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Photostability Study of Some Modified Poly(vinyl chloride) Containing Pendant Schiff's Bases

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Abstract

The polymers modified Poly(vinyl chloride) differ in their tendency to photo oxidation comparing with that unmodified. It has been studied Photostability for modified Poly(vinyl chloride) chains using Schiff's bases derivative of (5-amino-1, 3, 4-thiadiazole-2-thiol) in a manner casting of plastic chips with thickness (40) in a solvent Tetrahydrofuran. It has been determined the effectiveness Photostability of these modified polymers through the photo degradation rate constant for photostabilizer (k_d) for the modified Poly (vinyl chloride).
Attributed efficiency of these Poly(vinyl chloride) chips in Photostability by replace the atom Cl Poly(vinyl chloride) chains ends more stable than light stabilizer.

Key words: Poly(vinyl chloride), Photostability , Schiff's bases.

Introduction

Poly(vinyl chloride), better known by its abbreviation (PVC), is one of the most significant polymers due to its competent properties, the growth of the Polyvinyl chloride production is due to the stable expansion of its application fields [1]. Poly(vinyl chloride) is known from poor thermal and light stability. It subject rapid autocatalytic dehydrochlorination upon exposure to heat and light [2,3]. However, low photo stability of Poly(vinyl chloride) leads to hydrogen chloride loss, discoloration, and dangerous corrosion phenomena, accompanied by changes of physical and chemical properties of the Poly(vinyl chloride). The increased use of poly(vinyl chloride), a low-cost ratios and good performance, which make it more widely used in outdoor applications such as windows, doors cladding, and pipes [4]. Using effective stabilizers is designed to prevent or slow down the process of deterioration earn Poly(vinyl chloride) protection against thermal and photodegradation in order to extend their use in (outdoor) applications through their resistance photodegradation over long periods of exposure to the sun [5] .

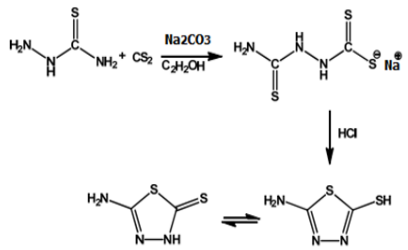
Scientists have used Schiff's bases compounds as Photostabilizers of poly(vinyl chloride) polymer against photodegradation by ultraviolate radiation [6]. It includes research studied of photostabilization for modified poly(vinyl chloride) using Schiff's's bases derivatives of 5-amino-1, 3, 4-thiadiazole-2-thiol .

Materials and Methods:

Synthesis of 5-Amino-1, 3, 4-Thiadiazole-2-Thiol Compound .

(Thiosemicarbazide) (10g , 0.1 mole) was pendent in (Ethanol $_{abs.}$) (50ml) in round bottom flask (250ml), (Anhydrous Sodium Carbonate) (6g, 0.05mole) and (Carbon disulfide) CS2 (11g ,0.14 mole) were then added respectively with continues stirring. The interaction mix was refluxed for five hours.

