PVC Films Performance Stabilized By Dibutyltin(IV) Complex For Sustainable Environment

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Abstract:
A new tin(IV) complex was synthesized to inhibit the effect of UV light on PVC films. The new dibutyl tin(IV) complex coordinated to captopril as a ligand (Bu$_2$SnL$_2$) were used as additive to reduce the deterioration of PVC films under irradiation of UV light. Tin (IV) complex efficiency was examined under accelerated UV irradiation conditions for 300h at ambient temperature. The shifts in the FTIR index of hydroxyl, carbonyl and carline, in addition to changes in weight, viscosity and surface morphology was used to evaluate the performance of the new complex as a photostabilizer for PVC films.

Keywords: Photostability, PVC stabilizer, Tin complexes
INTRODUCTION

Reducing and controlling the photodegradation of organic polymers is a worthwhile challenge to chemists and engineers\(^1\)-\(^3\). One of the most widely used polymers is poly(vinyl chloride (PVC). It is used in construction, health care, automobile, household appliances and many other applications. For this reason, PVC was produced in massive amount (23 million tons per year) to fulfill the huge demand in different industries\(^4\)-\(^8\). Therefore, there is a need to reduce PVC waste due to harmful by products resulted from incineration or abandoning of PVC as a waste treatment method. PVC undergoes photodegradation incidents when exposed to sunlight resulted in a damaging the chemical structure and consequently affecting physical properties of the polymer\(^9\)-\(^12\). Thus, using PVC in outdoor applications makes it more susceptible to photodegradation. In order to minimize the effect of UV light, small molecules were incorporated within the polymer particle as a photostabilizers\(^13\)-\(^17\). UV stabilizers are divided into two categories, organic photostabilizers, and inorganic photostabilizers. Organic stabilizers are usually fluorescent compounds with a low molecular weight such as benzotriazoles, benzophenone derivatives, benzoic acid, etc\(^18\), \(^19\). Inorganic photostabilizers attracts more attention recently due to their ability to work efficiently as UV absorbers\(^17\), \(^20\). This work focuses on organotin complexes, since it is mainly used as PVC thermal stabilizers in addition to other different applications. The dibutyltin(IV) complex containing a ligand were added to enhance the photostability of PVC\(^21\). Dibutyltin(IV) containing captopril as a ligand at low concentrations was effectively inhibit the degradation of PVC against long-term UV irradiation significantly.

2. Experimental

2.1. Materials and characterization

All chemicals are used directly without further purification. PVC (degree of polymerization = 800) was supplied from Petkim Petrokimya (Turkey). The rest of chemicals were purchased from Sigma-Aldrich Chemical Company (UK). FTIR-8300 Shimadzu Spectrophotometer (Kyoto, Japan) was used to record Fourier transform infrared (FTIR) spectra of pure and modified PVC films in the range of 400–4000 cm\(^{-1}\) using KBr disc. Surface morphology experiments was conducted using Veeco Instruments Inc., Plainview, New York, NY, USA to record SEM images of PVC films at an accelerating voltage of 15.00 kV. The photostability test was performed at room temperature using accelerated weather-meter QUV tester (Philips,
Saarbrücken, Germany). UV-Vis was recorded using Shimadzu UV-Vis 160A Ultraviolet spectrophotometer.

2.2 Synthesis of dibutyltin (IV) captopril complex

The captopril ligand (2 mmol) dissolved in 30 mL of methanol was added in drop wise to stirred solution of Bu₂SnCl₂ (1 mmol). The reaction mixture was then refluxed for 8h followed by filtration. Then the solvent was removed under vacuum. The obtained solid was purified by recrystallization from ethanol to give a white powder 22.

2.3 Preparation of PVC Films

5 g of PVC and 0.5% (by weight) of dibutyltin(IV) captopril complex were dissolved in 100 mL tetrahydrofuran (THF) an stirred for 30 min at ambient conditions. After that, the solution was casted onto a glass mold and left in the fume cupboard to let the solvent evaporate at ambient temperature to produce PVC films.

