

Microwave-assisted Degradation of Polystyrene Induced by 8-hydroxy quinoline Nickel (II) complex.

Tariq A. Mendeel* Hameed Kh. Ali** Ahmad O. Farhan***



*University of Anbar- College Of Science

*University of Anbar- College Of Education For Pure Science

***University of Anbar- Desert Research Center.

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ABSTRACT

The most serious problems encountered in polystyrene (PS) processing is due to a poisoning and pollution of environment because of the PS structure containing aromatic ring. This study suggests a clean and ecofriendly of (PS) degradation. To the PS film prepared [8-hydroxyquinoline nickel(II) complex added as inducing agent for degradation (PS) film exposed to the microwave radiation. A hand molding casting has been used for preparing specimens of the (PS) in percentages (0.0, 0.025, 0.05, 0.1, 0.2, 0.4%) of the complex. The Degradation were carried out using commercial microwave oven at constant power of 400 W for all experiments. Specimens were exposed to microwave radiation with multiple time (0.0, 15, 30, 60 minute), A degradation were followed via of the decrease in molecular weights averages (Mw-, Mn-) and the increase of absorbancy of the carbonyl index ICO and hydroxyl index IOH at the total time of 60 minutes with microwave radiation.

Introduction

Polystyrene (PS) is the most important of the polymers produced from petroleum, It occupies the fourth rank of the world production of polymers.[1]

The degradation of (PS) has been widely studied since 1940. Most of the early studies have been focused on the improvement the thermal stability of PS [2]. The environment receives large amounts of this polymer as a waste product. So the recent studies have focused on finding a safe way to dispose the PS wastes responding to optical, microwave, thermal , and high-energy radiation (gamma, x-rays) degradations. Plastic wastes are also composed of (PS) (mainly, foodservice packaging and protective packaging), which necessitates the recycling of the polystyrene wastes.[3,4]

The microwaves are electromagnetic waves of relatively low frequency ($10^9 - 10^1$ Htz) They produce heat by giving quantum amounts of energy to the substances through which they pass. [5]. Microwave irradiation is a well-known method for heating and drying materials and is utilized in many private households and industrial applications for this purpose.

Offering a number of advantages over conventional heating such as non-contact heating (circumventing the decomposition of molecules close to the walls of their action vessel instantaneous and rapid heating), resulting in a uniform heating of their action liquor, microwave ovens operate with electromagnetic on ionizing radiation with frequencies between 300GHz and 300MHz. The corresponding wave lengths span rang from 1mm to 1m. [6,7]. There has always been a keen interest in the industrial

* Corresponding author at: University of Anbar - College of Science;

E-mail address: tarik_jm@yahoo.com

application of microwave storm prove conventional processes microwave energy on ionizing energy source, because it creates heat deep inside the materials being processed as are suit of rapid alternations of the electromagnetic field at high frequency. Property results in much shorter process time, high yield and better quality of products than that obtained by conventional processing techniques, In microwave activation the sample is exposed to electromagnetic fields at microwave frequencies. Microwave activation occurs in times similar to that of light activation. [8- 11].

In this study microwave degradation of (PS) film containing small amounts of [Ni(8-HQ)] complex were examined under atmospheric oxygen, through calculating the carbonyl index I_{CO} , hydroxyl index I_{OH} , and the change of the molecular weights and poly dispersity M_w / M_n , as a function of the degradation

Materials and Methods

Chemicals; The PS is from Petkim Co. (Turkey). tetrahydrofuran (THF), petroleum ether, nickel chloride, 8-hydroxy quinoline, benzene were purchased from BDH . All chemicals were of analytical grade and used as received

Instrumentation; Nicolet FT-IR. IR100. Thermo Scientific . U.V- Vis. double beam cintaras 5 Spectrometer, M. Wts. measurements were taken using Ostwald viscometer, microwave oven (Korea) , LG 2.15 GHz.

Preparation of the Complex 8-hydroxy quinoline nickel(II) [Ni(8-HQ)].

The prepared [Ni(8-HQ)] were carried out by mixing (0.236g, 0.001 mol) of nickel chloride $NiCl_2$ which dissolved in 30 ml of distill water, worm solution of (0.2900g, 002 mol) of 8-hydroxy quinoline dissolved in the absolute Ethanol was added to the

mixture at room temperature with medium stirring speed, till the color changed from green to deep green, then the resulting solution was introduced in to 100ml a round flask, then dilute solution of sodium bicarbonate was added. The mixture was refluxed with stirring for 2h, after cooling the solution. The complex crystal was obtained by filtration and purified by recrystallization with absolute Ethanol. The product dried under vacuum for 10h.

Films preparation and Sampling;

PS was purified by dissolving it in the chloroform and precipitating in petroleum ether,, M.Wts were measured viscometrically. PS film was prepared with blend of PS solution (in THF) for several percentage with the complex (**0.0, 0.025, 0.05, 0.1, 0.2, 0.4**) % which were added to the solution with stirring in medium velocity, after that the mixed solution were poured into glass molds of dimensions 1×3 cm, once casted on transparency sheet thickness (65 ± 5) μm and were allowed to dry under ambient conditions for **24** h free standing films were obtained, further drying under 50 C^0 for **10** h was performed.

Degradation Procedures.:

A domestic microwave oven with magnetron source constant power of **400 W** for all experiments. The degradation of (PS) was carried out on the specimen as a film form, the specimens were placed at the center of the oven directly below the magnetron source and it was rotated on a turntable, to avoid the temperature gradients in the degradation reactions, the specimens were exposed to microwave with different times (**0.0 ,15 30 , 60** minutes), and specimens were taken out periodically from the device models then followed by FT-IR , UV. And M.Wts measurements.

