

Al-Nahrain Journal of Science

ANJS, Vol.23 (1), March, 2020, pp. 57 – 61



The Effect of UV Aging on the Structure of PVC in the Presence of Organotin(IV) Compounds

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Articles Information Abstract New photostabilizers of poly(vinyl chloride) (PVC) were synthesized and Received: investigated the photostabilizing efficiency of the polymer films by 15, 12, 2019 ultraviolet (UV) experiment. The rate of photodecomposition constant Accepted: 04, 02, 2020 have been calculated for PVC films as a method for evaluating the Published: efficiency of the organotin(IV) complexes that used as a photostabilizers 01, March, 2020 after 300 hour of irradiation. The results have showed that the additives had reduced the rate of photodecomposition constant of PVC films significantly with comparison to PVC (blank). The (kd) value for PVC films was the highest in the absence of any additives, and the lowest value in the presence of triphenyltin (IV) complex. Keywords: Telmisartan Photodecomposition **PVC** Films UV Poly(vinyl chloride) (PVC) HEAT

DOI: 10.22401/ANJS.23.1.08

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1. Introduction

Poly(vinyl chloride) (PVC) considers one of the most popular and important plastics because it used in different fields such as medicine, dolls, artificial leather, blinds, floors, wrapping material, pipes, etc. There are two types of PVC which are flexible and rigid plastics. PVC plastics are used widely because of its unique properties; it is cheap and easy modified. Even though, PVC poor flexibility and durability limits its application in industry field [1]. Many new stabilizers have been synthesized to mix with PVC to achieve the excellent flexibility such as Schiff bases [2-4], organotin complexes [5,6] and polyphosphates [7]. However, these stabilizers have effect on the environment. Three methods have been used to obtain suitable stabilizers. The first approach is utilizing eco-friendly stabilizers and second is reducing the amount of the stabilizers. Lastly the reacting of the stabilizers with the PVC polymer chain by covalent bond, so they will not release to environment easily [8]. Many studies discussed the PVC degradation, and it is well known involving a multi-step mechanism, through this process, including competing reactions [9-15]. When the hydrochloric (HCl) molecules release from the polymer chain, they react with the double bond to organic chlorinated compound. the PVC degradation process of is almost dehydrochlorination to produce polyene compounds with large amount of HCl and small amount of organic molecules such as benzene ring, anthracene,..etc. In comparison the C-C bond is stronger than C-Cl bond and the Cl atom is more electronegative than the C atom. Therefore, formation of Cl radicals is more preferred than formation of primary C radicals [12]. Emad's group used Polyphosphates as photostabilizers of PVC [13]. In this work, four stabilizers synthesized, telmisartan organotin(IV), to investigate the kd (photodecomposition constant) for the PVC polymer films. The UV experiment was utilized to study the stabilizing efficiency of these new stabilizers in the PVC films, measure their kd values of the stabilizer-doped PVC.

2. Materials and Methods

Materials used

Telmisartan and other chemicals supplied from Merck (Schnelldorf, Germany) and used received.

Methodology

Four organotin(IV) complexes, 1-4 (Figure 1) were synthesized from the reaction of telmisartan and the appropriate tin(IV) chloride salts as previous complexes reported [16].The have characterized by FTIR, ¹H-, ¹³C-and ¹¹⁹Sn-NMR spectroscopies, elemental analysis and Field Emission Scanning Electron Microscopy (FESEM), as reported [16].

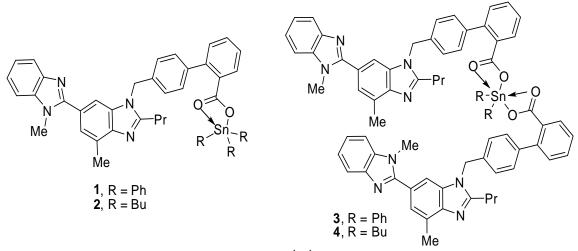


Figure 1. Organotin(IV) complexes 1-4.

The preparation of polymeric Films

5 g of PVC was dissolved in 100 mL of THF and left to stir for 30 min at 25 °C, after that 0.5 wt% of the new stabilizers (1, 2, 3, or 4) was added to the

mixture and left to stir for more 30 min. The combination was casted onto glass plates and the film was left (24 h) at 25 °C to get dry.

UV-Weathering measurements

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A self-prepared chamber connected with 40-W was used to test the accelerated UV-weathering. The films were exposure to continuous UV light using average irradiation intensity $(7.75\times10^{-7}\ \mathrm{Ein.Dm^{-3}.S^{-1}})$ and wave length 313 nm. The accelerated irradiation test was done after total time 300 h.

UV Spectrophotometer

To determine the variations in the UV-Vis spectra of prepared polymer films, the 160A-Ultraviolet/Visible (UV-Vis) (Shimadzu, Japan) Spectrophotometer was used. All the prepared films were irradiated at $\lambda_{max} = 313$ nm [17]. The Equation

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

Equation (3) was got by replacing a - x in Equation (1) by its value in Equation (2).

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

The plot of $ln(A_t - A_{\infty})$ against the irradiation time (t) gives straight line, where the slope is k_d . The photodecomposition of PVC shows a first order kinetics [17-20].

