#### **Research Article**

### Synthesis and Identification of Heterocyclic Compounds (Oxazepine, Tetrazole) Derived from Benzidine as Photostabilizing for Poly vinyl chloride

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ArticleInfo	Abstract
Received	This research describes preparation of new four compounds (A2-A5) having 1,3-oxazepine and Tetrazole rings. The first step involves reaction of benzidine (A1) with aromatic aldehyde (cin- namaldehyde) in ethanol as a solvent in the presence of acid as catalyst to yield the Schiff base (A2), Schiff base (A2) was condensed with maleic anhydride and phthalic anhydride in dry ben- zene to give a seven-membered heterocyclic ring derivative (A3, A4), In addition, we synthesis novel tetrazole derivative (A5) from the reaction of Schiff base (A2) with sodium azide in tetra-
Accepted	hydrofuran. The structure of synthesized compounds was identified by spectral methods [FTIR, <sup>1</sup> H-NMR, and <sup>13</sup> C-NMR] and measurement physical properties. The photo stabilization of poly (vinyl chloride) films by compounds (A1-A5) was studied. The Photo stabilization activities of these compounds were determined by monitoring the carbonyl and hydroxyl indexes values with irradiation time. The changes in viscosity average molecular weight of PVC with irradiation time were studied by using tetrahydrofuran as a solvent. The influence of concentrations additives (range 0.1-0.5wt) on the rate of photo degradation and Photo stabilization course was studied. Therefore, we found that was an increase Photo stabilization rates with increasing concentrations of additives. In addition, Studying the effect of film thickness and the results showed that an increase in film thickness would reduce the rate of photolysis. The results indicated that Photo stabilization proportion of plastic in the presence of additives follow the trend: (PVC blank) > PVC+A1>PVC+A2>PVC+A5>PVC+A4>PVC+A3. According to the results obtained, it proposed mechanisms depending on the structure of the additive. Keywords:1,3-Oxazepine,Photochemistry, PVC, Photo stabilizer, UV absorber, Tetrazole.
	الخلاصية
	يصف هذا البحث تحضير أربعة مركبات جديدة(A2-A5) تحتوي على Tetrazole، وTetrazole والخطوة الأولى تتضمن تفاعل البنزدين (A1) مع ألديهايد اروماتي (سينمالدهيد) في الإيثانول كمذيب بوجود حامض كعامل مساعد لتنتج قاعدة شيف (A2)، وعند تكثيف قاعدة شيف (A2) مع الانهيدريدات ( أنهيدريد الماليك وأنهيدريد الفثاليك) في البنزين الجاف لإعطاء حلقة سبعة غير متجانسة. (A3, A4) إلى جانب ذلك، حضرنا مشتق جديدة (A5) من تفاعل قاعدة شيف (A2) مع أذرد الصروريوم في تتربل هديد مفروران كمزير)
	(AZ) مع اريد المصوديوم في قدراميدرونيوران تصيب. وقد تم التعرف على تركيب المركبات المحضرة بالطرق الطيفية[ I3CNMR ، 1HNMR ، FTIR] وقياس الخواص الفنديائية مقد درس التثنيت الذينية الأفلار بدار الكلميد الفندار) بدعد الدكاري (A 1 A 5)
	القيريانية. وقد درس السبيب الصولي «كلام بولي (موريد القينين) بوجود المركبات (A1-A3). تم تحديد فعاليه التثيبت الضوئي لهذه المركبات من خلال رصد موشر ات قيم معاملات الكربونيل والهيدر وكسيل مع وقت التشعيب تمريد البية التغييرات في الأذم حة مأرجاد متمسط المذين الحذيث الزمل كامريد الفرندل مع مقت التشعيب استخدام
	التسعيم. لم دراسة المعيرات في المروجة والبعة متوسط المران الجريمي عبوري عبورية العيني مع وف الصحيح وسيسم رباعي هيدرو الفوران كمذيب. كذلك تمت دراسة تأثير تركيز المضافات (0.5wt) على معدل التحل الضوئي و عملية التثنين الضوئي ماذاك، محددا أن سرعه التثنيت الضوئي تزداد مع ذيادة تركيز ات المو إد المضافة السحاني ذلك، تو
	السبية المعلولي. وللله، وجد أن شرك الشيب المعلولي مردان مع ريدة مر ليرات المواد المسبب المي المرابع المار النتائج إلى أن نسبة در اسة تأثير سمك الفيلم وأظهرت النتائج إلى أن نسبة
	التثبيت الضوئي لبولي كلوريد الفاينيل بوجود المضافات تتبع الترتب التالي: 24 ـ DVC + A - DVC - A
	r v C brank) >r v C+A1>r v C+A2>r v C+A3>r v C+A3) (r v C brank) >r v C+A3>r v C+A3) (r v C brank) ووفقا للنتائج التي تم الحصول عليها اقترحت ميكانيكيه عمل تلك المضافات اعتمادا على تركيبها.

