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RESEARCH PAPER

Studying the Photostabilization activity of Poly(Vinyl Chloride) Films containing 4-amino-5-(((5-methyl-1H-benzo[d]imidazol-2-yl)thio)methyl)-2,4-dihydro-3H-1,2,4-triazole-3-thiol with a dibutyltin Complex

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Abstract

A new traiazole derivative (4-amino-5-(((5-methyl-1H-benzo[d]imidazol-2-yl)thio)methyl)-2,4-dihydro-3H-1,2,4-triazole-3-thiol, (L), was employed as a chelating ligand to form a dibutyltin chloride complex and improve the poly(vinyl chloride) (PVC) properties. The doped PVC films were characterized via FT-IR, UV-Vis spectrum, elemental analyses (C, H, N, and M (metallic)), and magnetic susceptibility and conductivity measurements. These characterizations were conducted at room temperature, and it was disclosed that the chelating ligand rules as a bidentate chelate. The photostabilization examination of plain and L-doped PVC films was conducted in the presence of ambient air using the accelerating weather tester, where the doping ratio was fixed to 0.5 wt.%. The photostabilization performance of the additive was evaluated by tracking the indexes of carbonyl (I_{CO}), polyene (I_{PO}), and hydroxyl (I_{OH}), and weight loss relationship with irradiation time. It was noticed that the values of I_{CO}, Ipo, and I_{OH} increased as the irradiation time increased, where this improvement relied on the presence of the Bu_2SnL complex.

Keywords: photochemistry; triazole; organotin complexes; PVC; photostability

INTRODUCTION

Poly(vinyl chloride) (PVC) is classified among the vastly utilized polymers due to its valuable properties; the growth of PVC production is attributed to the continuous expansion of its application fields (Naif, 2011). This polymer showed remarkable physical and mechanical properties, which promoted it to multiple industries, such as food foiling, blood bags, medical devices, wiring insulations, boots, window frames, automotive interiors, credit cards, packaging, and synthetic leather (de Souza et al., 2019) . Regardless of its wide techno-economic significance, PVC still, however, struggles with many obstacles, including poor stability when exposed to heat (Su et al., 1997). As PVC suffers degradation, the polymer's

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color turns from yellow to dark brown because of the unsaturated bonds. This change is associated with a reduction in stability against various solvents due to weak cross-linking and rapid deterioration in the mechanical properties (Al-Dossary et al., 2010) Photodegradation processes, such as photolytic, photooxidative, and thermo-oxidative reactions, occur on the surface of natural and manufactured polymers when they absorb UV radiation (Haddad, 2019). To avoid plastic degradation because of UV light exposure, UV stabilizers have been developed and added to the polymer to inhibit the photoinitiation processes (Salman et al., 2018). PVC degradation can be reduced by applying thermal stabilizers in four mechanisms: terminating the released HCl gas due to degradation, changing the labile chlorine in PVC, elapsing the free radicals produced throughout degradation, and, finally, interaction with the conjugated polyenes within PVC's chains (Wang et al., 2019). Reactions of oxidation could be tracked by the growth of C=O absorption peak at 1720 1/cm (Gesenhues, 2000). Various additives have been used to improve the photostability of polymeric films, such as plasticizers, heterocycles, aromatics, and organometallics (Ali et al., 2016). There are numerous light stabilizers and the nature of their work's mechanism is highly reliant on the absorption of UV light, such as radicals scavengers, excited state quenchers, light screeners, and peroxide decomposers (Hussain et al., 2019).

1, 2, 4-Triazole represents an attractive group of heterocyclic components that have three nitrogen atoms in a five endings ring, where its sub-derivatives are identified for their biological activates. These derivatives have vast biological and pharmacological properties (Abed et al, 2021), which allow them to engage in many medical applications (Singh et al., 2011). Furthermore, 1,2,4-Triazole's derivatives exhibit intense photo- and electro-luminescence (Gusev et al., 2011). In general, triazoles are considered noticeable coordinating ligands since they combine the hard nitrogen and soft sulfur atoms' characteristics in the thioamide group. These ligands are active to coordinate with multiple metal ions due to the presence of donor groups (Ahmed, et al., 2021).

One of these additives is organotin complexes; the main use of organotin (IV) compounds in this field is to stabilize the PVC against UV light (Vymazal et al., 1991), where they rule as antioxidants when PVC is exposed to the ultraviolet light (Rabinovitch et al., 1986). In the present study, an effectual and simple synthetic method was applied to produce high-quality organotin complexes that were applied to improve the PVC photostability. The activity of prepared complexes as photostabilizers after exposure to UV light for 300 h was tested, where different factors were considered to show the change after filling these additives. There are many advantages of using this type of fillers; these are represented by their low price, easy preparation, low eco bad impact, and availability.

MATERIAL AND METHODS

PVC is a white, odorless, and crystalline powder, which was supplied by Petkim Petrokimya company (Istanbul, Turkey) with a purity of 97%.

All complexes were characterized by elemental analysis, ultraviolet-visible (Uv-Vis) spectroscopy, melting point, Fourier transform infrared (FTIR) spectroscopy, magnetic susceptibility, and molar conductivity measurements. The microanalytical data elemental analysis was collected using Euro EA3000 and AA-680 Shimadzu atomic absorption spectroscopy. FTIR spectra of the synthesized complexes were recorded on a CsI disc using a Shimadzu and Perkin Elmer FTIR spectrometer. The electronic spectra of synthesized ligands and ligands-derivatives in the solution state were recorded on a Uv-Vis (1800 PC Shimadzu spectrophotometer). Magnetic susceptibility measurements of the complexes were made by using Balance Johnson Mattey Catalytic System division at 25 °C. The melting point of solid products was determined using Gallen Kamp M.F.B-60 apparatus.

Diorganotin(IV) complex was synthesized by dissolving the raw material in molar ratios of 2:1 L:M, respectively, of Bu_2SnCl_2 in methanol with drop-wise addition of methanolic solution, stirring for 10 minutes, and refluxing for 8 hours. The preparation was conducted at room temperature and atmospheric pressure. The resulted mixture was filtered, and white powder was collected upon recrystallization from methanol, which, ultimately, was characterized using analytical and spectroscopical methods.

