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Kinetics study of photo-degradation of poly(Vinyl Chloride) films in presence of organotin(IV) complex derivatives

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Abstract: As polymers became very important in our lives, their negative impact on general health and the environment raised a serious issue. Here, enhancing their life term is presented as a compromise solution between the need and harm. In the study, six PVC films, the plain and five filled with improvers, underwent radiation exposure for 300 hours at room temperature to investigate their photodegradation rates. The modified films were embedded with organotin(IV) complex derivatives (Ph_3SnL, Ph_2SnL_2, Bu_3SnL, Bu_2SnL_2, and Me_2SnL_2 (where L is levofloxacin)), and their effectiveness was evaluated. The PVC films were compared before and after exposure to various tests including UV-Vis spectroscopy, gel content analysis, theoretical calculations, and EDX microscopy. Findings indicated that the presence of organotin(IV) complex derivatives, particularly Ph_3SnL, notably decreased UV light absorbance and the amount of gel content in PVC sheets in comparison to untreated PVC. Furthermore, EDX analysis showed that the PVC-Ph_3SnL blend exposed to radiation exhibited the highest chlorine content, reaching 30 %. This blend demonstrated superior efficacy in stabilizing the polymeric materials.

Key words: PVC films, photodegradation, organotin(IV) complex derivatives, UV impact, gel content analysis, stabilization

1. Introduction

Over the years, there has been a steady increase in the production of plastics worldwide, primarily due to their extensive use in a variety of sectors and industries. Because plastic products are abundant,

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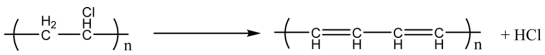
versatile, lightweight, resistant to deterioration, and reasonably priced, they provide consumers with significant convenience.[1,2] PVC, or poly(vinyl chloride), is a material that is widely used in both commercial and residential settings and finds application in a wide range of fields. PVC has characteristics like flexibility, rigidity, resistance to heat and weather, impact resistance, variable thicknesses, and a wide range of colors because of its inherent qualities. PVC is mostly used by the medical, electronics, automotive, construction, toys, and packaging industries.[3,4] Under extreme circumstances, PVC decomposes by dehydrochlorination in the presence of light, leading to the formation of macromolecules with C=C bonds. The following chemical equation represents the induction phase, which is the first stage of PVC dehydrochlorination:[5]



This degradation is inevitable. For instance, while PVC piping is often formulated with additives to mitigate damage from sunlight, it's recommended by most pipe manufacturers to protect PVC piping exposed to prolonged outdoor use. Studies show that UV aging of PVC pipe leads to a reduction in impact strength, yet the modulus of elasticity and tensile strength remain largely unchanged. Despite this, the essential qualities of PVC pipes, including pressure capacity and structural integrity, remain unaffected. UV degradation occurs once exposure to UV radiation starts and doesn't persist after termination. Knowing that fillers could represent a solution for this phenomenon, it's crucial to ensure that these additives are compatible with the PVC.[3] As the Additives are correctly selected, they could hold a critical role in improving various properties of PVC, including, clarity characteristics, thermal, electrical, color, light, and mechanical. These chemicals are typically blended with PVC through compounding methods.[6,7]

PVC exhibits inherent rigidity at standard temperatures due to close molecular proximity, facilitated by robust intermolecular interactions. The introduction of plasticizers into PVC causes these molecules to intercalate between PVC molecules, preventing them from close proximity. As a result, even under normal temperatures, polymer molecules remain separated, resulting in a softer texture.[8,9]

Dioctyl phthalate (DOP) is extensively employed as a plasticizer in the medical industry due to its exceptional efficacy, wide availability in a highly pure form, and cost-effectiveness. Other plasticizers such as di(n-decyl) phthalate (DnDP), tri n-hexyl citrate (BTHC), n-butyrul, and tri(2-ethylhexyl) mellitate (TOTM or TEHM) find applications in various medical contexts, including platelet preservation.[10,11] Thermal stabilization is crucial for PVC during high-temperature processing. Most heat stabilizers comprise metallic components that react with HCl and impede PVC breakdown. Metal salts and soaps are commonly utilized as heat stabilizers.[12,13] Mixed metal stabilizers are predominantly employed to shield PVC from the detrimental effects of UV light. DBL phosphate serves as a light stabilizer with UV-resistant properties. Light stabilizers are sophisticated compounds that, despite their higher cost, exhibit high effectiveness even at low concentrations (0.1–0.3 PHR).[12]

