Tin(IV) Compounds as Photo-Stabilizers for Irradiated Surfaces of Poly(Vinyl Chloride) Films

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Abstract: Dimethyl-organotin(IV) valsartan (Me_2SnL_2) and dichlorostannanediyl valsartan (SnL_2Cl_2) complexes were synthesized, characterized, and applied as Poly(vinyl chloride) (PVC) photo-stabilizers. The complexes were loaded within the PVC films in a weight ratio of 0.5%, and the modified films were irradiated to a UV light of 313 nm wavelength for 300 h at room temperature. The efficiency of the complexes-filled films was compared with the plain one and evaluated before and after irradiation by Fourier transform infrared spectroscopy, weight loss, gel content, change in viscosity, atomic force microscopy, and field emission scanning electron microscopy. The SnL_2Cl_2 complex had higher activity than the Me_2SnL_2 complex to retard the PVC's photodegradation by several mechanisms.

Keywords: PVC; UV irradiation; organotin complexes; photostability; polymeric films

1. Introduction

Poly(vinyl chloride) has been produced in Germany since the 1930s and used with plasticizers to manufacture flexible materials for flexible pipes, films, footwear, raincoats, and sheets [1]. The first use of organotin compounds as photo-stabilizers for the PVC was in 1940 [2]. As the PVC ranks the second-highest produced plastic material after polyethylene, it is used in various fields worldwide, such as piping, siding windows, wiring, etc. This commonness is due to their remarkable mechanical and chemical properties, non-flammability, resistance to ecological strain cracking, easy formation, strength, and low cost [3,4]. However, the PVC is gradually degraded by time mostly due to climate conditions, which can be observed by discoloration (yellowing), macro-cracking, loss of mechanical performance, and despicable surface layers. This deterioration is attributed to the structural defect that results from the monomer polymerization reaction, which appears in the double bond that results from the evaluation of hydrochloric acid. Moreover, the deterioration could be caused by branching, long-chain ends, and oxygenated compounds that form in the presence of atmospheric oxygen, which is very reactive toward alkyl radicals. As a result, hydrogen chloride and other volatile organic residues are released. Such processes clearly lead to weight loss and changes in viscosity. These deformations in the internal structure are assigned to the photo and oxidative degradation of PVC during weathering (such as heat and direct ultraviolet (UV) light for a long period), wherefore the PVC cannot be used without stabilizers. The presence of double or carbonyl bonds (C=C or C=O) was detected by the FTIR and UV spectrophotometry [5–7].

Here, additives production is desired to be easy and inexpensive, and these additives must tend to be well incorporated within the PVC polymeric chains. Furthermore, the additives should be non-toxic, non-volatile, and own high chemical stability, and should not influence the polymer's color or harm the environment [8–10]. Recently, several

organotin (IV) compounds [11], inorganic compounds [12], and Schiff bases [13] were used as photo-stabilizers for PVC.

The inorganic compounds of tin are commonly represented by tin sulfide, sulfur, oxygen, and halides (F_2, Cl_2, Br_2, and I_2). Tin(II) chloride ($SnCl_2$) could be the highly applied tin halide, where it can be prepared by dissolving tin in hydrochloric acid (HCl) [14]. When tin combines with some organic compounds, the products are called organotin compounds, which have a minimum of one covalent bond between the tin and carbon atoms. These compounds are known for their pharmaceutical and industrial importance [15].

The current work describes the preparation and use of valsartan–tin complexes, namely: Dimethyl-organotin(IV) valsartan (Me_2SnL_2) and dichlorostannanediyl valsartan (SnL_2Cl_2), as PVC improvers. They are colorless solids, commercially available, and contain heteroatoms (nitrogen) and aryl rings (aromatic moieties), where changes in the physicochemical features were tested. The additives can synergize with the PVC, absorb the UV light, do not influence the color, and inhibit radicals and peroxides. Furthermore, the cation of tin rules as an inhibitor of the produced HCl through PVC photodegradation. Thereby, valsartan–tin complexes own all the required characteristics as photostabilizers. Both additives enhanced the photostability properties of the PVC films, but SnL_2Cl_2-PVC films performed better than Me_2SnL_2 filled films. This result was obtained by using different assessment methods. It is expected that the implication of excess aromatic substituents (phenyl groups) in the structure of tin complexes enhances their ability to photostabilize PVC.

2. Experimental Methods

2.1. Materials and Devices

The degree of polymerization of the used PVC was 3000; the polymer was supplied by Petkim Petrokimya (Istanbul, Turkey). Tetrahydrofuran ($\geq$99.9%) was purchased from Sigma Aldrich and used to dissolve the polymer to prepare the films. The FTIR spectra were recorded via an FTIR 8300 Shimadzu spectrophotometer (Shimadzu, Tokyo, Japan). In order to accelerate the weather impact inspection, a QUV weather-meter unit from the Q-Panel Company (Homestead, FL, USA) was utilized to irradiate the PVC films with 313 nm UV light at 25 °C. The viscosity of PVC was measured by an Ostwald U-Tube viscometer. The films' surface morphology was examined via atomic force microscopy (AFM) and scanning electron microscopy (SEM) technologies. The AFM device was obtained from Veeco (Plainview, NY, USA), while the SEM was supplied from FEI Company (FEI Inspect-S50).

2.2. Preparation of Complexes

The two complexes, Me_2SnL_2 and $SnCl_2L_2$, were synthesized and characterized as shown in recently published researches from our group [16,17], where L is the ligand (valsartan). Based on the instrumental analysis, bonding takes place between tin and the hydroxyl oxygen of the carboxylic acid of the ligand. The complexes' structures are illustrated in Figure 1.