Solutions of polymer were prepared by dissolving 5 gm of PVC in 100 ml of THF, which were stirred for 30 min until a clear solution formed. Then, the solution was poured onto glass plates to prepare 40µm thick PVC films, where the thickness was estimated by a micrometer type 2610 A, Germany. The solutions were left to evaporate for a whole day at room temperature in order to remove the solvent and obtain polymeric films (Mohammed et al., 2021). The homemade frame was prepared by gluing laboratory glasses slides onto regular glass sheets to design small sinks of a volume capacity 4 ml.

A UV Light source of a spectrum range 290–360 nm was used to irritate the PVC films and simulate weather aging conditions, where a wavelength of λ=313 nm was applied. An accelerated weather meter (QUV tester) was employed for this purpose and the examination took place at room temperature. To ensure equal intensity exposure of the incident light on tested PVC films, the films were frequently rotated.

In a process to monitor the PVC films' photodegradation, a 4200 JASCO FTIR spectrophotometer of range 400−4000 cm^{-1} was utilized. As the degradation of polymeric compounds can be caused by ultraviolet irradiation (Fizer et al., 2017), absorption of C=C, OH, and C=O groups was evaluated to track PVC degradation (Al-Juibouri et al., 2013). This absorption was estimated from the indexes of carbonyl (I_{CO}), polene (Ic=c), and hydroxyl (I_{OH}). Hence, changes in the IR absorption bands of carbonyl, polyene, and hydroxyl groups at 1722 cm^{-1}, 1602 cm^{-1}, and 3500 cm^{-1}, respectively, were tracked and compared to the CH_2 group's reference peak at 1328 cm^{-1}. The above-mentioned indices were estimated via the band index method as illustrated in Equation 1. Here, the functional group index (I_s) relies on the peaks absorbance, particularly the under-investigation (A_S) and reference peak (A_r) peaks (Yousif et al., 2011).

$$I_S= A_S/A_r \qquad (1)$$

where A_S is the absorbance of peak under-investigation, A_r is the absorbance of reference peak, and I_S is the index of the group that is under investigation.

One of the determination methods of stabilization efficiency is via measuring the weight loss ratio of photodegraded PVC films. In order to comprehend the impact of adding additives, the weight loss of PVC that contain the additives was compared with the pristine one. The ratio could be estimated by applying the following equation (Rabie et al., 2012) :

$$\text{Weight loss \%} = (W_1 - W_2 /W_1)\, 100 \qquad (2)$$

where W_1 and W_2 are the weights of the specimen before and after irradiations, respectively.

Viscosity is a physical property that can be employed to estimate the molecular weight of a polymer (Xiang et al., 2010) using the Mark-Houwink equation.

$$[\eta]= KM_V^{\alpha}.. \qquad (3)$$

where $[\eta]$ represents the intrinsic viscosity, while K and α are constants that rely on the polymer-solvent system at a specific temperature.

The polymeric solution intrinsic viscosity is determined using the Ostwald U-tube viscometer. The polymeric solutions were prepared via dissolving an amount of the polymer in a solvent, as explained above, and the time of the solution and pure solvent flow, t and t_o, respectively, were used in the equation below to calculate the specific viscosity (η_{sp})

$$_{re} \qquad \frac{\quad}{t_o}\,. \tag{4}$$

where η_{re} is the relative viscosity.

$$\eta_{sp} = \eta_{re} - 1 \tag{5}$$

The single–point measurements are changed to intrinsic viscosities (La Mantia and Morreale, 2008) using the following equation:

$$[\eta] = \left(\sqrt{2}/c\right)\left(\eta_{sp} - \ln\eta_{re}\right)^{1/}\,. \tag{6}$$

where C stands for the polymer concentration in the solution (gm/100ml).

Also, PVC’s molecular weight before and after the filling can be estimated by the intrinsic viscosity values of the polymeric solution when the polymer is dissolved in THF solvent.

$$[\eta] = 1.38*10^{-4} M\mathrm{w}^{0.77} \tag{7}$$

RESULTS AND DISCUSSION

The obtained complex was an off-white powder that has high stability for a long time under the atmosphere. Table 1 summarizes the analytical data and physical properties of the ligand and its derivative.

Table 1. The physical properties, elemental, and metal content for the ligand and its complex

Comp.	**Color**	**M.Wt g/mol**	**m.p^{0}C**	**Yield %**	**Molar ratio (M:L)**	**Elemental analysis Found (Calc.)**				**Metal% Found (Calc.)**	***Molecular* Formula**
						C	**H**	**N**	**S**		
L_2	Beige	292.0	256- 258d	61	----	45.01 (45.20)	3.85 (4.10)	28.18 (28.76)	21.47 (21.91)	----	$C_{11}H_{12}N_6S_2$
Bu_2SnL_2	off-white	846.7	236-238	67	1:2	42.77 (43.93)	4.67 (5.19)	19.32 (19.84)	14.66 (15.11)	13.48 (14.01)	$SnC_{32}H_{44}N_{12}S_4O$

d : decomposition degree

The characteristic bands of the ligand (L) were determined by FTIR spectroscopy for the free ligand and its complex, and their adsorption data are provided in Table 2. This ligand has thioamide groups (–N=C–SH or H–N–C=S) (Symal and Bari, 1984; Alias et al., 2008) and nitrogen of the azomethine. The analysis displays an obvious ν(S-H) peak at 2573 1/cm and ν(N-H) peaks at 3130, 3030, and 2981 1/cm due to strong hydrogen bonding vibrations indicatives of both thiol and thion groups. These two bands disappeared in the spectrum of the metal complex; the NH band shifted to lower frequency from the original peak at 3130 1/cm, and the two peaks at 3030 and 2981 1/cm of the ligand. This is more obvious by observing the thioamide band (I), which is mainly due to (δ NH + ν C=C); however, this band disappeared in the spectrum of the metal complex. The IR spectrum of the complex in Table 3 showed medium to strong bands at 1597, 1357, 975, and 744 1/cm that could be attributed to the vibration of thioamide bands from I to IV, respectively (Abdullah et al., 2007). The coordination of both N and S atoms to the metal is further indicated by observing that the band (IV) had no change in position and is more supported for this proposed coordination. Nevertheless, there are new weak bands appear at the regions 536 and 459 1/cm, which refer to M-N and M-S bands stretching (Alias et al., 2007), respectively. Other bands in the spectrum of this compound are displayed in Table 2.

