

Study the Rate Constant of Photostabilization of PVC in Presence of Schiff's Bases of Sulphamethoxazole

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Abstract

The photostabilization of poly (vinyl chloride) (PVC) films by Sulphamethoxazole Schiff's bases compounds was investigated. The PVC films containing concentration of compounds 0, 5% by weight were produced by casting method from tetrahydrofuran (THF) solvent. The photostabilization activities of these compounds were determined by calculating the photodegradation rate constant for photostabilizer (k_d). The stabilizing efficiency of sulphamethoxazole–Schiff's base derivatives is attributed to the replacement of the labile chlorine atoms on the PVC chains by a relatively more stable moiety of the organic stabilizer.

Keywords: Schiff's bases, Poly(vinyl chloride), Sulphamethoxazole.

Introduction

Poly (vinyl chloride), better known by its abbreviation PVC, is one of the most versatile plastics. It is the second largest manufactured resin by volume worldwide [1]; However, PVC suffers from poor thermal and light stability. It undergoes rapid autocatalytic dehydrochlorination upon exposure to heat and light [2,3] during its molding and use, respectively. As a result, conjugated polyene sequences are formed from the beginning of the reaction, and they give rise to discoloration of the polymer and seriously change its physical properties [4]. The low cost and the good performance of poly (vinyl chloride) products have increased the utilization of this polymer in building, mainly in exterior application, such as window profiles, cladding structure, and siding [5]; However, ultimate user acceptance of the PVC products for outdoor building applications will depend on their ability to resist photodegradation over long periods of sunlight exposure. To ensure weatherability, the PVC resin needs to be compounded and processed properly using suitable additives, leading to a complex material whose behavior and properties are quite different from the PVC resin by itself [6]. Recently, scientists have used Schiff's bases compounds as Photostabilizers of poly (vinyl chloride) polymer against photodegradation by ultraviolet radiation [7-9]. As part of our on-going research in the photostabilization of poly (vinyl chloride),

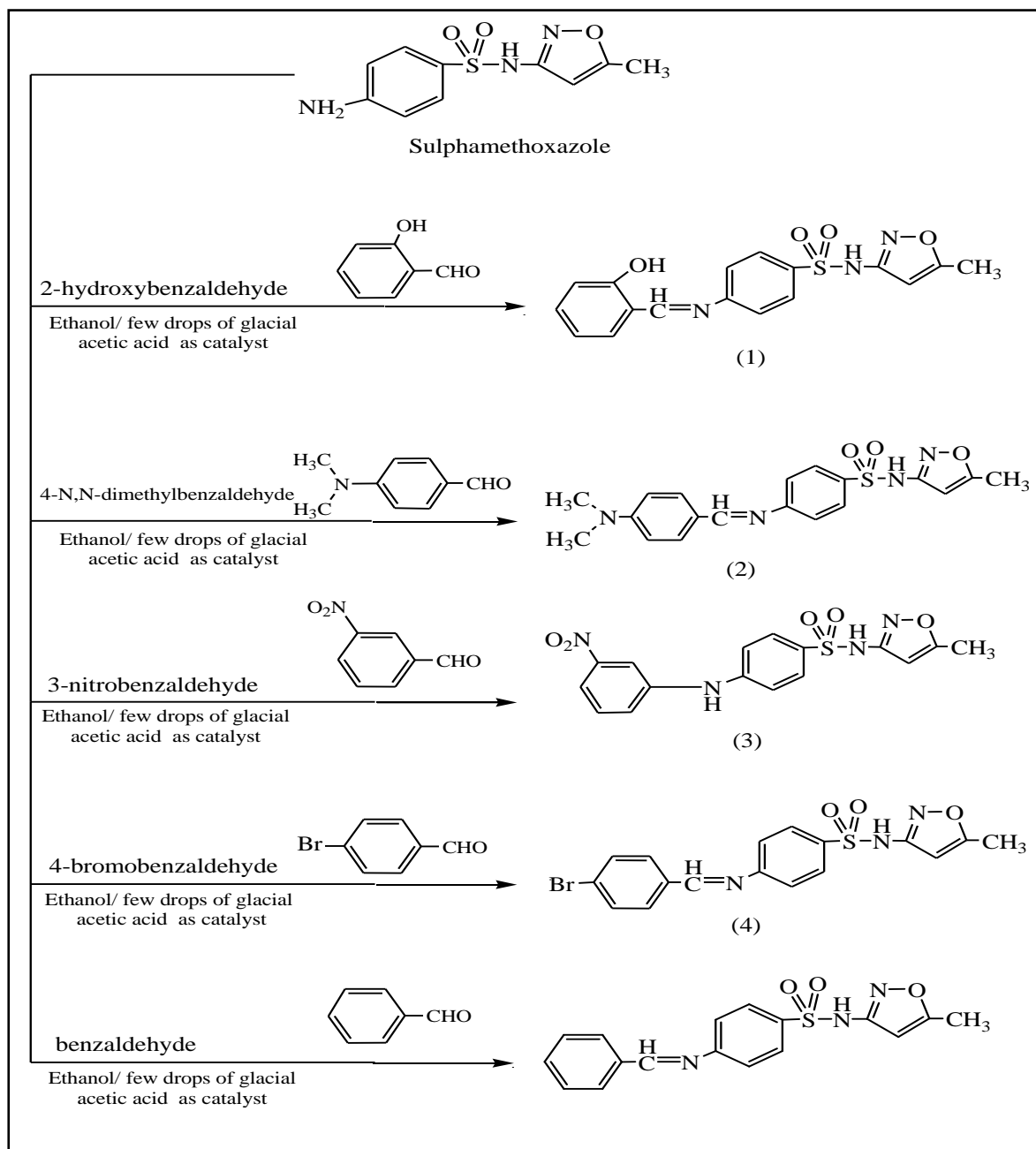
the photostabilization of PVC was studied using five Schiff's bases derivatives of sulphamethoxazole have been prepared in alcoholic medium.

