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Reducing Environmental Pollutants by using Triorganotin(IV)-Tyrosine Complexes that Prolong the Life of the Polymers used in Outdoor Patios

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ABSTRACT

When exposed to UV light at ambient temperature, three tri organotin (IV) complexes with tyrosine as a ligand (85–97% yields) were utilized as additives to prevent the photo-degradation of PVC films (40 µm thickness). The compounds were described using NMR (^{1}H, ^{13}C and ^{119}Sn), IR, and elemental analysis. The compounds formed were assigned trigonal bipyramidal geometry depending on the spectrum data. Several Triorganotin (IV) tyrosine complexes were synthesized and mixed with polymers to form thin films (vinyl chloride). Up to 300 hours of UV light (wavelength: 313 nm) exposure was given to these films. A microscope, atomic force microscopy, and scanning electron microscopy were used to examine the surface morphology of the PVC films. Rapid UV-weathering was employed to determine weight loss and the production of certain functional groups, including carbonyl and polyene. Compared to pure PVC film, the films with manufactured complexes showed less undesired alterations. By absorbing UV light and scavenging peroxides, hydrochlorides and radicals. The polymer was photo stabilized by the triorganotin (IV)-tyrosine complexes (vinyl chloride). It was discovered that Ph3SnL has the fastest rate of PVC photostabilization.

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INTRODUCTION

Environmental impact of polymeric substances is largely decided with the aid of the low molecular mass compounds launched from the materials. For the safety assessment of plastic materials in food packaging and medical applications, the qualitative and quantitative

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determinations of these compounds are particularly essential and a key to success. Reducing applicable landfill ability, environmental stability, and chemical, and calorific value loss of plastics makes plastic landfilling an unfavorable, unlikely option, which shows a major problem for future generations. A further appropriate way is recycling. At most, there are four kinds of plastic recycling, categorised as primary (re-extrusion), secondary (mechanical), tertiary (chemical recycling), and quaternary recycling (energy recovery) (Yousif et al., 2019). Polyvinyl chloride has several advantages, including low cost, inflammability, proper flexibility, and adaptability as a plastic for a wide range of applications, but it has poor heat and light stability [Tomi et al., 2017]. It presents substantial environmental difficulties when it decomposes quickly when heated or exposed to sunlight for an extended length of time due to hydrogen chloride loss from the polymer via autocatalytic dehydrochlorination [Yousif et al., 2015]. Degradation is produced by a considerable change in the mechanical and physical features of the polymer, which is accompanied by a change in the average molecular weight owing to chain crosslinking [Tomi et al., 2017; Yousif et al., 2015]. There are a number of flaw locations in the polymer chain that are thought to be the source of this instability. Potential defect structures in polyvinyl chloride chains include chlorine atoms, hydroperoxides, double bonds, chloroallyl groups, carbonyl groups, peroxide residues, and head-to-head configurations. The toxicity (steric arrangement of the monomer units) may affect degradation in addition to these anomalies. To prevent the possibility of degradation, suitable additives are added to polyvinyl chloride, resulting in a complex polymer with behavior and properties that differ significantly from PVC alone. Polymer additives should be non-volatile and chemically stable, have lower manufacturing costs, be suitable with the polymer and be employed in small quantities [Yousif et al., 2015; Martins et al., 2016]. Additives come in powders, flakes, pellets, and spheres and perform a variety of tasks such as antioxidants, UV absorbers, energy quenchers, and radical decomposers. Polyphosphates, organotin chemicals, Schiff bases and heterocyclic compounds are the most often used PVC additives. The aromatic residues in the skeleton of additives are vital for enhancing oxidant resistance and acting as UV absorbers to stabilized a wide range of polymeric products, including films, plastics, and cosmetics [Yaseen et al., 2021; Yousif et al., 2023]. Common photo stabilizers and antioxidants, such as organotin chemicals help to preserve polymers. The first commercially effective organotinW stabilisers were dibutyltin dilaurate, dibutyltin maleate, and dibutyltin methyl maleate [Rabie et al. 2013; Yousif et al., 2018; Alotaibi et al., 2019]. Since 1940, stabilizers made of organotin chemicals have been used to stop this deterioration [Arraq & Hadi, 2023]. Organotin complexes have been evaluated for their effectiveness as photodegradation and photooxidation inhibitors of polyvinyl chloride [Arraq & Hadi, 2023]. This article reviews the function of tyrosin tin complexes as additives to prevent or inhibit polymer photodegradation. The most recent developments in the field of photodegradation are reviewed and addressed in the part that follows. The methods now in use will help to address this problem. The utilization of tyrosin tin complexes as UV additives and their potential advantages for preventing and reversing the photodegradation of polymers are indeed the main topics of the third section of this manuscript.

MATERIALS AND METHODS

General

Chemicals from Merck were used as well as solvents and reagents (Gillingham, UK). Petkim Petrokimya contributed PVC with an approximate molecular weight of 180,000. (Istanbul, Turkey). The FTIR spectra were captured using a Shimadzu FTIR-8300 spectrophotometer (Tokyo, Japan). Using a Q-Panel tester, samples were exposed to UV light with a maximum wavelength (max) of 365 nm and a light intensity of 6.2×10^{-9} Einstein dm^{-3} s^{-1} (Homestead, FL, USA). Each side of the tester includes a 40-watt UV fluorescent light with a maximum wavelength of 365 nanometers. The films were positioned parallel to the UV lamps and 10 cm distant from the source of the irradiation light. The films were sometimes turned to provide equal illumination from all sides. In order to determine the extent of the damage induced by irradiation to the film surface, the surface of the PVC films was evaluated using a Meiji Techno microscope (Tokyo, Japan), FEI Inspect S50 microscope (Czechia, Czech Republic), and Veeco equipment (Plainview, NY, USA).