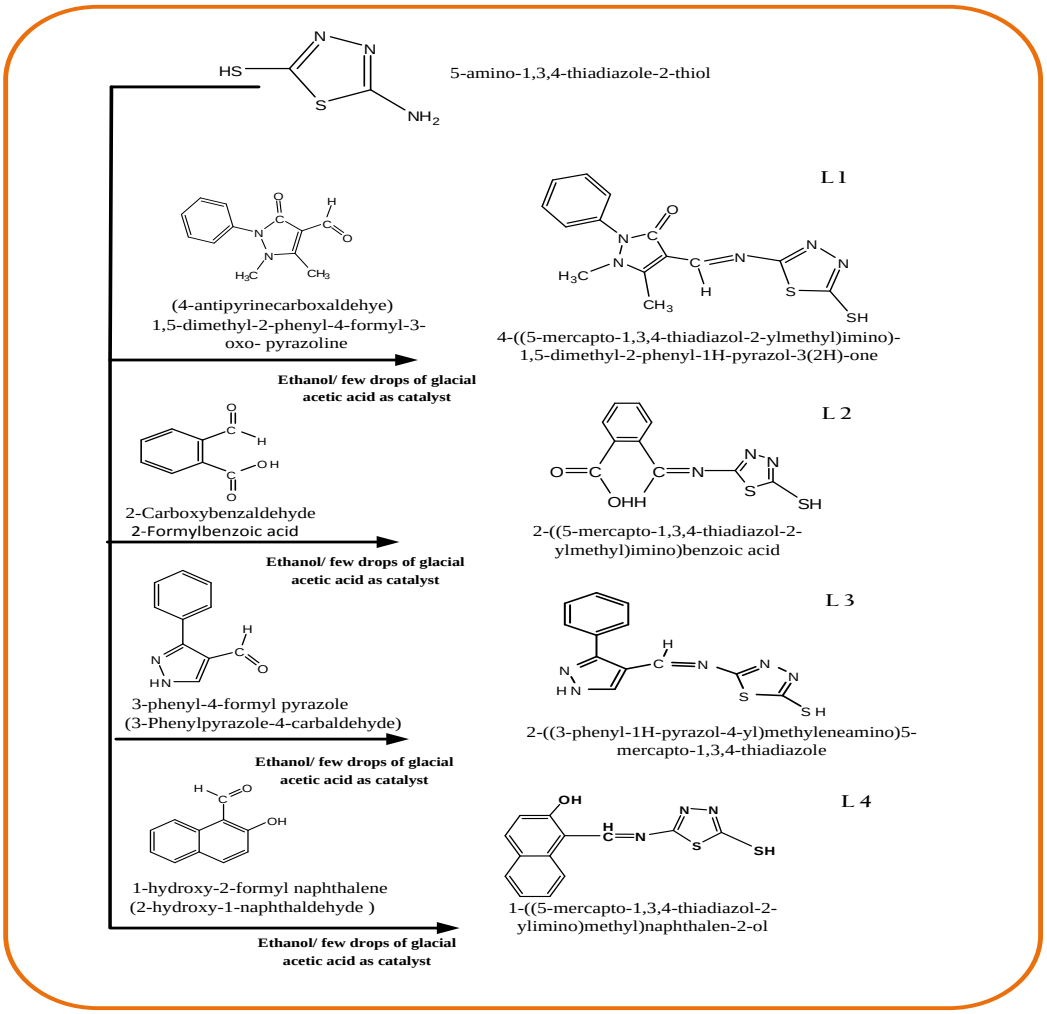
The interaction admixture was then allowed to cool to room temperature and filtered. The filtrate was vaporized under vacuum then (50 ml) (cold distilled water)was added, acidification with HCl drop(conc.) by drop was executed white – yellowish, precipitate was formed, the precipitate was composed by filtration, and distilled water with washed , re-crystallized using hot distilled water.



Scheme 1 :Preparation of 5-amino-1, 3, 4-Thiadiazole-2-Thiol

Synthesis of Schiff's Bases of 5-amino-1,3, 4-Thiadiazole-2-Thiol Compound.

Schiff's bases is prepared from melting different aldehyde in absolute ethanol in a glass beaker circular capacity (200 ml) and added of (**5-amino-1, 3, 4-thiadiazole-2-thiol**) dissolved in 20 ml of absolute ethanol and two drops of acetic acid glacial. The interaction by paying (1: 1) of the Secretary-record and aldehyde in respectively, climbing mix (Reflux) with stirring a period of time ranging from two and a half to four hours consists precipitation is sucked off and wash the amount of alcohol (85%) and are re-crystallization by a mixture of ethanol and methanol (20:80) respectively .



Scheme 2 : Preparation of Schiff's Bases from 5-Amino-1, 3, 4-Thiadiazole-2-Thiol

Table 1: Physical Properties of Schiff's Bases Additives.

