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INORGANIC TIN(IV) COMPLEXES AS PHOTO-STABILIZER FOR PVC

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ABSTRACT. Five organotin(IV) complexes including captopril (ligand) were employed in small amount as photostabilizers for poly(vinyl chloride) (PVC) when irradiated by UV light. Polymer's samples were cast into films in order to conduct the UV exposure impact. The photodegradation rate constant (k_d) of blank and organotin(IV) complexes embedded PVC specimens were investigated in this work. The k_d values of filled samples were lower than the blank one, which indicates higher stability of these embedded films. Among these additives, triphenyltin(IV) showed the highest stability effect.

KEY WORDS: PVC, Organotin(IV) complexes, Photostability, Photodegradation, UV light

INTRODUCTION

Poly(vinyl chloride) is the third widely applied polymer across the globe after polyethylene and polypropylene [1]. This polymer has multiple outdoor applications, such as window frames, pipes, packings, wires, and coatings. However, PVC undergoes photodegradation when facing a long term exposure to ultraviolet (UV) light, this degradation could result in defects in the mechanical and physical properties for the polymer [2, 3]. The photodegradation of PVC leads to loss of hydrogen chloride, discoloration, and micro-cracking; this changes the appearance of PVC. The photodegradation of PVC were decrease by using different additives, such as organometallics, including complexes of organotin [4, 5], organic [6, 7], Schiff bases [8, 9], and others [10]. In general, organotin compounds contain one or more carbon–tin covalent bond(s), and usually own a tetravalent structure [11]. These chemicals were discovered in 1894 by Edward Frankland, the first one was diethyltin diiodide ($(C_2H_5)_2SnI_2$). Organotin compounds containing two oxidation numbers (+2 and +4) are known as tin; the species of organotin(II) and organotin(IV) are sp2 and sp3 hybridized, respectively. It was reported that the oxidation state of (+IV) is more stable than (+2); yet, the +2 can be simply oxidized to the +4 state [12]. This promoted the organotin complexes to be used in different applications [13, 14]. In this work, five organotin complexes were tested as photo-stabilizers for the PVC. Using different techniques, the photodegradation rate constant was calculated and studied as a function of exposure time.

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EXPERIMENTAL

Materials

Captopril and other chemicals were supplied from Merck (Gillingham, UK) and used without any additional purification and/or treatment steps.

Methodology

The di and tri-organotin(IV) complexes, **1-5** were synthesized from the reaction of organotin(IV) with captopril (1-(3-mercapto-2-methylpropanoyl)-pyrrolidine-2-carboxylic acid) as a ligand in a methanolic medium at different ratios, as previously reported in a study from our group [19]. The complexes were characterized by FTIR, ^{1}H-NMR, UV-VIS spectroscopy, conductivity measurements, and elemental analysis, as reported in our previous paper [15]. Figure 1 shows the structure of these compounds.

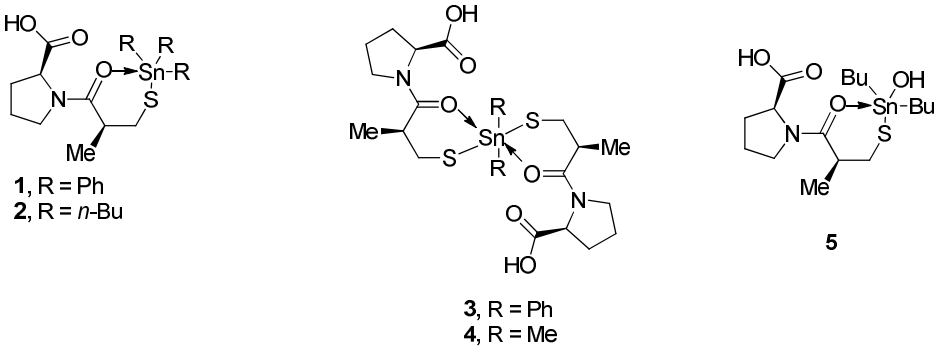


Figure 1. Organotin(IV) complexes **1**–**5**.

Films preparation

A 5 g/100 mL concentration of the PVC/tetrahydrofuran (THF) solution was used to synthesize polymeric films. However, PVC films filled with the organotin complexes were prepared by adding 0.5 wt.% of these components within the cast solution [16].

Accelerated testing technique

The prepared PVC sheets were continuously exposed to UV light for 300 h at 25 °C. The UV light had properties of intensity = 1.052×10^{-8} ein·dm^{-3}·s^{-1} and λ_{max} = 313 nm, and was obtained using a QUV tester weather-tester (Q-Panel Company; Homestead, FL, USA) [17, 18].