2.3. Films Preparation

The PVC films were prepared by dissolving 5 g of PVC in 100 mL of Tetrahydrofuran (THF) at room temperature and stirred for two hours. Then, the complexes were added to PVC solution at a ratio of 0.5 wt.% and stirred for one hour more. Later, the solution was cast onto a glass plate to a thickness of 40 μm. The PVC films were left to dry and ultimately collected for further investigations [18].
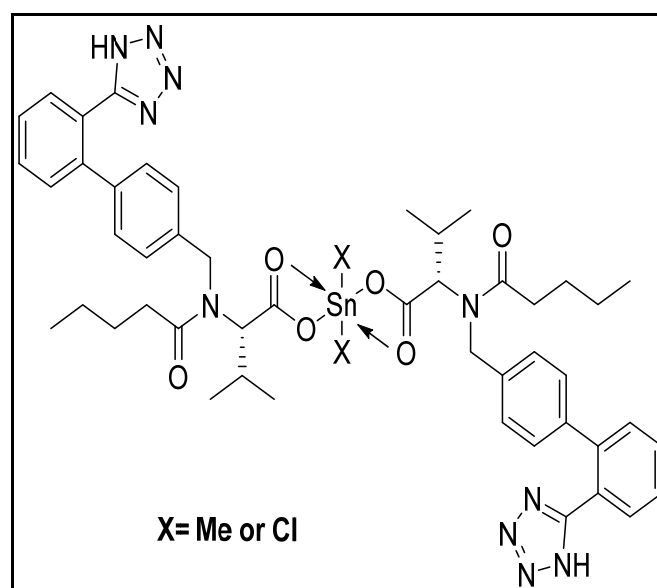
Figure 1. Structure of Me_2SnL_2 and SnL_2Cl_2 Complexes.

2.4. Films Irradiation

The accelerated UV-weathering test is an important method that shortens the time and simulates the climatic changes that polymers are exposing for months or years. UV-Light was used for the irradiation of PVC films at a wavelength of 313 nm, temperature of 25 °C, the pressure of 1 atm, and under atmospheric air (non-isolated system). The maximum light intensity in the test was 6.02×10^{-9} ein·dm^{-3}·s^{-1}.

2.5. Estimating the Tin(IV) Compounds Activity as PVC Photo-Stabilizers

2.5.1. Using FTIR Spectrophotometry

The photodegradation process of the PVC films was tracked using FTIR spectrophotometry, where rises in the intensities of the absorption peaks of carbonyl (C=O, 1722 cm^{-1}) and polyene (C=C, 1602 cm^{-1}) groups demonstrate this process. These peaks appear due to the formation of compounds containing C=O and C=C groups, which improve PVC photo-oxidation. The reflected signals intensities from films' surfaces could be tracked during the photo-oxidation, and compared with the C–H bond signal intensity of the CH$_2$ moieties (1328 cm^{-1}) that the polymer consists of. The absorption of the C–H bond is not altered during the irradiation process. Equation (1) was used to calculate the functional group (C=O or C=C) index (I_s) from the absorbance of functional group (A_s) and the standard (A_r) peaks. The absorbance (A) values for each functional group were calculated from the transmission percentage (%T) in FTIR spectra using Beer–Lambent law [19].

$$I_s = \frac{A_s}{A_r} \qquad (1)$$

2.5.2. Using Weight Loss

The blank and additives-filled PVC films were irradiated and weighted based on multiple time intervals. The weight loss percentage was calculated according to Equation (2), where W_0 and W_t are the weights of films before and after irradiation, respectively [20].

$$\text{Weight loss (\%)} = \frac{W_0 - W_t}{W_0} \times 100 \qquad (2)$$

2.5.3. Measuring the Variation in Gel Content of PVC Films

The gel content of the plain and modified PVC films before and after irradiation was determined by dissolving 0.1 g of each film in 4 mL of THF at room temperature; the

mixture was left overnight to ensure complete dissolving. However, the insoluble fractions were filtered, washed, and dried in an air oven. The gel content percentage was calculated using Equation (3), where W_1 and W_2 are the weight of the original sample and gel content, respectively [21].

$$\text{Gel content\%} = \frac{W_2}{W_1} \times 100 \tag{3}$$

2.5.4. Using Viscosity Average Molecular Weight (M_V)

The viscosity average molecular weight (M_V) is another testing method, in which the PVC films before and after irradiation in the absence and presence of tin(IV) complexes were tested in THF solvent at 25 °C via an Ostwald U tube viscometer. The intrinsic viscosity [η] values were calculated to determine the molecular weight from the Mark–Houwink equation (Equation (4)) [22].

$$[\eta] = 1.63 \times 10^{-2} \, \text{Mv}^{\,0.766} \tag{4}$$

3. Results and Discussion

3.1. Stabilizing Appraisal of PVC by FTIR Spectroscopy

The activity of tin(IV) complexes to retard the photochemical process of PVC films was monitored using FTIR spectroscopy. The PVC films underwent photo-oxidative degradation via UV irradiation (λ_{max} = 313 nm) for 300 h in the presence of an oxygen source. As a result, polymeric clots form due to the presence of carbonyl (C=O) group from the carboxyl and ketone and the presence of carbon–carbon double bond (C=C) from the polyene residues [23–25]. These functional groups are monitored via FTIR spectroscopy. The intensity of FTIR signals detected during the photo-oxidation was compared with the intensity of the original film's signals, mainly for the C–H bond at 1328 cm^{-1} originated from CH$_2$ moieties within the polymeric chains. From Figure 2, it can be noticed that the absorption of C–H bond did not change during the irradiation process, while the intensities of C=O and C=C signals at 1722 cm^{-1} and 1602 cm^{-1}, respectively, were significantly lower for the irradiated modified PVC films comparing with the plain one.

The PVC film filled with SnL$_2$Cl$_2$ had the lowest intensity of the functional groups, followed by the PVC film filled with Me$_2$SnL$_2$. However, both films performed better than the blank irradiated PVC film in terms of corresponding peaks. In order to study the effect of organotin complexes on the photodegradation of PVC, the rate of peaks growth was estimated by comparing the absorbance of the main peaks with a reference peak at 1328 cm^{-1}. Equation (1) was used to calculate the functional group indices ($I_{C=O}$ and $I_{C=C}$) for the blank and modified PVC films when irradiated to UV light. The irradiation time impact on the indices, $I_{C=O}$ and $I_{C=C}$, values were studied in 50 h intervals for a period of 300 h, as illustrated in Figures 3 and 4, respectively.