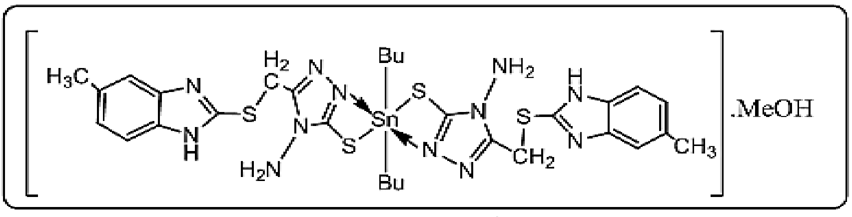
Table 2. FTIR Absorption data of the free ligand and its organotin complex.

Formal	**ν NH_2 Asym. Sym.**	**Thioamide I δ NH + ν C=N**	**Thioamide II νC=N+C=C**	**Thioamide III ν N--C--S**	**Thioamide IV ν C-S**	**ν M-N**	**ν M-S**	**others**
L	3270 3200	1597 154٧	1٣٥٧	9٧٥	7٤٤	---	---	----
But_2SnL	3270 3200	1640, 1612, 1558	١٣٧٢	975 v.w.	745	536	459	ν CH_3OH= 3320-3280 ν M-C=439

The UV-vis spectrum of the free ligand appeared in three absorption bands. The first and second absorption bands exhibited at 238 and 260 nm, which are corresponding to $\pi \rightarrow \pi^*$ transition. The third band is attributed to the $n \rightarrow \pi^*$ transition at 330 nm, which refers to the donor atom of S and N atoms in the C=N group (Joshi et al., 2019).

The absorption spectrum (200–600 nm) for the organotin complex was recorded in Dimethylformamide (DMF). The bands were marginally moved to a higher wavelength subsequent to complexation and exhibited at 30769, 38167, 41322 1/cm, which are corresponded to the intraligand charge transfer (ILCT). The molar conductivity for the organotin complex was measured in DMF at room temperature and found to be 8.3 µS/cm. The measurement of conductivity for this organotin complex was non-electrolytic. The magnetic moment of this complex is diamagnetic. From analysis data and spectroscopy techniques, and from all results, the octahedral form for this complex can be assumed.

The proposed structural model of this newly prepared complex, which was characterized by the physical and spectroscopic analysis, is shown in Scheme 1.



Scheme 1. The proposed structure of the organotin complex

When a UV light of wavelength λ=313 nm irradiates PVC films, photo-oxidation of PVC occurs and produces components with hydroxyl (OH), carbonyl (CO), and polyene (C=C) groups (Joshi et al., 2019). Peaks at 1604, 1724, and 3450-3400 1/cm appeared and are attributed to the formation of polyene, carbonyl groups, and hydroxyl band (Gardette et al., 1989; Boughattas et al., 2016; Hasan et al., 2015), respectively. These bands were compared with the reference peak at 1328 1/cm that refers to the CH_2 band in the PVC chain (Hassan and Otaiwi, 2008). The mentioned groups are used to measure the quantity of degraded polymer overtime when the sample is exposed to UV radiation while oxygen presents (Gaumet and Gardette, 1991). The increase in carbonyl index is a way to evaluate the extent of degradation; I_{CO} of PVC film with Bu_2SnL additives showed a slower generation rate of carbonyl index along with irradiation time compared to the PVC pristine sheet. Therefore, the Bu_2SnL complex is a more active Photostabilizer than the free ligand (L).

The changes in indexes values along the 300 h irradiation time for the blank and embedded PVC films are shown in Figures 1-3. The Ic=o, $I_{P=O}$, and $I_{O=H}$ indices were calculated in intervals of 100 h and plotted versus the irradiation time. During the photooxidation of PVC, carbonyl groups are formed, which extend the sheet's absorption to longer wavelengths. Thus, the light of wavelength between 200-700 nm could be absorbed; it is activating the singlet and triplet excited states, which exciting multiple consequences of photooxidation reactions (Maouz et al., 2020).

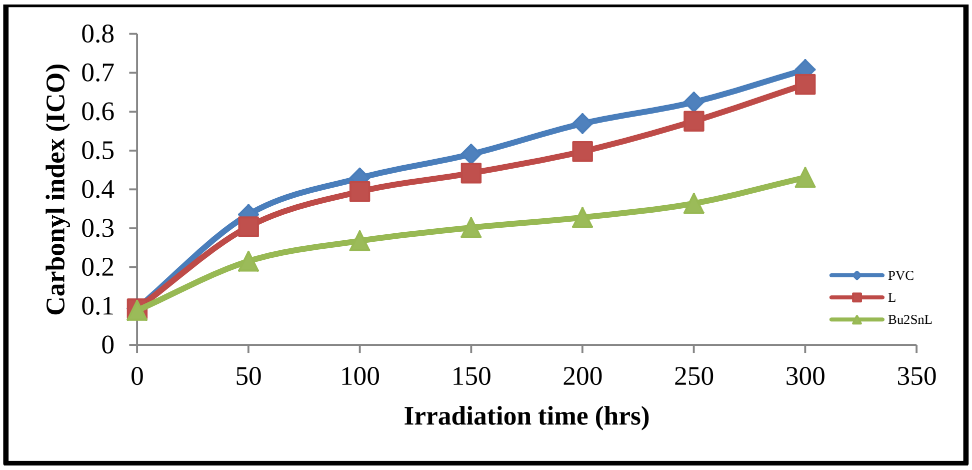


Fig 1. Relationship between the I_{CO} and irradiation time of plain and modified PVC films