#### Introduction

The chemistry of carbon-nitrogen double bonds has played a basic role in March of chemical sciences. Because there is a lone pair of electrons on the nitrogen atom and general electron donating character of the double bond, it has found these compounds is very large applications in the field of chemistry . It is known that the com-





pounds containing >C=N group as imines or azomethines or anils or ligands, but in general, which is known as "Schiff bases" in honors of Schiff who synthesized these compounds for the very first time [1] [2].Oxazepine derived was presented in 1965 for use in mental ease characterized by anxiety and stress [3]. Oxazepine Is an unsaturated, seven membered containing heteroatoms and oxygen in the position (1) and nitrogen in position 3 in addition to five carbon atoms. It is prepared by the pericyclic cycloaddition of Schiff bases with anhydrides [4]. Oxazepine and derivatives have medical and biological importance and they have medicinal and pharmaceutical application [5], [6]based on its spectrum therefore many of industrial and medical applications like photo stabilizer, pigments, and dyes take place in these fields [7], [8]. Tetrazole ring is unsaturated five-membered heterocyclic containing four nitrogen atoms and one carbon atom in position (5). Tetrazoles also serve as precursors for the synthesis of further interesting heterocyclic. Tetrazole derivatives were prepared by the

reaction of Schiff bases derivatives with sodium azide

There is considerable importance at present in the photo-oxidative degradation of polymeric compounds as large molecules have ever more rife merchant applications. When exposed to synthetic polymer, semi-synthetic and natural environment [9].

All commercial organic polymers destroy in air when exposed to rays, as energy from sunlight is sufficient to cause the collapse of the C-C bonds because of polymer degradation. Synthetic polymers require almost all the stability against the negative impact with the improvement of synthetic resin has become essential that looking at ways and means for the prevention, or at least a limit, the damage due to ecological light, air and heat factors. This can be accomplished by adding the chemicals and optical stabilizers special or stabilizers, UV, which must be adjusted to the specific nature of the resin and the application in mind. Photostabilization polymers has achieved in many ways. It has been developed following the stability of systems. That rely on the work of stabilizer: - (1) Screeners light, (2) the excited state quenchers, (3) UV absorption), (4) analyzers peroxide, and (5) scavengers free radical, this is generally believed that the types 2 and 4 and 5 is the most effective [10].

In our research we were studied Photostabilization of PVC using four compounds derived from benzidine and contain 1,3-Oxazepine and Tetrazole rings.

#### **Materials and Methods**

**Preparation methods of organic compounds** Melting points were determined on Gallen Kamp Melting Points apparatus MFB-600-Olof, and Stuart Scientific Co. LTD melting point SMP1 in the University of Mustansiriyah, College of Science.

FT-IR spectra were recorded using Shimadzu FT-IR 8000 series Fourier Transform, Infrared Spectrophotometer in the University of Mustansiriyah, College of Science.

<sup>1</sup>H-NMR spectra were recorded on a Fourier transform spectrometry [11], company Bruker, model, ultra-shield 300 MHz, and origin: Switzerland, in DMSO-d6 solution with the TMS as internal standard, measurements were made at the Chemistry Department, AL-Albait University, Jordan.

