

Improving the Photostabilization of Poly(vinyl chloride) Using 4-(benzylideneamino)benzenesulfonamide Tin Complex

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ABSTRACT

The photostabilization of poly (vinyl chloride) (PVC) film filled with an organotin complex in its structure was examined and compared with the blank PVC film. The organotin (IV) complex that contains 4-(benzylideneamino) benzenesulfonamide as a ligand was synthesized and applied as a PVC photostabilizer. The impact of the complex on the polymer was assessed by comparing the properties of the films with and without the complex, before and after irradiation, using Fourier transform infrared spectroscopy, weight loss, viscosity change, atomic force microscopy, and field emission scanning electron microscopy (FE-SEM). Results showed that the complex film had lower weight loss, gel content, and molecular weight deterioration than the plain PVC film. Also, surfaces of the complexes-filled films were smoother, less lumpy, and more homogeneous. These findings were obtained via the FE-SEM and light microscope images and confirmed by measuring the roughness factor. The organotin (IV) complex proved its activity in delaying the photo-degradation of PVC by several mechanisms. Ultimately, the Tin complex has effectively protected the PVC film against irradiation.

Keywords: 4-(benzylideneamino)benzenesulfonamide, weight loss, viscosity change, gel content, photo-degradation

INTRODUCTION

In many modern applications, plastics are used to replace glass, metals, and wood [1]. In contrast with conventional materials, plastic has superior properties and special performance [2]. During the manufacturing process of plastics, properties such as hardness, density, colour, transparency, and rigidity, are possibly controlled [3]. Poly (vinyl chloride) is among the widely applied plastics; it ranks the second most synthesized resin in the world after polyethylene. Furthermore, PVC is the third most extensively used plastic in chemical engineering, architecture, packaging, transportation, and electronics after polyethylene and polypropylene [4]. Poly (vinyl chloride) is among the commonly used materials in the production of food packaging, and it has good technical properties and high polarity, which ensures its high compatibility with a vast range of polymers [5]. One of the main properties of PVC is its high chlorine concentration (about 57 wt.%), which makes it non-combustible [1]. PVC has excellent chemical and physical properties, and its low production cost allows it to enter diverse applications [6]. PVC is the cheapest polymer in the market; nevertheless, it is non-toxic and stable and has high resistance to acids, alkalis, and corrosion [7, 8]. PVC is a thermoplastic polymer with a polyethylene-like linear structure replacing one of the hydrogens with a chloride atom [9].

Polymerization of vinyl chloride monomer (VCM) has been recognized since the late 19th century when Baumann accidentally manufactured PVC. The inventor exposed PVC's monomer to sunlight heat and obtained a white powder that could be heated up to 130 °C without disintegration [10]. It was firstly produced in Germany and the USA around 90 years ago in small quantities that contributed to different products.

However, its intensive use began during the second world war, when highly flexible mixtures were produced and used as substitutes for rubber, particularly when natural rubber suppliers were hard to reach [11]. In the early sixties, the development and use of rigid PVC had significantly increased. Now, Poly (vinyl chloride) has been commercially produced in high amounts for more than 50 years [8].

It is known that the sun has a big role in degrading all types of plastics. Several different stabilizers were successfully added and used to solve the issue of polymers' poor stability [9, 10]. Thereby, the durability of PVC products for outdoor use, such as building sheds, frames, and structures, is an important factor to endure photodegradation over long periods of sunshine exposure. This will determine the polymers' acceptance and conformity to the set standards [12, 13]. To assure weather resistance, the PVC resin must formulate homogeneously, and the additives should adjust with the total matrix. These complexes result in modified PVC with properties that significantly differ from the plain PVC resin [14].

Organic UV stabilizers of low molecular weights, including hydroxylbenzophenone, phenyl ester of benzoic acid, benzotriazole, fluorescent compounds, and others, were recently

applied [12]. Nevertheless, adding stabilizers to the plastic materials, problems such as incompatibility, solvent extraction, and volatility. This results in a significant reduction in the application window. Multiple approaches were developed to solve such problems, such as the preparation of reactive UV stabilizers [12, 13], the addition of suitable side chains, and attaching the additives to the polymer's backbone [15-17].

Recently, some researchers studied the effect of organotin complexes as photo stabilizers for PVC. Among these compounds, the effect of di- or tri- organotin (IV) complexes with ligand (carvedilol) were studied [18]. Similarly, many organotin complexes were synthesized and studied for their effect as PVC's stabilizers and proved their high effectiveness [16, 17]. In this work, an organotin(IV) complex was synthesized and filled in the PVC structure to test the stability of this polymer after the irradiation of UV light. Different measurement methods and characterization techniques were applied to study the change. This additive showed a good improvement in PVC films' structure, morphology, and performance.

EXPERIMENTAL

Instruments and Chemicals

The spectra of Fourier-transform infrared (FT-IR) were monitored via Jasco spectrometer FTIR-4200 (Tokyo, Japan). The spectra of 500 MHz ^1H NMR and ^{13}C NMR were detected using Varian INOVA spectrometer (Palo Alto, CA, USA). Furthermore, the spectra of ^{119}Sn NMR (107 MHz) were recognized by DRX spectrophotometer from Bruker (Zürich, Switzerland). An accelerated weather meter QUV tester used to irradiate the PVC samples with UV light ($\lambda_{\text{max}} = 365 \text{ nm}$) at room temperature was purchased from Q-Panel Company (Homestead, FL, USA). The viscosity of the polymer was measured using Ostwald U-Tube viscometer, while films' morphology was examined using devices from Veeco (Plainview, NY, USA) and scanning electron microscopy (SEM) MIRA3 LMU from TESCAN (Kohoutovice, Czech Republic) at 10 KV accelerating voltage. All used chemicals were purchased from Merck (Gillingham, UK). Exceptionally, PVC of a molecular weight cut =171,000 was provided by Petkim Petrokimya (Istanbul, Turkey). However, Table 1 shows the ligand and Bu_2SnOHL properties.

Synthesis of Organotin(IV) Complex

First, a mixture was made of 4-(benzylideneamino) benzenesulfonamide (0.260 g, 1.0 mmol) and Bu_2SnO (0.248 g, 1 mmol). Then, it was dissolved in 30 ml of MeOH solvent and refluxed for 6 hours at 65°C to get the final product as shown in Figure 1. The yield mixture was filtered, washed, dried and recrystallized to form an off-white colored powder [21].