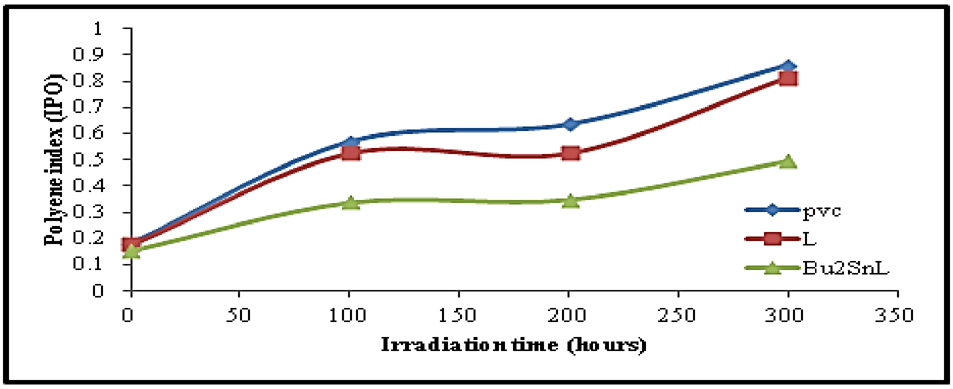


Fig 2. Relationship between the Ipo and irradiation time of plain and modified PVC films

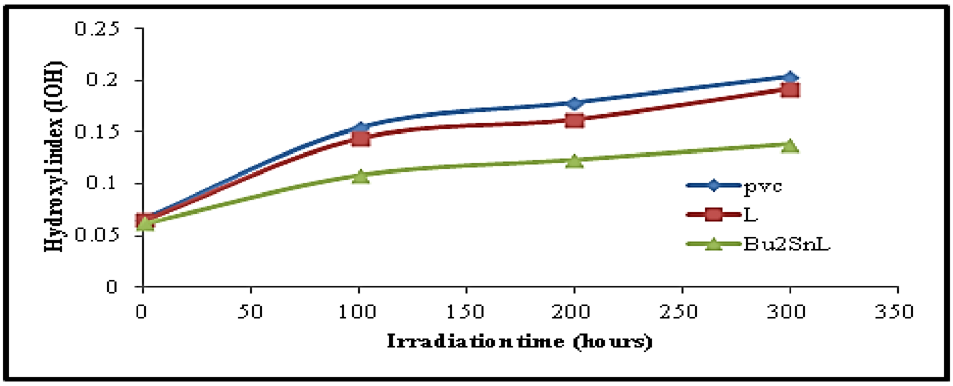


Fig 3. Relationship between the I_{OH} and irradiation time of plain and modified PVC films

After 300 h of irradiation, the $I_{C=0}$ value was higher in the case of the plain PVC sheet (0.70) compared with Bu_2SnL-PVC doped film (0.43). Additionally, the $I_{P=O}$ of the plain PVC film was 0.86, which is furtherly higher than -PVC doped film (0.49). Similarly, after 300 h, the hydroxyl index I_{OH} for the blank PVC film was (0.20) compared with the obtained for doped PVC film (0.13). The synthesized organotin complex, Bu_2SnL, increases the ability to absorb the UV light and rule as a remarkable UV absorber. The films efficacies followed the order:

$$PVC+Bu_2SnL > PVC+L > PVC$$

In this context, it was reported that around 70 % of the annually produced organotin compounds and their derivatives are applied as photo and thermal stabilizers in the plastics, and as catalysts in the silicones and polyurethane foams (Awad et al., 2016). However, the PVC is easily decomposing by heating, where certain organotins, such as mono and dialkylated derivatives, were filled to overcome this degradation (Maouz et al., 2020); diorganotin compounds are other types of stabilizers (Awad et al., 2016).

The weight loss that occurs in PVC film when irradiated to UV light could be utilized as a method of measuring the photodegradation degree (Okoro et al., 2011). The loss in weight changed depends on the presence/absence of fillers, where it is calculated by applying equation (2). The weight loss ratio relationship with irradiation time provides an evidence of photodegradation degree as shown in Figure 4.

From the figure, the plain PVC film exhibited the highest weight loss compared to other PVC films containing the Bu_2SnL complex. For instance, the weight loss ratios after 300 h irradiation were 0.42 and 0.23 wt.% for the pristine and Dibutyltin PVC films, respectively. These results indicate that complexes improved the photostability of the polymer. Once again, the performance followed the same previous order:

$$PVC+Bu_2SnL > PVC+L > PVC$$

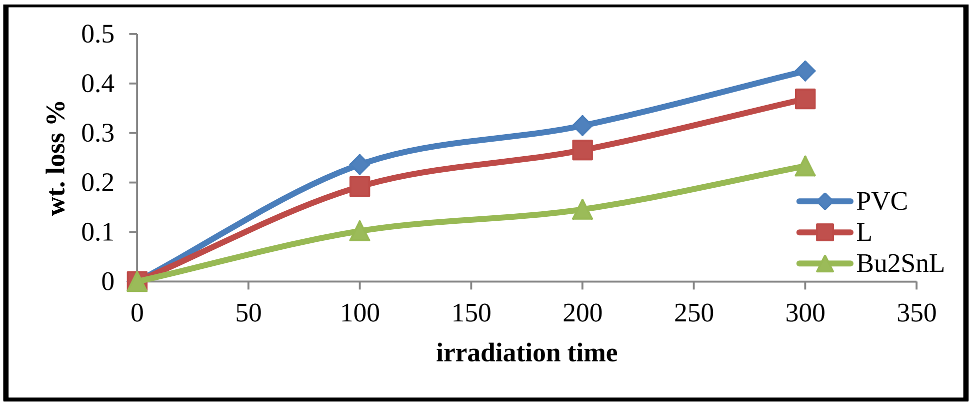


Fig 4. Variation of the weight loss of PVC films over the irradiation time of plain and modified PVC films

Measuring viscosity is an easy and popular method to estimate the average molecular weight of a polymeric substance (Hadi et al., 2019). This method is based on the proportional relationship between the polymeric solution viscosity and average molecular weight. The Mark–Houwink equation that was mentioned previously was applied in this work to estimate the relative molecular weight of PVC- THF solution at the testing temperature of 25 ºC.

