Development of atenolol-tin complexes as PVC photostabilizers for outdoor applications

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Abstract
New tin complexes were made from the reaction of various tin reagents with atenolol. These complexes were mixed with PVC to produce the stabilized polymeric films. The stability of the films was evaluated using UV/Vis absorption spectroscopy and field emission scanning electron microscopy.

The rate of photodecomposition constant have been calculated for PVC films as a method for evaluating the efficiency of atenolol-tin complexes that used as a photostabilizers after 300 hour of irradiation. The results have showed that the additives had reduced the rate of photodecomposition significantly with comparison to PVC (blank). The rate constant of photodecomposition (kd) value for PVC films was higher than that after addition of atenolol tin complexes as photostabilizers.

Keywords: poly(vinyl chloride); atenolol-tin complexes; photostabilization

1. Introduction
Polyvinyl chloride (PVC) is one of the most abundant polymers used in different industries with respect to commercially available polymers. It is rated as the second polymer in the plastic industry just after polyethylene due to its characteristics and performance under use as well as the ease of processing for different applications [1]. Commonly, PVC used in piping, packaging, insulation, frames, doors, medical devices textile and cleansing materials and many other applications [2]. The variety and growing number of applications where PVC is
essential raised a question about the waste disposal of PVC in order to protect our environment [3].

The increasing demand for PVC products, even though its products are long life under service conditions, will increase its waste progressively raising not only environmental issues but economic problems in term of energy required to deal with PVC waste [4, 5].

One of the suggested solutions for such problem is to introduce a tin complex to reduce the effect of the UV light on PVC, in addition to increase it lifetime under working condition [6]. When the hydrochloric (HCl) molecules release from the polymer chain, they react with the double bond to produce organic chlorinated compound. The degradation process of the PVC is almost dehydrochlorination to produce a polyene compounds with large amount of HCl and small amount of organic molecules such as benzene ring, anthracene. 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 [7-14].

Additives must have different characteristics to considerate as suitable stabilizers such as manufacturing cost. In addition to its chemical properties like its chemical stability and the effective concentration of stabilizer in use. The physical properties are important as well i.e., the stabilizer dose not effect the mechanical properties or the color of the final product, also has the ability to disperse homogenously within the polymer matrices. [15]. Our group have been previously reported a number of Schiff base [18–21], aromatic [22, 23], polyphosphates [24, 25] in addition to tin complexes [26–31] as a photostabilizers for PVC polymer. In this work, four stabilizers have been synthesized, atenolol organotin(IV), to examine the kinetic of the reaction by measuring the $k_d$ (photodecomposition constant) of the new polymeric system. UV spectrophotometric analysis was utilized to evaluate the efficiency of atenolol complexes as a new photostabilizers for PVC polymer via measuring their $k_d$ values.

2. Materials and Methods

2.1. General

PVC was purchased from Petkim Petrokimya (Istanbul, Turkey). A QUV- accelerated weather-meter tester used for the irradiation. This device was supplied by Q-Panel Company, Homestead, FL, USA. The wavelength centered at 313nm with intensity of $6.43 \times 10^{-9}$ ein dm$^{-3}$ s$^{-1}$ at room temperature. Field emission scanning electron microscopy (FESEM) images were recorded using a Tescan MIRA3 LMU instrument (Tescan Orsay Holding; Brno-Kohoutovice, Czech Republic.

2.2. Synthesis of atenolol-tin complexes 1–4

Four organotin(IV) complexes, 1–4 (Figure 1) were synthesized from the reaction of atenolol with suitable tin (IV) chloride salts as previously reported [8]. These complexes have been characterized by FTIR, $^1$H- and $^{13}$C-NMR spectroscopies, elemental analysis atomic force microscopy (AFM) and Field Emission Scanning Electron Microscopy (FESEM), as reported [8].

![Figure 1. Atenolol-tin complexes 1–4.](image-url)
2.3. The preparation of polymeric Films

5 g of PVC solubilized in 100 mL of THF, then left to stir for 30 min at 25 °C. After that, 0.5 wt% of atenolol-tin complexes 1–4 was added to the above solution. The reaction mixture was left to stir for additional more 30 min. Reaction mixture poured onto glass plates mold. The film which were left for (24 h) at 25 °C to give a polymer film.

2.4. UV-Weathering measurements

A self-prepared chamber was used to test the accelerated UV-weathering. The films were exposed to continuous UV light with average irradiation wavelength of 313 nm. The accelerated irradiation test was done after total of 300 h.

2.5. UV/Vis absorption Spectroscopy

To determine the variations in the UV-Vis spectra of prepared polymer films, the 160A-Ultraviolet/Visible (UV-Vis) (Shimadzu, Japan) Spectrophotometer was used [9]. The Equation (1) was utilized to measure the rate constant \((k_d)\) of photodecomposition for prepared films.

\[
\ln(a - x) = \ln a - k_d t
\]  

(1)

Where, \(a = A_0 - A_\infty, x = A_0 - A_t, a = PVC \) concentration prior the exposure to UV light, \(x = \) the change in PVC concentration at a certain time \(t\) during the exposure to UV light as presented in Equation (2), \(A_0 = PVC \) absorption intensity at \(t_0, A_\infty = PVC \) absorption intensity at \(t_\infty\) and \(A_t = PVC \) absorption intensity after irradiation time \(t\).  

\[
a - x = A_0 - A_\infty - A_0 + A_t = A_t - A_\infty
\]  

(2)

Equation (3) was got by replacing \(a - x\) and a Equation (2) by their values from Equation (2).

\[
\ln(A_t - A_\infty) = \ln(A_0 - A_\infty) - k_d t
\]  

(3)

\(k_d\). Photodecomposition was calculated from the slope of the strait line obtained from \(\ln(A_t - A_\infty) \) versus time \((t)\) of irradiation with UV light.[10].