Analysis of degradation;

Temporal absorption spectral changes during the degradation of substrate film were shown by FT-IR and U.V-Visible Spectrophotometer to determinate the I_{CO} and I_{OH} , to follow the change in the number average molecular weight Mn^* . Intrinsic viscosity method is applied using ubbelohde viscometer and weight average molecular weight Mw^* was estimated using the following Marke Houwink equation : [12]

$$\eta_0 = 7.8 \times 10^{-5} MW_w^{0.75}$$

Degradation product were changed in the weight average molecular weight Mw^* and poly despersity Mw^* / Mn^* .

The rate constant for Degradation of the complex

The rate constant for degradation by oxidation with microwave radiation for complex (K_d) is calculated by using the first order eq.

$\ln(a - x) = \ln a - K_d t$ 1, as **a = concentration of complex before radiation**

X = change in concentration of complex after time t, t = irradiation time

a = $A_\infty - A_0$, as A_∞ = adsorption at infinity time, A_0 = adsorption before irradiation.

x = $A_t - A_0$, as A_t = adsorption after time t of irradiation.

$$a - x = A_\infty - A_0 - A_t + A_0 = A_\infty - A_t$$
 2

By substitution of the value of a, (a - x), in Eq.

No 1 and 2

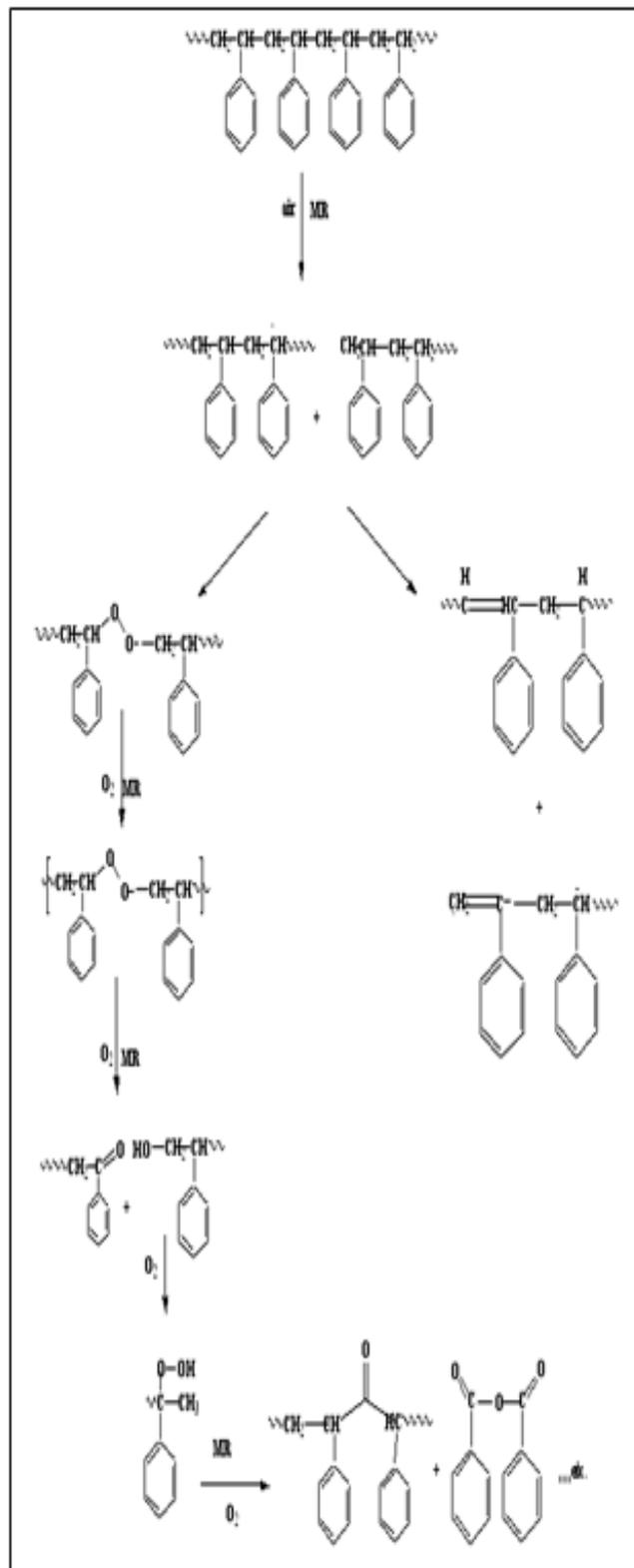
$$\ln(A_\infty - A_t) = \ln(A_\infty - A_0) - K_d t$$
 3

The a relationship between $\ln(A_\infty - A_t)$ and irradiation time(minutes) resulting straight line, its slope represents the ($-K_d$). This indicates that degradation of the additives is from a first order.

Results and Discussion

The degradation of PS was investigated under the microwave irradiation and in the presence of the complex [(Ni - HQ)] which accelerates the

degradation processes. In order to confirm the degradation mechanism, the reaction is carried out in the presence of radiation only and without heating, the suggested mechanism of the PS degradation is the following.



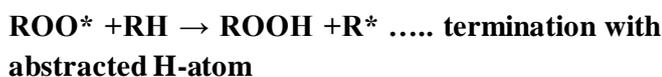
It showed the strong absorption on at the site of the carbonyl group C = O , and for the hydroxyl group OH, this refers to the formation of acetophenone and hydroperoxide respectively, due to the reaction of radicals with the impurities in the polymer under atmospheric oxygen that are lead to oxidation of the surface of polymer. Acetophenone degradation in the presence of oxygen begins via an initiation which produces the radical precursors initiation step may be represented as follow



Which induced by microwave ,When oxygen is allowed to react with the newly formed chain radical (R*), a peroxy radical intermediate is produced during the propagation step.



Highly reactive ROO* then abstracts a labile hydrogen from another polymer molecule giving rise to the hydroperoxide species.



Monomolecular decomposition of hydroperoxide should have a relatively high activation energy which would be comparable to the energy of an O- O bond scission.

$\text{ROOH} \rightarrow \text{RO}^* + \text{OH}^* \dots\dots$ alkoxy radical, RO* can also effectively abstract hydrogen from the remaining polymer .