NO.	**compounds**	Molecular Weight	yield	Comp.
1	4-((5-mercapto-1,3,4-thiadiazol-2-ylmethyl)imino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one	331.42	86%	L1
2	2-((5-mercapto-1,3,4-thiadiazol-2-ylmethyl)imino)benzoic acid	265.31	83%	L2
3	2-((3-phenyl-1H-pyrazol-4-yl)methyleneamino)5-mercapto-1,3,4-thiadiazole	287.36	79%	L3
4	1-((5-mercapto-1,3,4-thiadiazol-2-ylimino)methyl)naphthalen-2-ol	287.36	88%	L4

Table 2: Schiff's Bases from 5-Amino-1, 3, 4-Thiadiazole-2-Thiol.

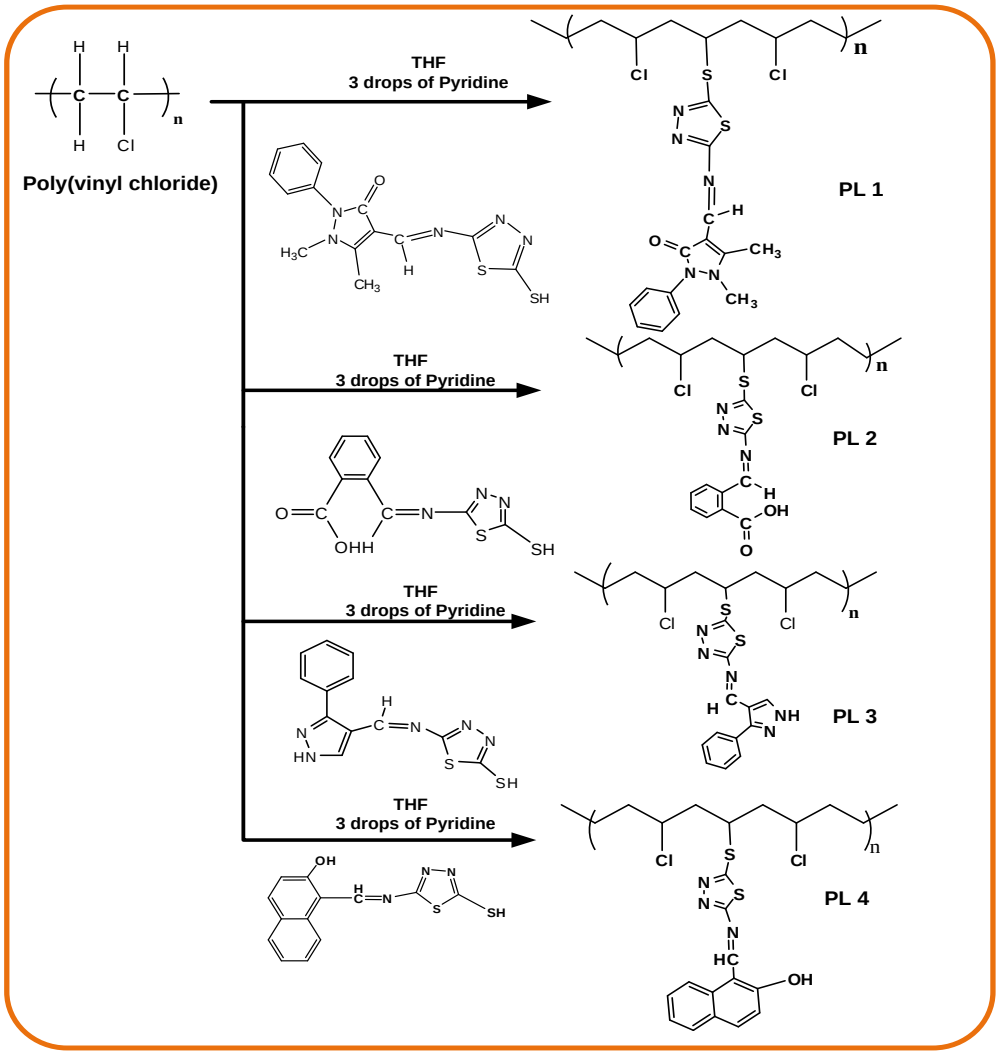
Comp NO..	**Molecular Formula**	**Color**	**M.P C^0**	**Elemental analysis, theoretical (actual)**				
				% C	% H	% N	% O	% S
L1	**$C_{14}H_{13}N_5OS_2$**	**Dark yellow**	**197-201**	50.74 (51.59)	3.95 (3.50)	21.13 (22.04)	4.83 (4.41)	19.35 (18.46)
L2	**$C_{10}H_7N_3O_2S_2$**	**White**	**256-259**	45.27 (46.14)	2.66 (2.90)	15.84 (15.59)	12.06 (11.63)	24.17 (23.74)
L3	**$C_{12}H_9N_5S_2$**	**Yellow**	**136-140**	50.16 (49.92)	3.16 (3.41)	24.37 (24.63)	---	22.32 (22.04)
L4	**$C_{13}H_9N_3OS_2$**	**Orange**	**265-269**	54.34 (55.12)	3.16 (3.64)	14.62 (14.16)	5.57 (5.22)	22.32 (21.86)