The changes in PVC film's Mv after UV irradiation for 300 h (of 100 h intervals) are shown in Figure 5. A sharp reduction in the molecular weight can be noticed in the blank PVC film compared to those observed in PVC films that contained organotin complexes along with the irradiation time. For instance, the molecular weight average of the plain PVC sheet reduced from approximately 165929.1 to 21793.19 after 300 h of irradiation. In contrast, the decrease in Mv was lower for PVC sheets embedded with organotin complexes. The smallest reduction in Mv was remarked for the PVC film filled with dibutyltin complex, from 168888 to 79810.95.

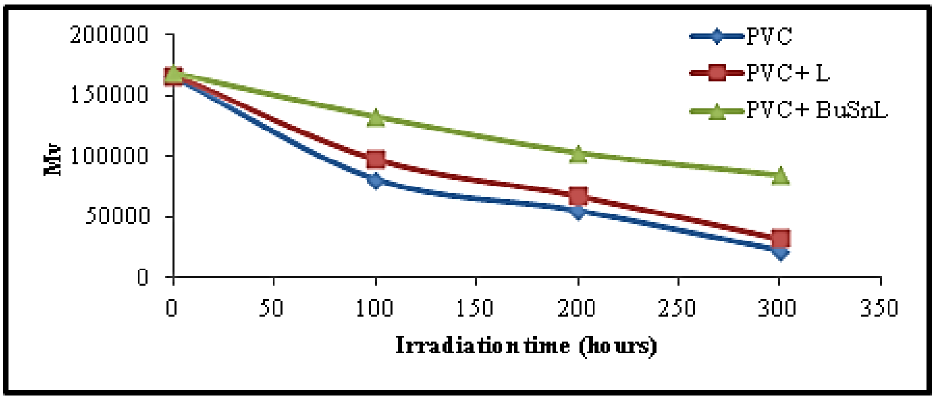


Fig 5. Variation of the viscosity average molecular weight and irradiation time of plain and modified PVC films

After irradiating samples with sunlight, the surface morphology and color gradually turn from white to chalky, and finally dark yellow. While crackles on the surface grow over the aging time (Mark, 2007) that concomitant discoloration of the polymer is due to polyene formation (Yang et al., 2017). This deformation of the surface is attributed to PVC's photodegradation due to dehydrochlorination (Decker and Balandier, 1981).

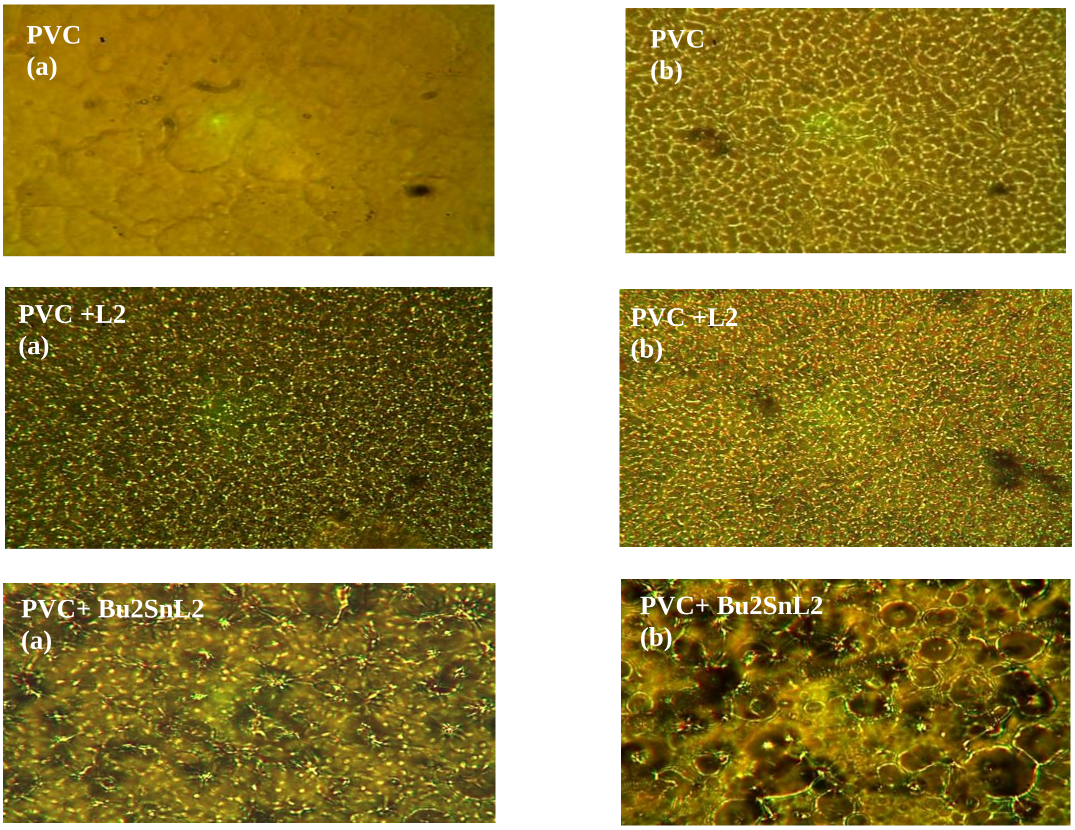
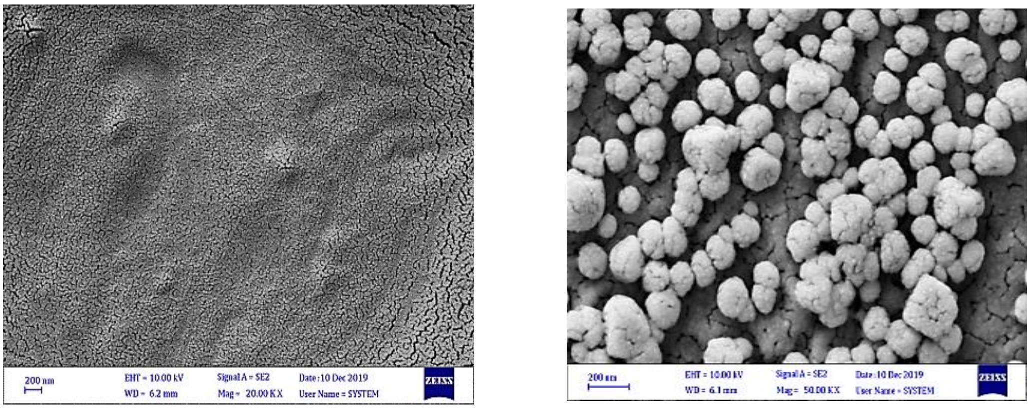
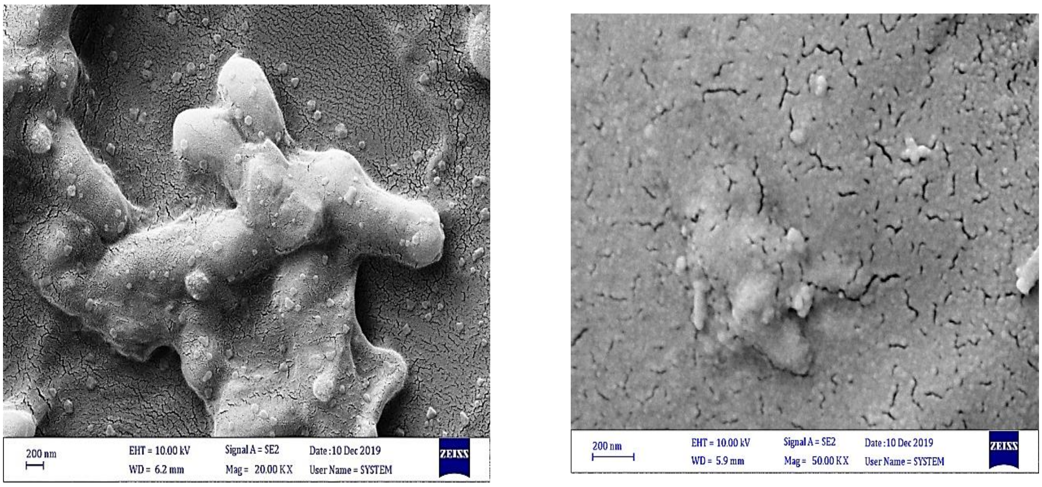