From the above figures, the complexes increased the PVC stability. For example, the $I_{C=O}$ values after 300 h of irradiation were 0.271, 0.228, and 0.199 for the PVC, PVC/Me$_2$SnL$_2$, and PVC/SnL$_2$Cl$_2$ films, respectively. Similarly, the $I_{C=C}$ of the blank PVC film was 0.485 after 300 h irradiation compared to 0.363 and 0.325 for the PVC/Me$_2$SnL$_2$ and PVC/SnL$_2$Cl$_2$ films, respectively. The growth rate of carbonyl and polyene groups increases with irradiation time increasing and decreases with tin(IV) complexes addition. Hence, the minimum change in the C=O and C=C groups indices was achieved when SnL$_2$Cl$_2$ was used.
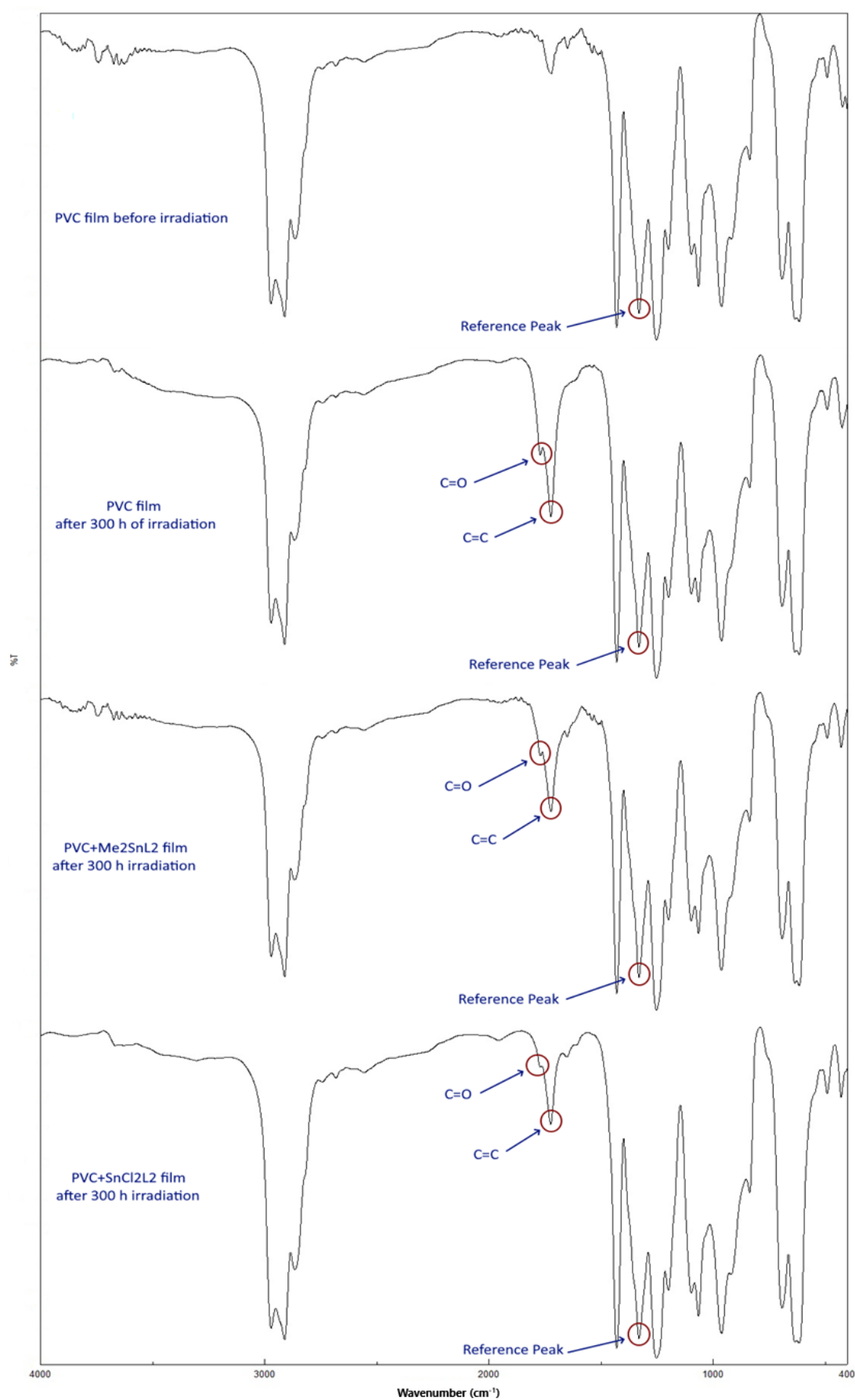
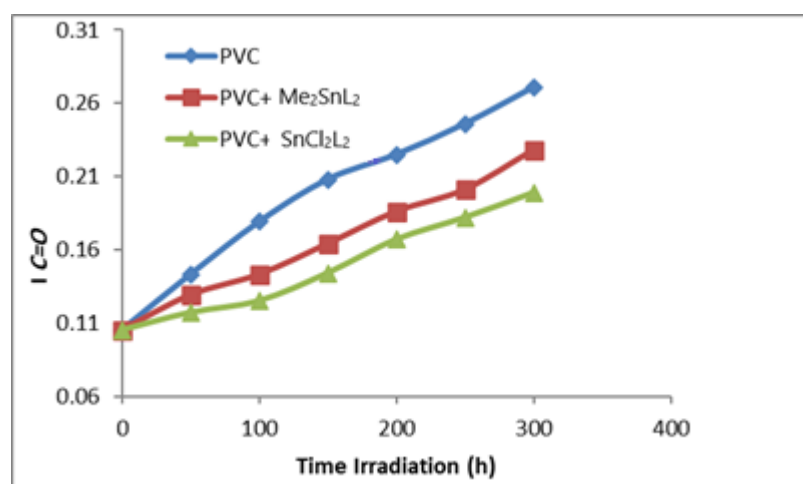**Figure 2.** FTIR spectra of PVC films.