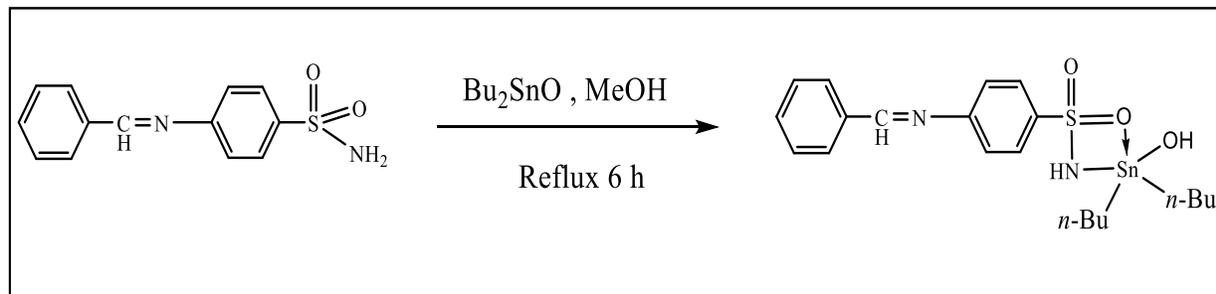


Figure 1: Synthesis of organotin (IV) complex

PVC Films Preparation

25 mg of the Tin complex was mixed with 5.0 g of PVC powder and together dissolved in 100 mL of tetrahydrofuran (THF) solvent with stirring for two hours at 25⁰C . The mixture was then poured on a glass plate and casted to 40 μm thick. Ultimately, the films were dried for 18 hours under vacuum [18].

Evaluation of PVC Peaks Using FTIR Spectroscopy

FTIR spectroscopy was investigated to identify the activity of the organotin (IV) complex on PVC films' photostability. Irradiating the film with 313 nm UV light for 300 hours causes a change in the reflected FTIR spectra. After irradiation, the FTIR spectrum of PVC film showed two absorption peaks because of the formation of polyene and carbonyl at 1604 cm⁻¹ and 1722 cm⁻¹, which are attributed to the C=C and C=O groups, respectively [22]. The growth rate of these peaks is in relation with the reference peak 1328 cm⁻¹ that could be used to determine the PVC photodegradation rate. [23]. From the absorbed spectra of the functional group (A_s) and standard peak (A_r), equation (1) is used to compute the functional group (C=C or C=O) index (I_s) [24] .

$$I_s = A_s/A_r \quad (1)$$

Evaluation of PVC Photodegradation Using Weight Loss Method

Weight loss of the polymer caused by the photodegradation is another indication of the radiation effect. It is determined by tracking the weight before (W₀) and after irradiation (W_t) using equation (2) [25, 26].

$$\text{Weight loss (\%)} = [(W_0 - W_t)/W_0] \times 100 \quad (2)$$

Evaluation of PVC Photodegradation Using Average Molecular Weight (\bar{M}_V)

The \bar{M}_V of polymeric materials after irradiation is determined from the intrinsic viscosity $[\eta]$ of the polymeric solution using the Mark–Houwink equation, which is illustrated in equation (3) [27].

$$[\eta]=1.63\times 10^{-2} \bar{M}_V^{0.77} \quad (3)$$

Evaluation of photodegradation by the Gel Content Method

The gel content of the irradiated PVC films was determined by dissolving 0.1 g of a film in 4 ml of THF at room temperature and left to stir overnight. The insoluble fractions were filtered, washed, and dried in an air-circulated oven. The content percentage was calculated using equation (4), where the W_1 and W_2 are weight of the original sample and gel content, respectively [28].

$$\text{Gel content (\%)} = [W_2/W_1]\times 100 \quad (4)$$

RESULTS AND DISCUSSION

Synthesis of Organotin Complex

Organotin complex (Bu_2SnOHL) was synthesized by reacting the dibutyltin oxide with 4-(benzylideneamino) benzenesulfonamide (ligand) in a medium of MeOH solvent (refluxed for 6-8 times) as mentioned in Figure 1 [23, 24].

Table 1: Physical properties of ligand and organotin complex.

Compounds	M. Wt.	Yield %	Color	M.P. °C
Ligand	260.20	-	Yellowish white	160 -162
Bu_2SnOHL	509.2	88.5	White	202-204

Characterization

The FTIR spectrum of the ligand is shown in Figure 2. Figure 2 shows bands of sulfonamidic amino group ($-\text{SO}_2\text{-NH}_2$) at 3290 cm^{-1} that disappear and convert to a primary amino group at 3457 cm^{-1} in the organotin complex. This could be attributed to the generation of a covalent bond between the nitrogen atom of ($-\text{SO}_2\text{-NH}_2$) and the tin atom of organotin compounds, Figure 3. The IR spectrum of the ligand shows bands at 1326 cm^{-1} and 1184 cm^{-1} that belong to the asymmetrical and symmetrical vibrations of the $-\text{SO}_2$ group, respectively. However, shifting towards lower or higher wavenumbers has occurred because of the formation of a coordination bond between oxygen and atoms of $-\text{SO}_2$ and tin of organotin compounds as shown in Table 2. The FT-IR spectral data of the organotin complex showed three new bands; these bands are assigned to Sn-O, Sn-N, and Sn-OH at 538 cm^{-1} , 435 cm^{-1} , and 3215 cm^{-1} , respectively [31].