Intrinsic viscosities were determined with viscometer.

#### **Preparation of Schiff base (A2)**

1mmole (0.184 gm) of Benzidine was dissolved in 20ml absolute ethanol with 2 mmole (0.264gm) of Cinnamaldehyde in presence (2-3) drops of glacial acetic acid and the mixture was stirred and refluxed for 7 hours. The precipitate was filtered to give(A2). The product was washed with cold water and recrystallized from ethanol to give the pale yellow color solid.

N4-Allylidene-N4'-(3-phenyl-allylidene)biphenyl-4, 4'-diamine (A2)

Yield:82%;M.p:200°C;FTIR(v,cm<sup>-1</sup>):3057.3032( CHaro-

matic),2947.2874(CHaliphatic),1627(CH=N),16 02,1581(C=C) ,833,746.692(CH out of plane) Figure 18;<sup>1</sup>H-NMR (300 MHz, DMSOd6,δ,ppm):8.6-7.2(m,,Ar-H),9.1(signal,1H 5.6(d, 2H, CH=CH) Figure 19;

<sup>13</sup>C-NMR DMSO-d6): 163 (CH=N), 148 (C aro-N), 138 (Caro-CH=), 137(Caro- Caro), CH aro. (129 -110) Figure 20

## **Preparation of Oxazepine compound.** (A3, A4):

A mixture of (A2) (0.0012mole) and (phthalic anhydrides) (A3), maleic anhydrides (A4) (0.0025mole) was melted in (20mL) solvent (dry benzene). The mixture was stirred and refluxed at 9-10 hours. Excess solvent was distilled; the precipitate was filtered and recrystallized from ethanol to give the Orang color solid for (A3) and the Deep Orange color solid for (A4).

#### 4,4-biphenyl-diyl)bis(3(cinnymyl)-3,4dihydrobenzo[e]1,3-oxazapine-1,5dione)(A3)

Yield:68%;M.p:230°C(Dec);FTIR(v,cm<sup>-1</sup>):3055-3194(CH aromatic),2994,2872(CHaliphatic), 1600,1555(C=C),825,813,746.69(CH out of plane) ,1697 (C=O lactam) , 1723 (C=O lacton) Figure 21; <sup>1</sup>H-NMR (300 MHz, DMSO-d6,  $\delta$ , ppm): N-CH, (d,1H7.12 N)-HC-CH, =tri,1H ( 6.17-576)= ,CH H1(d, 7.20), Ar CH (m, ,8.59.-67.7) Figure 22 <sup>13</sup>C-NMR DMSO-d6):125, 129, 78 (CH=CH-CH-N), 150 (C aro-N), 139 (Caro-CH=),140-148(Cphtha), CH aro. (129 -110) 165 (C=O ester), 164 (C=O amid) Figure 23.

#### 3,3--biphenyl-4,4--diyl)bis(2-(phenyl-3,4dihydro -[1,3]oxazapine-4,7-dione )(A4)

Yield:72%;M.p:235°C;FTIR(v,cm<sup>-1</sup>):3045.3138( CHaro-

matic),2992,2854(CHaliphatic),1535(C=C) ,817,850,755.613(CH out of plane) ,1639 (C=O lactam ) , 1722 (C=O lacton) Figure 24 ; <sup>1</sup>H-NMR (300 MHz, DMSO-d6,  $\delta$ , ppm): Maleic + CH=CHN-7 (d,1H, CH,N) -CH-( tri,1H, =CH 656.-76) ,6. =CH (d, 1H .28), 7Ar (m, CH 6.7-76 7)Figure 25;<sup>13</sup>C-NMR DMSO-d6) : 129,128,79(C=C-C-N), 135 (C aro-N) ,134 (Caro-CH=) , 156-158(C =C oxa ), CH aro.( 123 -114 ) 169 (C=O ester), 164 (C=O amid) Figure 26

# Preparation of Tetrazole compound (A5):

Compound (A2) 0.001mole (0.412gm) was melted in (20mL) solvent (tetrahydrofuran) and mixed with 0.002mole (0.134gm) sodium azide. This mixture was stirred and refluxed for 12hours. Excess solvent was distilled; the precipitate was filtered and recrystallized from Methanol to give the Pale Yellow color solid.