Figure 3. Changes in the $I_{C=O}$ index for PVC films versus irradiation time.
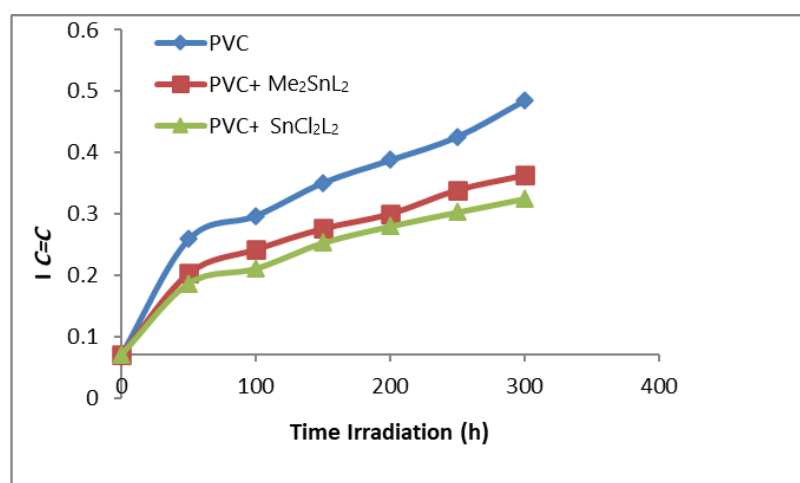

Figure 4. Changes in the $I_{C=C}$ index for PVC films versus irradiation time.

3.2. Stabilizing Appraisal of PVC by Weight Loss

During the photo-oxidation of PVC films, free radical moieties will generate and affect the cross-linking of the structural chains. As a consequence, dehydrochlorination for the chains takes place, and hydrogen chloride gas generates in addition to disassembling the volatile organic compounds. The released compounds leave organic residues that are responsible for the PVC discoloration. Such processes lead to weight loss at relatively high temperatures [26–28]. The weight loss was tracked at time intervals of 50 h, and the examination continued for 300 h to identify the impact of tin(IV) complexes as photo-stabilizers. The weight loss was estimated using Equation (2), and the results are shown in Figure 5. The PVC weight loss was sharp at the beginning of irradiation and gradually decreased until it reached the end of the test after 300 h. In the presence of complexes, the PVC weight loss ranged from 0.199 to 0.219% after 300 h of continuous irradiation, while the weight loss was around 0.39% for the plain film. The minimum weight loss was obtained when the SnL_2Cl_2 complex was added. Without a doubt, the complexes improved the photostability of the PVC films.

3.3. Stabilizing Appraisal of PVC by Variation in Gel Content

The gel content that appears when PVC films dissolve after irradiation in THF is an indication of the polymeric chains cross-linking release during the photodegradation [21]. The gel content ratios were calculated according to Equation (3) and plotted against the

irradiation time as shown in Figure 6. The blank PVC film shows higher gel content ratios when compared with the additives-filled PVC films. The gel content increased as the irradiation time increased and decreased with the addition of tin(IV) complexes. The complexes increased the links among polymer chains, according to the mechanism that is explained later.
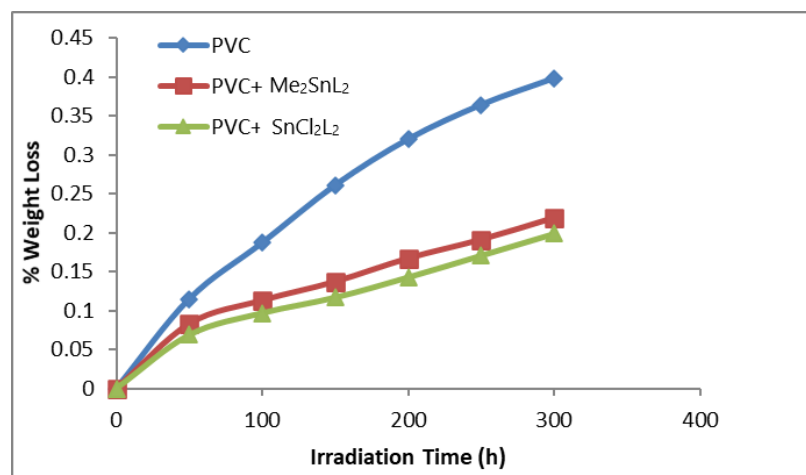

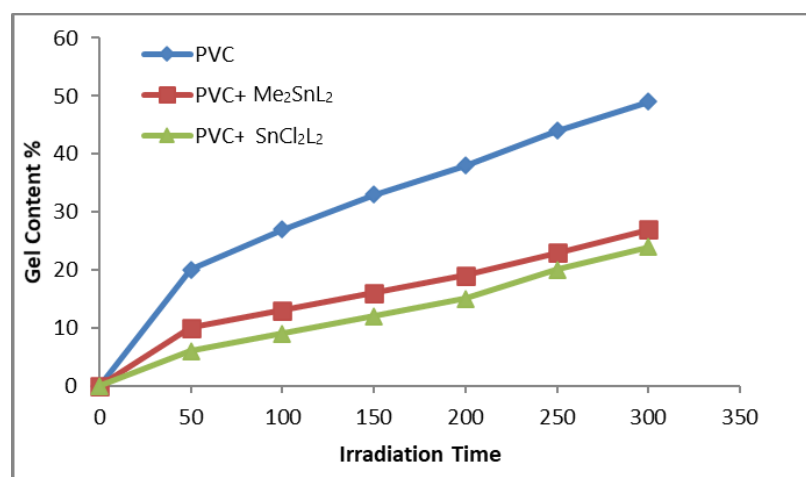**Figure 5.** Changes in weight loss of PVC films with irradiation time.

Figure 6. Gel content ratio relation with the irradiation time for the plain and modified PVC films.

3.4. Stabilizing Appraisal of PVC by Variation in Viscosity Average Molecular Weight

The photodegradation of PVC leads to a reduction in its molecular weight that is attributed to the main polymeric chains' scission [29]. The potency of the tin(IV) complexes was proved by estimating the viscosity of PVC irradiated films and comparing it with the blank film. The viscosity of the polymeric solution was employed as a function to indicate the $\overline{M}_V$. The films that were irradiated to UV light for various periods were dissolved in THF, where mixtures' viscosity was determined via a viscometer [22]. The $\overline{M}_V$ for each film at different irradiation times was computed using the Mark–Houwink equation (Equation (4)), and the change in $\overline{M}_V$ was plotted against time irradiation, as illustrated in Figure 7.

An obvious dropping in the $\overline{M}_V$ was noticed during the irradiation process, which was more intensive for the blank PVC film. For example, the $\overline{M}_V$ for blank PVC was approximately 186,345 at the start of the irradiation process and declined to 66,738 after 300 h.