Experimental

Materials

The following Schiff's bases compounds were all prepared by the method described by Hussain et al. [10]:

- (1) ξ -[(γ -hydroxy-benzylidene)-amino]-*N*-(α -methyl-isoxazol- γ -yl)-benzene sulfonamide.
- (2) ξ -[(ξ -dimethylamino-benzylidene)-amino]-*N*-(α -methyl-isoxazol- γ -yl)-benzene sulfonamide.
- (3) *N*-(α -methyl-isoxazol- γ -yl)- ξ -[(γ -nitro-benzylidene)-amino]-benzene sulfonamide.
- (4) ξ -[(ξ -bromo-benzylidene)-amino]-*N*-(α -methyl-isoxazol- γ -yl)-benzene sulfonamide.
- (5) *N*-(α -methyl-isoxazol- γ -yl)- ξ -[(ξ -nitroox-benzylidene)-amino]-benzene sulfonamide.



Scheme (1) Scheme of preparation of Schiff's bases from sulphamethoxazole.

Experimental Techniques

Films preparation

Commercial poly(vinyl chloride) supplied by Petkim company (Turkey) was re-precipitated from THF solution by alcohol several times and finally dried under vacuum at room temperature for 24 hours. Fixed concentrations of poly(vinyl chloride) solution ($0.5 \text{ g}/100 \text{ ml}$) in tetrahydrofuran were used to prepare polymer films with $30 \mu\text{m}$ thickness (measured by a micrometer type 2610 A, Germany). The prepared compounds (0.5% concentrations) were added to the films. The

films were prepared by evaporation technique at room temperature for 24 hours, to remove the possible residual tetrahydrofuran solvent.

Irradiation Experiments

1. Accelerated testing technique

UV light was used for irradiation of polymer films. The lamp giving spectrum range between (200–280) nm and the light intensity is $6.2 \times 10^{-4} \text{ ein dm}^{-2} \text{ sec}^{-1}$. The polymer films samples were fixed vertically and parallel to the lamps to be sure that UV incident radiation is vertically incident on the

samples, the irradiation samples are changed places from time to time to be sure that the intensity of light incident on all samples is equal. The distance between the polymer films and light source was 10 cm.

**2.2. Photodegradation measuring method
Measuring the photodegradation rate of Poly (vinyl chloride) films using ultraviolet - visible spectrophotometer**

The ultraviolet-visible spectrophotometer type Shimadzu UV-VIS. 160 was used to measure the changes in the UV-visible spectrum during the irradiation time for each compound at the maximum absorption band (λ_{max}). The absorption spectrum was measured in the range of (200-800) nm and the (λ_{max}) at each absorption was also recorded for different irradiation times. The infinite irradiation time was considered and the infinite absorption (A_{∞}) was assumed to be after the infinite irradiation time. To determine the photodegradation rate constant for photostabilizer (k_d), the first order equation was used:

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

where a, represent the stabilizer concentration before irradiation, x represents the change in stabilizer concentration after irradiation time (t).