#### Bis (4, 4-(5-styryl-2, 5-dihydro-tetrazol-1-yl)biphenyl (A5)

Yield:60%;M.p:260°C;FTIR(v,cm<sup>-1</sup>):3045.3138( CHaro-

matic),2922,2885(CHaliphatic),1600,1581(C=C) ,833,812,746,692(CH out of plane),1453 (N=N ring), 3174 (NH) Figure 27; <sup>1</sup>H-NMR (300 MHz, DMSO-d6,  $\delta$ , ppm): ) .aro H8(m,-7]a11 9.3( singlet, NH )[ reference =CH),CH-,1H( CH tri( 35.,)CHCH=-( CHH1(d, 6, 5. CH=)-CH-1H (N, d (3.7) Figure 28; <sup>13</sup>C-NMR DMSOd6):81[reference, 121,124(N-CH-CH=CH), 149 (C aro-N), 139 (Caro-CH=), (138,129,118,107) CH aro Figure 29.

#### Process of preparing the films:

Poly (vinyl chloride) (PVC) [supplied from Batteries factory in (Iraq) (the origin of the United States)] was re-precipitated from THF solution by methanol several times and lastly dried under vacuum at room temperature for (24) hours. Fixed concentrations of PVC solution (4 gm in 100 ml) in THF were used to get thickness (measured through a micrometer type 2610A, Germany). The prepared compounds (0.4% concentrations) were added to the films starting at 0 concentrations (control). It was essential to control the dimension of humidity and the rate of solvent vaporization during casting to maintain good visual quality is very narrow.

The films were get ready by vaporization method at room temperature for 24h. for removing the solvent. Films prepared were fixed on stands specially used for irradiation. The stand is provided with an aluminum plate (0.6 mm in thickness) by Q-panel Company.

#### Method for the accelerated test:

Weather accelerator meters QUV test (panel Q, Inc., USA), and was used for the irradiation of polymer films. Accelerated weathering test panel include stainless steel, which has two of the holes on the front side, and other behind. Each side contains side a lamp (type fluorescent UV lights) 40W each. These lamps are the type of UV-B 313 tender spectrum range between 290



and 360 nm with a maximum wavelength of 313 nm. Polymer film samples were fixed vertically parallel to the lamps to make sure that ultraviolet radiation is incident perpendicular to the samples. Irradiated samples have been rotated from time to time to make sure that the incident light intensity on all samples is same.

### Measuring photolysis rate of polymer films using infrared spectroscopy:

This was followed by the degree of photolysis of samples of polymer film by monitoring FTIR spectra in the range of 4000- 400 cm<sup>-1</sup> using 8400S Shimadzu FTIR spectrum. It is determined by the position of the hydroxyl and carbonyl absorption (3430.1720) cm<sup>-1</sup>respectively. The provide photo deteriorating at different times of irradiation followed by monitoring changes in hydroxyl and carbonyl peaks. Then calculated hydroxyl (I<sub>OH</sub>) and carbonyl (I<sub>CO</sub>) comparing the absorption peak in the FTIR (3430.1720) cm<sup>-1</sup> with a peak signal at 1332 cm<sup>-1</sup>, respectively. This method is called the band the way the index, which contain

$$Is \left[ CO \text{ or } OH \right] = \frac{As}{Ar} \tag{1}$$

Where (As) represents the absorbance of peak below study. (Ar) represents absorbance of reference peak. (Is) is the index of carbonyl or hydroxyl group below study. The actual absorbance difference between the absorbance of the highest peak and the baseline (A Top beak-base line) is calculated using the baseline method [12] [13].