Usually, fillers are inert inorganic substances that serve to reduce the cost of manufacturing PVC and improve its mechanical qualities, including impact performance and fracture strength. They serve as a pigment and enhance the chemical resistance of PVC. The predominant types of fillers are calcium carbonate, titanium dioxide, talc, glass, and calcined clay.[14,15] Nevertheless, a number of novel tin complexes incorporating the fusidate unit were synthesized and evaluated as photostabilizers for PVC.[16]

In this paper, the chemical kinetic method was used to study the degradation phenomenon of modified PVC by examining the stability of radiation-exposed PVC films. Five organotin (IV) complex derivatives were utilized to enhance the stabilization of PVC under radiation exposure. Different techniques were applied to examine the modification and compare the properties of PVC films with and without the complexes. The research findings may pave the road for future industrial applications.

2. Experimental

2.1. Materials and apparatuses

All the organotin(IV) complexes, Ph_3SnL, Ph_2SnL_2, Bu_3SnL, Bu_2SnL_2, and Me_2SnL_2 (where L is levofloxacin), have been synthesized, characterized, and applied as PVC photostabilizers. *Scheme* 1 shows the structures of the complexes, while the preparation of PVC films was presented in our previous research.[17] The synthesized films underwent comprehensive characterization to evaluate their properties. The UV-Vis absorption spectra of both the unmodified (blank) and modified PVC sheets were acquired using a Shimadzu UV-1601 spectrophotometer subsequent to irradiation. The irradiated modified PVC film surface morphology was examined by scanning electron microscopy using a SIGMA 500 VP microscope (ZEISS Microscopy, Jena, Germany).

2.2. PVC films absorbance

The study examining the physical properties of PVC films during irradiation utilizing UV-Vis spectroscopy. The photo-degradation process was conducted at three distinct temperatures (298, 303, and 308 K) following the principles of first-order kinetics. The photo-decomposition rate constant (K_d) of PVC films after post-irradiation has been calculated using Eq. (1):[18]

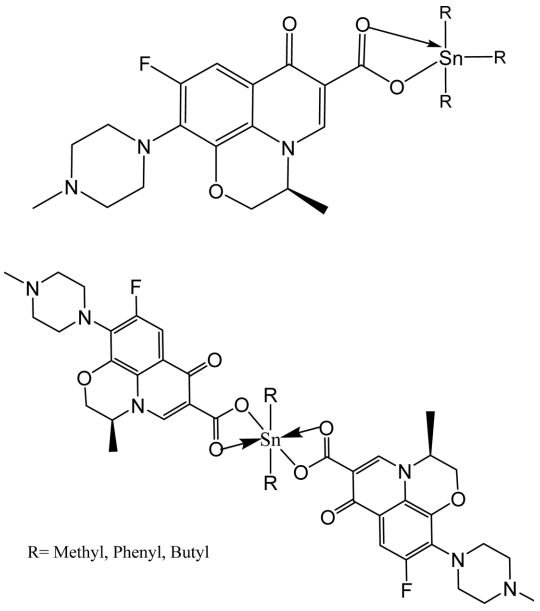
$$\ln(a-x) = \ln a - K_d t \quad (1)$$

where $a = (A_0 - A_\infty)$, $x = (A_0 - A_t)$

By substituting the provided variables into Eq. (1), we can derive Eq. (2), where a represents the stabilizer concentration before irradiation, x indicates the change in stabilizer concentration after time t of irradiation, A_0 represents the absorption intensity of PVC films at the initial time t_0, A_∞ denotes the absorption intensity at the final time (t_∞), and A_t signifies the absorption intensity after irradiation time (t).

$$\ln(A_t - A_\infty) = \ln(A_0 - A_\infty) - K_d t \quad (2)$$

Plotting $\ln(A_t - A_\infty)$ against the irradiation time (t) gives a straight line in which the slope equals K_d.