Fig 6. Microscopic images of PVC films (a) before irradiation, (b) after 300 hr irradiation time

The scanning electron microscope (SEM) images of PVC films are shown in Figure 7, the surface of pristine PVC was essentially smooth and neat before exposure to ultraviolet light. Images of PVC in different magnifications show rough and irregular microstructures on the surface of PVC (Mohamed et al., 2021). SEM analysis was also carried out to investigate the top surface and cross-sectional morphology (Ma et al., 2020).



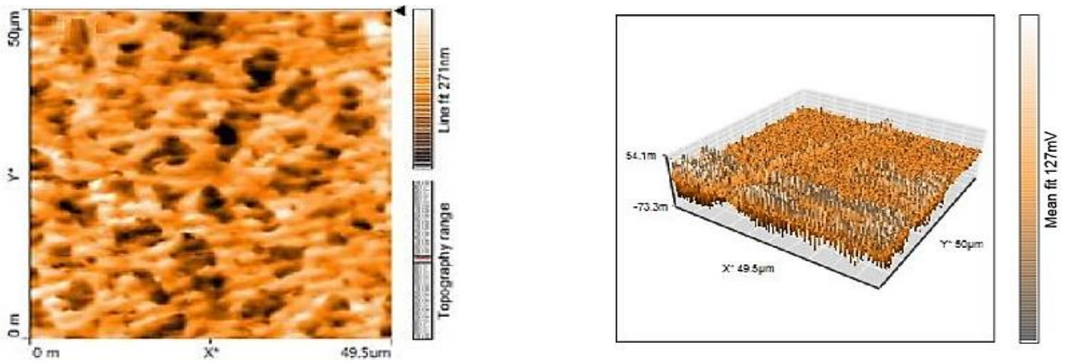
PVC (before 300 h) **PVC (after 300 h)**



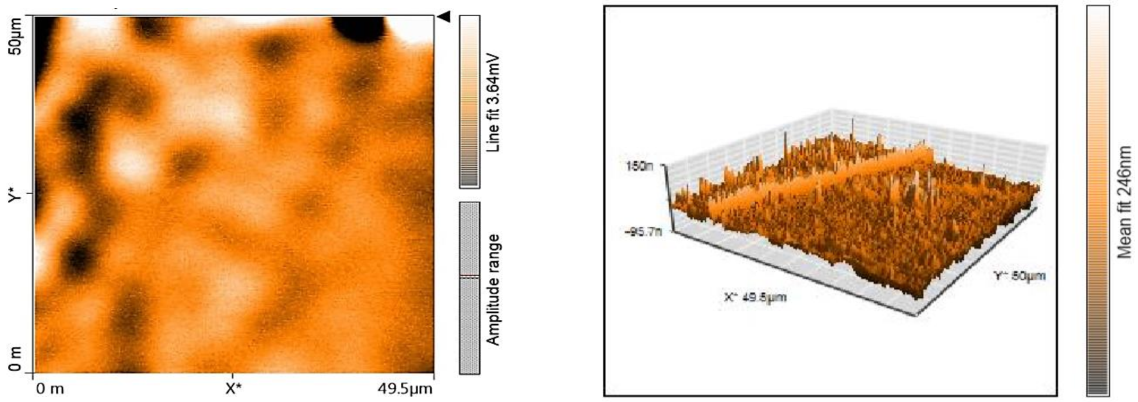
PVC + L **PVC + Bu_2SnL**

Fig 7. SEM images of plain and filled PVC films before and after 300 hrs irradiation time