The oxidative radiolysis is accelerated by metallic contaminant which could cause an extreme oxidative degradation Possibility of PS, the results of experimental microwave irradiation of PS lead to the polymer chains scission, and a reduction in the molecular weight .

The degradation of (PS) was studied by following the changes in OH stretch at (3350)cm⁻¹ .The area of the peak at (3350) cm⁻¹ is an indicator of the concentration of polymer hydroxide, As the

degradation progresses, the peak of of OH (produced from the reaction between radicals and atmospheric oxygen) of the polymers increases in intensity and expansion in such a way that the degradation made changes in C= O stretch at (1660) cm⁻¹ Table (1). The area of the peak increases in length and intensity, The % conversion of the reaction was therefore determined by following the increase in the integrated peak area of OH and C= O peaks of PS at (3350,1660 cm⁻¹) respectively, generally to offset any change in these bands. The peak at the (3350, 1660 cm⁻¹) band could be used quantitatively to determine the % conversions of the degradation reactions without any internal references.

Microwave Degradation;

Microwave technology is environmentally friendly techniqu and the nature of MW heating is also much more efficient compared to resistance heating, microwaves are located between infrared radiation and radio waves in the region of the electromagnetic spectrum. More specifically, as all electromagnetic waves, microwaves consist of electric and magnetic field components, both perpendicular to each other. as it is well known that PS has a high dielectric constant, and absorbs microwave energy better than other plastic grades.

The microwave strength absorption of PS is given by the following equation:

$\text{P} = \text{kft}^2 \text{E} \tan \phi = 0.55 \text{E}^2 \text{f} \text{E} \tan \phi \cdot 10^{-10}$, f is frequency of applied MW; E is strength of electro-magnetic field E is dielectric constant of materials and δ is loss angle; k is constant ($= 2\mu \epsilon_0 = 2\mu \cdot 8.85 \cdot 10^{-12}$). From Eq. above it can be stated that the absorbed microwave energy is depended on the strength of electro-magnetic field and dielectric characteristics of irradiating materials. The strength of electro-magnetic field is given as a function of the microwave power

frequency, PS has higher loss factor ($\epsilon \tan \phi$), than that of other plastic species and it reveals that (PS) has much advantages to absorb microwave than other plastic species. The variation of the number average molecular weight was also studied with reaction time which indicated that the degradation processes for PS led to decrease of the molecular weight due to the division of polymeric chain as a result of the degradation Table (2).

Spectral study:

Fig (1) shows spectra of FT-IR with absorption peaks of a reference sample with Stretching ($1630 - 1720\text{cm}^{-1}$) for the C=O group and shows all the peaks of other samples after addition of [(Ni - HQ)] complex indicating more degradation, as a sequence of the reaction between the produced radicals and atmospheric oxygen to form (peroxides and hydroxide), Fig(2) for absorption peaks of stretching ($3200-3650\text{cm}^{-1}$) due to OH group for reference sample, all other peaks for samples containing a complex salts showed more adsorption and intensity compared with the reference sample. UV-Vis spectra of prepared specimens doped with complex showed absorptions with different peak of PS before and after radiation which are shown in fig (3--8), For the neat specimen (reference) is of low absorption, where a doped complex specimens exhibit red shifts of absorption and significant enhancement of visible light absorption with reference accompanied with the changes of color from yellow to reddish, and shift toward longer wavelengths. the absorption of reference peak is low adsorption, but all absorption peaks is higher than the reference, so we show an increase in the value of I_{OH} and I_{CO} , with increment of the concentration of [(Ni-HQ)] complex and radiation time. Fig (7). fig (8). It is found that the value of the adsorption increases with the concentration of the

complex increment in such manner that the highest concentration (0.4) have the largest value in absorption Table (9) and (10). [14]

To study the effect of [(Ni - HQ)] complex on the degradation. The relationship between the natural logarithm of the complex concentration of the PS film with the time and The results correspond to the values of the calculated degradation constant from slope of the straight line Fig (11–15), values were Proportional to the increment of the complex concentration, 0.4 percentage of complex gave the highest value of the degradation constant. While the percentage of 0.025 given the lower value for degradation constant Table (5). This is in consistent with previous studies of the PS degradation by U.V radiation.

Conclusion

This study showed that the degradation of PS film is directly proportional to concentration of the added percentage of complex with increasing time of microwave radiation and didn't stabilize the polymer with complex against energy of radiation. That microwave radiation with 400W in different times cause decrease in the molecular weight of (PS) as the result of degradation, also of resulted change of the films color from yellow to yellow – orange the color change increases with the increasing of radiation time, that means the microwave radiation caused oxidation of the surface, in the first stages of the polystyrene degradation. And using of microwave radiation in degradation study is reducing the time and cost. Also This study showed that the use of the chemical methods for the degradation of (PS) is better than conventional processing such as incineration and landfill to reduce the environmental pollution

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Table.1. U.V – Visible adsorption value of (PS) film of thickness (65± 5) micron with complex (Ni-HQ) concentrations for microwave radiation at 400W

| Concentration Complex | Adsorption | | | |
|-----------------------|------------------------------------|-------|-------|-------|
| | Microwave Radiation / Time Minutes | | | |
| | 0.0 | 15 | 30 | 60 |
| PS | 0.171 | 0.185 | 0.191 | 0.202 |
| PS + 0.025 | 0.208 | 0.213 | 0.222 | 0.231 |
| PS + 0.05 | 0.214 | 0.231 | 0.254 | 0.268 |
| PS + 0.1 | 0.225 | 0.258 | 0.306 | 0.326 |
| PS + 0.2 | 0.234 | 0.270 | 0.356 | 0.515 |
| PS + 0.4 | 0.251 | 0.366 | 0.721 | 0.824 |