Scheme 1. Structures of the complexes.

2.3. Gel content percentages of modified PVC films

Each film, weighing 0.2 grams, was dissolved in 8 milliliters of tetrahydrofuran (THF) at room temperature overnight. Afterward, the insoluble fractions (referred to as gel content) released in the solution were filtered, washed, and dried in an oven. The percentage of gel content for each film at various irradiation times was calculated using the following equation, where W_1 and W_2 denote the weight of the original sample and the gel content, respectively.[19]

$$\text{Gel content } \% = \frac{W_2}{W_1} \times 100 \quad (3)$$

3. Results and Discussion

3.1. Calculation of kinetic parameter

The change in color observed in PVC films after irradiation is ascribed to the formation of unsaturated groups and oxidized structures, including carbonyl and polyene, which possess the capacity to absorb UV light with wavelengths exceeding 220 nm.[20,21] When additives are incorporated, PVC films demonstrate resistance to color alteration. Analysis of the films for absorption was conducted using a UV-Vis

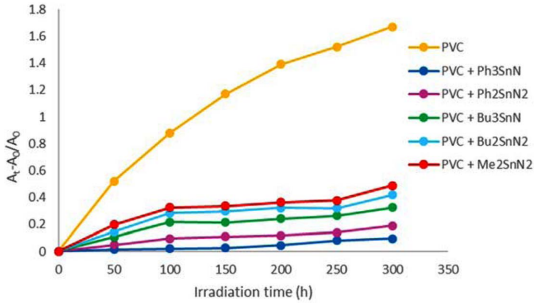


Fig. 1. The absorbance of PVC films at 313 nm for 300 h of irradiation.

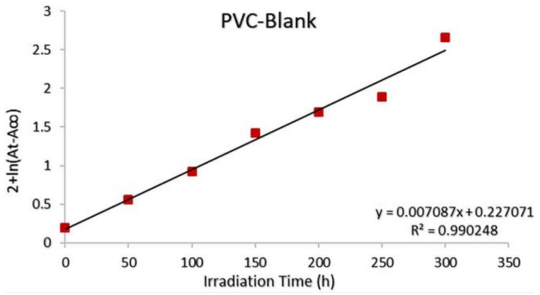


Fig. 2. Changes in $\ln(A_t-A_\infty)$ for blank PVC film with irradiation time for the plain PVC film.

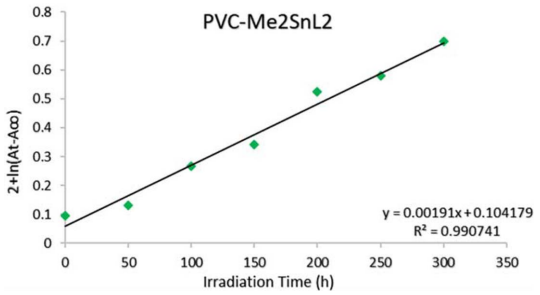


Fig. 3. Changes in $\ln(A_t-A_\infty)$ for the PVC film filled with Me_2SnL_2.

spectrophotometer, specifically measuring at a wavelength of 313 nm. *Fig.* 1 illustrates the fluctuation in absorbance of PVC films throughout radiation exposure.

The photodecomposition of the films has been investigated depending on the photodecomposition rate constant (k_d), which was obtained from plotting the $\ln(A_t-A_\infty)$ against irradiation time (t) according to the equation 1. The graph showed a straight line obeying the first-order kinetics. *Figs.* 2 to 7 show the change in $\ln(A_t-A_\infty)$ against irradiation time (t) for k_d PVC films in the absence and presence of additives, while

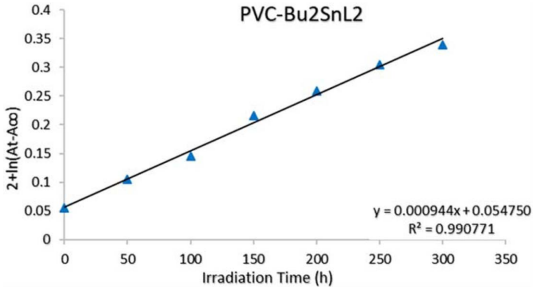


Fig. 4. Changes in $\ln(A_t-A_\infty)$ for the PVC film filled with Bu_2SnL_2.