Organotin (IV)-tyrosine complexes synthesis

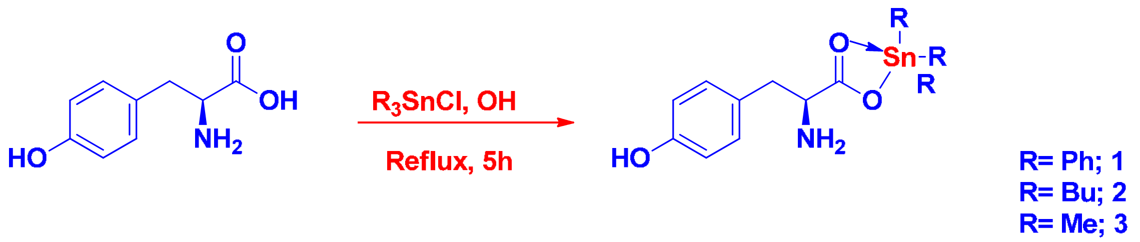
Tyrosine (1 mmol, 181.1 mg) was combined with triphenyltin chloride (1 mmol, 385.5 mg), tributyltin chloride (1 mmol, 325.5 mg), trimethyltin chloride (1 mmol, 199.2 mg), or trimethyltin chloride (Me_3SnCl) in methanol (20 mL) and refluxed for five hours (Scheme 1). The blend was given time to cool to 25 ◦C, and the solid was sifted, washed with MeOH (2 × 10 mL), and dried, yielding either 1 (96%) as an off-white solid or 2 (58%) as a greenish-yellow solid or 3 (97%) as an off-white solid (Table 1).

Fourier Transform Infrared Spectroscopy

The bands associated with the stretching vibration of the O-H bonds that should be observed in the area of 3300-2400 cm-1 for the ligand (L-tyrosine) as a result of the complexation with tin atom were absent from the FTIR spectra of triorganotin (IV)-tyrosine complexes [Arraq et al., 2023]. Evidence of the complexity between a metal ion and the carboxyl group of the ligand includes a shift in the stretching frequencies of the C=O group, which has the wave number 1613 cm^{-1}. Moreover, the Sn-C and Sn-O groups emerged in areas 534-528 and 448-424 cm^{-1}, respectively, in the FTIR spectra of complexes, as shown in Table 2.

Nuclear Magnetic Resonance Spectroscopy

The ^{1}H-NMR spectra of the ligand and Triorganotin (IV) complexes **1-3** indicated the elimination of the carboxylic group proton ($-CO_2H$), which shows as an exchangeable singlet in the ligand band at 12.40 ppm. The findings were consistent with the oxygen atom of the carboxylate group complexing with the tin atom. The up field shifting for complexes reduces as a result of the ligand's chelation with the Triorganotin (IV) moiety [Pospíšil & Nešpurek,



Scheme 1. Synthesis of triorganotin (IV)-tyrosine complexes.

Table 1. Physical data of ligand (Tyrosine) and its complexes.

Compounds	**Colors**	**M.P (°C)**	**Yields (%)**	**Calculated % (Measured %)** C	H	N	Sn
Tyrosine (L)	white	268	-------	59.66 (59.71)	6.12 (6.22)	7.73 (7.75)	--------
1	Off white	95-97	96	61.16 (61.18)	4.75 (4.81)	2.64 (2.68)	22.39 (22.41)
2	Greenish yellow	175-177	85	53.64 (53.66)	7.93 (7.95)	2.98 (3.02)	25.24 (25.26)
3	Off white	245-247	97	41.90 (41.96)	5.57 (5.63)	4.07 (4.10)	34.51 (34.55)

Table 2. FTIR information of prepared Triorganotin (IV) - tyrosine complexes (**1-3**).

Complex	C=O	C-O	Sn-C
1	1597	1246	529
2	1598	1244	528
3	1595	1242	534
Complex	C=O	C-O	Sn-C

Table 3. The ^{1}H-NMR spectra (DMSO-d_6) of tyrosine and its complexes.

No	^{1}H-NMR
L	δ12.77 (s,1H,COOH), 9.24 (s,1H,Ar-OH), 7.05 (d, J=8.50 Hz.2H,Ar), 6.68 (d, J=8.50 Hz,2H,Ar), 3.51 (br, 2H,NH_2), 3.15 (t, J=4.0 Hz,1H, CO-CH-), 2.75 (m ,2H,2 PhCH-).
1	δ7.99 (s,1H,Ar-OH), 7.88 (t,J=30Hz,3H,Ar), 7.64-7.58 (m,6H,Ar), 7.56 (d , J=2.36 Hz , 6H, Ar), 7.48 (d , J=1.07 Hz ,2H, Ar), 7.46 (d , J=2.07 Hz ,2H, Ar), 3.39 (br,2H, NH2), 2.79 (t,J=8.09 Hz , 1H, CO-CH-), 2.35 (m, 2H, 2PhCH-).
2	δ 9.10 (s,1H,Ar-OH), 6.99 (d , J=7.80 Hz ,2H, Ar), 6.88 (d , J=7.80 Hz ,2H, Ar), 3.41(br,2H, NH_2), 3.20 (t, J=5.20 Hz , 1H, CO-CH-), 2.76 (m, 2H, 2PhCH-), 1.60 (qut, J= 7.50 Hz, 6H,3CH_2), 1.29 (sex, J=7.50 Hz ,6H,3CH_2), 1.07 (t, J= 8.08 Hz,9H,3Me), 0.87 (t, J=7.5 Hz,6H,2CH_2).
3	δ 9.27 (s,1H,Ar-OH), 7.07 (d,J=7.5Hz,2H,Ar), 6.69 (d, J=7.5 Hz , 2H, Ar),3.30 (br,2H, NH_2), 3.01 (t, J=6.30 Hz ,1H , CO-CH), 2.86(d, J=12Hz,2H, PhCH-), 1.26 (s,9H,3Me).