Estimation of the photodegradation rate (k_d) for PVCs' sheets

In regard to determining the changes in PVC films, UV-Vis spectra reflection from the surface were analysed using a Shimadzu UV-Vis 160A - spectrophotometer for ultraviolet (Shimadzu Cooperation, Kyoto, Japan). The whole PVC films, blank and filled, were irradiated at λ_{max} = 313 nm. The constants of photodegradation rate (k_d) for all films were estimated by using Equation (1) [19].

$$ln(a - x) = lna - k_d\, t \quad (1)$$

where $a = A_0 - A_\infty$, and $x = A_0 - A_t$, a is the concentration of PVC prior to the irradiation, x is the differences in PVC concentration after a certain irradiation time (t), as shown in Equation (2):

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

A_0 = the polymer's absorption intensity before irradiation (at t_0). A_∞ = the polymer's absorption intensity at t_∞. A_t = the polymer's absorption intensity after exposing to irradiation for a certain time (t). Ultimately, Equation (3) was calculated by substituting $(a - x)$ of the first equation in the second one [20].

$$(At - A\infty) = (A0 - A\infty) - k_d\, t \quad (3)$$

RESULTS AND DISCUSSION

The impact of filling five organotin(IV) components, numbered from **1** to **5**, within the PVC films was investigated. These complexes were added in a weight ratio of 0.5% and performed as photostabilizers, where the films were examined under the radiation of UV light (λ_{max} = 313 nm) for 300 h. These additives resulted in a clear improvement in the decomposition rate of PVC films. Figure 2 shows the relationship of $(A_t - A_\infty)$ versus irradiation time (t); the plot was a straight line. The graph showed 1st order kinetics behaviour, where slope equals to the rate of decomposition constant (k_d) for the plain film. Figures 3-7 show the changes in $(A_t - A_\infty)$ versus time of irradiation for PVC films filled with organotin(IV) stabilizers during UV light exposure.

It has been noted that during the photolysis process, all additives used are photodecomposed. All the k_d data for PVC samples with and without organotin(IV) chemicals were summarized in Table 1. From the table we notice that the photostabilizers always have lower level of k_d values, so these modified polymers are stable towards ultra-violet light. We can predict that the type of additives could effect on the k_d values. The k_d values for the organotin(IV)-filled PVC films were lower than the blank PVC.

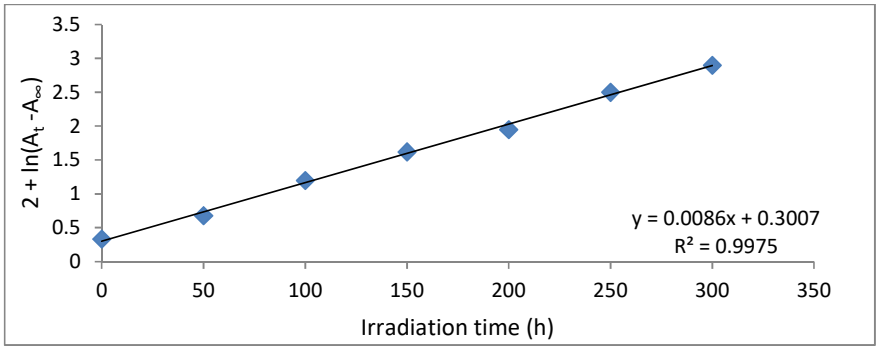


Figure 2. Changing in $(A_t - A_\infty)$ versus UV irradiation time for blank PVC film.

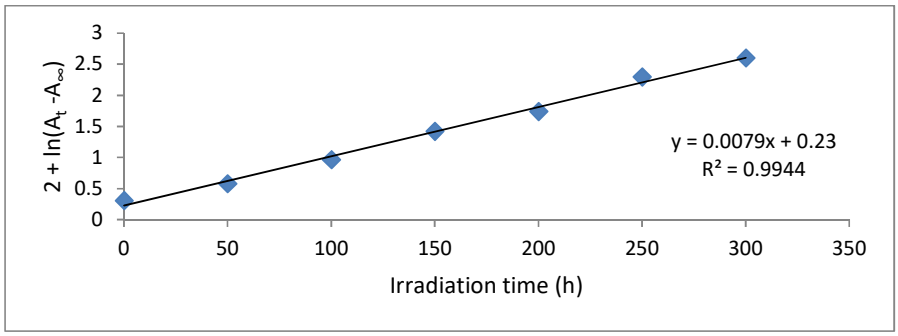


Figure 3. Changing in ($A_t - A_\infty$) versus UV irradiation time for PVC film filled with organotin(IV) number **5**.