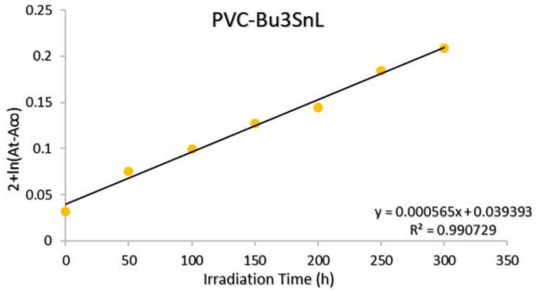


Fig. 5. Changes in $\ln(A_t-A_\infty)$ for the PVC film filled with Bu_3SnL.

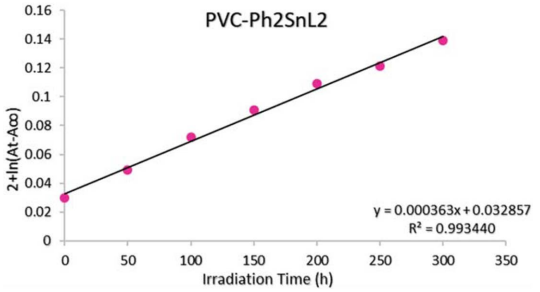


Fig. 6. Changes in $\ln(A_t-A_\infty)$ for the PVC film filled with Ph_2SnL_2.

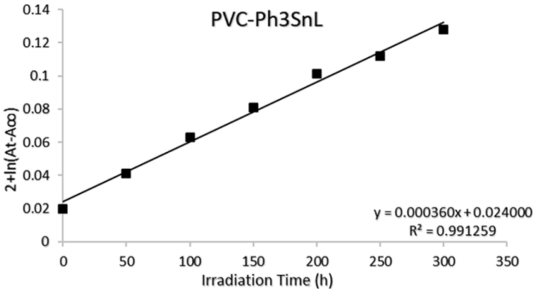


Fig. 7. Changes in $\ln(A_t-A_\infty)$ for the PVC film filled with Ph_3SnL.

Table 1 shows the values of k_d of the films. The results reveal that k_d values of modified PVC films

Table 1. The values of the rate constant (k_d) for the PVC films

Film	k_d (h^{-1}) × 10^{-4}
PVC	70.87
Me_2SnL_2	19.10
Bu_2SnL_{2d}	09.44
Bu_3SnL	05.65
Ph_2SnL_2	03.63
Ph_3SnL	03.60

were lower than the blank PVC film.

During the photolysis process, it was noted that insoluble PVC traces formed in THF when the irradiated film remained immersed in the THF solvent overnight. These residues observed in the study could potentially indicate PVC crosslinking or branching resulting from irradiation, as suggested in previous research.[22] To offer further insights, the average number of chain scissions S was determined using Eq. (4).[23] The S value is significantly influenced by the viscosity average molecular weight, calculated in a recent study, both initially ($\overline{M}_{V,O}$) and at a time (t) during irradiation ($\overline{M}_{V,t}$).

$$S = \frac{\overline{M}_{V,O}}{\overline{M}_{V,t}} - 1 \quad (4)$$

Fig. 8 demonstrates the influence of irradiation time on the value of S for PVC films containing organotin (IV) complexes. The PVC samples subjected to irradiation display a higher degree of branching and/or cross-linking compared to those with additives. Notably, the S value experienced a significant rise for the control PVC samples between 100 to 300 hours of irradiation. Complexes containing Ph_3SnL exhibited a decreased presence of insoluble residual polymers in PVC.[23]

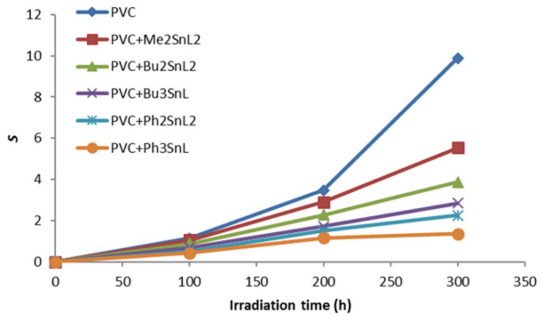


Fig. 8. Changes in the main chain scission (S) for PVC films versus irradiation time.