2000]. The chemical shift increases as more tin atoms are in coordination [Ahmad et al., 2007]. The N-H proton of the ligand appears as a singlet in every compound, indicating that the N atom did not coordinate with the Sn center. In ^{13}C-NMR due to the decrease in electron density at carbon atoms when oxygen is coupled to an electropositive tin atom, the complexes' C_1-carboxyl was moved down the field in comparison to the ligand. This data supports the concept that complexation occurred through carboxyl group oxygen shown in Table 4. Both the shape of the complexes and the coordination number have an impact on the chemical shift in ^{119}Sn-NMR [Molyneux, 2004]. The chemical shift range of penta-coordinated tin derived from organotin (IV) complexes is (-90 to -190) ppm [Bukhari et al., 2008]. The complexes Ph_3SnL, Bu_3SnL and Me_3SnL have trigonal bipyramidal geometry and their respective resonances are -190.03, -140.02 and -96.95 ppm [Bukhari et al., 2008; Karayıldırım et al., 2005; Mohammed et al., 2023; Gaumet & Gardette, 1991; Pospíšil & Nešpurek, 2000].

PVC Films preparation

THF (100 mL) was combined with PVC (5 g) and 5% weight of the suitable compound. After 2 hours of stirring at 25 °C, the homogeneous solution was poured into a plate with a thickness of 40 µm. To eliminate the THF, the plate was maintained at 25 °C for 24 hours. The generated films were then dried in a vacuum oven for eight hours at 40 °C to remove any THF residue completely.

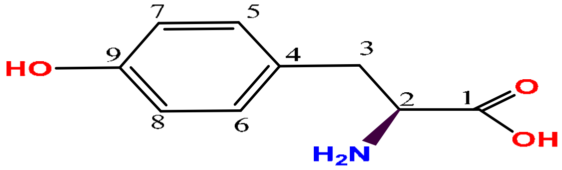
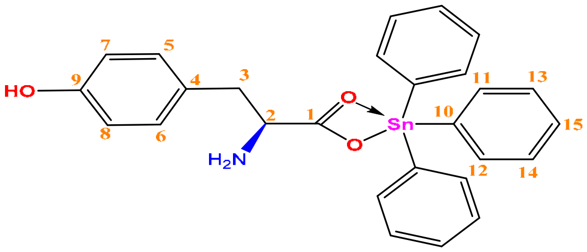
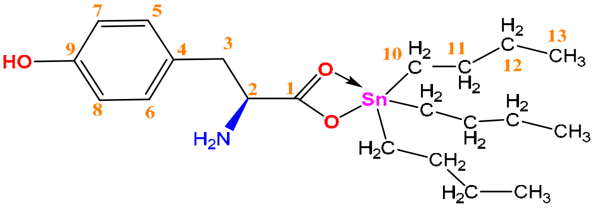
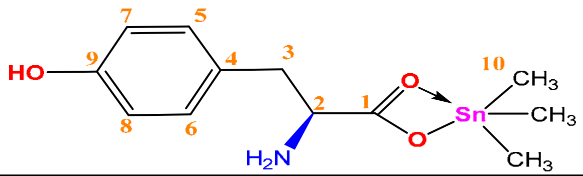
RESULTS AND DISCUSSION

Monitoring the photodegradation on PVC films by applying the following techniques:

IR Spectroscopy

The first step in photodegradation is photon absorption by polymer chains. Upon absorption, the molecules' energy rises, and they enter an excited state, which causes bonds to dissolve and

Table 4. Shows the ^{13}C-NMR spectra (DMSO-d6; ppm) of tyrosine and its complexes.

Comp.	**^{13}C-NMR**
	(C_1-Carboxyl, 1C, 184.8), (C_9-Phenolic , 1C,168.3),(C_4,1C,139.4),(C_5,C_6,2C,132.5), (C_7,C_8,2C 118.1),(C_2,1C,65.2) , (C_3,1C,21.8).
	(C_1-Carbonyl,1C,177.3),(C_9-Phenolic,1C,145.9),(C_{10},3C,140.9),(C_4,1C, 137.2),(C_5,C_6,2C,129.5),(C_{13},C_{14},6C,128.3), (C_{11},C_{12},6C,127.8),(C_7,C_8,2C,120.0),(C_{15},3C,115.4), (C_2,1C,57.8),(C_3,1C,38.8).
	(C_1-Carbonyl,1C,177.4),(C_9-Phenolic,1C,160.2),(C_4,1C,130.7),(C_5,C_6,2C,115.0),(C_7,C_8,2C,103.5),(C_2,1C,57.2),(C_3, 1C,28.3),(C_{11},3C,27.0),(C_{12},3C,20.9) ,(C_{10},3C,16.6) ,(C_{13},3C,14.5).
	(C_1-Carbonyl,1C,176.4),(C_9-Phenolic,1C,157.5),(C_4,1C,132.1),(C_5,C_6,2C,129.8),(C_7,C_8,2C,116.3),(C_2,1C,57.7), (C_3, 1C,38.4),(C_{10},3C10.1).