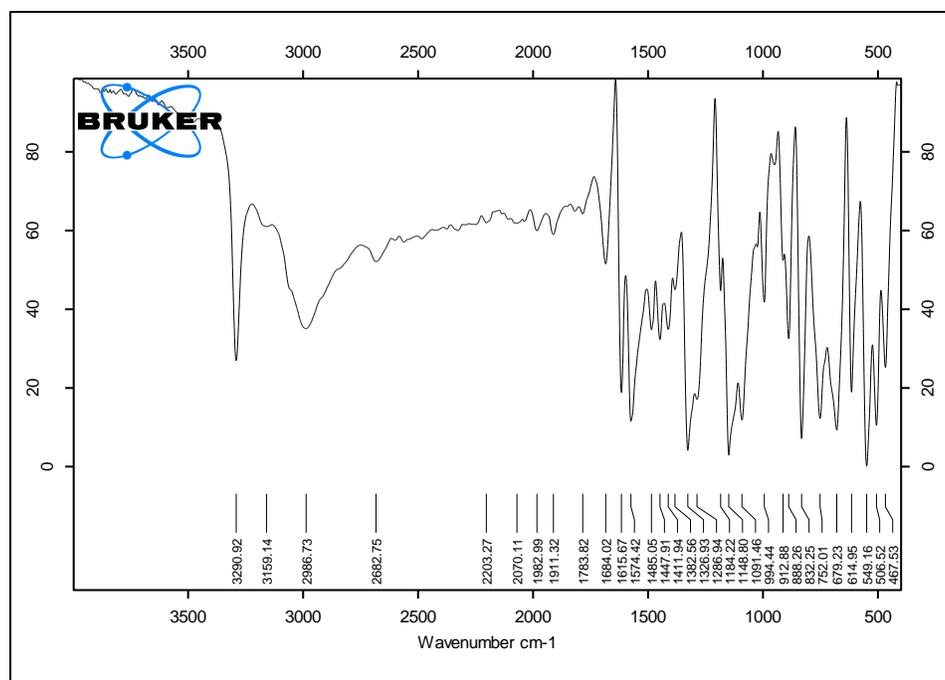


Figure 2: FTIR spectrum of ligand

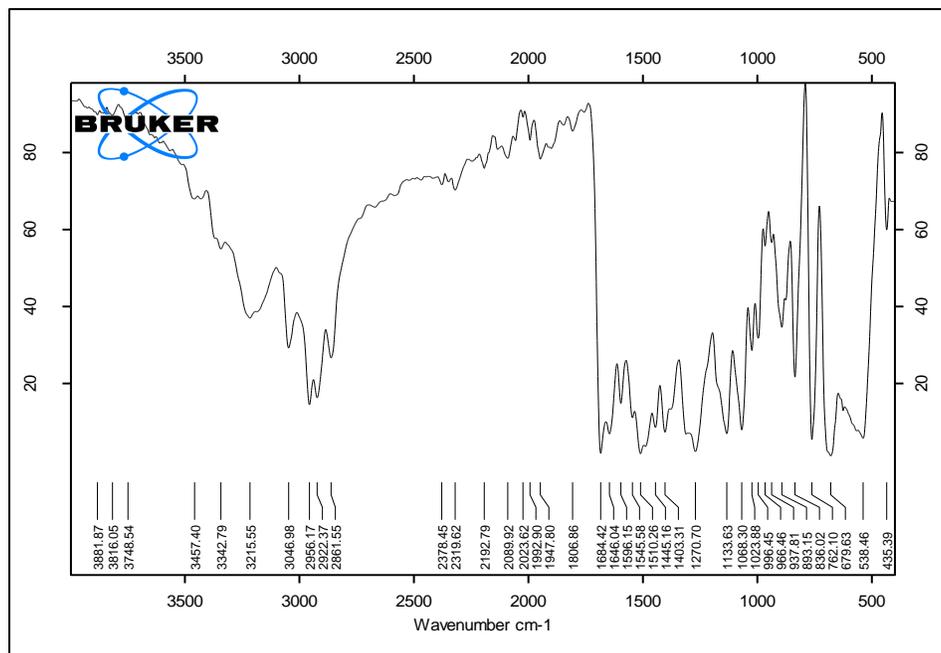


Figure 3: FTIR spectrum of Bu_2SnOHL

Table 2: Functional groups for ligand and organotin (IV) complex.

Vibrational Mode	Ligand	Bu_2SnOHL
ν asym (Ar-NH ₂)	-	-
ν sym (Ar-NH ₂)	-	-
ν (-SO ₂ -NH ₂)	3290	-
Amido ν (NH)	-	3457
ν C=N	1684	1684
ν asym (SO ₂)	1326	1403
ν sym (SO ₂)	1184	1133
Sn-N	-	435
Sn-O	-	538
Sn-OH	-	3215

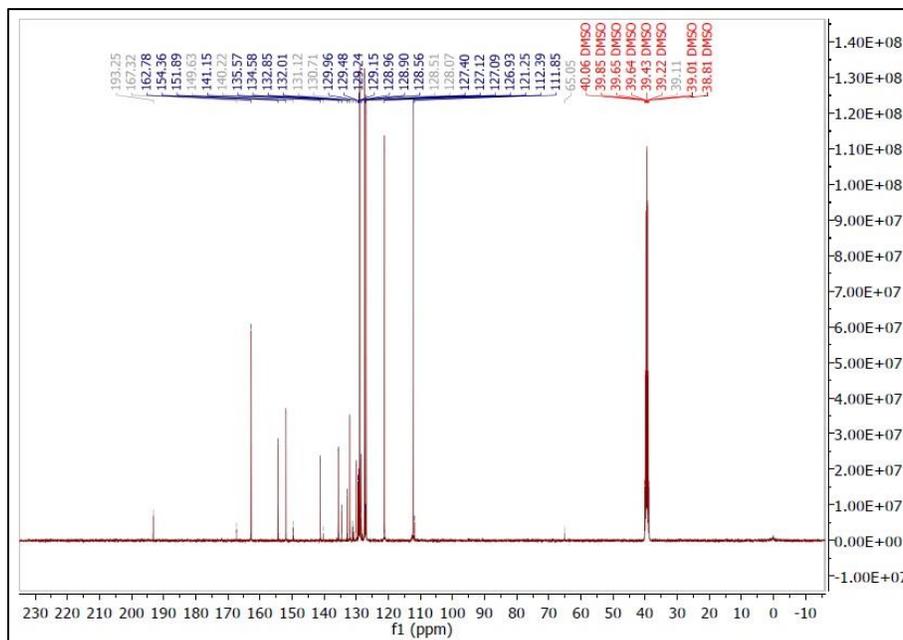


Figure 6: ¹³C-NMR spectrum of ligand

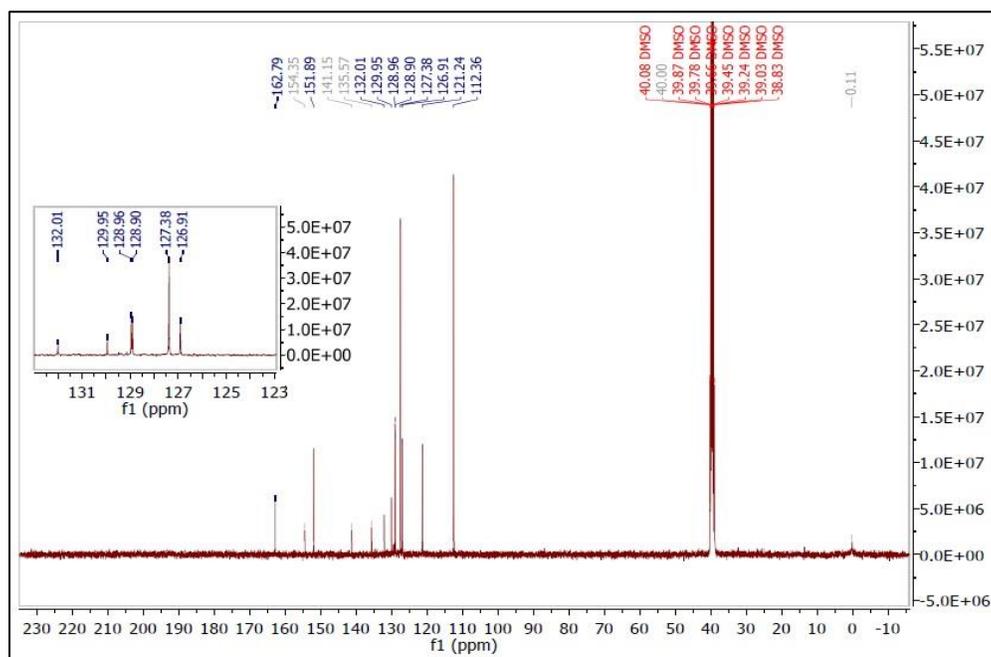


Figure 7: ¹³C-NMR spectrum of Bu₂SnOHL

The ^{119}Sn -NMR spectrum of Bu_2SnOHL complex was measured in DMSO- d_6 solvent. Figure 8 shows the ^{119}Sn -NMR spectrum for the complex. The resonance of Bu_2SnOHL complex appears at -131.2 ppm, which means the geometry of this complex was penta-coordinated organotin(IV) [33].