**Determining the average molecular weight by using the method of measuring the viscosity:** Determining the viscosity average molecular weight of the polymer property was used using the relationship Mark Houwink [14] [15].

$$\left[\eta\right] = K\left(\overline{M}_{\nu}\right)^{\alpha'} \tag{2}$$

Where " $[\eta]$  is the intrinsic viscosity, K and  $\alpha$  constants based on polymer- solvent system at a given temperature". It was measured viscosity of the polymer solution with the U-tube measure viscosity Ostwald. The solutions provided by dissolving the polymer in a solvent (g / 100 ml), and the times the flow of the polymer solution and the solvent is pure (t) and (t<sub>o</sub>) respectively. The specific viscosity account  $\eta_{sp}$  as follows:

$$\eta_{sp}$$
 (specific viscosity) =  $\eta_{re}$ -1 (4)

Intrinsic viscosities by the relation (5) which is then converted to the average viscosity molecular weight by using

$$\left[\eta\right] = K\left(\overline{M}_{\nu}\right)^{\alpha'} \tag{2}$$

:

$$|\eta| = \left[ \left( \sqrt{2} / C \right) (\eta_{sp} - \ln \eta_{rel}) \right]^{\mathcal{A}}$$
(5)

Where C is the concentration of polymer solution (g/100 ml).

#### **Results and Discussion**

One new Schiff base (A2) have been synthesized from the condensation of Cinnamaldehyde with amino compound (A1)

$$H_{2}N \longrightarrow H_{2} + PhCH=CH-CHO \longrightarrow Ph-C=C-C=N-(Q)-(Q)-N=CH-C=C-Ph$$

The formation of compound (A2) was indicated by presence in their IR spectra of (CH=N) stretching bands at  $1627 \text{ cm}^{-1}$  combined with the disappearance doublet bands of NH<sub>2</sub> stretching bands. <sup>1</sup>H- NMR of compound (A2): 9.1 (s, 1H, CH=N), 6.6-5.6 (d, 2H, CH= CH), 8.6-7.2 ppm which belonged to aromatic protons [16]. The <sup>13</sup>C- NMR spectra provide further support for the structural characterization of the Schiff base: 163ppm due to (CH=N) group and signals at (110 -148) ppm due to aromatic carbons. In addition, in the present work two new Oxazepine compounds (A3, A4) were prepared by reaction compound (A2) with (phthalic anhydride (A3) and maleic anhydride (A4) in good yields.



The structures of prepared compounds were identified by FTIR spectral and Magnetic resonance (<sup>13</sup>C, <sup>1</sup>H-NMR, the FTIR-spectra of these compounds shows the appearance of the absorption bands at (1722-1639)cm<sup>-1</sup> characteristic to (C=O) of (lacton - lactam) and the disappearing of the two absorption bands at (1750-1800) cm<sup>-1</sup>of pure anhydrides. The <sup>1</sup>H-NMR spectrum of compound (A3) showed the following characteristic signals at: (7.67-8.59) multiplet signal due to aromatic protons ,7.20 (d,1H CH=) ,6.57-6.17 (tri,1H, =CH-CH-N) 7.12 (d,1H, CH-N) while <sup>13</sup>C-NMR spectrum of the same compound showed signal at :125,129,78 (CH=CH-CH-N), signal (107-150) due to carbon aromatic and signals at 165 ppm due to (C=O ester) signal at 164 ppm due to (C=O amide).

The <sup>1</sup>H-NMR spectrum of compound (A4) showed the following characteristic signals <sup>1</sup>H-NMR (300 MHz, DMSO-d6,  $\delta$ , ppm): 7.2, 7.7 (m, Ar-H) 6.6,5.67,6.17 (d,2H, tri,1H CH= CH-CH), <sup>13</sup>C-NMR DMSO-d6) :129,128,79(C=C-C-N), 135 (C aro-N),134 (Caro-CH=), 156-158(C = C oxa), CH aro.(123 -114) 169 (C=O ester), 164 (C=O amid)

Tetrazole derivatives (A5) was prepared by the reaction of Schiff base derivative (A2) with sodium azide in tetrahydrofuran as solvent.