Synthesis of Poly(vinyl chloride) compounds .

Poly(vinyl chloride) was dissolve in Tetrahydrofuran solvent (20ml) then add from Schiff's bases The reaction mixture was heated under reflux for Three hours. The hot mixture is transferred to molding. Polymer modified the precipitate detached chip by evaporated the solvent.[7]. The chips were prepared by vaporization at room temperature for 24 hours to take out the possibility residual tetrahydrofuran solvent, chips samples are further exsiccated at room temperature for (3) hours under reduced pressure. The chips prepared through molding of Poly(vinyl chloride) (5 gm /100 ml) in (Tetrahydrofuran) Which are (40µm) thickness of polymer chips [measured by a micrometer type 2610 A]. [8].

Accelerated tested technique

The samples were placed in Accelerated weathering tester (Q.U.V) it used for the irradiation of polymeric chips. The sources Uv-Visible giving range (250-380) nm and the light intensity is 6.2×10^{-9} ein dm^{-3} sec^{-1} . The polymer chips samples were fixed vertically and parallel to the lamps to be sure that light incident radiation is vertically incident on the samples, the irradiation samples are changed places from time to time to be sure that the ntensity of light incident on all samples is equal. The distance between the polymer chips and light source was 10 cm [9].



Scheme 3: Elaboration of Modified Poly(vinyl chloride).

Measuring the Photodegradation Rate of Polymer Chips

By useing the UV/Vis Spectrophotometers (Perkinelmer LAMBDA 25) to measure the change in the UV - visible spectrum during the irradiation time for each polymer chips at the maximum absorption band. The absorption spectrum was measured in the range of ($\swarrow_{max}$ = 200-400) nm . The photodegradation rate constant for photostabilizer (k_d) calculated using the first order kinetic equation,

$\ln(a-x) = \ln a - k_d t$ ..... (1)

Where:

a : represents the stabilizer concentration before irradiation.

x : represents the change in stabilizer concentration after irradiation time (t) .

If (A_O) represents the absorbance of the film Poly(vinyl chloride) containing a certain concentration of compound added before irradiation . process (At) absorbance after the passage of time (t) on the irradiation process. And (A∞) represents the absorbance at infinity, than:

$a = Ao - A\leftarrow$

$x = Ao - At$

$a - x = Ao - A\leftarrow - Ao + At = At - A\leftarrow$....(2)

substitution of (2) in (1) from equation gives:

$\ln(At - A\leftarrow) = \ln (Ao - A\leftarrow) - k_d t$.... (3)

Thus a plot of In (A_t - A_∞) exchange for irradiation time (t) in seconds produces a straight line is a tendency (K_d) and this shows that photodecomposition of additives are first order [10].