free radicals to develop. The initial stage in photodegradation is the generation of such free radicals [Gardette et al., 1989; Khalil et al., 2016, Arraq& Hadi, 2022]. The presence of chemical groups in the polymer known as chromophore groups, which can absorb specific wavelengths from sunlight (280-400 nm), is a fundamental need for photodegradation to begin (Ch) [Pospíšil et al., 2006, Jafari et al., 2009]. The types of chromophores are internal and external impurities, which are not a part of the polymer structure. External substances (such as residues of catalysts, solvents, additives, etc.) or functional groups in polymer chains might be impurities (in-chain or end-chain). They start the photodegradation process and generate free radicals. The residues that are most easily eliminated when polymeric materials are subjected to UV radiation include C=O (ketones, chloroketones, chlorocarboxylic acid, and acid chloride) (polyene) [Gardette et al., 1989; Khalil et al., 2016]. Tin-tyrosine complexes **1-3** with PVC were combined and after being exposed to radiation for up to 300 hours, IR spectra were taken (Fig.1).

C=O (1734 cm^{-1}) and C=C (1607 cm^{-1}) absorption bands were compared to those of the C-H bond (1328 cm^{-1}). The results are graph shown in Figs. 2 and 3. Given that the carbonyl and alkene indices for the pure film are significantly higher than those for the films with additives, it is clear that Triorganotin (IV) complexes **1-3** have significantly stabilized the PVC.

Weight Loss of PVC films

C-C, C-H, and C-Cl bonds, which make up PVC chains, do not exhibit any absorption peak wavelengths that are longer than 190–220 nm. Nevertheless, the impurities that are introduced throughout the polymerization and processing process start the photodegradation process and generate primary radicals. Dehydrochlorination and the creation of HCl are the results

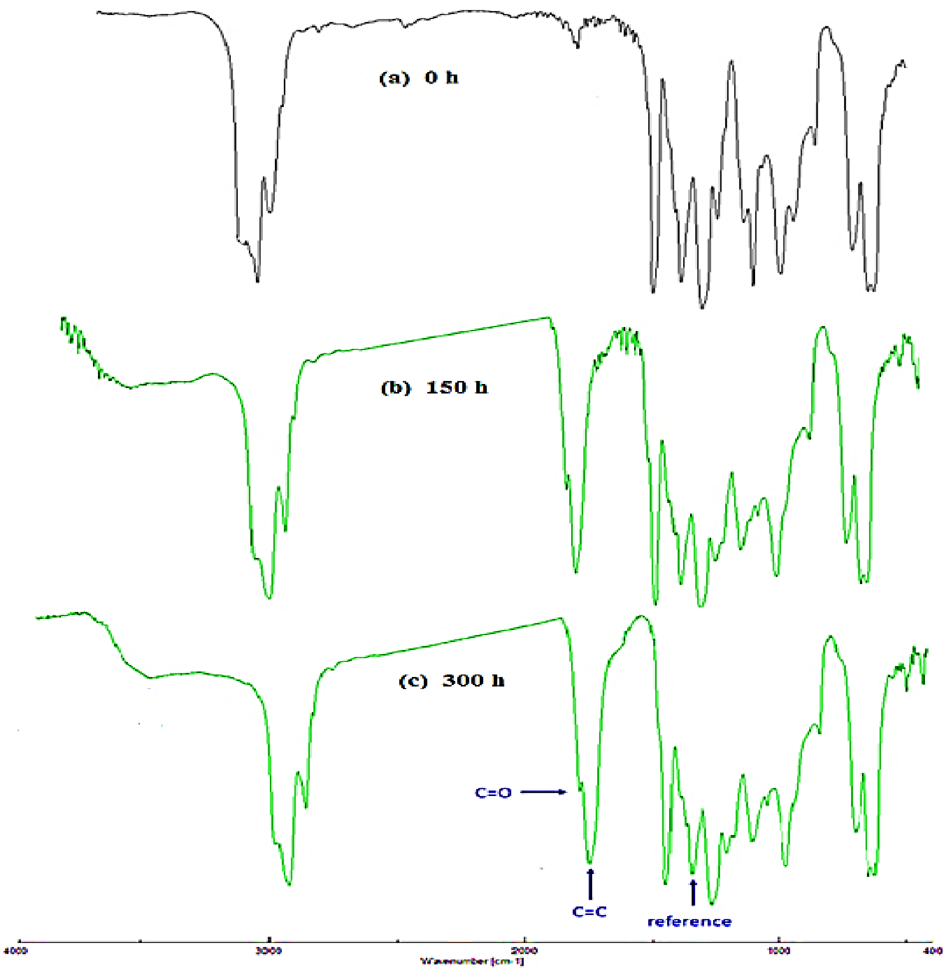


Fig. 1. FT-IR spectra of PVC film containing Me_3SnL complex at 0, 150 and 300 hours of irradiation.