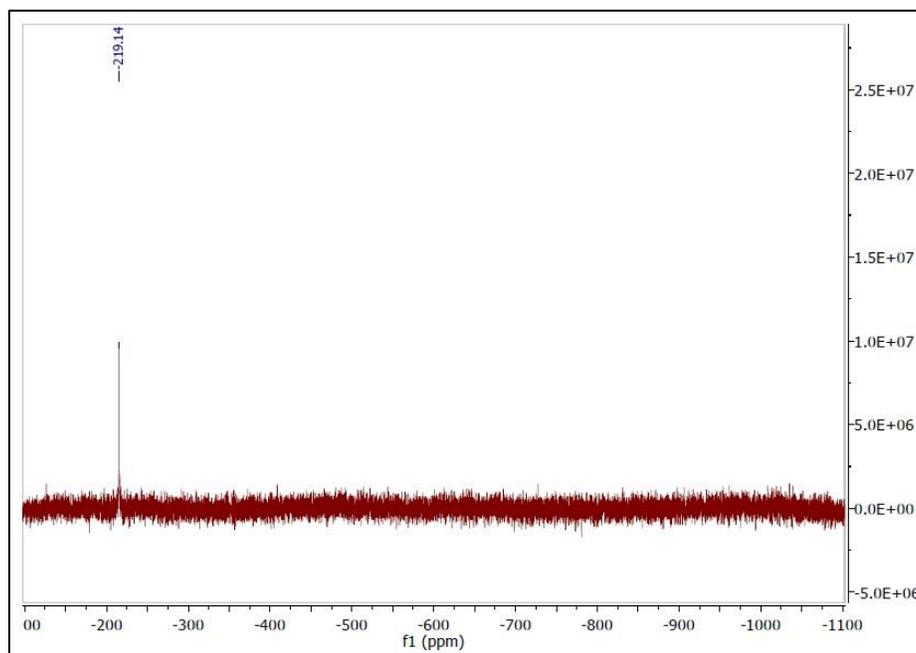


Figure 8: ^{119}Sn NMR spectrum of Bu_2SnOHL

PVC Stabilization Evaluation Using FTIR Spectroscopy

The photoactivity of the organotin (IV) complex that was used as an additive to photostabilize PVC films was examined using FTIR spectroscopy. Irradiating the PVC film for 300 hr to the UV light ($\lambda_{\text{max}} = 313 \text{ nm}$) causes a change in the reflected FTIR spectrum. The FTIR spectrum of PVC film after irradiation showed two absorption bands due to the formation of polyene ($\text{C}=\text{C}$) at 1604 cm^{-1} and carbonyl ($\text{C}=\text{O}$) at 1722 cm^{-1} [22]. The rate of growth of these peaks is referenced to the peak 1328 cm^{-1} and could be used to estimate the PVC photodegradation in order to study the effect of organotin complexes on the photodegradation of PVC [23]. Figure 9 shows the FTIR spectra of PVC film before and after 300 hours of irradiation.

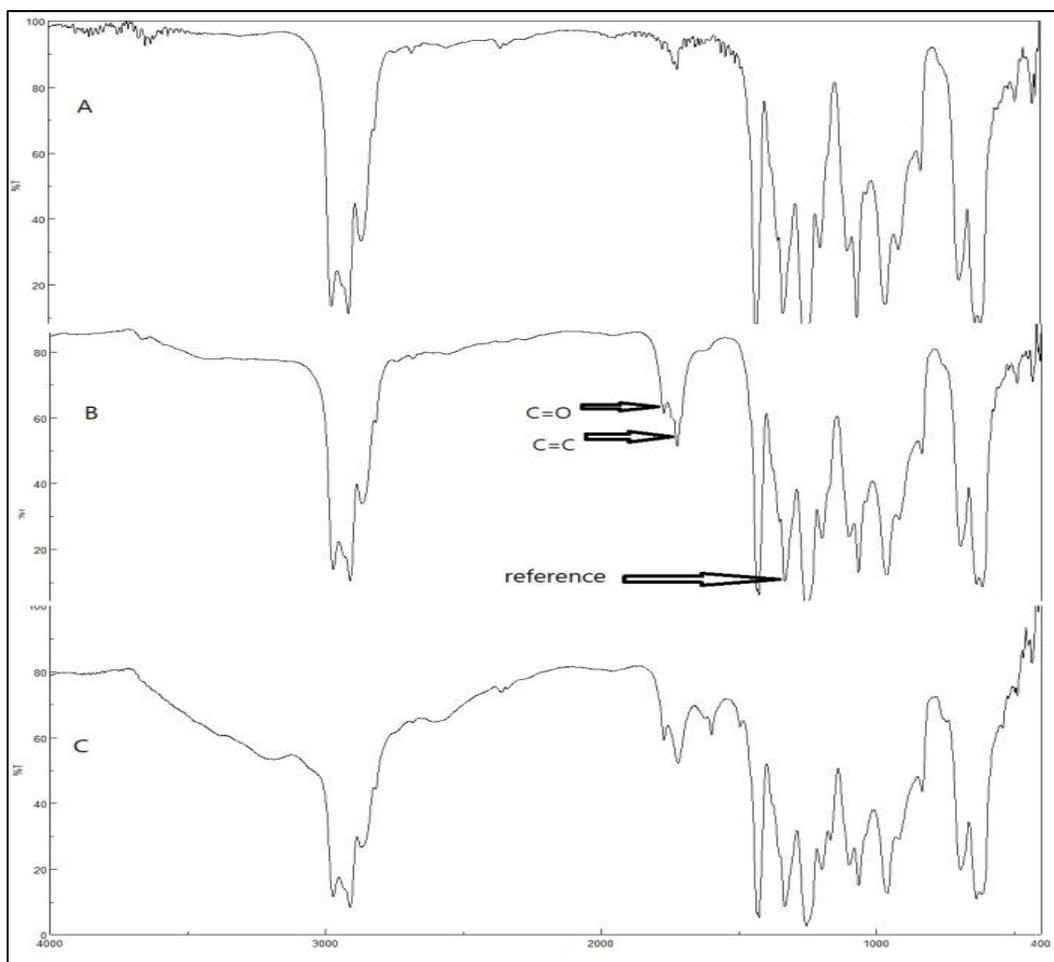


Figure 9: Changes in FT-IR spectrum of PVC film (A) before irradiation, (B) after 300 h irradiation, and (C) after 300 h irradiation and Bu_2SnOHL addition

Changes in levels of intensity of carbonyl group (1722 cm^{-1}) and polyene group (1604 cm^{-1}) of PVC film that contains organotin(IV) complex were calculated and plotted against the irradiation time (50-300 h) as shown in Figures 10 and 11. The growth rates of the carbonyl group (C=O) and polyene group (C=C) were lower for the PVC film that contains 0.5 wt.% organotin (IV) complex, comparing to the plain PVC. Both $I_{\text{C=O}}$ and $I_{\text{C=C}}$ have changed significantly for the blank PVC film comparing with the modified PVC film, which was more stabilized. For example, the $I_{\text{C=O}}$ after 300 h irradiation was 0.54 and 0.42 for the PVC films before and after filling Bu_2SnOHL , respectively. Similarly, the $I_{\text{C=C}}$ of blank PVC after 300 h irradiation was 0.55 compared to 0.41 for the Bu_2SnOHL - PVC film. The results proved that Bu_2SnOHL is an active photostabilizer for

PVC; similar results were obtained from our previous work [8]. As shown in the carbonyl ($I_{C=O}$) and polyene ($I_{C=C}$) groups Figures, Bu_2SnOHL addition gave photostability to the PVC film.