Results and Discussion:

Uv radiations are known to have deleterious effects on most polymers inducing chemical modification and cleavage of polymer chain, which ultimately lead to an unwanted loss of the mechanical and surface properties of the irradiated material. The prepared Schiff's bases were used as photostabilizers to modified Poly (vinyl chloride) films comparing with unmodified PVC chips [11].

The added substances used to be totally soluble in Tetrahydrofuran solvent. It has been be noticed that the added substances used in this work are photodecomposed during the photolysis. Thus the photodecomposition rate constant (k_d) was calculated .The (k_d) values were computed using the UV spectra changes of poly(vinyl chloride) chips thickness (40 ↘m) containing groups of Schiff's bases. The photolysis. Along these lines the photodecomposition rate steady (k_d) was calculate The (k_d) qualities were registered utilizing the UV spectra changes of [12]

The plot of illumination time versus ln(At-A∞) gives straight line which indicates primarily the first order reaction. The slope equal to the decomposition rate constant k_d. Fig. (1) demonstrates the variety of ln(At - A ∞) with irradiation time for all added substances in poly(vinyl chloride) chips at the wavelength 365nm.

Table (3): Photodecomposition Rate Constant (kd) of PVC Chips Thickness (40µm)

Compounds	Polymer	Kd (sec^{-1})
PVC	B	5.35×10^{-3}
PVC + L1	PL1	1.78×10^{-3}
PVC + L3	PL3	6.15×10^{-4}
PVC + L2	PL2	4.99×10^{-4}
PVC + L4	PL4	3.36×10^{-5}