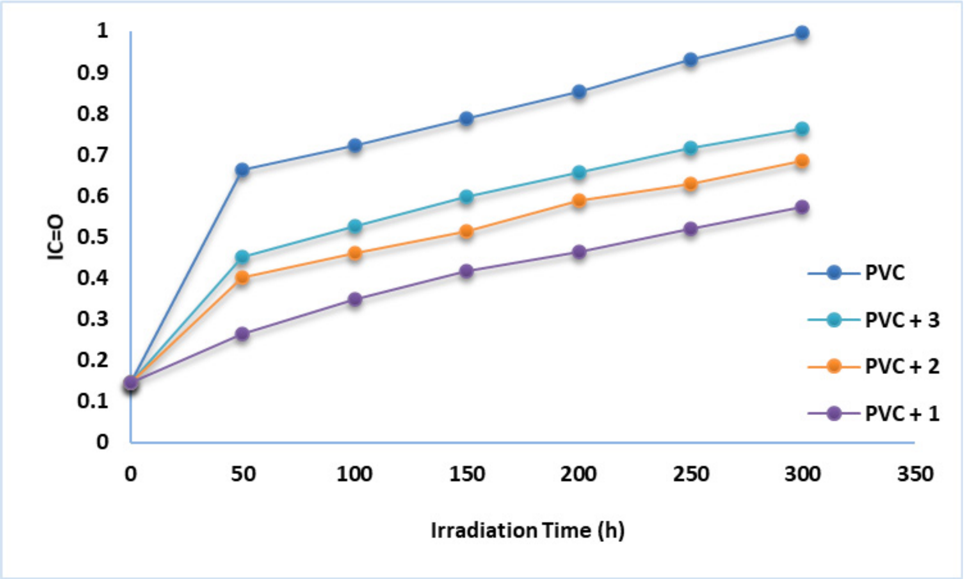


Fig. 2. Impact of radiation exposure period on PVC film's IC=O.

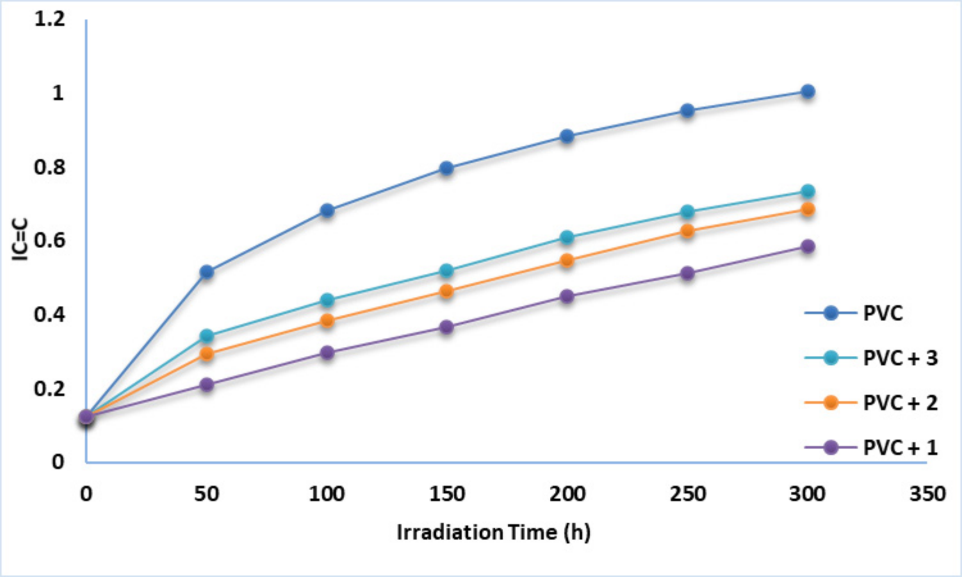


Fig. 3. Impact of the radiation time on the PVC films' IC=C.

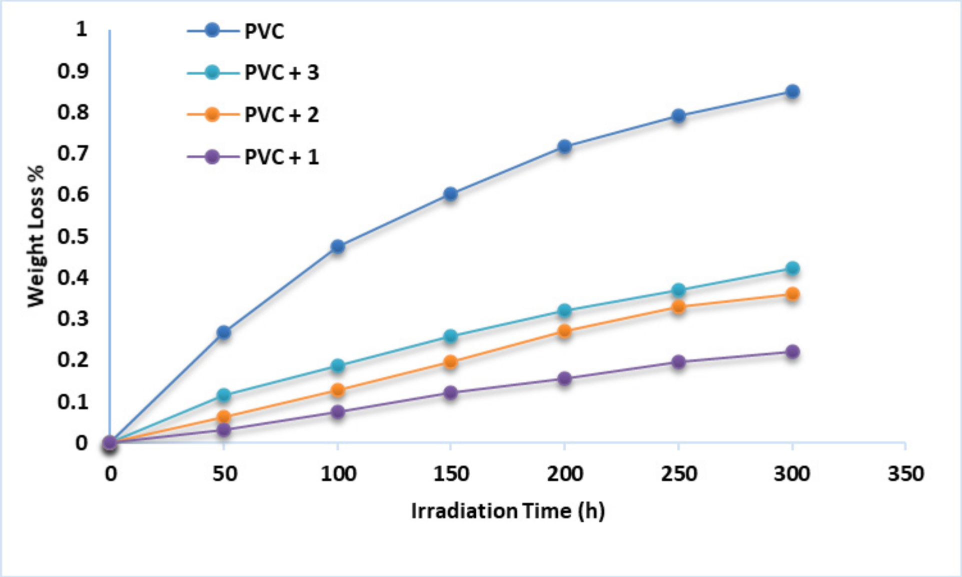


Fig. 4. Shows the effect of irradiation time on the weight of PVC films.

of these processes. The photodegradation of PVC is then sharply accelerated by the presence of HCl, resulting in low photostability [28,30]. Ketone and hydroperoxide groups, which are chromophore groups, are produced in polymer chains during polymerization and processing techniques like extrusion. These groups absorb UV and increase the photosensitivity of polymer chains [Sawyer et al., 2008]. The polymer chains incorporate chromophores. The presence of the chromophore group in the polymer structure raises light absorption and lowers photostability. Exposure of PVC to heat, light and humidity leads to autocatalytic dehydrochlorination. Hydrogen chloride (HCl) removal results in color change, unsaturated fragment formation, significant changes in mechanical and physical characteristics, weight loss, and a reduction in molecular weight [Pospíšil et al., 2006, Jafari et al., 2009]. Figure 4 demonstrates that the higher