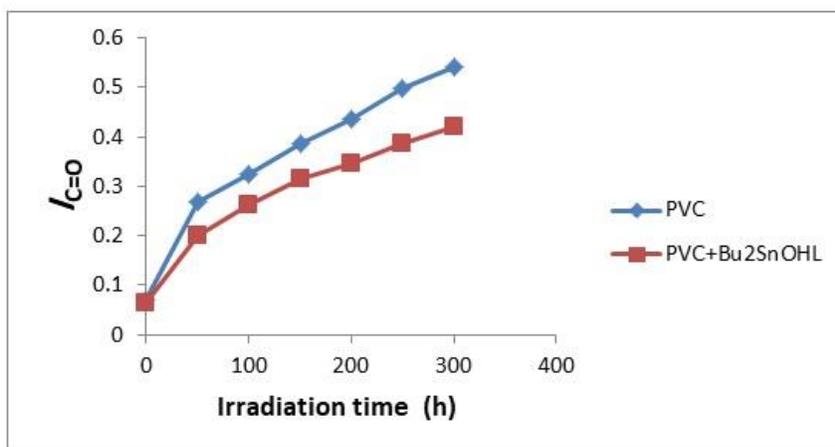


Figure 10: Difference in $I_{C=O}$ of PVC film with and without organotin complex after irradiation

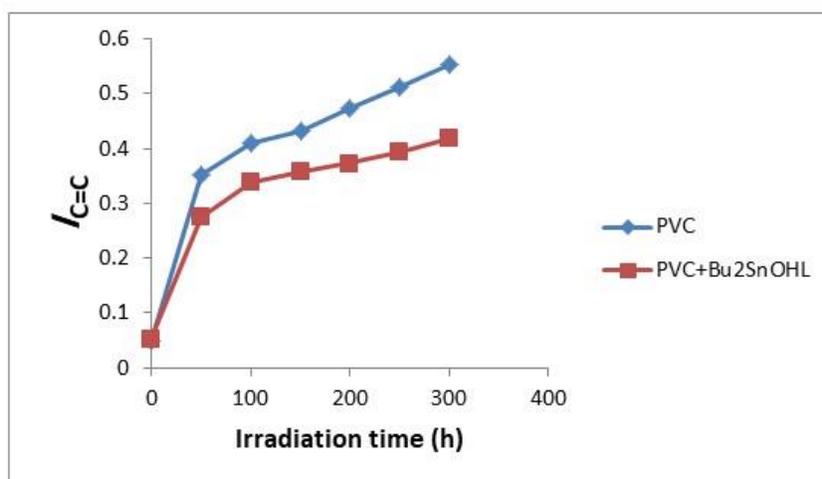


Figure 11: Difference of $I_{C=C}$ of PVC film with and without organotin complexes after irradiation

Evaluation of PVC Stabilization Using Weight Loss Method

The degree of photodegradation can be determined by measuring the weight loss of PVC during irradiation [26]. The photo-oxidation of PVC generates the cross-linking within the polymeric chains as a result of the creation of free radicals. As a consequence, PVC discoloration is eliminated together with hydrogen chloride (dehydrochlorination), and traces of organic residues are volatilized. [28, 29]. To determine the efficiency of the organotin (IV) complex as a stabilizing agent, PVC films were irradiated with UV light for various periods of time. During the irradiation, the weight loss was determined at 50 hr intervals using equation (2); the obtained results are shown in Figure 12. PVC weight loss was high at the start of irradiation (the first 50 hr), then it increased at a lower rate until reaching the maximum after 300 hr of continuous irradiation. When the Bu₂SnOHL complex was employed as an additive, the weight loss of PVC was decreased.

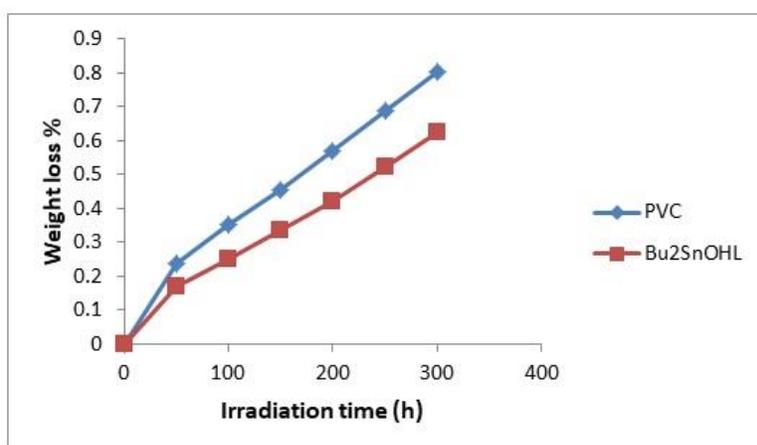


Figure 12: Change in weight loss for PVC films

PVC Stabilization Evaluation Using Viscosity Average Molecular Weight Variation

PVC is experiencing a reduction in its molecular weight as a result of photodegradation due to the main polymeric chains scission [35]. By measuring the viscosity of irradiated PVC film, the potency of the organotin (IV) complex is proven. The viscosity of PVC film that was irradiated for various periods was measured using a viscometer after it was dissolved in THF [27]. \bar{M}_v was calculated using the Mark-Houwink (equation (3)) for every film at various irradiation times (50-300 h). The change in molecular weight was plotted against irradiation time as shown in Figure 13.

During the irradiation process, a clear decrease in the \bar{M}_V of PVC films was noticed, where the decrease in the blank PVC film was more significant. Obviously, Bu₂SnOHL stabilized PVC to a remarkable degree against irradiation.

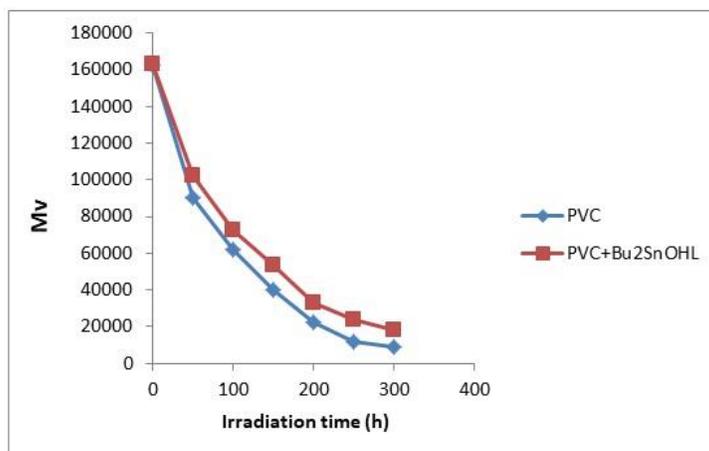


Figure 13: Change in \bar{M}_V for PVC films

PVC Stabilization Evaluation Using gel content

The gel content that appears when PVC films are dissolved in THF after being irradiated indicates the cross-linking of polymeric chains that are released during the photodegradation [28]. Equation (4) was used to obtain the percentage of gel content, which was then plotted against time of irradiation, as shown in Figure 14. The gel content of blank PVC film is higher than that of the additive. The gel content increases with irradiation time and decreases with the organotin(IV) complex ratio. The reason was explained as the complex increases the links of polymer chains.