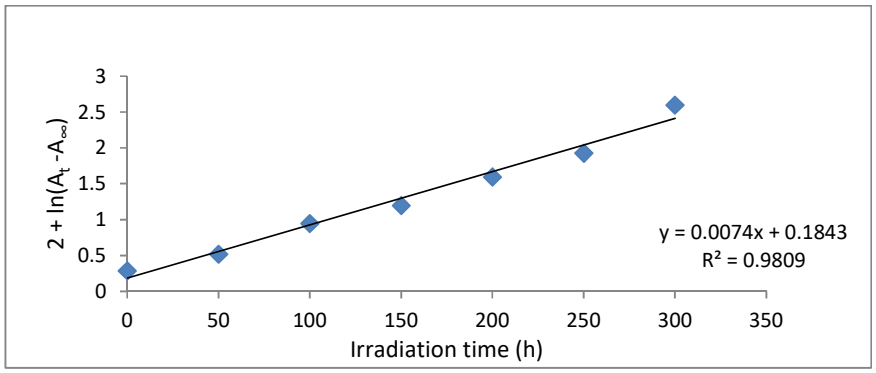


Figure 4. Changing in ($A_t - A_\infty$) versus UV irradiation time for PVC film filled with organotin(IV) number **4**.

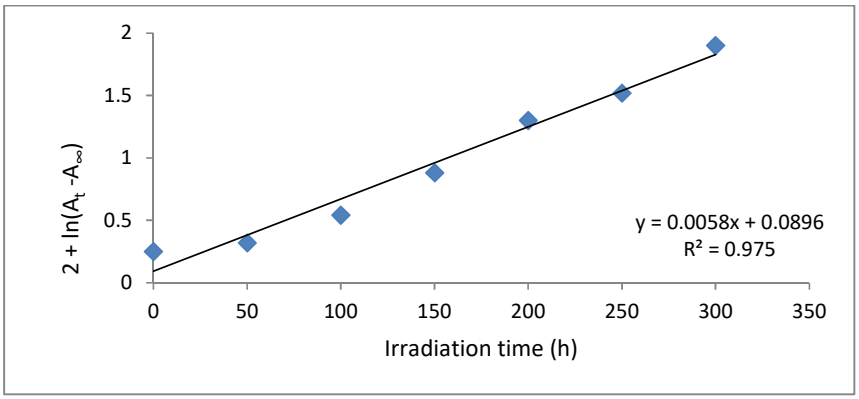


Figure 5. Changing in ($A_t - A_\infty$) versus UV irradiation time for PVC film filled with organotin(IV) number **3**.

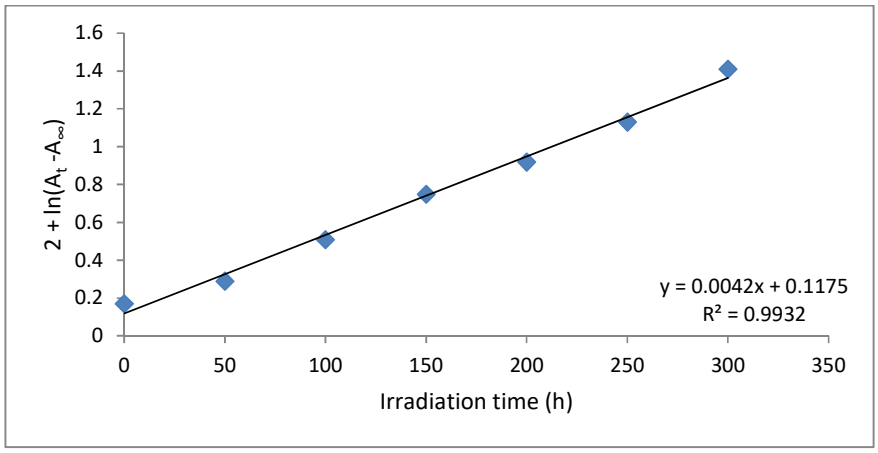


Figure 6. Changing in ($A_t - A_\infty$) versus UV irradiation time for PVC film filled with organotin(IV) number **2**.