Table.2. The values of the polydispersity after degradation at 60 minutes in 400W of microwave radiation

| Concentration | \overline{M}_w | M_v | \overline{M}_w / M_v |
|---------------|------------------|--------|------------------------|
| PS + 0.0 | 95.898 | 20.811 | 4.608 |
| PS+025 | 88.201 | 19.601 | 4.499 |
| PS + 0.05 | 84.512 | 18.920 | 4.466 |
| PS + 0.1 | 69.033 | 16.291 | 4.237 |

| | | | |
|----------|--------|--------|-------|
| PS + 0.2 | 60.436 | 14.011 | 4.313 |
| PS + 0.4 | 48.931 | 11.723 | 4.173 |

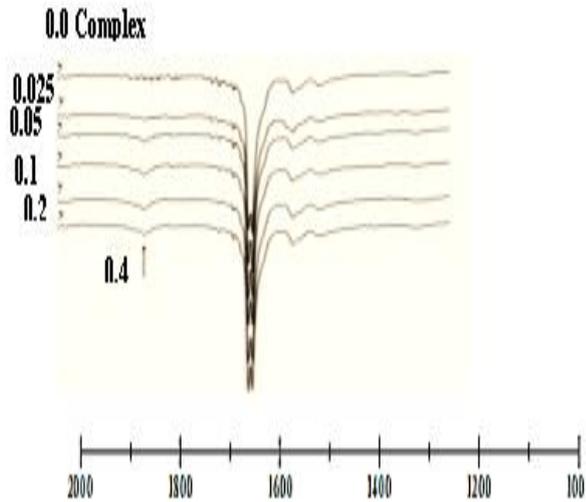


Fig. 1. FTIR spectra for Stretching CO of Microwave radiation PS

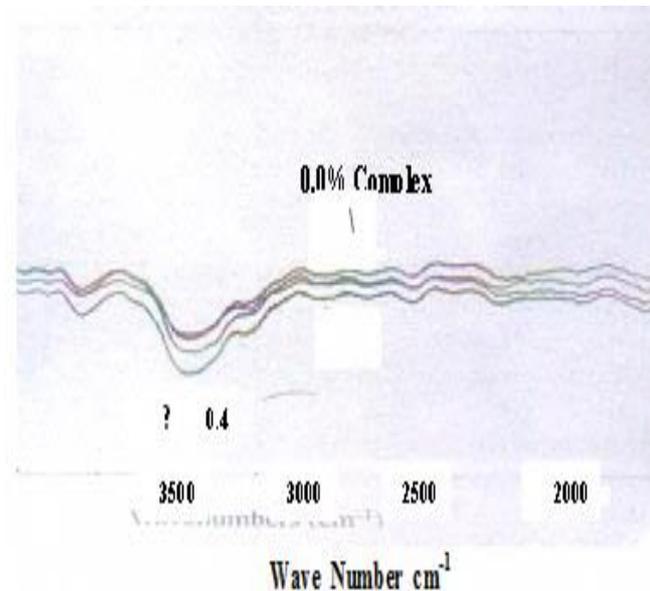


Fig. 2. FTIR spectra for Stretching OH of Microwave radiation PS

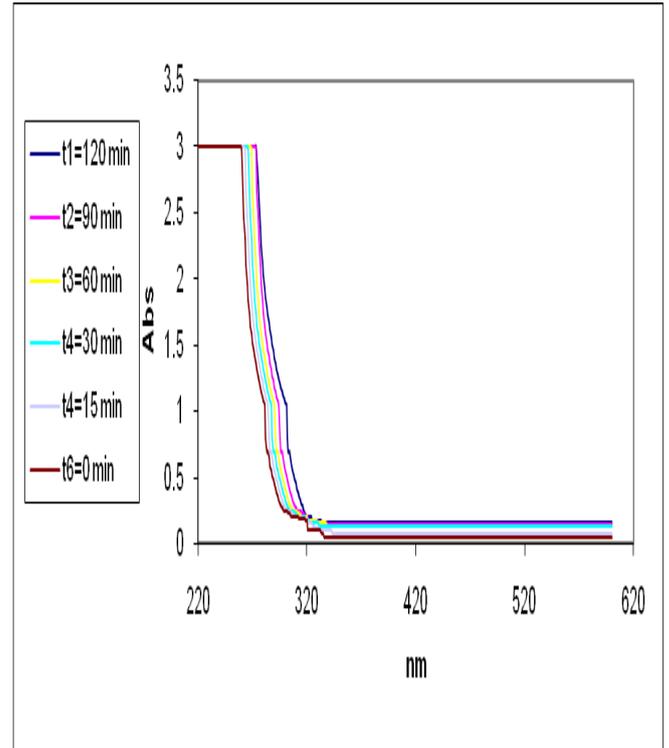


Fig. 3. U.V-Visible spectra change for (PS) film without additives of different times with Thickness of (65± 5) micron

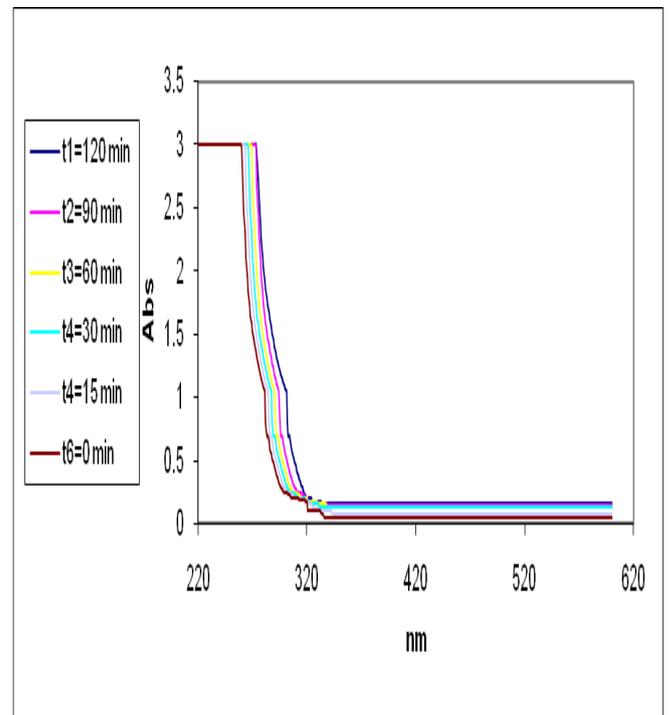


Fig.4. U.V-Visible spectra change for (PS) film with (%0.025) concentration of complex [(Ni - HQ)] in different time with Thickness of (65 ± 5) micron.