2.4. Weight loss photostability test

The resistance of the PVC films stabilized by tin(IV) complex to UV radiation was measured depending on the weight loss of the films before and after irradiation. The efficiency of the new tin(IV) complex stabilizer was evaluated using Eq (1):

\[
\% weight\ loss = \left( \frac{W_1 - W_2}{W_1} \right) \times 100
\]  ...1

Where, W1 and W2 represent the weight of the films before and after irradiation 23.

2.5. Viscosity photostability test

Another way, Viscosity[$\eta$], was applied to evaluate the photostability performance of tin(IV) complex when added to PVC films. This approach was used to track the changes in the molecular weight of the PVC after being exposed to UV light. Mark-Houwink equation was used follow the relationship in viscosity and its relationship with molecular weight as shown in Eq (2):

\[
[\eta] = KM_v^a
\]  ...2

Where $M$ is the molecular weight viscosity, $a$ and $K$ are constants24.

The Molecular weight of PVC was measured from intrinsic viscosities measured by using Eq (3).

\[
[\eta] = 1.38 \times 10^{-4} M_v^{0.77}
\]  ...3
3. Results and Discussion

3.1. Synthesis of dibutyltin(IV) Complex

The dibutyltin(IV) Complex were synthesized via the reaction of captopril (2mmol) and dibutyltin(IV) chlorides(1mmol) (Figure 1). The physical properties of ligand and Sn(IV) complex are reported in Table1.

![Figure 1. Synthesis of Bu₂SnL₂(IV) complex.](image)

Table 1. Physical data for L and dibutyltin(IV) complex.

| Compounds    | M.WT  | Yield % | Color  | M.P(°C) |
|--------------|-------|---------|--------|---------|
| L            | 217.29|         | White  | 103-104 |
| Bu₂SnL₂      | 665.49| 67.7    | White  | 185-187 |

The structure of dibutyltin(IV) complex were established using FTIR and UV spectroscopy (Tables 2). The FTIR spectrum of ligand displays peaks at 2565, 3414 and 1589 cm⁻¹ assigned to vibrational stretching of SH, OH and CO (amide), respectively. On the other hand, the infrared spectrum of the complex showed the absence of vibrational stretching of SH bond and suggesting the successful reaction and losing of SH absorption band on complexation reaction. Also, the absorption band of carbonyl in amid group was shifted toward lower wave number (1577 cm⁻¹). The UV spectra of ligand and complex showed absorption bands 243 and 249 nm electronic transitions respectively²⁵,²⁶.

Table 2. FTIR and UV spectral data changes for ligand and complex.

| FRIR (cm⁻¹) | Absorption (nm) |
|-------------|-----------------|
| Compound    | SH | OH | (CO)Car. | (CO)Amide | Sn-C | Sn-O | π–π* |
| L           |    |    |          |           |      |      |      |
| Bu₂SnL₂     |    |    |          |           |      |      |      |
3.2 Weight loss photostability test

The photostability of PVC and stabilized PVC with tin (IV) complex were investigated using accelerated weather-meter QUV tester. All experiments were performed at ambient temperature. The exposure of PVC film to UV light may cause damage to polymer structure via dehydrochlorination process, resulted in lighter weight films due to the loss of these small molecules. Figure 2 illustrates the behavior of pristine PVC and PVC in the presence of the stabilizer under irradiation with UV light. The results showed that the weight loss of pristine PVC sample was significantly higher than PVC film in the presence of tin(IV) complex due to it acts as better primary photostabilizer.

![Figure 2: the effect of UV radiation on the stability of PVC films determined by the difference in the weight loss of PVC bland and PVC film stabilized by tin(IV) complex.](image-url)
3.3 Photodegradation of PVC by Fourier Transform Infrared (FTIR) Spectroscopy.