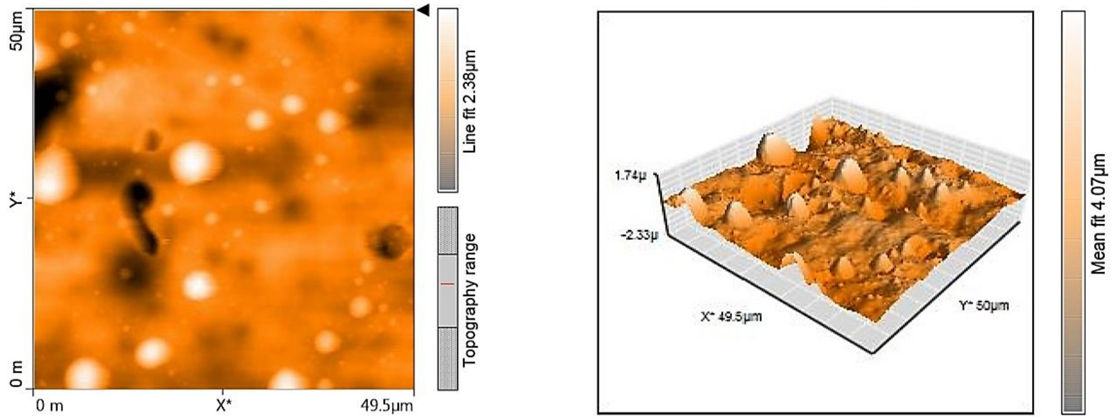
The roughness factor (R_q) of PVC films' morphology could be identified via the atomic force microscope (AFM) technique (Ahmed et al., 2018). This examination presents two- and three-dimensional topographic images (Su et al., 2000) as shown in Figure 8.



PVC (2D) PVC (3D)



PVC+L (2D) PVC +L (3D)



PVC+Bu_2SnL (2D) PVC + Bu_2SnL (3D)

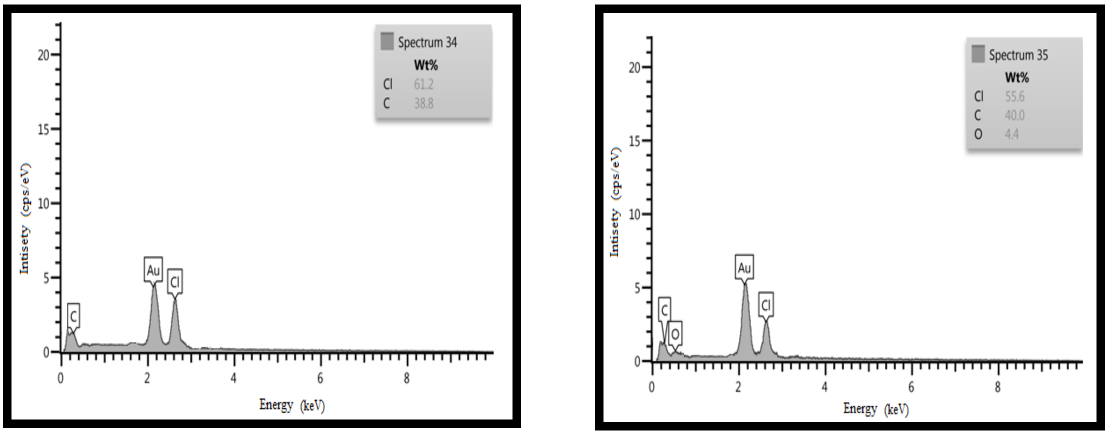
Fig 8. 2D and 3D AFM images of plain and modified before and after 300 hr irradiation time

The surface roughness factors (Rq) of irradiated PVC films were estimated and the data were listed in Table 4. The value of this factor for the pristine PVC was high (198.6) compared with the modified films (Rq =35.44–74.91). The high value of the Rq in the plain film case could be attributed to the high dehydrochlorination rates that result in a termination of the leachable residue from the polymeric sheets.

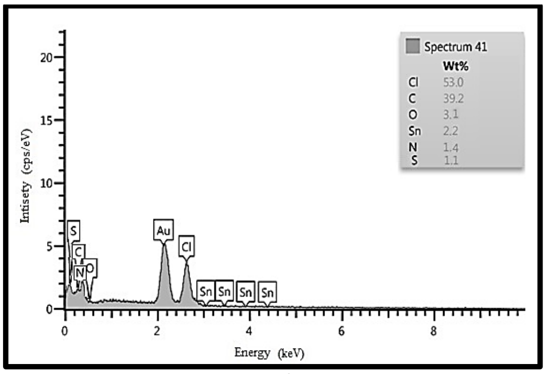
Table 4. Rq values of PVC films after irradiation

Films after irradiation	**Rq values**
PVC	198.6
PVC+ L	74.91
PVC+ Bu_2SnL	35.44

The Energy-dispersive X-ray (EDX) test was utilized to investigate the total chemical composition and distribution of particular elements for the plain and modified films (Ali, et al., 2016). The obtained spectra showed strong absorption bands, corresponding to the chlorine atom, in addition to the tin, sulfur, and nitrogen bands resulting from the organotin complexes, as shown in Figure 9.