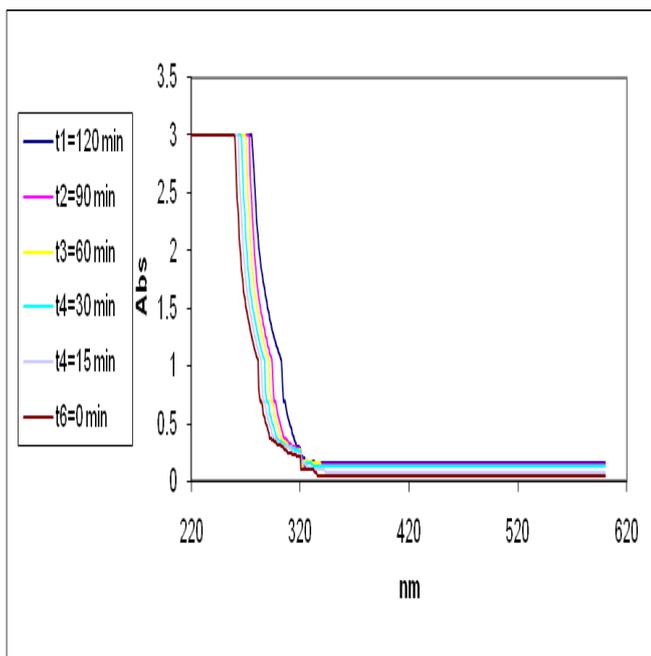


Fig. 5. U.V-Visible Spectra change for (PS) film with (%0.05) concentration of complex in different time with Thickness of (65± 5) micron

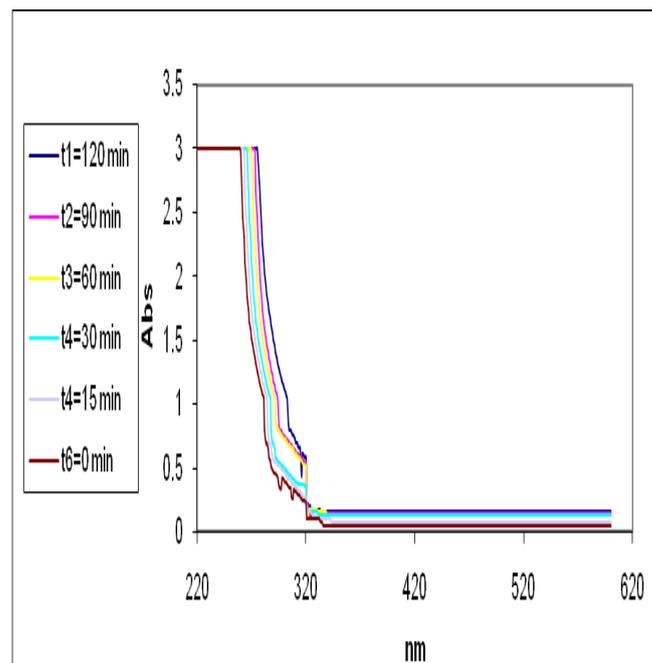


Fig.7.U.V-Visible Spectra Change for PS Film With (%0.2) Concentration of Complex in different time with Thickness of (65± 5) micron

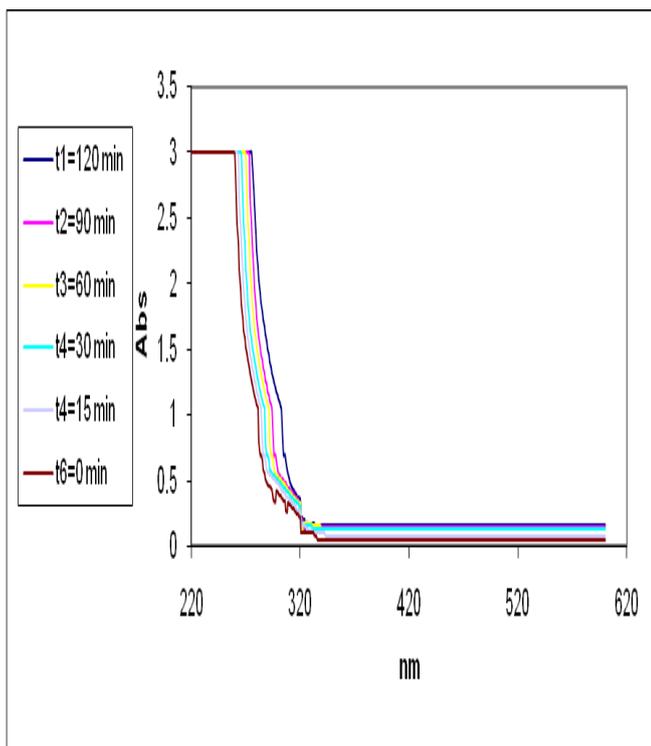


Fig. 6. U.V-Visible spectra change for (PS) film with (%0.1) concentration of complex in different time with Thickness of (65± 5) micron