As discussed before that the irradiation with UV light can degrade the PVC matrix producing small molecules. FTIR spectroscopy was used to follow the variation in the structure of PVC films before and after irradiation for 300 h as shown in figure 3. A new peaks appears in the FTIR spectra due to the photo-oxidation reaction resulted in appearance of new absorption bands at 3500, 1602 and 1722 cm$^{-1}$ attributed to OH, C=C and C=O functional groups respectively. The change in the index of functional group ($I_s$) was calculated based on the absorbance of the functional group ($A_s$) after being exposed to UV and the reference group light before irradiation ($A_r$) using Eq.4.

$$I_s = \frac{A_s}{A_r}$$  \hspace{1cm} \ldots 4

The variation in the FTIR spectra of the peaks intensities of OH, C=C and C=O groups was remarkably changed after exposure to UV light in comparison to those before irradiation for PVC films. The indices for the polyene ($I_{C=C}$), carbonyl ($I_{C=O}$) and hydroxyl ($I_{OH}$) groups were collected after irradiation for different time intervals. Figure 4 illustrates the changes in the intensities along with the increase of illumination time for the PVC film with and without tin(IV) complex. The results showed that the growth of the functional groups index, for PVC with the additive, is much lower than PVC pristine sample. Therefore, the $\text{Bu}_2\text{SnL}_2$ was efficient as photostabilizers for PVC polymer.

![Figure 3. FTIR spectra of PVC film (blank) (a) before and (b) after irradiation](image.png)
3.4 PVC Photodegradation by Viscosity

The photostability of the polymers was further investigated via following the change in the viscosity average molecular weight \( (M_v) \). Up on exposure to UV light, the \( M_v \) for the blank PVC polymer was drastically reduced in comparison to the polymer containing tin(IV) complex. The reduction in \( M_v \) is attributed to the chain session when exposed to UV light. Figure 5 shows the relationship between changes in \( M_v \) and irradiation time for PVC.
3.5 Scanning Electrons Microscopy (SEM) Analysis

The surface morphology of PVC films was studied via SEM analysis before and after exposure to UV light 28, 29. The PVC film surface before irradiation by UV light was smooth and neat. After 300h of irradiation, both pristine PVC and PVC containing tin(IV) complex specimen surface were damaged. The formation of cracks on the surface of the polymer was larger in length and depth and more visible in PVC blank compared to PVC containing dibutyltin complex (figure 6). The cracks on the surface of the PVC films are due to dehydrochlorination and chain session and crosslinking. Therefore, The SEM image for PVC with dibutyltin(IV) complex showed the least surface damage compared to PVC blank. These results are in a good agreement with results obtained in weight loss, FTIR and Viscosity experiments.
Figure 6: SEM images for PVC films with and without tin(IV) complex.

3.6 Suggested Mechanisms of Photostabilization of PVC:

Tin(IV) complex can stabilize the PVC films by several mechanisms. Tin(IV) acts as a good HCl scavenger (figure 7) due to it is strong Lewis acid. Therefore, Tin(IV) atom can displace of chlorine atom within PVC chains by sulfur atom in the complex. The dibutyltin(IV) complex can improve long-term stability of PVC polymer as secondary stabilizers.

Another group that can damage the PVC structure via photo-oxidation reaction is hydroperoxides. Hydro-peroxides can react with tin(IV) complex, and thus inhibit photo-degradation of the PVC polymer due to their act as peroxide decomposers (figure 8).
Figure 8: Suggested mechanism of tin(IV) complex as peroxide decomposers.

Also, Tin(IV) complex interactions with PVC through the coordination with C-Cl bonds which can enhance the photo stability of the polymer matrix, in addition to their role in absorbing UV light as a primary stabilizer as shown in figure 9.

Figure 9: Dibutyltin(IV) complex as primary stabilizers.

Conclusions

Tin(IV) complex were synthesized and used as photostabilizers for PVC (0.5% by weight) films. Different approaches were applied to measure the effect of tin(IV) complex in reducing the photodegradation of PVC films under UV exposure. The results exhibit a significant performance of tin(IV) complex in reducing the weight loss and viscosity of the polymer as well as the intensities of the functional groups (I_C=O, I_C=C and I_OH) up on irradiation in comparison to
blank PVC films. The dibutyltin(IV) complex stabilize the PVC films through several mechanisms such as HCl scavenging, peroxide decomposers and primary stabilizers.

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