The structure of synthesized compound was shown in Scheme 4.The synthesized compound was characterized by its melting point, FT-IR, <sup>1</sup>H-NMR. and <sup>13</sup>C-NMR, FT-IR spectrum of compound (A5) Figure 27 showed absorption bands at 1453 cm<sup>-1</sup>, 3174 cm<sup>-1</sup>due to $\sqrt{(N=N,NH)}$ . The <sup>1</sup>H-NMR spectrum of compound (A5) Figure 28 showed singlet signal at 9.3 ppm due to NH group, multiplet signals at (7-8) due to aromatic protons.

<sup>13</sup>C-NMR spectrum of compound (A5)Figure 29 showed signals at (138-107) ppm due to aromatic carbon and at 121,124 ppm due to (N-CH-CH=CH) and 139 ppm due to Carbon arom-CH=).

#### Mechanism of photodegradation of PVC:

It may be outlined steps photochemical degradation of PVC as follows:-

1. Free radicals (P1) and (Cl<sup>·</sup>) were Formed by homolytic cleavage of (C-Cl) bond in (2).



2. Peroxy radical (4) was produce by reaction of free radical (3) with oxygen.

3. Hydro peroxide polymers (5,6) were produced by abstraction of hydrogen atom in polymer chain by peroxy radicals (4).



4. The free radical polymers (5) react with  $O_2$  to give chloro alkyl peroxy radical (7).



5. The radical (7) abstraction from PVC with the formation of hydroperoxide (8) and (9) or it reaction with  $PO_2$  leads to formation of Peroxide bridge and alkoxy radicals (10).

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6. Alkoxy radical (10) suffered some interactions such as:

i) Abstraction of hydrogen atom from polymer chain to give polymeric alcohols (11).

ii)  $\beta$  – scission reaction to produce ketonic polymers.

Forming a keto group in the polymer chain plays an important role in increasing the oxidative degradation of the polymer chain through the defection of a key chain for the production of acyl radical mechanism. The Oxazepine-tetrazole compounds usage as additives for the polymeric films. In order to studying the optical activity of these additives for Photostabilisation of plastic films, Led, irradiation of plastic films using light of wavelength  $\lambda$ =313nm new changes in their FTIR spectrum. Appearance of bands at range  $\sqrt{}$ (1770 - 1720) cm<sup>-1</sup>, and  $(\sqrt{3430})$  cm<sup>-1</sup>, attributable respectively to form a carbonyl and hydroxyl groups. These absorptions account as carbonyl and hydroxyl index. It is reasonable to assume that the growth indicators carbonyl and hydroxyl is a measure of the extent of polymers degradation.

Nevertheless, in the Figure 30, Figure 31 the  $I_{CO}$  and  $I_{OH}$  of (A3), (A4), (A5), (A2), (A1) and (PVC control) showed fewer growth rate with irradiation time with respect to the (PVC control) film without additives. Since the growth of carbonyl and hydroxyl index with irradiation time is lower than PVC blank, as seen in the Figure 30, Figure 31 it is suitable to conclude that these additions can be considered photo stabilizers of PVC polymer.

Photo stabilizer shows the efficiency of the induction period is longers. Therefore, the (A3) studies such as photo stabilizer more active, followed by of (A4), (A5), (A2) and (A1), which is the least active.

In this work the Photostabilization of PVC films of 40  $\mu$ m thickness was examined with changed additive concentration, Figure 32, Figure 33 shows the relationship between carbonyl index and hydroxyl index with irradiation time for additive (3) concentrations Figure 34, Figure 35 shows the relationship between the (3) additive concentrations and carbonyl or hydroxyl index for PVC film at fixed irradiation time (150) hours and fixed thickness 40µm.

In addition, in this work studying the relationship between the carbonyl and hydroxyl indexes with various different thicknesses for PVC samples Figure 36, Figure 37 could be explained considering the relatively important permeability of polymer to oxygen, which results in the care zone of the selected films thickness being rich in oxidation product in addition to the superficial. However, Figure 36, Figure 37 presented decrease of photodegradation with increasing of thickness of the film.