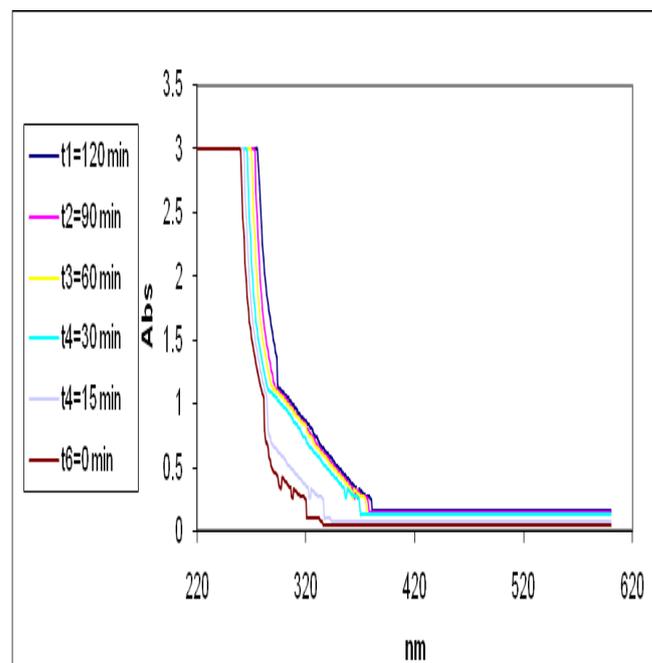


Fig. 8. U.V-Visible spectra change for (PS) film With (%0.4) concentration of complex in different times with Thickness of (65± 5) micron

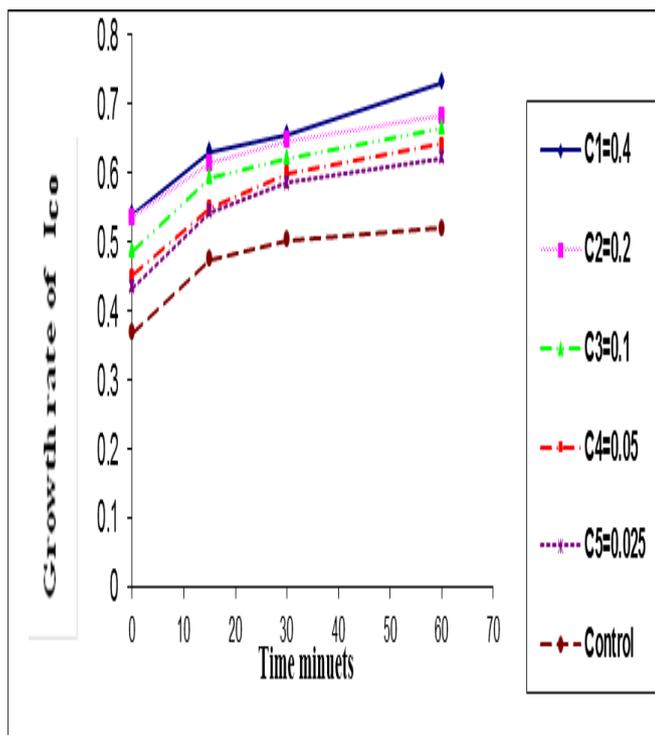


Fig.9. Relationship between absorption of the carbonyl index ICO and time of radiation

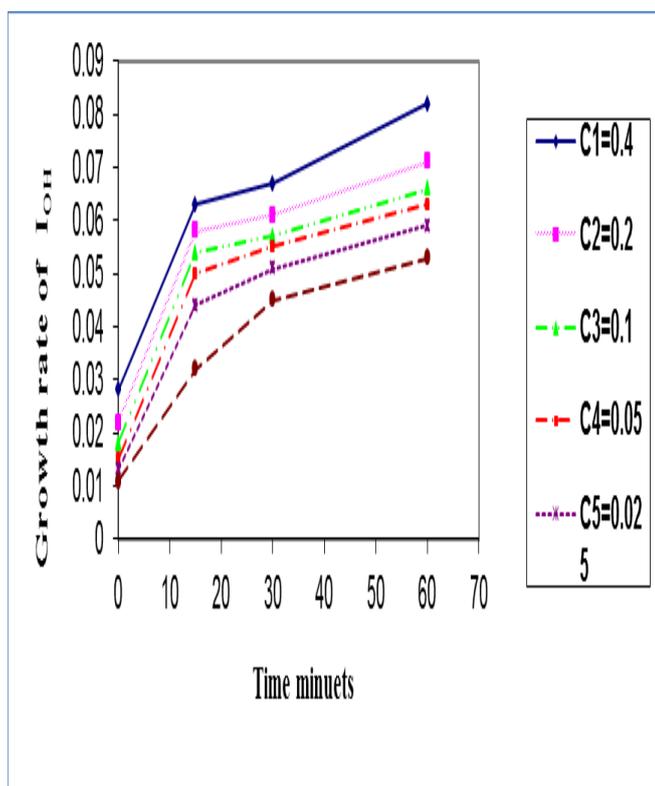


Fig.10. Relationship between absorption of the hydroxyl index IOH and time of radiation

Table.3. The values of the carbonyl index ICO with different radiation time

| Additives % | Microwave Radiation Tim(minuets) | | | |
|-------------|-----------------------------------|-------|-------|-------|
| | 0.0 | 15 | 30 | 60 |
| P.S | 0.369 | 0.475 | 0.504 | 0.521 |
| P.S + 0.025 | 0.434 | 0.544 | 0.586 | 0.623 |
| P.S + 0.05 | 0.451 | 0.550 | 0.601 | 0.642 |
| P.S + 0.1 | 0.488 | 0.594 | 0.622 | 0.666 |
| P.S + 0.2 | 0.536 | 0.614 | 0.647 | 0.683 |
| P.S + 0.4 | 0.541 | 0.630 | 0.657 | 0.732 |

Table.4. The values of the hydroxyl index IOH with different radiation time

| Additives % | Radiation Time (minuets) | | | |
|-------------|---------------------------|-------|-------|-------|
| | 0.0 | 15 | 30 | 60 |
| P.S | 0.011 | 0.032 | 0.045 | 0.053 |
| P.S + 0.025 | 0.013 | 0.044 | 0.051 | 0.059 |
| P.S + 0.05 | 0.015 | 0.050 | 0.055 | 0.063 |
| P.S + 0.1 | 0.018 | 0.054 | 0.057 | 0.066 |

| | | | | |
|-----------|-------|-------|-------|-------|
| P.S + 0.2 | 0.022 | 0.058 | 0.061 | 0.071 |
| P.S + 0.4 | 0.028 | 0.063 | 0.067 | 0.082 |