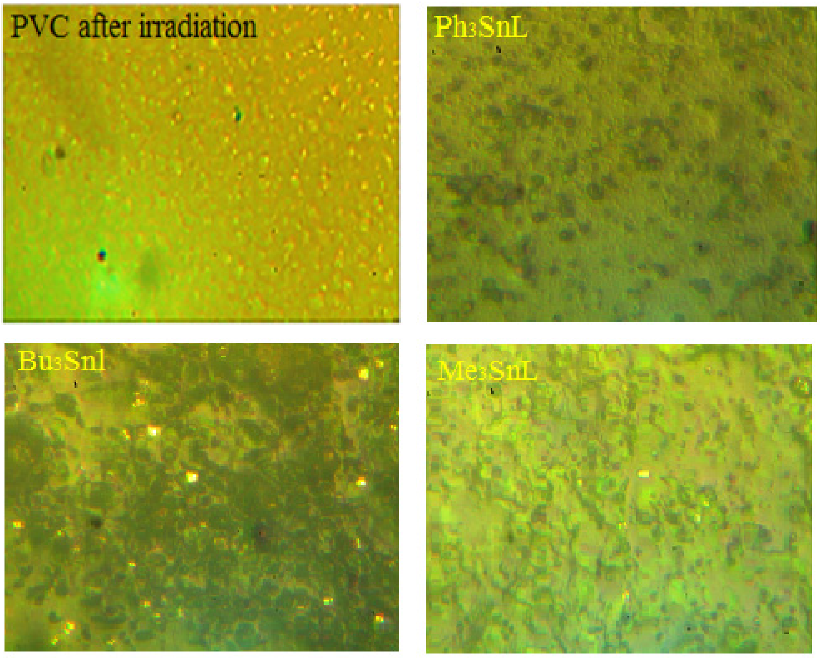


Fig. 5. Microscope images of (PVC + complexes) films after 300 h irradiation

the weight reduction, the longer the irradiation period. The weight loss of PVC films containing triorganotin (IV)-tyrosine complexes is smaller than PVC blank. Complex **1** was obviously the most efficient PVC stabilizers due to being the least steric hindrance among numerous additives studied, therefore functioning as a higher photostabilizer than the others.

PVC Surface Morphology

Effective surface roughness and the emergence of black spots, cracking, and other damage caused by photodegradation in PVC may be monitored using microscopy. Prior to irradiation, optical microscope photographs of the polyvinyl chloride revealed very few black patches and a smooth surface with no apparent defects. The removal of HCl is a major cause of surface damage to polyvinyl chloride [Sawyer et al., 2008; Valko et al., 2001]. The surface degradation was less apparent in films containing triorganotin (IV)-tyrosine complexes because the tin atom assists in the elimination of HCl. as seen in figure 5.

The films are imaged in two and three dimensions using Atomic Force Microscopy (AFM). Bond breaking occurs as a result of long term irradiation, leading to a rough and cracked surface [Kara et al., 2014; Shinato et al., 2020; El Hetti et al., 2019]. Comparing the results obtained for the films combined with triorganotin (IV)-tyrosine complex additives to those for the surfaces of the irradiation polymers, as shown in Fig. 6, the roughness factor (Rq) for the surfaces of the irradiated polymers was typically high.

The pure PVC that had been exposed to radiation showed significant irregularity, including white spots, grooves, and lumps, which suggested severe photodegradation. Following irradiation, the surface of the PVC containing the triorganotin (IV)-tyrosine complexes was smoother and had less cracks than the blank polyvinyl chloride. These fractures may occur as a result of chain crosslinking and the evaluation of HCl and other volatile degradation chemicals (Figure 7) [El-Hiti et al., 2021, Shi et al., 2008; Hashim et al., 2018].