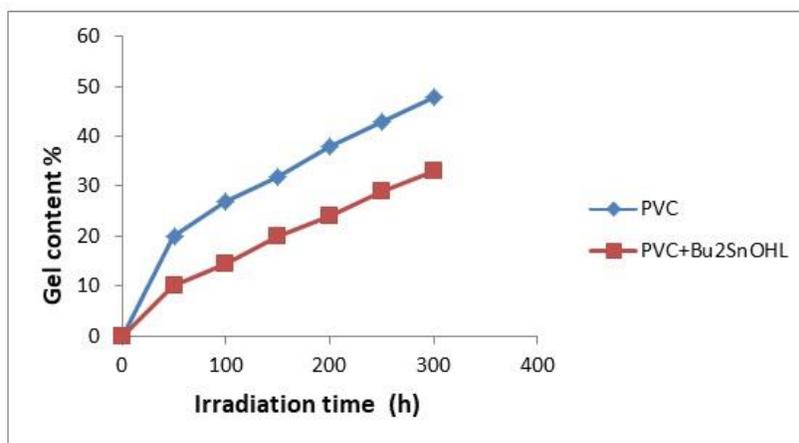


Figure 14: The percentage of gel content for PVC films

Surface Analysis of PVC

Stabilization Assessment of PVC by Atomic Force Microscope

The atomic force microscope (AFM) test was used to examine the surface morphology of PVC films. This technique provides the desired information to characterize the roughness in two- and three-dimensional topography of the PVC surface. Long-term irradiation of PVC causes bond breakage that results in a rough and broken surface [31-32]. Before and after 300 hours of irradiation with and without the additive, topographic AFM images of the PVC film surface are shown in Figure 15. The addition of the complex increased the photostability of PVC films substantially; the surface of irradiated and modified PVC was less rough than that of blank PVC film. PVC roughness factor (Rq) before irradiation was 14.0, but the values of PVC and PVC/Bu₂SnOHL films after irradiation were 42.2 and 34.1, respectively. Obviously, the Bu₂SnOHL complex improved the PVC roughness. The organotin (IV) complex inhibits the process of dehydrochlorination due to irradiation, which leads to breaking the bonds within the polymer chain.

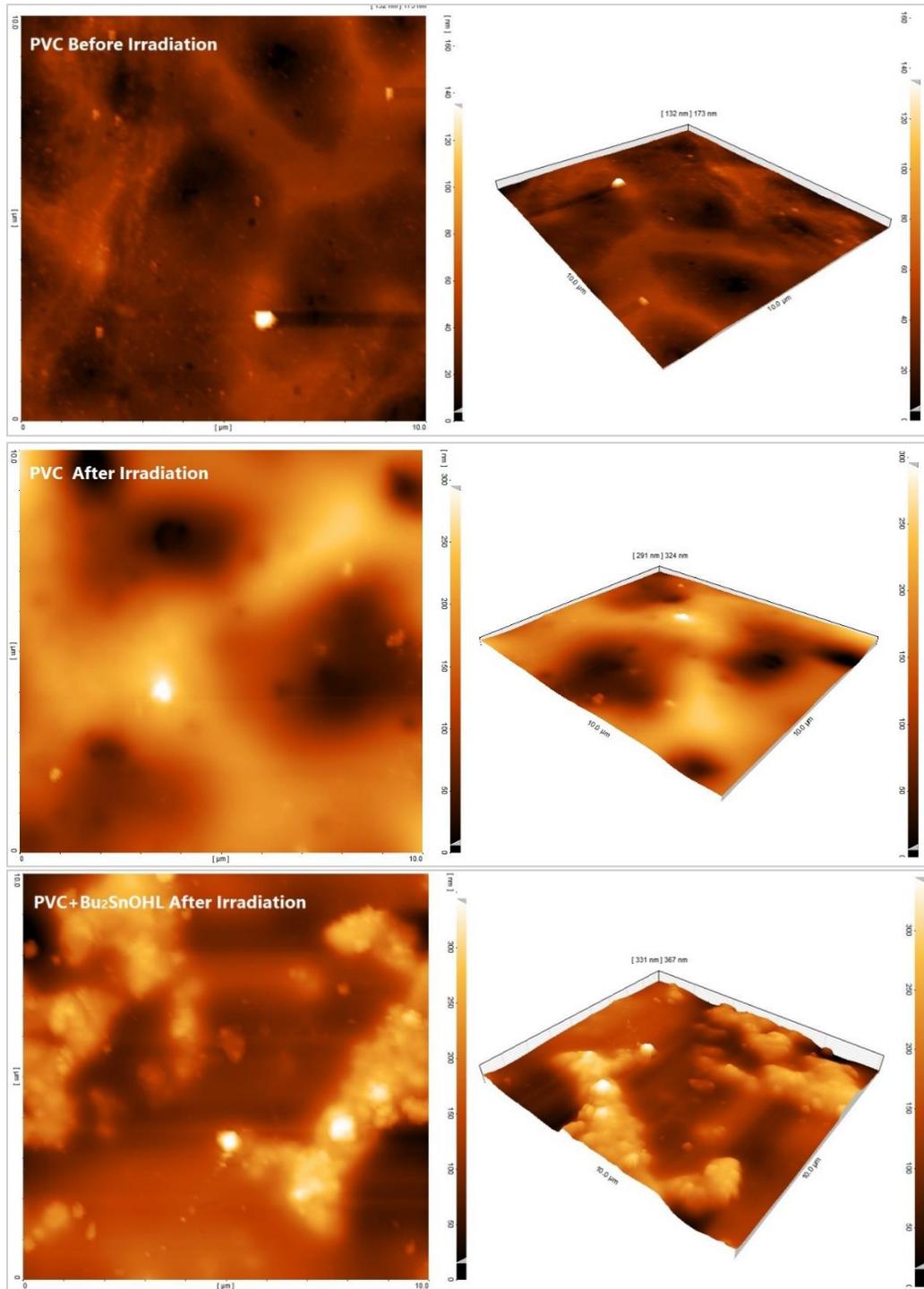


Figure 15: Images of AFM for PVC films

Stabilization Assessment by FE-SEM of PVC films

SEM examination was used to analyze the surface morphology of PVC films. It was demonstrated that the plain PVC film was less lumpy (smooth surface) and had a high level of homogeneity prior to radiation exposure. After irradiation, bonds breaking within the polymer chains and HCl inducement led to form cracks and roughness on the PVC surface [38]. The PVC/Bu₂SnOHL blend had a smoother and cleaner surface after irradiation to 300 hr compared to the irradiated plain PVC film as shown in Figure 16.