#### Variation of PVC molecular weight during photolysis in the presence 1,3-Oxazepine-Tetrazole:

Viscosity of PVC solution depends on concentration and size of the dissolved polymer Measuring the solution viscosity and idea about molecular weight [17]Figure 38show the plot of  $M_v$  versus irradiation time for (PVC) film with and without 0.4% (wt/wt) of the additives selected. M<sub>v</sub> is measured using Equation 2 with tetrahydrofuran as a solvent at 25 °C. It is worth mentioning that hints of the films with additives are not soluble in tetrahydrofuran representing that cross-linking or branching in the (PVC) chain does occur during the course of photolysis. To provide the best support from this point of view, the number of average chain scission (average number cut per single chain) (S) [18] was calculated using the relation:

$$S = \frac{M\nu, 0}{M\nu, t} - 1 \tag{6}$$

Where:" Mv, o and Mv, t are viscosity average molecular weight at initial (0) and (t) irradiation time" respectively. It shows a plot of the (S) versus time Figure 39. In addition, it indicates an increase in the degree of branching that may arise, such as the occurrence of cross-linking curve. It was observed that the material is soluble formed during irradiation, which provided additional evidence on the idea that cross-linking occurs. For randomly distributed weak bond links [19], which break down quickly in the early stages of photolysis, and given the degree of deterioration ( $\alpha$ ) as follows:

$$\alpha = \frac{m}{M\nu, 0} S \tag{7}$$

Where m is the initial molecular weight. The scheme of  $\alpha$  as a function of irradiation time in the Figure 40. In addition, the values of samples irradiated higher when absent and lower additions in the presence of additives compared to the corresponding values of PVC free additive [20]. In the early stages of the photolysis of PVC, and the value of ( $\alpha$ ) increases rapidly with time, these indicators point to a random breaking of bonds in the polymer chain.



Scheme 2:Suggested mechanism of Photostabilisation of 1,3-Oxazepine ring as UV absorber.



Scheme 3: Suggested general mechanism of Photostabilisation of Tetrazole ring as UV absorber.



Scheme 4: Suggested mechanism of Photostabilisation of PVC by Schiff base as UV absorber.









Figure 20: <sup>13</sup>CNMR spectrum of compound (A2).







Figure 30: The relationship between the ( $I_{CO}$ ) and irradiation time for PVC films (40  $\mu$ m) thickness Containing 0.4% additive.



Figure 31: The relationship between ( $I_{OH}$ ) and irradiation time of PVC films (40  $\mu$ m) Thickness containing 0.4% additives.



Figure 32: The relationship between the  $(I_{CO})$  and irradiation time for PVC films (40 µm) thickness containing different concentrations of compound (A3).



Figure 33: The relationship between the  $(I_{OH})$  and irradiation time for PVC films (40  $\mu$ m) thickness containing different concentrations of additive (A3).



Figure 34: The relationship between the ( $I_{CO}$ ) and irradiation time at (150hrs) for PVC films (40 µm) thickness containing different concentrations of compound (A3).



Figure 35: The relationship between the  $(I_{OH})$  and irradiation time at (150hrs) for PVC films (40  $\mu$ m) thickness containing different concentrations of compound (A3).



Figure 36: The relations ship between the carbonyl indexes with different thicknesses ( $\mu$ m) at (150hrs) irradiation time containing (0.4%) Wt. of additives.





Figure 37: The relations ship between the Hydroxyl indexes with different thicknesses ( $\mu$ m) at (150hrs) irradiation time containing (0.4%) Wt. of additives.



Figure 38: Variation of the viscosity-average molecular weight with irradiation time of PVC films (40µm) (control) and 0.4% wt. of additives.



Figure 39: Changes the average number cut per single chain (s) during irradiation of PVC films ( $40\mu m$ ) (control) and with 0.4% wt. of additives.



Figure 40: Changes in the degree of deterioration during irradiation of PVC films ( $40\mu m$ ) (control) and with 0.4% wt. of additives.