(a) EDX pattern of PVC (b) EDX pattern of PVC after 300h

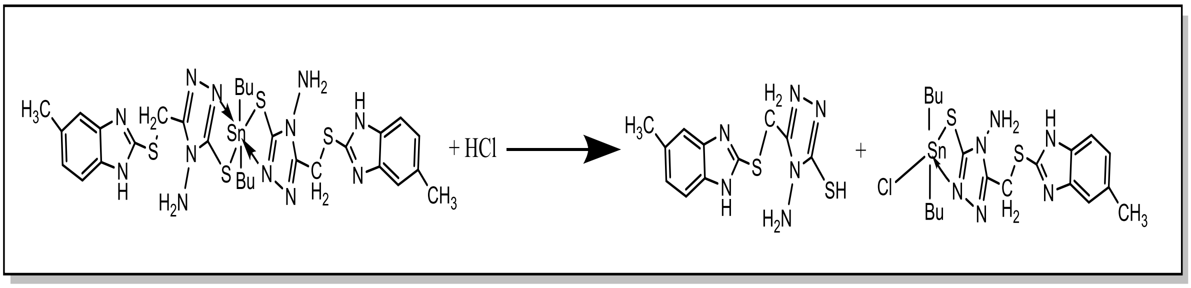


(c) EDX pattern of PVC+ Bu_2SnL

Fig 9. EDX of the tested samples

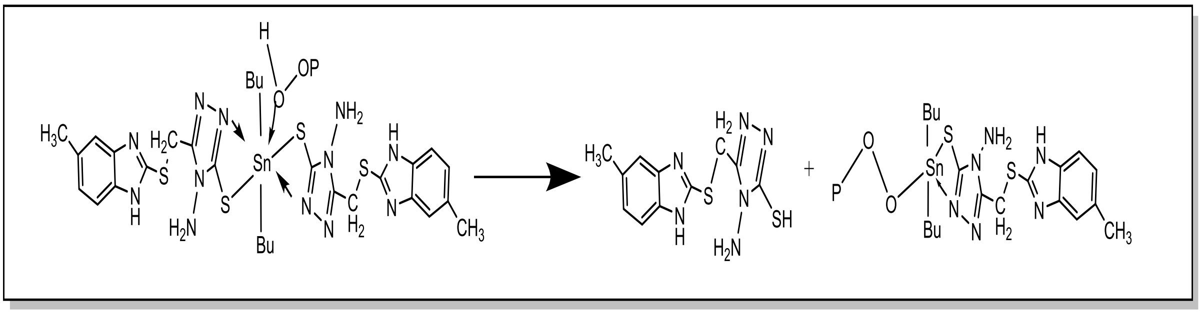
The dibutyltin (IV) complexes performed as photostabilizers in this work for PVC prepared films, where Sn(IV) worked on reducing PVC photodegradation. However, these compounds could stabilize the films by multiple mechanisms. Here, tin could affect the stability because it is a strong Lewis acid, where it has secondary stabilization characteristics and works as an HCl scavenger as shown in Scheme 2. The main expected reason for the photostabilization is the replacement of chlorine atoms that exist within the PVC structure by carboxylate oxygen groups. Based on previous studies, many organic compounds were reported as long-term PVC stabilizers (Folarin and Sadiku, 2011). Depending on the reported outcomes, the stabilizer's performance can be engineered in accordance with the carbonyl and hydroxyl concentrations changes (Watheq et al., 2020), where the improvement in this work followed the order below:

$$Bu_2SnL+PVC > L+PVC > PVC$$



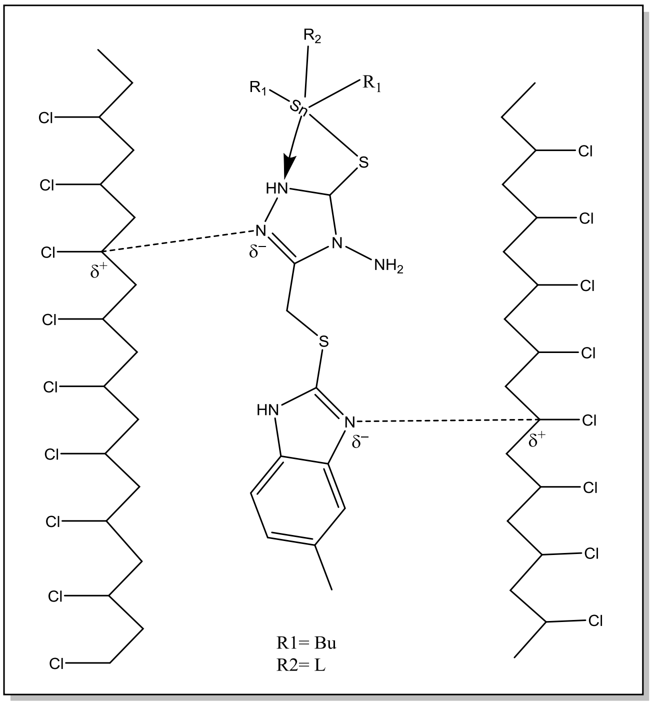
Scheme 2. Organotin complexes act as HCl scavengers

The other mechanism assumes the photooxidation of PVC occurs in the presence of hydroperoxides. Metal chelate could be called photostabilizers for the PVC through decomposing the peroxide and quenching the excited state (Gugumus et al., 1990). Hence, it is anticipated that these compounds behave as peroxide decomposers as shown in Scheme 3.



Scheme 3. Organotin complexes as peroxide decomposers

The final assumption considers an attraction between organotin(IV) complexes' polarized bonds and the C-Cl bonds of PVC chains is taking place, which stabilizes the polymer as shown in Scheme 4. This attraction affects the stability of PVC by converting the energy level from the excited state to a lower level that has no harmful impact on the polymeric chain.



Scheme 4. Organotin complexes as primary stabilizers

CONCLUSION:

In this study, a dibutyl tin was used as a filler in the polymer for the purpose of improving the photostability properties of PVC films. To comprehend the impact of this additive, indexes of carbonyl, hydroxyl, and polyene, $I_{C=O}$, I_{OH}, and $I_{C=C}$, respectively, and the weight loss methods were applied to investigate the photodegradation of PVC films. The plain and modified PVC films followed the order below in the photostabilization activity.

$$PVC+Bu_2SnL > PVC+L > PVC$$

Stabilization mechanisms of PVC films were presented to explain the occurred improvement; namely: HCl scavenging, peroxide decomposers, primary stabilizers, free radical scavenger, and UV absorption.

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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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