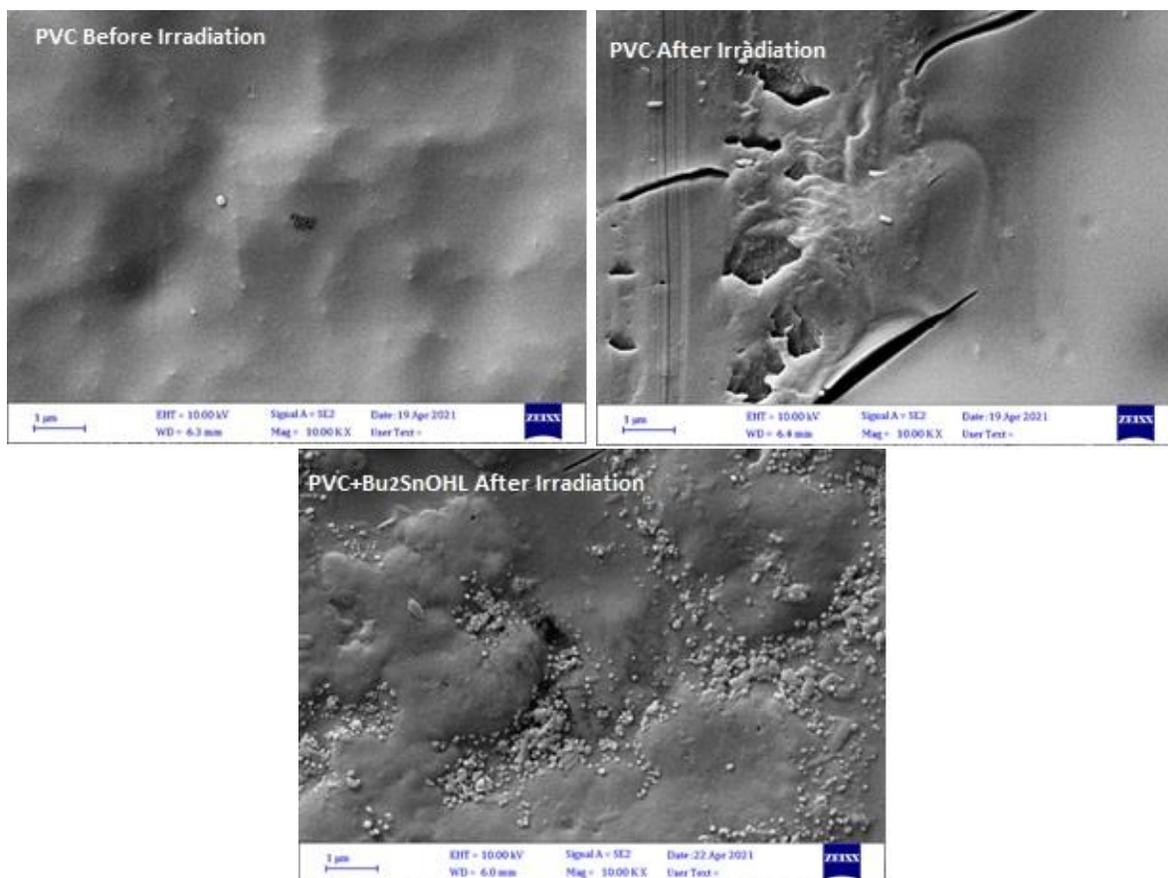


Figure 16: FESEM images of PVC films and complex

Energy Dispersive X-ray Spectroscopy Analysis (EDX) of PVC films

EDX technology was used to examine PVC films in the absence and presence of the organotin (IV) complex additive. The films of PVC were exposed to UV light for 300 hours and the elemental composition was analyzed by the EDX [39]. Due to photodegradation, the chlorine content in the blank PVC films decreased from 68.0 % before irradiation to 50.6 % after irradiation, where hydrogen chloride was eliminated from the blank PVC, indicating significant dehydrochlorination. The decrease in chlorine content of the modified PVC film after irradiation was lower than that of the plain film as shown in Figure 17. A higher chloride percentage indicates less bond breaking and less photodegradation of the polymeric film.

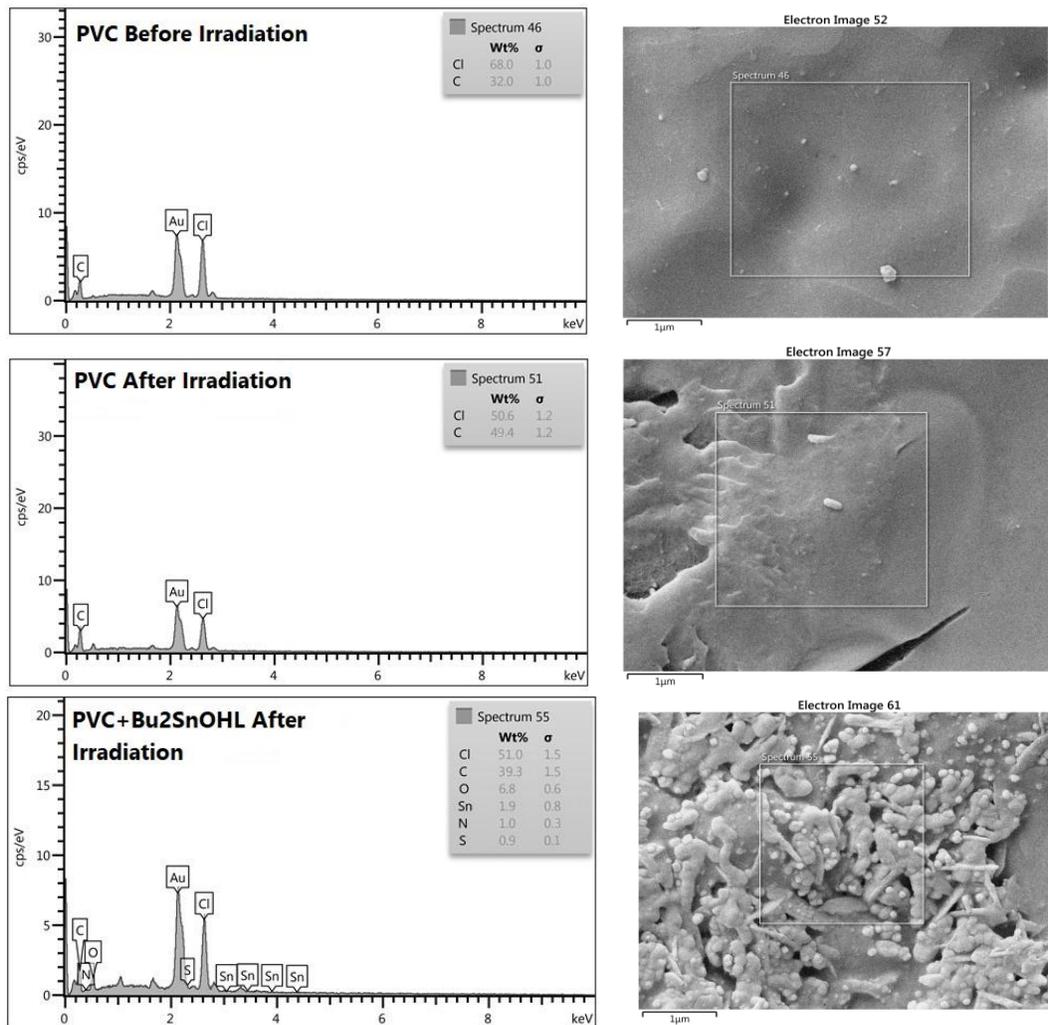


Figure 17: Energy dispersive X-ray mapping of PVC films

Suggested Mechanisms of Organotin Complex Efficiency

Bu_2SnOHL complex was used as a photostabilizer of PVC. The use of the tin complex as an additive has significantly decreased the photodegradation of PVC film. The Bu_2SnOHL complex is able to directly absorb UV light, and gradually release the adsorbed energy at a pace that does not degrade the PVC chains [20]. The Bu_2SnOHL complex containing tin atoms acts as an acidic center. The atom of tin absorbs the chloride ion from hydrogen chloride, which is released from PVC chains after UV irradiation, to produce stable substitute tin chloride, Figure 18. Therefore, the Bu_2SnOHL complex is a PVC photo-stabilizer that acts as a scavenger for hydrogen chloride [40].