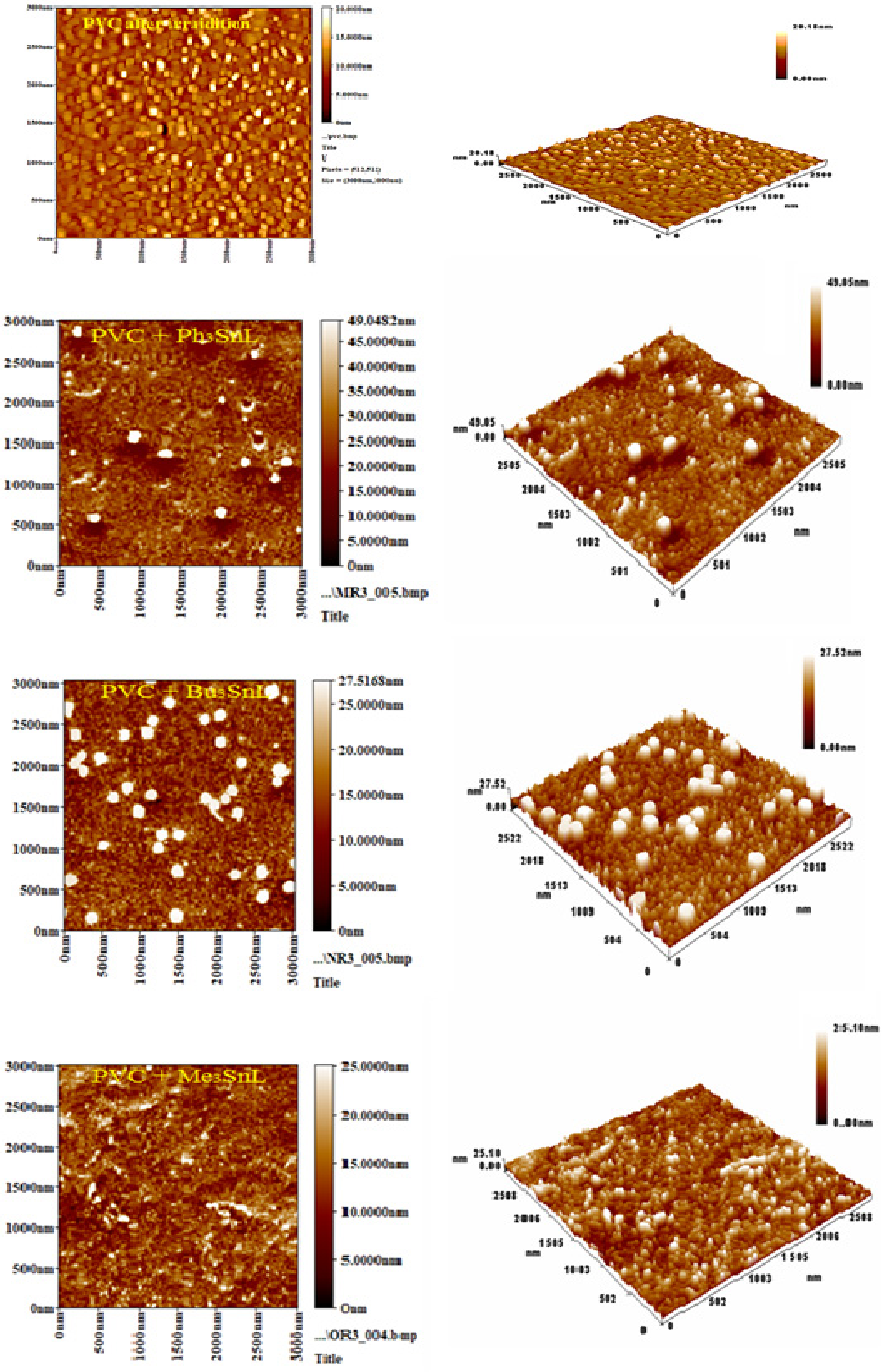


Fig. 6. After 300 hours of radiation, complexes are evident in two and three-dimensional AFM pictures of PVC blank and films.

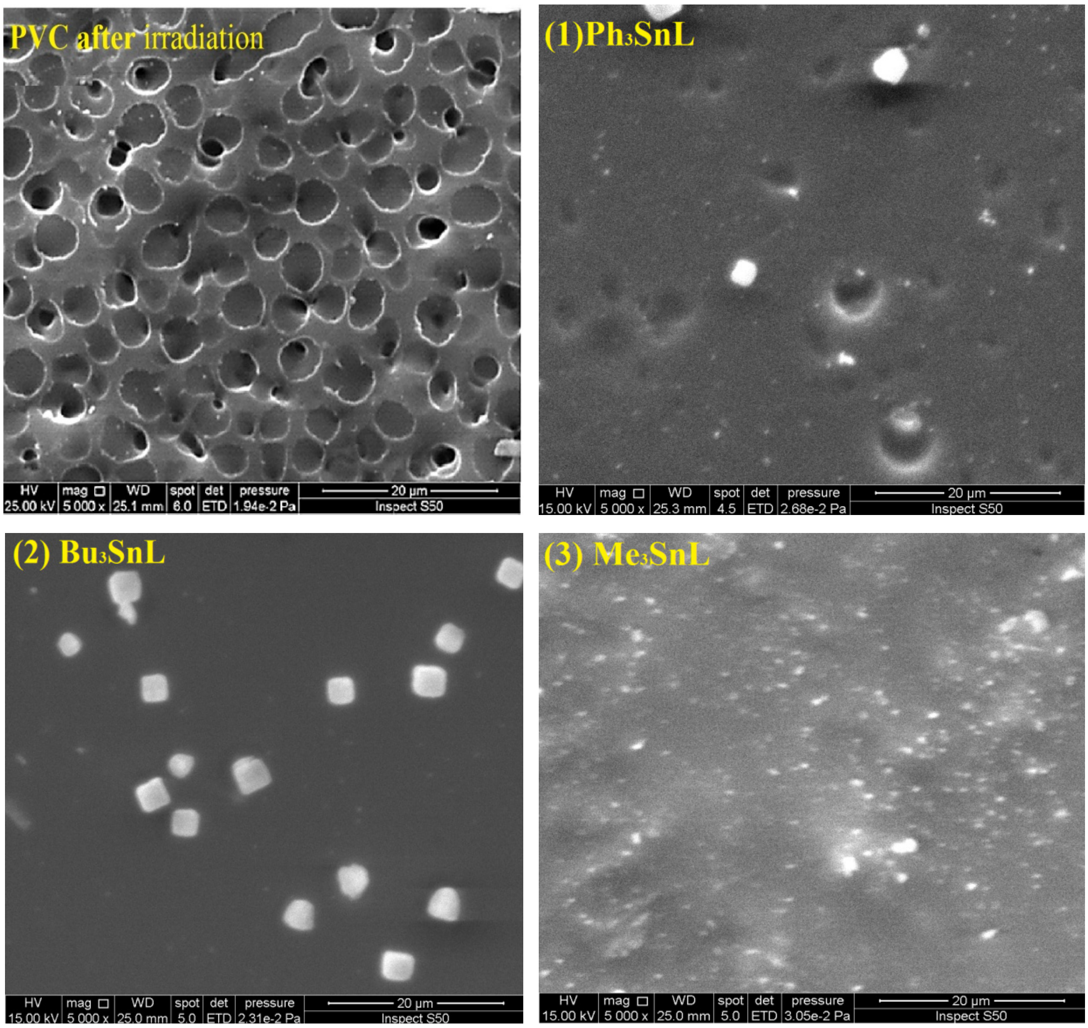


Fig. 7. SEM images for PVC films after irradiation at 20 µm magnification.