At the end of the irradiation process, the $\overline{M}_V$ for PVC/SnL$_2$Cl$_2$ and PVC/Me$_2$SnL$_2$ blends was 102,416 and 93,292, respectively. Again, the tin complexes, and particularly SnL$_2$Cl$_2$, stabilized the PVC against irradiation to a remarkable degree.
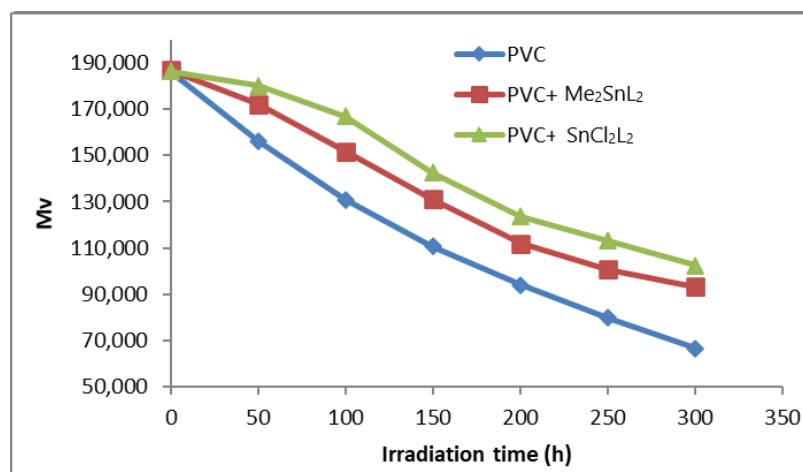

Figure 7. Changes in $\overline{M}_V$ for PVC films versus irradiation time.

3.5. Surface Analysis

3.5.1. Stabilizing Appraisal of PVC by Atomic Force Microscope

The morphology of studied PVC films was explored by the atomic force microscope (AFM) technique as this method can provide two- and three-dimensional images for the films. Here, as the topology of the films becomes clear, information about the surface's roughness and features could be obtained. Irradiation for long periods creates bond breaking, which produces rough and cracked surfaces [30,31]. In our work, the topographic examination via AFM was conducted for the plain and modified PVC films, and three-dimensional images of the surface after 300 h irradiation were listed in Figure 8. From the figure, filling the complexes improved the photostability of the polymeric films after UV irradiation by reducing the roughness of the surfaces compared with the plain film. The roughness average (Sa) after irradiation for 300 h of plain PVC, PVC/Me$_2$SnL$_2$, and PVC/SnL$_2$Cl$_2$ are 7.46 nm, 3.04 nm, and 2.51 nm, respectively. Once again, the use of the SnL$_2$Cl$_2$ complex enhanced the smoothness of the PVC sheet and reduced the roughness. The tin(IV) complexes inhibited the process of dehydrochlorination during the irradiation that broke the polymeric chains bonds and ultimately increased the surface roughness.
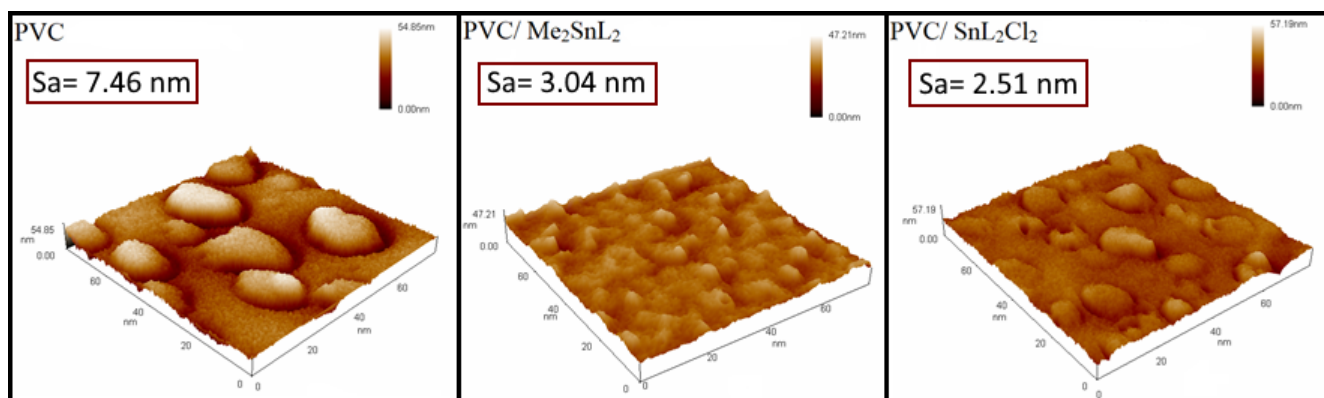

Figure 8. AFM images with Sa values of PVC films after irradiation for 300 h.