Table.5. The values of the speed of dissociation constants of the complex [(Ni - HQ)].

| Concentration | (Sec) ⁻¹ × 10 ⁻⁴ K _d |
|---------------|---|
| 0.025 | 2.35 |
| 0.05 | 2.41 |
| 0.1 | 2.97 |
| 0.2 | 3.84 |
| 0.4 | 4.09 |

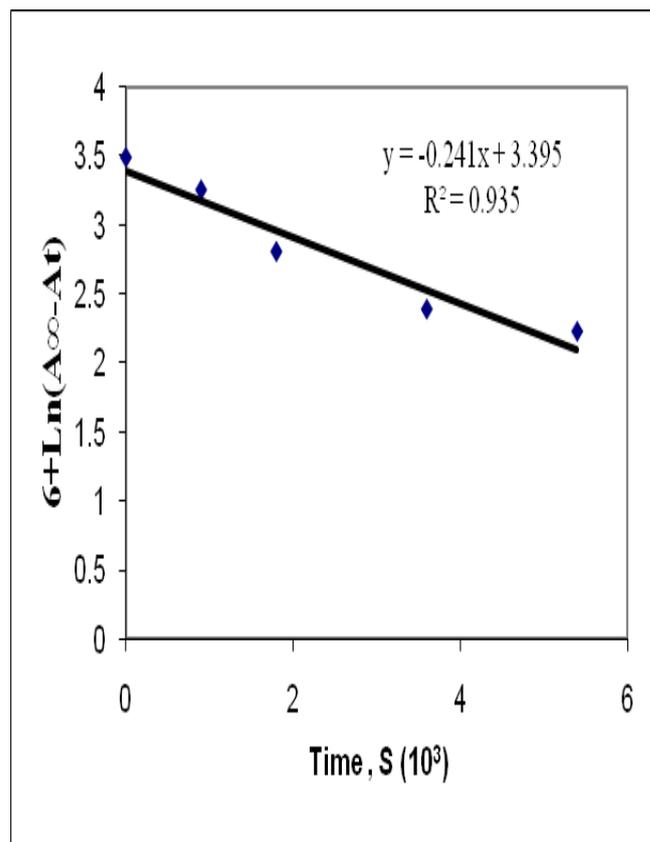


Fig. 11. The relationship between the natural logarithm of the complex [(Ni - HQ)] in(PS) film With (%0.025) concentration for complex with time of irradiation

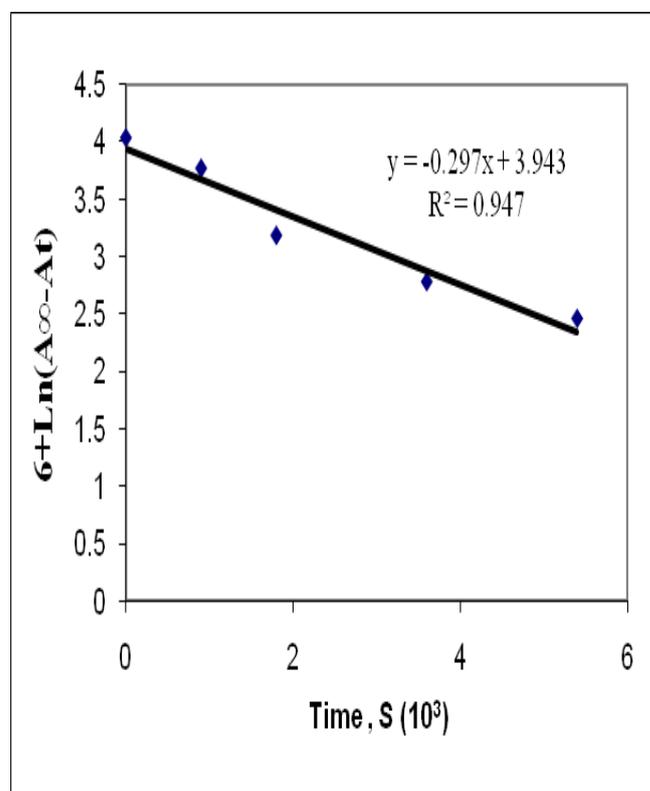


Fig. 12. The relationship between the natural logarithm of the complex [(Ni - HQ)] in PS film with (%0.05) concentration for complex with time of irradiation

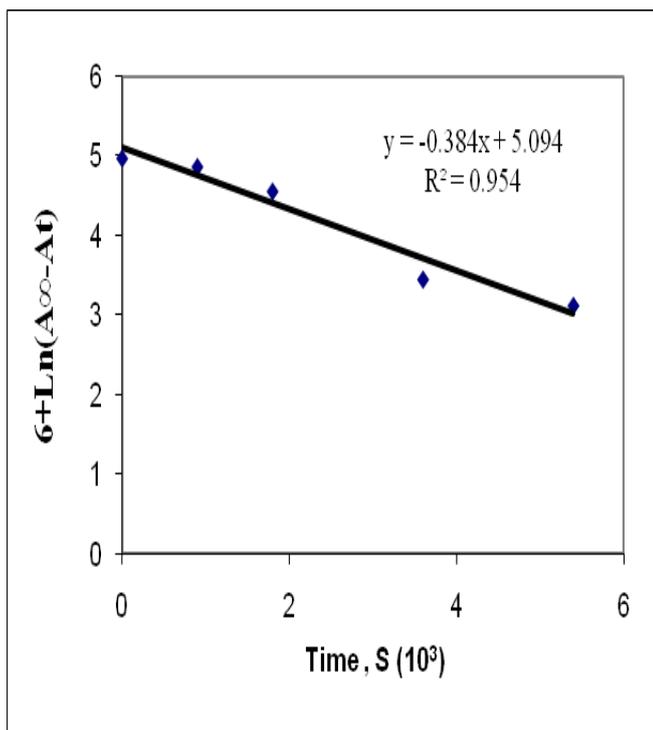


Fig. 13. The relationship between the natural logarithm of the complex [Ni - HQ] in PS Film With (%0.1) concentration for complex with time of irradiation.