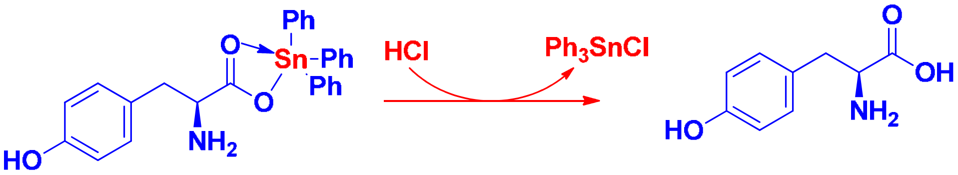
Suggested Mechanisms for PVC Photo stabilization by Triorganotin (IV)-Tyrosine Complexes

Organotin (IV)-tyrosine complexes stabilize PVC in a variety of ways, including absorbing UV light and scavenging free radicals. Additionally, the tin atom in the additions is very acidic and may neutralize the HCl produced during the dehydrochlorination, as shown in Scheme 2. Trimethyl tin (IV) demonstrates the most remarkable photostabilization among the synthesized compounds that stabilized PVC [Fadhil et al., 2022].

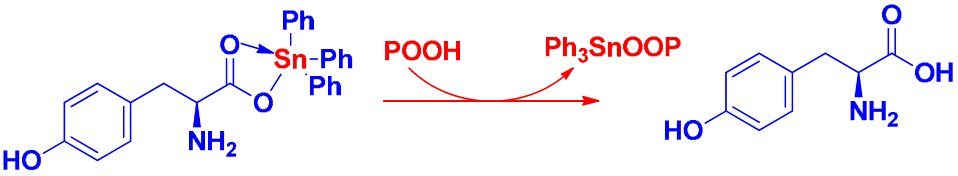
Hydroperoxides are well known for having a negative effect on PVC chains, resulting in photooxidation [Hadi et al., 2019]. Because the synthesized triorganotin (IV) compounds may breakdown hydroperoxides, they can protect PVC films from photooxidation, as shown in Scheme 3.

Organotin (IV) compounds have the capacity to serve as radical scavengers when a chromophore (POO) is present [Yousif & Haddad, 2013]. Triorganotin (IV) molecules interact with the polymeric surrogate radicals of chromophores (POO) [Mohamed et al., 2021]. The influence of the absorbed energy may be neutralized, stabilized, and then distributed over a large number of atoms by the resonance of aryl groups.

The polarized N and O atoms of the amine and carboxylate moieties, respectively, of the tin (IV) compounds and the polarized carbons of the C-Cl bonds in PVC, may work



Scheme 2. Trimethyltin (IV) -Tyrosine Complex as HCl Scavengers.



Scheme 3. Trimethyltin (IV) -Tyrosine Complex Acting as a Peroxide Decomposer.

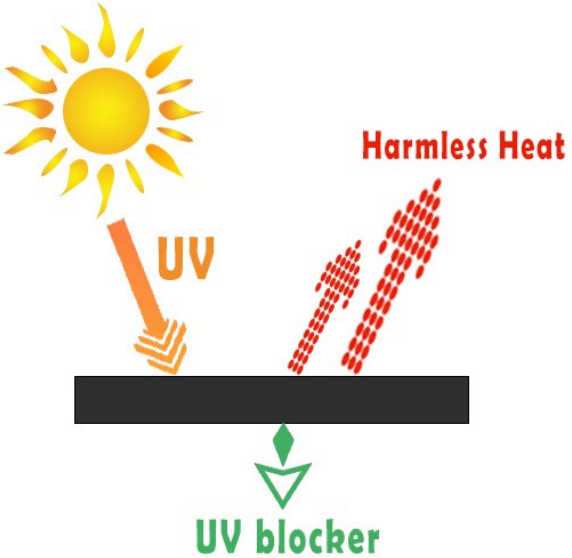


Fig. 8. Photoprotection process of organotin (IV) tyrosine complexes.

together to stabilize the polymeric polymers. This coordination promotes the conversion of excited state energy into a stable level in the polymeric chains [Balakit et al., 2015; Hadi et al., 2019; Bufaroosha et al., 2020].

Sun UV light provides the energy needed to initiate the incorporation of oxygen into the polymeric chains. Plastics are degraded into small polymeric fragments and then metabolized by microorganisms in the surrounding environment. Microorganisms tend to convert the polymeric chain carbons to either carbon dioxide or biomolecules. However, such a process is very slow. Plastic natural degradation is initiated through photodegradation followed by thermooxidative degradation as shown in figure 8. UV absorbers play an important role in absorbing harmful radiation from light and dissipating it as harmless thermal energy. In addition, they block the formation of free radicals that are produced at the early stages of degradation [El Hiti et al., 2022].

CONCLUSION

Three organotin (IV) tyrosine complexes have been produced and evaluated as PVC additives. The additives were applied sparingly and showed to slow down PVC photodegradation dramatically. In the presence of additives, the development of functional groups, weight loss, and surface deformation were all significantly inhibited compared to the pure film. The organotin (IV) tyrosine function as energy quenchers, absorbers of damaging radiation, and scavengers for active species like peroxides, volatiles like hydrogen chloride and volatiles. Being the additive with the least steric restriction among the several investigated, complex (Ph3SnL) was the most effective PVC stabilized and performed better as a photostabilizer than the others.

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CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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