#### Conclusions

#### References

- [1] H. Schiff, Ann. Chem. , vol. 131, p. 118, 1864.
- [2] P. Saul, "The chemistry of the carbon nitrogen double bond," *Ltd., London,* (1970.
- [3] Ahmed, A., Sarah, M., Anwar, H., Ayad, H. and Emad, Y, "Antibacterial Study of Some Oxazepine Derivatives," *Journal of Al -Nahrain University*, vol. 18, pp. 22-26, 2015.
- [4] Dhanya Sunil 1, Ranjitha C1, Rama M 1, "Oxazepine Derivative as an Antitumor Agent and Snail1 Inhibitor against Human Colorectal Adenocarcinoma," *international Journal of Innovative Research in Science*, vol. 3, pp. 15357-15363, 2014.
- [5] Matsuzaki, H., Takuchi, I., Hamad, Y. and Hatano, K, "Studies on the 1, 4-oxazepine ring formation reaction using the molecular orbital method," *Chemical and Pharmaceutical Bulletin*, vol. 48, pp. 755 -756, 2000.
- [6] Hamak, K. F., Eissa, H. H, "Synthesis, Characterization, and Biological Evaluation and Anti Corrosion Activity of Some Heterocyclic Compounds Oxazepine Derivatives from Schiff Bases," Organic Chemistry Current Research, vol. 2, no. 3, pp. 1-7, 2013.
- [7] H. Ayad, "Microwave Synthesis of Some New 1, 3 -Oxazepine Compounds as Photostabilizing Additives for Pmma Films," *Journal of Al -Nahrain University*, vol. 15, pp. 47-59, 2012.
- [8] T. A. A. –. Khitam, "Synthesis, Identification and Evaluation the Biological Activity for Some New Heterocyclic Compounds Derived from Schiff Bases," *Journal of Applied Chemistry*, vol. 9, no. 5, pp. 1-11, 2016.
- [9] Andrady, A., Hamid, S., Hu, X.and Torikai, A, "Effects of increased solar ultraviolet radiation on materials in Environmental

Effects of Ozone Depletion," *J. Photochem. Photobiol*, vol. 46, p. 96–103, 1988.

- [10] Grassie N., Scott, G, "Polymer Degradation and Stabilization," *Cambridge University Press, London,* 1985.
- [11] Diana C. G. A. Pinto., Clementina, M. M. Santos. and Artur, M. S. Silva, "Advanced NMR techniques for structural characterization of heterocyclic structures," *Recent Research Developments in Heterocyclic Chemistry*, vol. 81, pp. 397-475, 2007.
- [12] Arct J., Dul, M., Rabek, J.F. and Ranby, B, "Studies on modified benzotriazoles as photostabilizers for poly (vinyl chloride)," *Eurp. Polym.J*, vol. 17, pp. 1041-1048, 1981.
- [13] Ranby B.G., Rabek, J.F, "Photodegradation, Photooxidation and Photostabilization of Polymers," *London: John Wiley & Sons*, 1975.
- [14] J. Mark, "Physical Properties of Polymers Handbook," *Springer, New York,* 1988.
- [15] Mori, F., Koyama, M.and Oki, Y, "Studies on photodegradation of poly (vinyl chloride)," *Die Angewandte Mak-omolekulare Chemie*, vol. 64, no. 1, p. 89–99, 2007.
- [16] Silverstein, R.M., Basslar, G.C, "Spectroscopic identification of organic compound," 2005.
- [17] Fisher, P.E., Lawrence, W, "Selection of Engineering Materials and Adhesives," CRC Press, 2005.

- [18] Shyichuk A., White, J, "Analysis of chain scission and crosslinking rates in the photo –oxidation of polystyrene," *Appl. Poly. Sci*, vol. 77, no. 13, pp. 3015-3023, 2000.
- [19] F. Gugumus, "Mechanism of Polymer Degradation and Stabilization," 1990.
- [20] A. N. Olfat, "Photostabilization of polyvinyl chloride by some new thiadiazole derivatives," *Eur. J. Chem*, vol. 3, no. 6, p. 242-247, 2015.