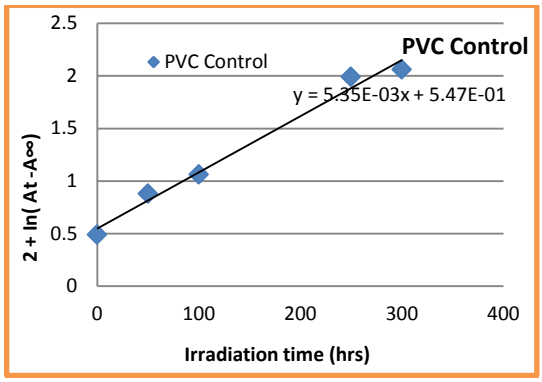


Fig. 1: In (At–A∞) with Irradiation Time of PVC Control Chips

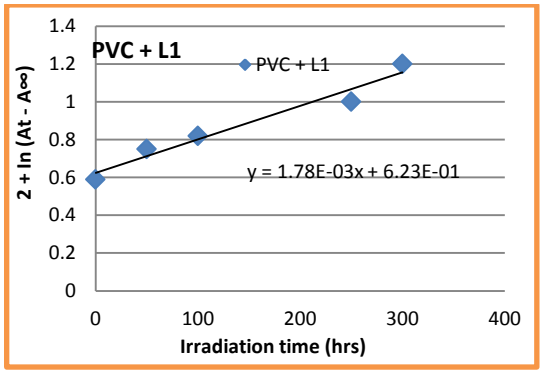


Fig. 2: In (At–A∞) with Irradiation Time of PL1 for Modified PVC Chips

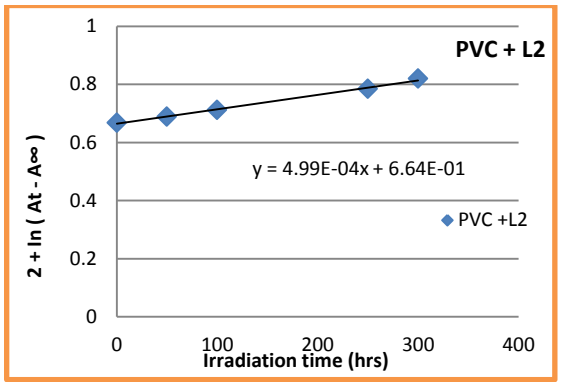


Fig.3: In (At–A∞) with Irradiation Time of PL2 for Modified PVC Chips

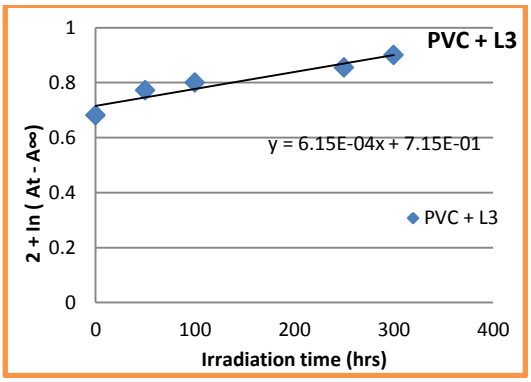


Fig. 4: In (At–A∞) with Irradiation Time of PL3 for Modified PVC Chips

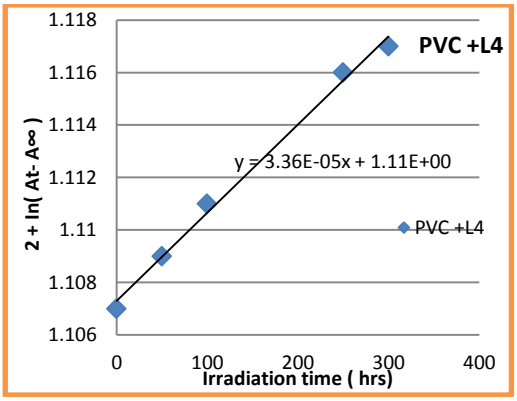


Fig. 5: In (At–A∞) with Irradiation Time of PL4 for Modified PVC Chips

The photostabilizers possess depressed kd values, which mean that these modified polymers are steady near U-Visible light. One could notice that kd values are critical to the kind of additives in Poly(vinyl chloride) chips, which decrease in the following order:

(B)> (PL1) > (PL3) > (PL2) > (PL4)

Increase the activity

Conclusions

The added substances of Schiff's bases work successfully as photostabilization for poly(vinyl chloride) chips**.** The photostabilizers always posses low kd values, which mean that these modified polymers are stabilized towards Ultraviolet-Visible light. The additives take photostabilization activity according to their reduction in observed rate constant in the following arrange :

(B) > (PL1) > (PL3) > (PL2) > (PL4)

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دراسة التثبيت الضوئي لبعض بوليمرات متعدد كلوريد الفاينيل والحاوية على مجاميع متدلية من قواعد شف

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الخلاصـة:

تختلف بوليمرات متعدد كلوريد الفاينيل المحورة في تاثرها بالأكسدة الضوئية بمقارنتها بمتعدد كلوريد الفاينيل غير محور حيث تم دراسة التثبت الضوئي لـرقائق متعدد كلوريد الفاينيل المحورة باستخدام قواعد شـف المشتقة مـــن (5-amino-1, 3, 4-thiadiazole-2-thiol) بطريقة الصـب الرقائـق البلاستيكية وبسمك (40) والحاوية على قواعـد شف في مذيـب (THF) . وتم تحديد فعالية أفلام متعدد كلوريد الفاينيل المحورة في التثبيت الضوئي عن طريق حساب ثابت سرعة التحلل الضوئي للمثبت الضوئي(k_d). يعزى كفاءة هذه البوليمرات في التثبيت الضوئي لرقائق متعدد كلوريد الفاينيل المحورة من خلال استبدال ذرة Cl في متعدد كلوريد الفاينيل بمجاميع فعالة من قواعد شف.

الكلمات المفتاحية : متعدد كلوريد الفاينيل ، التثبت الضوئي ، قواعد شف.