3.5.2. Stabilizing Appraisal of PVC by Scanning Electron Microscopy

For further examination of the topology of the films, scanning electron microscopy (SEM) was used to provide less distorted, clear, and high-resolution images of the PVC films [32–35]. Figure 9 shows SEM images of PVC films' surface before (a) and after (b) irradiation. It was reported that non-irradiated polymers commonly have smooth surfaces and a high level of homogeneity [36]. When the two images are compared, holes are generated, and the roughness of the PVC surface increases due to polymeric chains breaking and hydrogen chloride elimination [37]. As the SnL_2Cl_2 and Me_2SnL_2 are added, the holes and roughness after irradiation decreased, as shown in Figure 9c,d, respectively. The best morphology specifications of PVC film were when SnL_2Cl_2 was added, where the holes were smaller, and their number was lower.
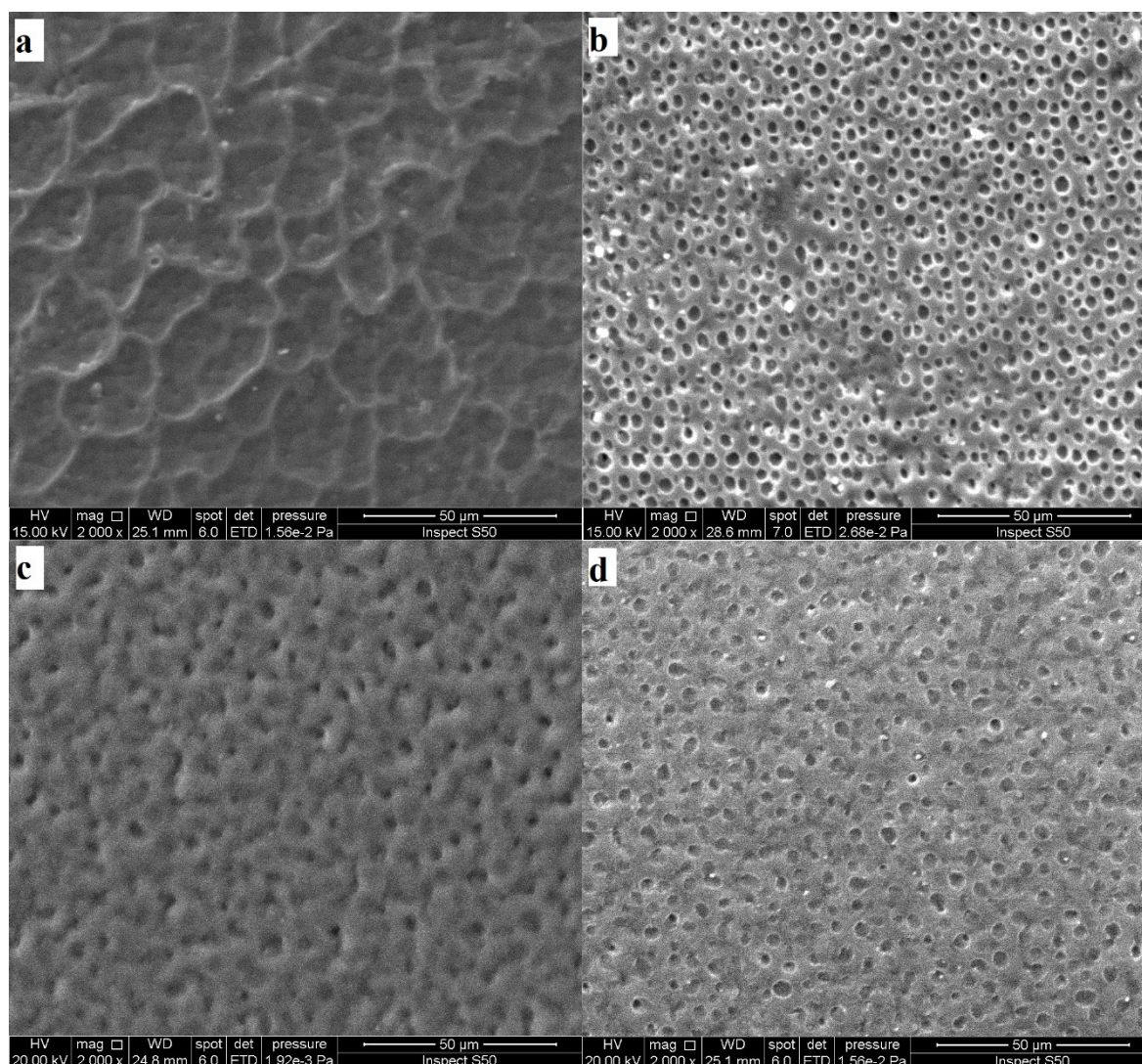

Figure 9. SEM images of (**a**) plain PVC film before irradiation, (**b**) plain PVC film after irradiation, (**c**) PVC/SnL_2Cl_2 film after irradiation, and (**d**) PVC/Me_2SnL_2 film after irradiation for 300 h.

3.5.3. Assessment of Photodegradation of PVC Using Energy Dispersive X-ray (EDX) Mapping

The elemental composition of PVC sheets with and without the tin(IV) complexes was analyzed using an energy-dispersive X-ray (EDX), as illustrated in Figure 10. The figure shows the reflected elemental peaks from the plain PVC films before and after irradiation and from complexes-filled PVC films after irradiation. The EDX graphs revealed that

