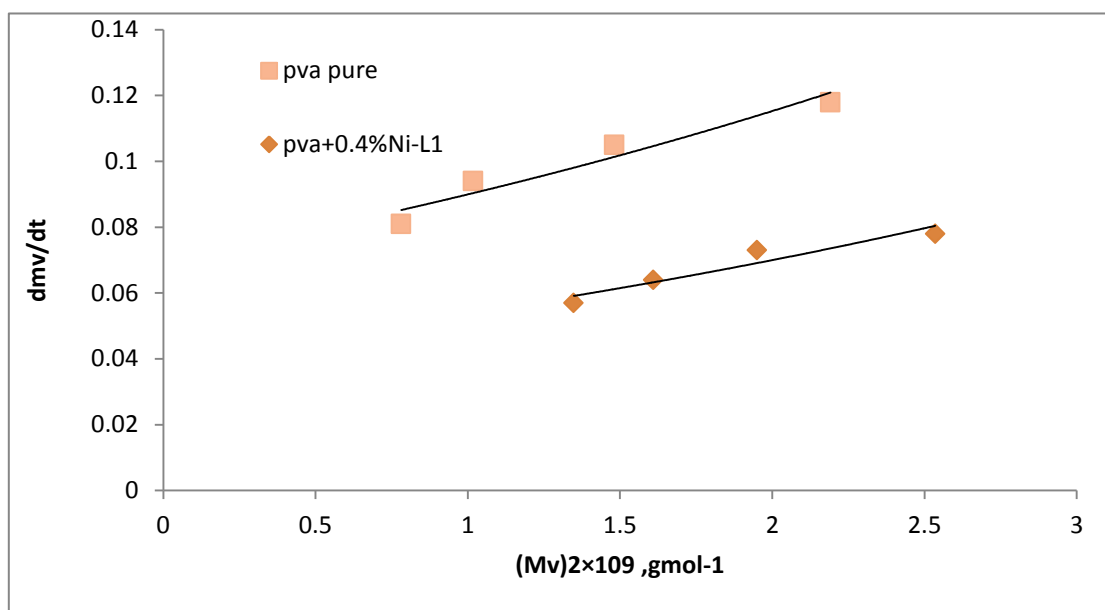


Figure 15. The relationship between the speed of decrease in the molecular weight average (dMv/dt) and the square of the average viscous molecular weight of PVA films with or without 0.4% of the Ni-Leu complex

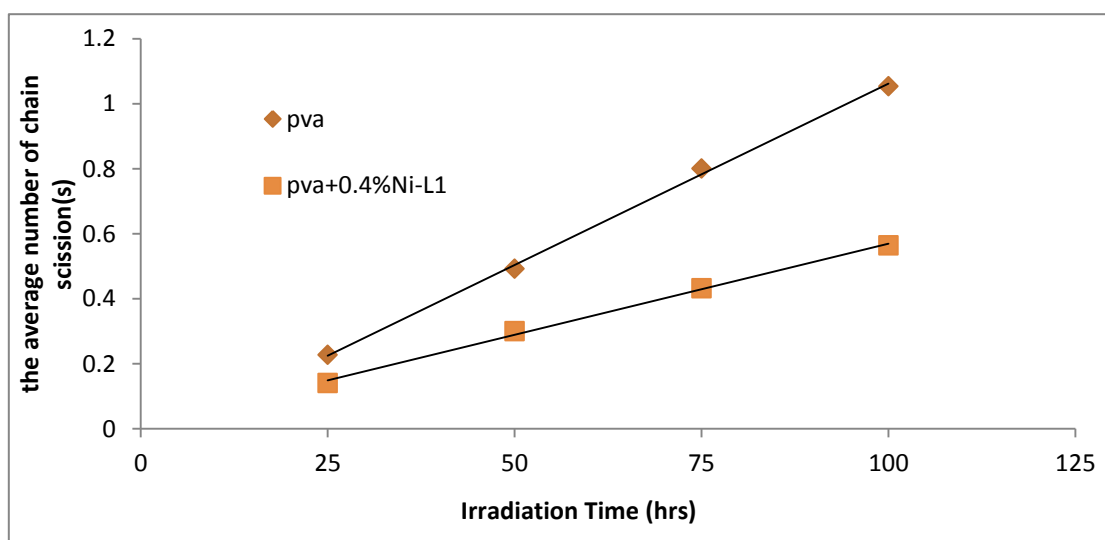


Figure 16. The relationship of the numerical rate of the chain scission with the irradiation time of PVA films with thickness  $75 \pm 5 \mu\text{m}$  in the presence and absence of 0.4% of the complex Ni-Leu

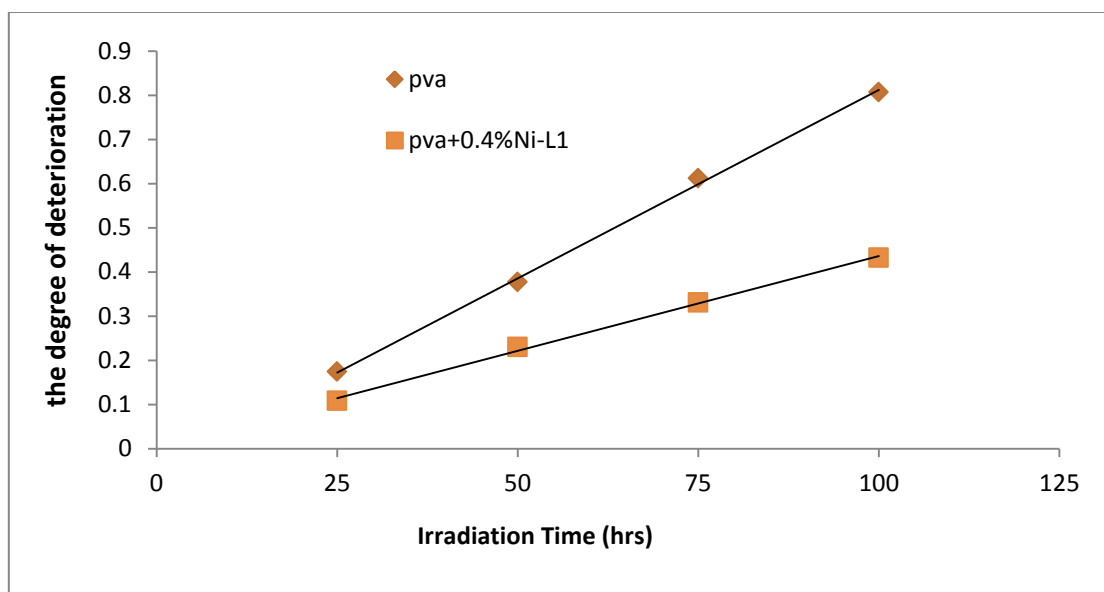


Figure 17. The relationship of the degree of degradation with the irradiation time of PVA films with thickness of  $75 \pm 5 \mu\text{m}$  in the presence and absence of 0.4% of the complex Ni-Leu