3. Results and discussion

The effect of organotin(IV) complexes 1-4 as new photostabilizers on the prepared PVC films was investigated. The irradiation demonstrated obvious alteration in the PVC prepared films and the photo degradation was observed. Figures 2-6 show the plot between $ln(A_t - A_{\infty})$ against t (irradiation time) which presented a straight line. The diagrams confirmed first order kinetics where the slope equalled kd of prepared films. The plot between $ln(A_t - A_{\infty})$ against irradiation time (t) of PVC

While, the alternations between the $ln(A_t - A_{\infty})$ versus the irradiation time of PVC prepared films mix with the new photostabilizers organotin(IV) compounds are shown in Figure 3-6. The additive stabilizers percentage was 0.5% by weight.

(1) was utilized to measure the rate constant (k_d) for prepared films.

$$ln(a-x) = lna - k_d t \tag{1}$$

Where, $a=A_0-A_\infty$, $x=A_0-A_t$, $a=\mathrm{PVC}$ concentration before irradiation with UV light and x= alteration in PVC concentration at time t throughout the irradiation by UV light as presented in Equation (2), $A_0=$ the PVC absorption intensity at t_0 , $A_\infty=$ the PVC absorption intensity at t_∞ and $A_t=$ the PVC absorption intensity after irradiation time t.

prepared films, without any stabilizers, shows in figure 2.

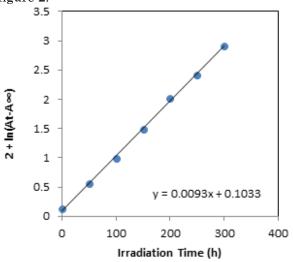


Figure 2. Plot for $ln(A_t - A_{\infty})$ versus irradiation time of blank PVC prepared film.

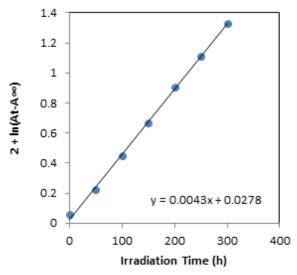


Figure 3. Plot for $ln(A_t - A_{\infty})$ versus irradiation time of PVC + 1 prepared film.

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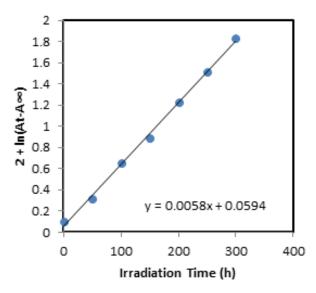


Figure 4. Plot for $ln(A_t - A_{\infty})$ versus irradiation time of PVC + 2 prepared film.

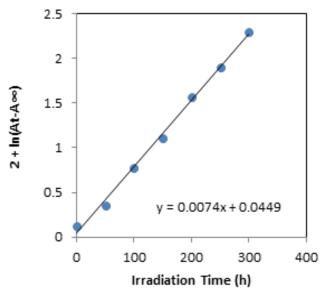


Figure 5. Plot for $ln(A_t - A_{\infty})$ versus irradiation time of PVC + 3 prepared film.

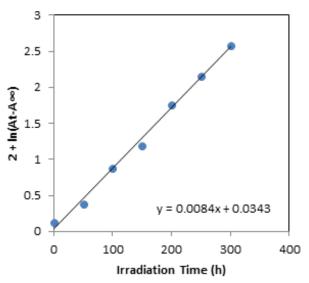


Figure 6. Plot for $ln(A_t - A_{\infty})$ versus irradiation time of PVC + 4 prepared film.

Table 1. The kd data for PVC prepared films after irradiation by UV light for 300 h.

Film	$K_d (\mathrm{sec}^{-1})$
PVC (blank)	9.30×10^{-3}
PVC + 1	4.30×10^{-3}
PVC + 2	5.80×10^{-3}
PVC + 3	7.40×10^{-3}
PVC + 4	8.40×10^{-3}

All the k_d data for PVC (blank) film and PVC films mixing with organotin(IV) complexes 1-4 are summarized in Table 1. Table 1 and Figures 3-6 demonstrate the effectiveness of the existence of organotin(IV) complex and its type on the k_d values for PVC prepared films. As shown in Table 1, the highest k_d value $(9.30 \times 10^{-3} \text{ sec}^{-1})$ was for the blank PVC film without any stabilizers. The rate constant decreased considerably (8.40–4.30 \times 10⁻³ sec⁻¹) when organotin(IV) complexes were used as additives. The highest k_d value was recorded for the blank PVC and the lowest value was recorded in the existence of 1 organotin(IV) complex. In the future, many researches will carry out to discuss why a different PVC stabilizer has different influence on the discoloration of the PVC films.

4. Conclusions

Adding the organotin(IV) complexes to the PVC films as photostabilizers show high efficiency through reducing the rate of photodecomposition constant compared to blank PVC that showed highest value. PVC films containing organotin(IV) showed lower values.

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Acknowledgments

This work was supported by UAE University, Universiti Kebangsaan Malaysia, Babylon University, Al-Mansour University College and Al-Nahrain University.

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