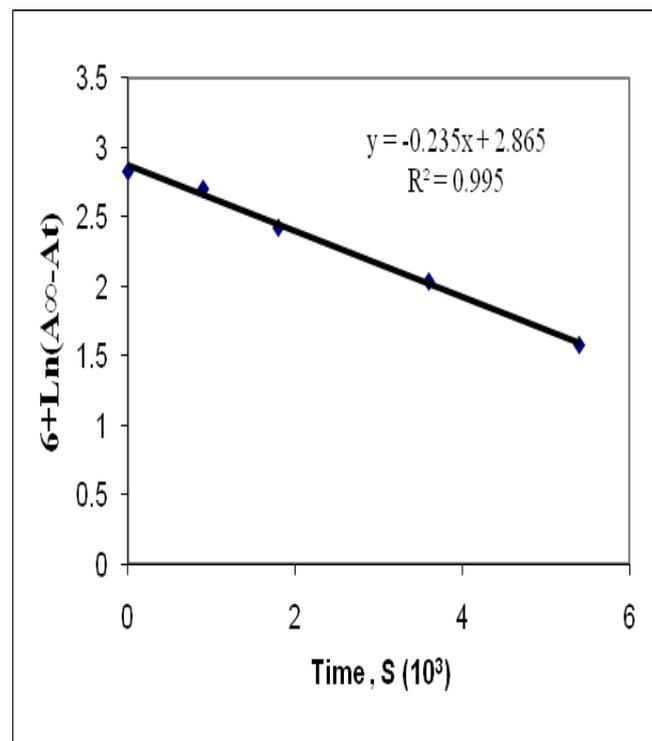


Fig.15. The relationship between the natural logarithm of the complex [Ni - HQ] in PS film with (%0.4) concentration for complex with time of irradiation

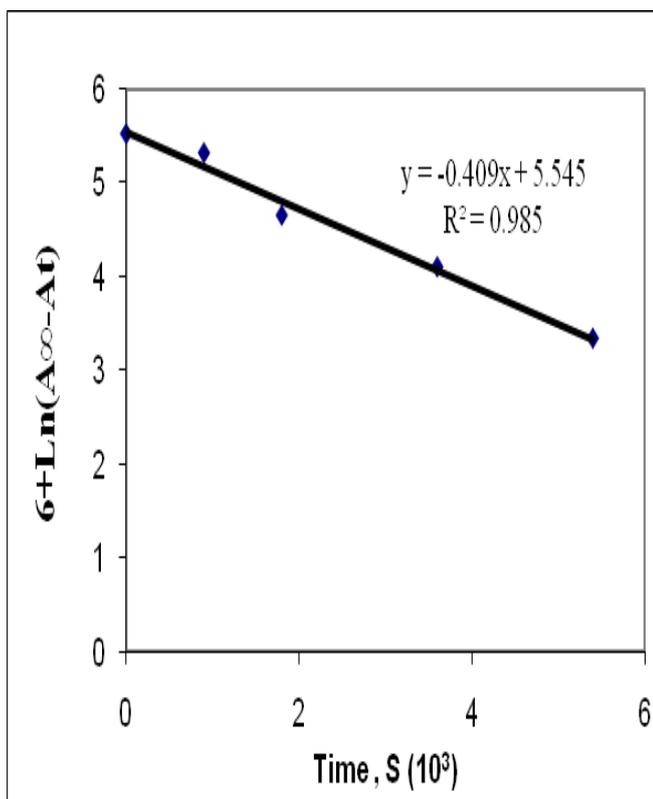


Fig. 14. The relationship between the natural logarithm of the complex [Ni - HQ] in (PS) film With (%0.2) concentration for complex with time of irradiation

التفكك المعجل بالميكروويف لمتعدد ستايرين المحتث بواسطة 8-hydroxy quinoline Nickel (II) complex

طارق عبدالجليل منبيل حميد خالد علي احمد عبيد فرحان

E. mail: tarik_jm@yahoo.com

الخلاصة :

بسبب المشاكل البيئية المتواصلة والناجمة من طرح الكميات الكبيرة من متعدد ستايرين كفضلات الى البيئة ولاحظته على الحلقة الأرماتية في تركيبه فإنه يشكل عامل تلوث وسمية للبيئة . هذه الدراسة تقترح طريقة نظيفة للتخلص من الفضلات البلاستيكية بطريقة التفكك اللبولي ستايرين باستخدام أشعة المايكروويف كمصدر للطاقة . ولكون الطرق التقليدية الحالية للتخلص من هذه الفضلات تتم بالحرق او الطمر وهي ملوثة للبيئة أيضا . تم في هذا العمل تحضير نماذج الدراسة على شكل أفلام من PS المضاف اليها المعقد الأنقالي (Ni-HQ) كمادة محفزة للتفكك وبنسب وزنية 0.05, 0.1, 0.2, 0.4 (0.025, 0.0)% تحت تأثير أشعة المايكروويف بطاقة مقدارها 400W ولفترات زمنية مختلفة (0.0, 15, 30, 60 دقيقة) . كطريقة كيميائية للتفكك , ولتجنب عمليات الحرق الملوثة للبيئة . تم متابعة نتائج التفكك للنماذج تحت الدراسة , من خلال نقصان معدل الوزن الجزيئي (Mw-, Mn-) ومعدل التوزيع له, وكذلك الزيادة الحاصلة في معاملات التفكك الى ICO, IOH, كنواتج عرضية من التفكك . باستخدام مطيافية FT-IR, U.V و بزمن مقداره 60 دقيقة تحت أشعة المايكروويف.