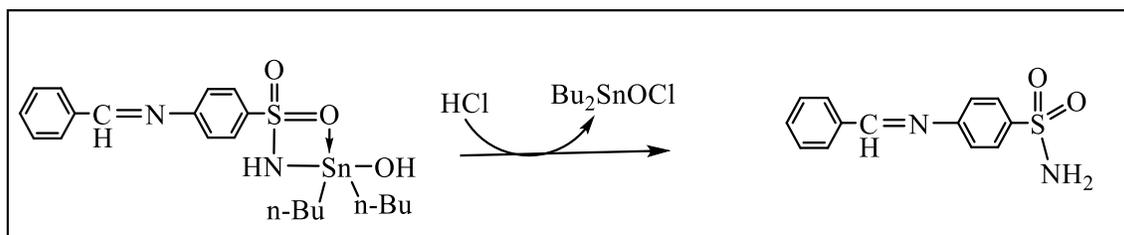


Figure 18: Bu_2SnOHL function as scavengers for hydrogen chloride

PVC undergoes photooxidation in the existence of oxygenated species like the hydroperoxides (POOH) [32, 36]. The tin complex may cause hydroperoxide decomposition by removing the acidic tin atom from the additive as shown in Figure 19. This procedure significantly reduces PVC photodegradation.

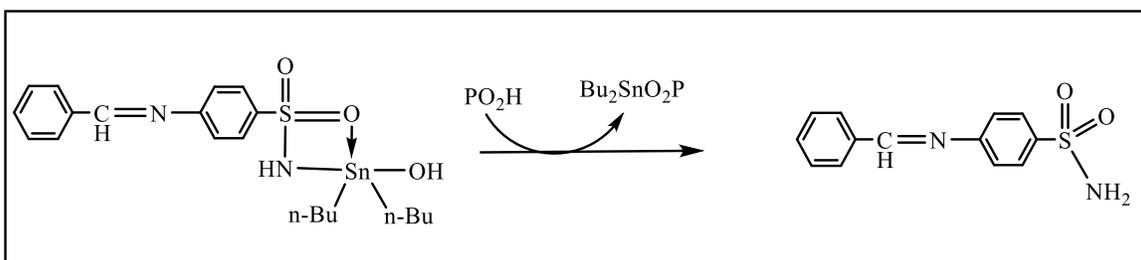


Figure 19: Bu_2SnOHL complex function to induce decomposition of hydroperoxide

Peroxide radical (POO^\bullet) has a negative effect on PVC film and resulting in the formation of various photo-oxidative products. The tin complex that has been synthesized may behave as radical scavengers [32, 37]. The complex inhibits photo-oxidation of PVC and gives a certain level of stability against irradiation, Figure 20.

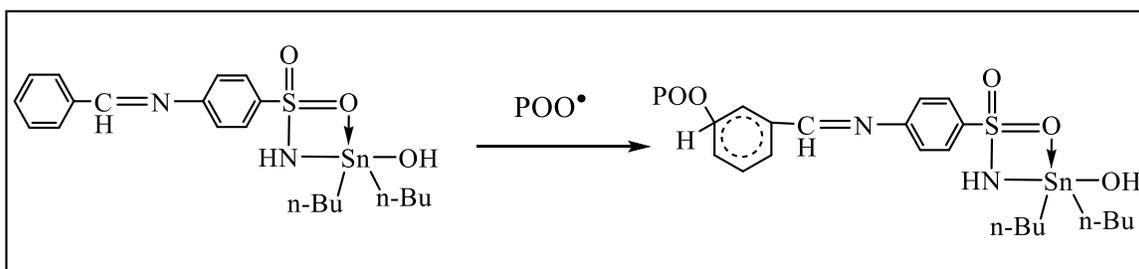


Figure 20: Bu_2SnOHL complex function as a radical scavenger

The polarity of C–Cl links in PVC chains, and nitrogen and oxygen of sulfonyl and amide groups, might enhance favorable interactions between PVC and the additive. These are all factors to consider; Figure 21 shows the possible scenarios of interaction. Before the photo-irradiation energy dissipated, this attraction may accelerate energy transfer from the polymer chains to the additive. This hypothesis, however, does not account for the complications caused by steric hindrance within macromolecules [20].

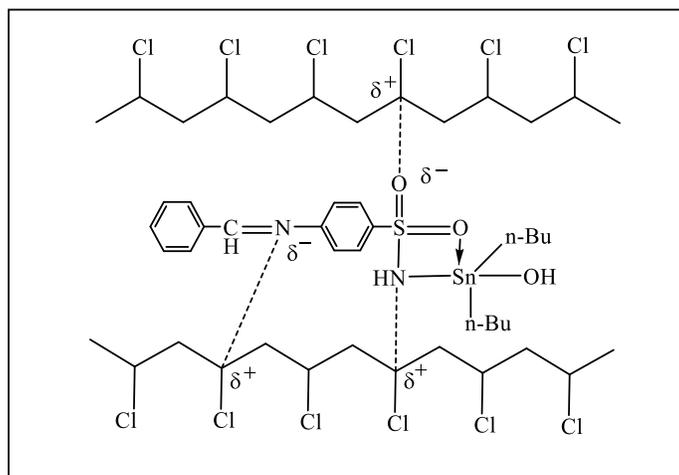


Figure 21: Interaction between complex Bu_2SnOHL and PVC



CONCLUSION

The organotin (IV) complex Bu_2SnOHL was synthesized from the reaction of di- or-ganotin(IV) oxide and 4-(benzylideneamino) benzenesulfonamide as ligand. The organotin complex and ligand were characterized using FT-IR, 1H , ^{13}C , ^{119}Sn NMR, and EDX. PVC films were irradiated for 300 hr at a wavelength of 313 nm at room temperature. A remarkable effectiveness of the complex was noticed when the modified film's performance was compared with the plain one before and after irradiation. Organotin (IV) complex was shown to be effective in reducing degradation of PVC film, and this was evaluated using the microscope, FE-SEM, and AFM techniques; these images show that the PVC films with the additive had fewer cracks and roughness.

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AUTHOR'S CONTRIBUTION

Hassan Ghani carried out the research, wrote and revised the article. Emad Yousif conceptualised the central research idea, provided the theoretical framework, designed the research, supervised research progress, and approved the article submission. Mohammed Kadhom, Waled Abdo Ahmed, Muhammad Rahimi Yusop and Muna Bufaroosha designed the research, supervised research progress; anchored the review, revisions and approved the article submission.

CONFLICT OF INTEREST STATEMENT

The authors agree that this research was conducted in the absence of any self-benefits, commercial or financial conflicts and declare absence of conflicting interests with the funders.

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