If A_0 represents the absorption intensity of the polymer film containing stabilizer before irradiation, A_t represents the absorption intensity after (t) time of irradiation, then:

$$\begin{aligned} a &= A_0 - A_{\infty} \\ x &= A_0 - A_t \\ a - x &= A_0 - A_{\infty} - A_0 + A_t = A_t - A_{\infty} \dots\dots (2) \end{aligned}$$

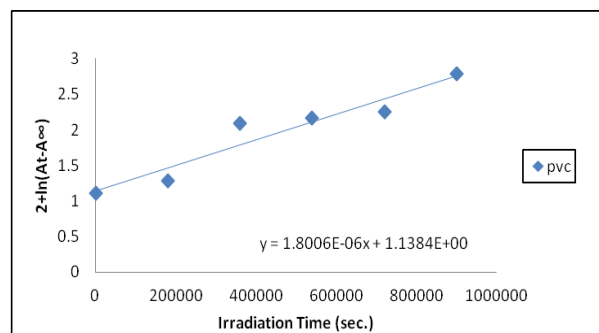
substitution of a and a - x from equation (2) in (1) gives:

$$\ln(A_t - A_{\infty}) = \ln(A_0 - A_{\infty}) - k_d t \dots\dots\dots (3)$$

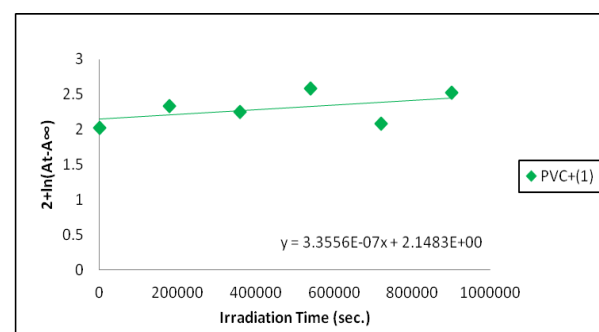
Thus a plot of $\ln(A_t - A_{\infty})$ versus irradiation time (t) gives straight line with a slope equal (k_d) which indicates that photodecomposition of the additives is first order [11].

**Results and Discussion
Study of the efficiency of prepared Schiff's bases as photostabilizers of Poly (vinyl chloride) films by ultraviolet spectroscopy**

Ultraviolet radiations are known to have deleterious effects on most industrial polymers inducing chemical modification and scission of polymer chain, which ultimately lead to an undesirable loss of the mechanical and surface properties of the irradiated material [12]. Poly (vinyl chloride) suffers from poor thermal and light stability. The prepared Schiff's bases were used as photostabilizers to Poly (vinyl chloride) films comparing with Poly (vinyl chloride) films (blank). The physical properties of additives and polymers play a very important role in determining the additive efficiency in photostabilization or photodegradation of polymers [13]. The additives used in this study were chosen to be completely soluble in polymer solvent, THF. It has been noticed that the additives used in the present work are photodecomposed during the photolysis. Thus the photodecomposition rate constant (k_d) was calculated (see paragraph (2)). The (k_d) values were computed using the UV spectra changes of PVC films thickness (30 μ m) containing 0.5 % of additives. The plot of irradiation time versus $\ln(A_t - A_{\infty})$, gives straight line which indicates primarily the first order reaction. The slope equal to the decomposition rate constant k_d . Fig. (1) shows the variation of $\ln(A_t - A_{\infty})$ with irradiation time for all additives in Poly (vinyl chloride) films at the wavelength 360 nm.



(a)



calculated by the same way and shown in Table (1).

Table (1)

Photodecomposition rate constant (k_d) of PVC films ($3 \cdot \mu m$) thickness containing $\cdot, \circ\%$ of additives.

Compounds	$k_d (sec^{-1})$
PVC+(1)	$3,3006 \times 10^{-7}$
PVC+(2)	$7,6222 \times 10^{-7}$
PVC+(3)	$1,0738 \times 10^{-7}$
PVC+(4)	$1,2097 \times 10^{-7}$
PVC+(5)	$1,5714 \times 10^{-7}$
PVC(blank)	$1,8006 \times 10^{-7}$

The photostabilizers always possess low k_d values, which mean that these modified polymers are stable towards UV light. One could notice that k_d values are sensitive to the type of additives in Poly(vinyl chloride) films, which decrease in the following order: **PVC (blank) > (5) > (4) > (3) > (2) > (1)**

$\xrightarrow{\hspace{10em}}$
 PVC with additives

And this might point out to increase the photostability of these additives in this term.