Results and discussion

The effect of atenolol-tin compounds (1–4) as new photostabilizers on the prepared PVC films was investigated. After irradiation, an obvious alteration in the PVC prepared films and the photo degradation was observed. Figures 2-6 show the plots between \(\ln(A_t - A_\infty)\) against \(t\) (irradiation time) which presented as straight lines. Diagrams confirmed first order kinetics reactions where the slope represents \(k_d\) of prepared films. The plot between \(\ln(A_t - A_\infty)\) against time of exposing to UV light \((t)\) for PVC films, without any stabilizers, illustrated in Figure 2.

![Figure 2](image-url)

**Figure 2.** Plot for \(\ln(A_t - A_\infty)\) versus time of UV light exposure of blank PVC.
While, the alternations between the $\ln(A_t - A_\infty)$ versus the irradiation time of PVC prepared films mix with the new photostabilizers atenolol-tin complexes 1–4 are shown in Figure 3-6. The additive stabilizers percentage was 0.5% by weight.

**Figure 3.** Plot for $\ln(A_t - A_\infty)$ versus time of UV light exposure of PVC + 1 prepared film.

**Figure 4.** Plot for $\ln(A_t - A_\infty)$ versus time of UV light exposure of PVC + 2 prepared film.
Figure 5. Plot for $\ln(A_t - A_\infty)$ versus time of UV light exposure of PVC + 3 prepared film.

Figure 6. Plot for $\ln(A_t - A_\infty)$ versus time of UV light exposure of PVC + 4 prepared film.

All the $k_d$ data for PVC (blank) film and PVC films mixed with atenolol-tin compounds 1–4 are listed in Table 1.

Table 1. $k_d$ data for PVC prepared films after irradiation by UV light for 300 h.

| Film          | $k_d$ (sec$^{-1}$) |
|---------------|--------------------|
| PVC (blank)   | $10.0 \times 10^{-3}$ |
| PVC + 1       | $6.20 \times 10^{-3}$ |
| PVC + 2       | $7.20 \times 10^{-3}$ |
| PVC + 3       | $8.70 \times 10^{-3}$ |
| PVC + 4       | $9.10 \times 10^{-3}$ |

Table 1 and Figures 3–6 demonstrate the effectiveness of the existence of atenolol-tin complexes and its type on the $k_d$ values for the prepared PVC films. As shown in
Table 1, the highest $k_d$ value ($10.0 \times 10^{-3}$ sec$^{-1}$) belongs to blank PVC film without any stabilizers. The rate constant decreased considerably ($9.10 - 6.20 \times 10^{-3}$ sec$^{-1}$) when atenolol-tin complexes were used as UV stabilizers. The highest $k_d$ value was recorded for the blank PVC and the lowest value was recorded in the existence of 1 atenolol-tin complex. Adding atenolol-tin 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.

The surface of PVC blends was investigated further using the FESEM. The FESEM images provide information about the morphological characteristics of the polymer surface such as shape, size as well as to homogeneity and cross section of the particle [11]. Previous reports showed that FESEM images of PVC films before irradiation have a high level of homogeneity with more or less smooth surface [12]. The FESEM images of blank PVC film after irradiation (Figure 7) showed rough surface with a number of cracks due to bonds breaking and elimination of HCl [11,12].

![FESEM images of blank PVC film after irradiation.](image)

**Figure 7.** FESEM images of blank PVC film after irradiation.

The irradiated blank PVC, roughness and heterogeneity were very noticeable along with formation of cracks that are long and deep. However, the surface of PVC containing additives 1–4 after irradiation were smoother with a limited number of cracks. The film containing complex 1 exhibit a homogeneous and clear smooth surface before irradiation in comparison to other films. It was clear from that complexes 1–4 acted as PVC stabilizers (Figure 8).
The new atenolol complexes contain an aromatic moiety within its structure which increase the ability of the polymeric system to absorb the harmful UV light via the resonance process, followed by the harmless release of energy over a long period of time [16]. Since tin are characterized by highly acidic (Lewis acid) features, it has the ability to effectively capture the HCl formed through the dehydrochlorination of PVC [17]. The degradation of PVC in the presence of oxygen will generate a peroxide resulted from the radicals formed during the degradation process. Tin complexes can act as a peroxide decomposers via the reaction with peroxide and converting it to a harmless side products(Fig. 9), therefor; tin complexes can extended the polymer lifetime under working conditions via enhancing its stability against photolysis [13,14].
Conclusion
Addition of atenolol-tin complexes 1–4 to the PVC films as photostabilizers shows high efficiency through reducing the rate of photodecomposition constant compared to blank PVC. PVC films containing atenolol-tin complexes 1–4 showed lower values.

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