the tin(IV) complexes were well-distributed throughout the films [38]. EDX graph for PVC blank film before irradiation shows 26.7% of chlorine content, while this percentage reduced to 24% after irradiation for 300 h. These ratios indicate that dehydrochlorination has occurred due to photodegradation. When PVC was doped with tin(IV) compounds and irradiated for 300 h UV light, the chlorine content percentages were 25.8% and 26.3% for PVC/Me$_2$SnL$_2$ and PVC/SnL$_2$Cl$_2$ films, respectively. Here, it is clear that the presence of tin(IV) compounds keeps the chlorine content in PVC films higher than the blank PVC after irradiation. The high chlorine content proposes fewer bonds break and likewise less photodegradation of PVC film.
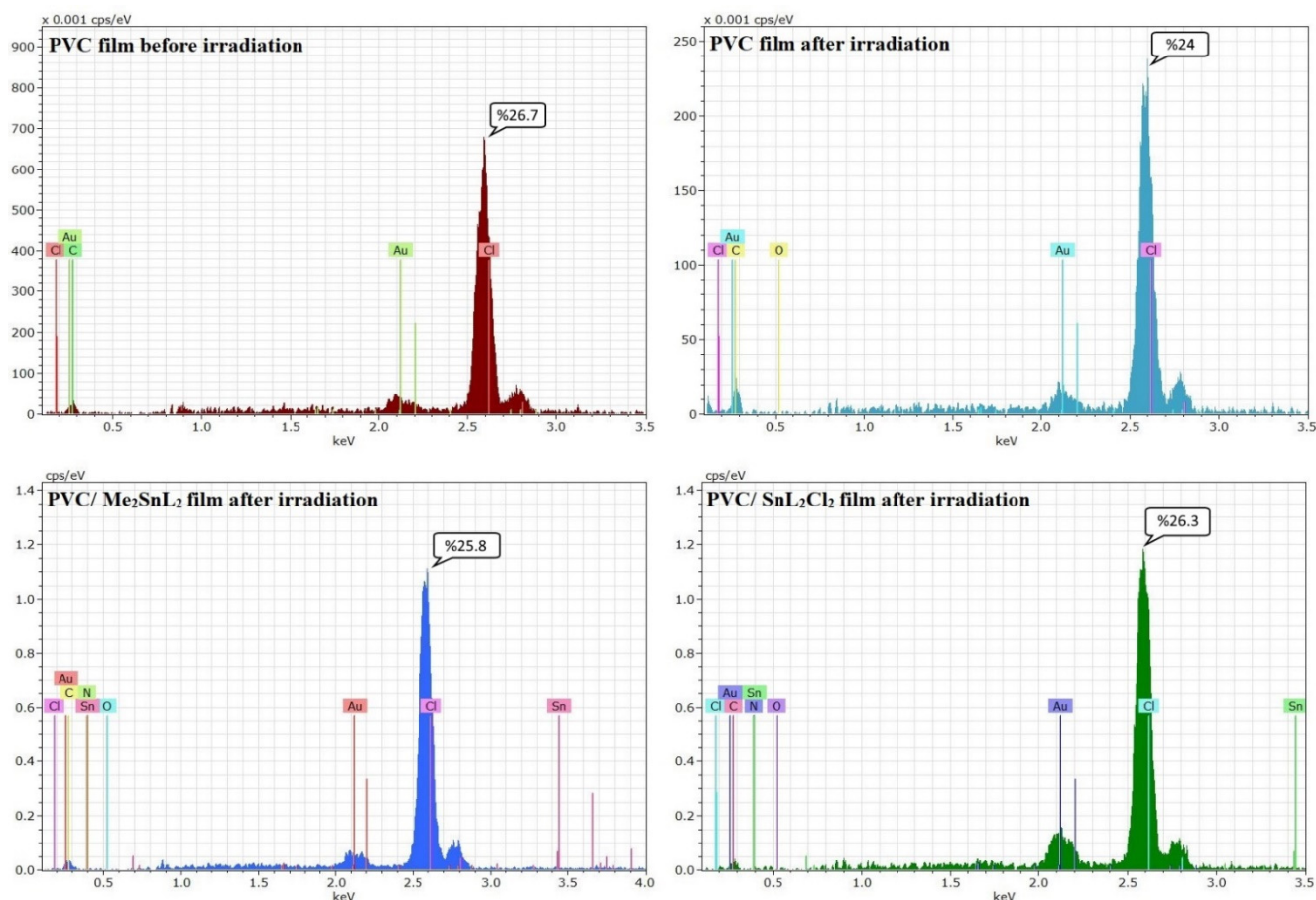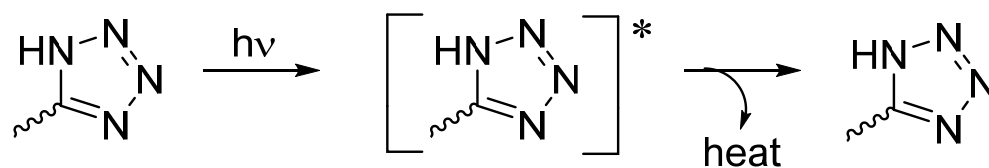

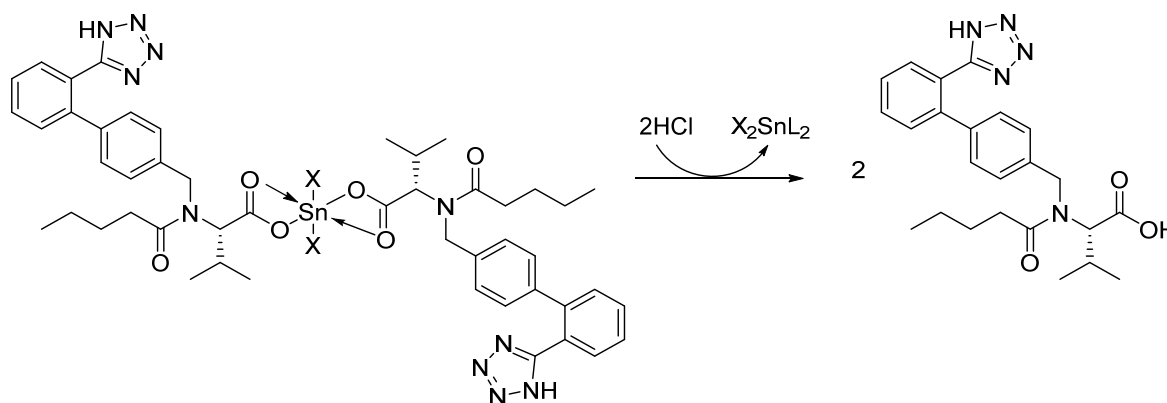**Figure 10.** Energy-dispersive X-ray graph of PVC films.

3.6. Suggested Mechanisms of Organotin Complexes Efficiency

The addition of tin(IV) complexes as additives significantly reduced the photodegradation of PVC sheets. Among the two tested tin(IV) complexes, SnL$_2$Cl$_2$ resulted in higher photostability for the PVC film than Me$_2$SnL$_2$, where both improved the polymeric films' properties. However, both tin(IV) complexes contain two aryl groups and one tetrazole ring within their skeletons, which allow them to absorb UV light directly. As the PVC becomes irradiated, the additives emit the absorbed radiation as heat at a rate that does not affect the polymeric chains (Scheme 1). Furthermore, the high energy level of tetrazole or aryl group, could be stabilized by the aromatic moieties' resonance [18].
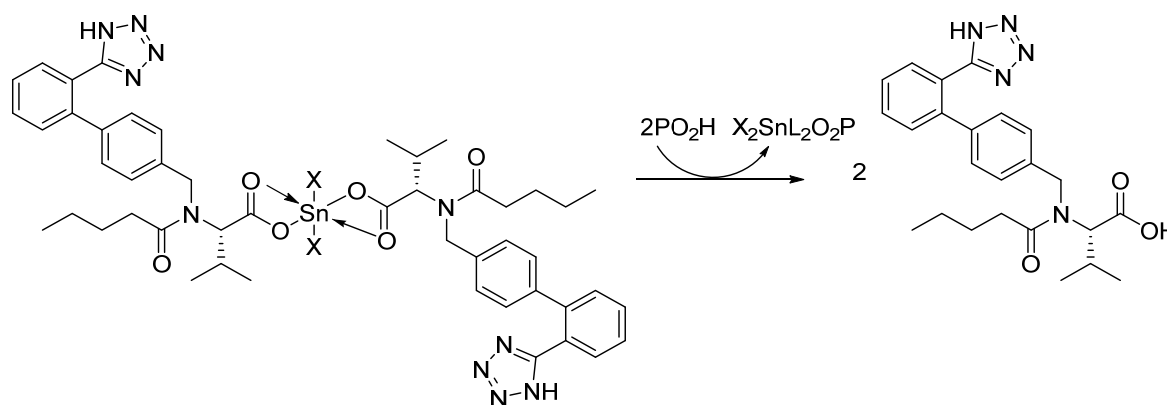
Scheme 1. Function of tetrazole unit as a UV absorber [18].