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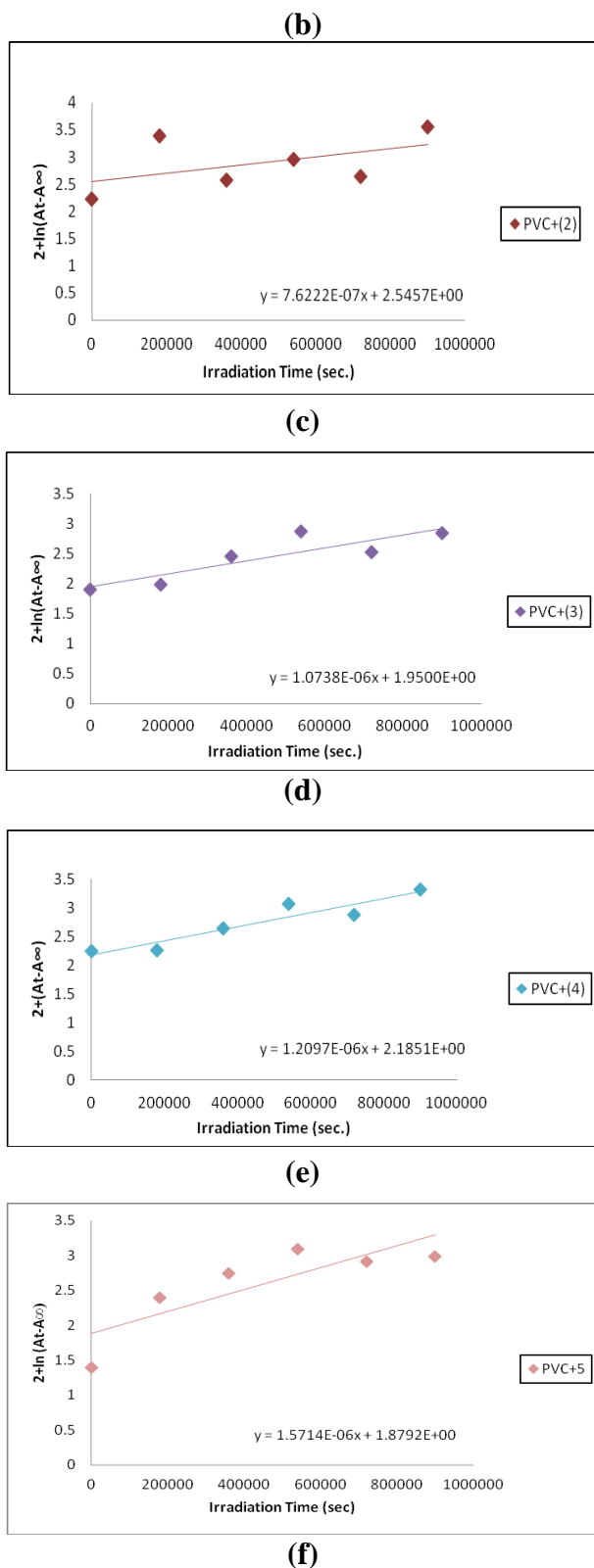


Fig. (1) Variation of natural logarithm of $\ln(A_t - A_\infty)$ with irradiation time for prepared Schiff's bases in PVC films. a. PVC(blank) b.(1) c.(2) d.(3) e.(4) f.(5).

The values of the first order rate constant of all the additives decay in PVC films (k_d)

الخلاصة

في هذا البحث تم دراسة التثبيت الضوئي لرقائق متعدد كلوريد الفينيل باستخدام قواعد شيف مشتقة من المركب sulphamethoxazole. تم انتاج الرقائق البلاستيكية التي تحتوي على 0,5% وزناً من قواعد شيف بطريقة الصب من مذيب Tetrahydrofuran. وتم تحديد فعالية هذه المركبات في التثبيت الضوئي عن طريق حساب ثابت سرعة التحلل الضوئي للمثبت الضوئي (k_d). وتعزى كفاءة هذه المركبات في التثبيت الضوئي لرقائق PVC الى استبدال ذرة Cl في سلاسل PVC بنهايات اكثر استقرارا من المثبت الضوئي.

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