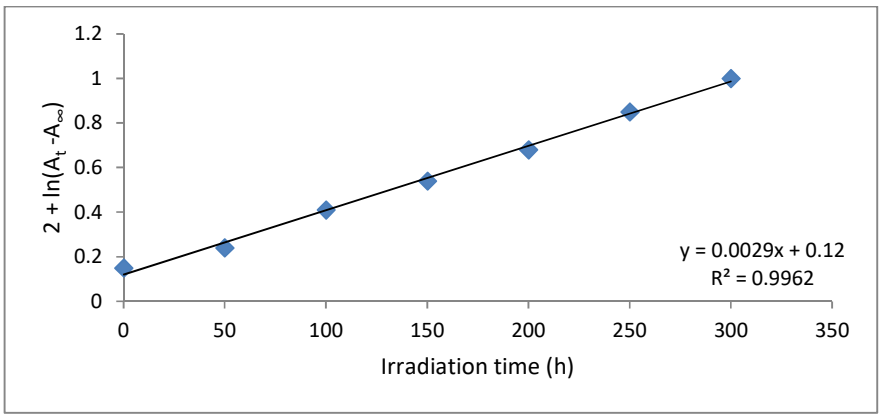
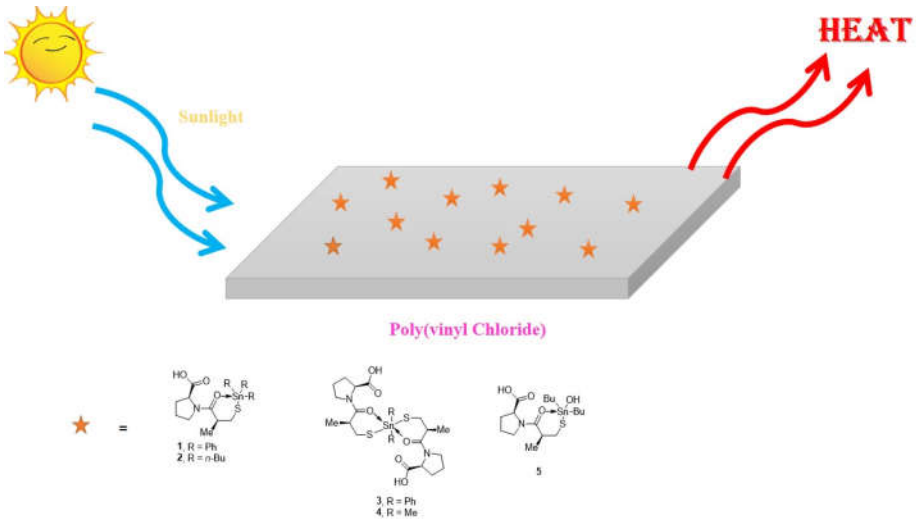


Figure 7. Changing in ($A_t - A_\infty$) versus UV irradiation time for PVC film filled with organotin(IV) number **1**.

Table 1. Rate of photodecomposition constant (k_d) for PVC films after UV. Light irradiation (300 h).

Film	k_d (s^{-1})
PVC (blank)	8.6×10^{-3}
PVC + **5**	7.9×10^{-3}
PVC + **4**	7.4×10^{-3}
PVC + **3**	5.8×10^{-3}
PVC + **2**	4.2×10^{-3}
PVC + **1**	2.9×10^{-3}

Table 1 and Figures 2–7 demonstrate the effectiveness of the existence of captopril-tin complexes and its type on the k_d values for PVC prepared films. As shown in Table 1, the highest k_d value (8.60×10^{-3} s^{-1}) was for PVC film without any stabilizers (blank). The rate constant decreased considerably ($7.90–2.90 \times 10^{-3}$ s^{-1}) when complex of captopril-tin are used as additives in this work. The highest k_d value was recorded for the blank PVC and the lowest value was recorded in the existence of 1 captopril-tin complex. Hence, complex 1 was the most effective photostabilizer for PVC films. From the table we notice that the sequence is as follows PVC (blank) > complex **5** > complex **4** > complex **3** > complex **2** > complex **1**. So these complexes decrease the effect of UV light on PVC films (Scheme 1) show the photochemical process of PVC films containing organotin complexes. So these complexes were used as photostabilizers against degradation. Many researches will carry out to discuss why a different PVC stabilizer has different influence on the discoloration of the PVC films [21].



Scheme 1. Photochemical process of PVC films containing organotin complexes.

CONCLUSION

Photostabilizers of organotin(IV) complexes were filled in PVC films and showed high efficiency compared to blank PVC film, which can be noticed by reducing the photodecomposition rate constant. Triphenyl-tin(IV) complex showed the highest stability improvement for PVC films during irradiation. The k_d values of filled PVC films ($2.9\text{-}7.9 \times 10^{-3}$ s^{-1}) were lower than the constant's value of blank PVC (8.6×10^{-3} s^{-1}).

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