The tin atom within complexes acts as an acidic center. The chloride ion is pulled by tin, which is eliminated from the PVC chains as hydrogen chloride due to irradiation, to produce a stable substituted tin chloride (Scheme 2). Thereby, the tin compounds rule as secondary PVC photo-stabilizers and hydrogen chloride scavengers [39,40].
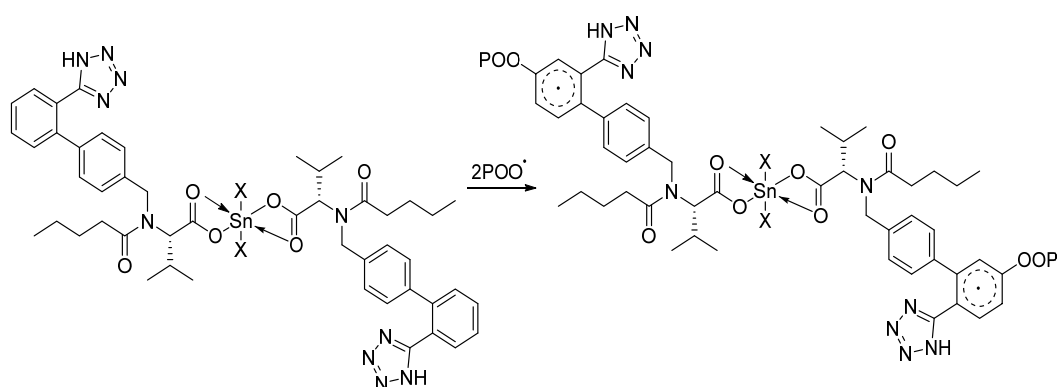

Scheme 2. Function of tin complex as a hydrogen chloride scavenger.

However, the Hydro-peroxides (PO_2H), which result from PVC photo-oxidation, are decomposed by tin(IV) complexes by displacing with the acidic tin atom of the additive (Scheme 3) [31,41]. This process inhibits PVC photodegradation significantly.
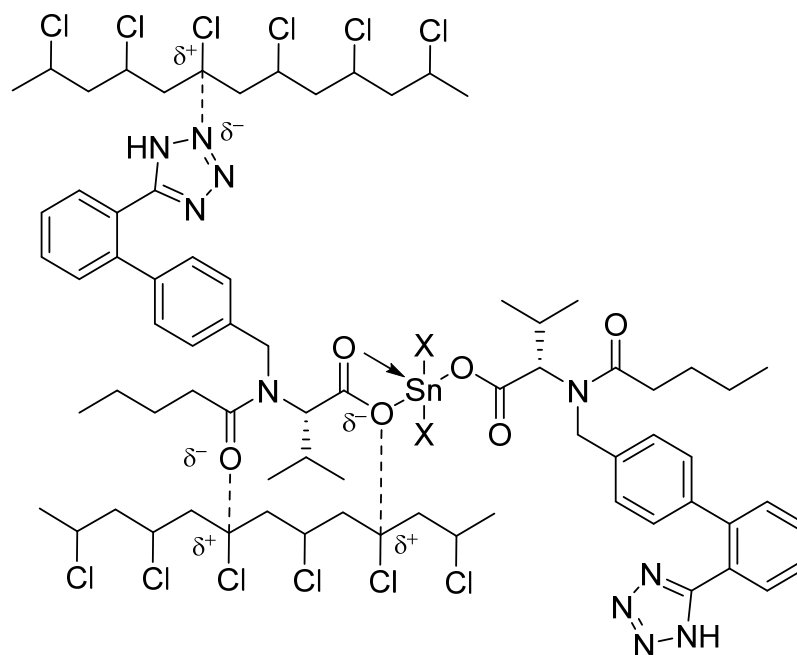

Scheme 3. Function of tin complex to induce hydroperoxide decomposition.

One of the most harmful products generated through photo-oxidation of PVC is peroxide radicals (POO$^\bullet$), which continue to form various photo-oxidative products. The tin(IV) complexes can act as radical scavengers, which form intermediates that contain peroxide radicals and aryl moieties within the additives (Scheme 4). The intermediates are highly stable via resonance [21,41]. Therefore, the complexes inhibit PVC photo-oxidation and provide a degree of stabilization against irradiation.

Scheme 4. Function of tin complex as a radical scavenger.

Due to the polarity of C–Cl bonds within the PVC chains, the interaction between PVC chains and tin additives, which also have electron density, occurs. The electron density is represented by the nitrogen atoms of the tetrazole ring and the oxygen of the carboxylate and amide groups (Scheme 5) [40].

Scheme 5. Interaction between tin complex and PVC.

4. Conclusions

Two tin(IV) complexes, namely SnL_2Cl_2 and Me_2SnL_2, were prepared and used as photo-stabilizers for poly(vinyl chloride). Films of the PVC were prepared and doped with the complexes at a weight ratio of 0.5% to study the effect of photo-stabilization. The films were irradiated with UV light of a 313 nm wavelength at room temperature for 300 h. The impact of these complexes was evaluated by comparing the physicochemical properties of the blank and modified PVC films before and after irradiation. Techniques of Fourier transform infrared spectroscopy, weight loss, gel content, change in viscosity, atomic force microscopy, and field emission scanning electron microscopy was employed to inspect the change. Irradiating the PVC films leads to generating a clear change in color due to degradation; however, when tin complexes are filled, the films show resistance against color change. The presence of additives within the PVC films after irradiation showed a dramatic decrease in weight loss and gel content compared to blank PVC. The morphology

images reveal that PVC films with additives display less roughness and cracks because tin complexes remarkably deactivate the potential initiation sites within the polymer.

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Conflicts of Interest: The authors declare that they have no known conflict for this work.

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