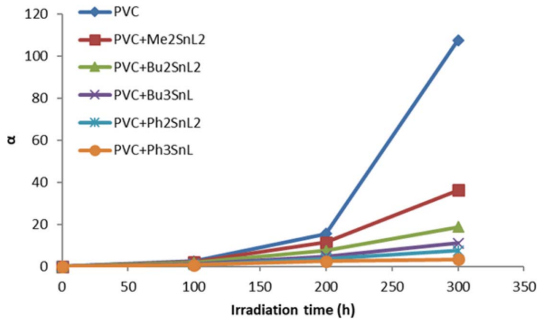


Fig. 9. Changes in the degree of deterioration (α) for PVC films versus irradiation time.

The degree of degradation α for PVC films can be assessed using Eq. (5). This outcome depends on the initial molecular weight (m), S, and $\overline{M}_{V,t}$. The value of α correlates directly with the disruption of randomly distributed weak bonds, which typically occurs rapidly during the initial stage of irradiation.

$$\alpha = \frac{m \times S}{\overline{M}_{V,t}} \quad (5)$$

Fig. 9 illustrates the effect of irradiation on PVC films. Irradiation time directly influenced the increase in the α value. For blank PVC (control), the α value sharply increased, peaking after 300 hours, indicating probable random bond breakage within the PVC chain. The α value was lower for PVC samples containing Sn(IV) complexes, reaching its minimum with the triphenyltin(IV) complex. The use of these additives notably reduced the photodegradation of PVC films under radiation exposure.[24]

3.2 Gel content measurements

The formation of insoluble fractions in irradiated PVC films dissolved in THF is attributed to the cross-linking of polymeric chains, a consequence of the photo-degradation process.[19] The gel content percentage was computed and plotted against the irradiation time, as illustrated in *Fig.* 10, utilizing Eq. (3). PVC films containing complexes demonstrated a lower gel content percentage compared to the blank

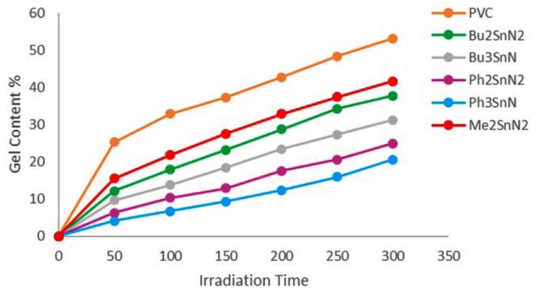


Fig. 10. Variation of the gel content of the PVC films in the absence and presence of additives.

PVC film post-irradiation. Specifically, the PVC-Ph_3SnL film exhibited a gel content percentage of approximately 20.6 % after 300 hours of irradiation, whereas the blank PVC film recorded a gel content percentage of 53.1 % under identical conditions. The modification of PVC films enhances the interconnections between polymer chains.

3.3. Photo-degradation of PVC Using energy dispersive X-Ray (EDX) mapping

Energy dispersive X-ray (EDX) mapping was utilized to analyze the elemental composition of PVC films containing organotin(IV) complexes, as depicted in *Figs.* 11 to 15. These films were subjected to UV irradiation for 300 hours, and their polymer blends' elemental composition was assessed using EDX. The mapping images from EDX indicated a homogeneous distribution of the tin complexes within the films.[25] The findings reveal a significant dehydrochlorination process, wherein hydrogen chloride was eliminated from the PVC films due to photodegradation. Among the irradiated PVC/Ph3SnL blend, the highest chlorine content was observed, reaching 30 %. The compound Ph3SnL, comprising three phenyl, two aryl, and one tetrazole moieties, emerged as the most effective additive for enhancing the stability of polymeric materials. A higher chloride percentage results in fewer bond breaks and less photodegradation of the polymeric film. Ph3SnL directly absorbs UV radiation and gradually releases the absorbed energy over an extended period, without causing harm to the PVC chains.

Several mechanisms have been proposed to elucidate

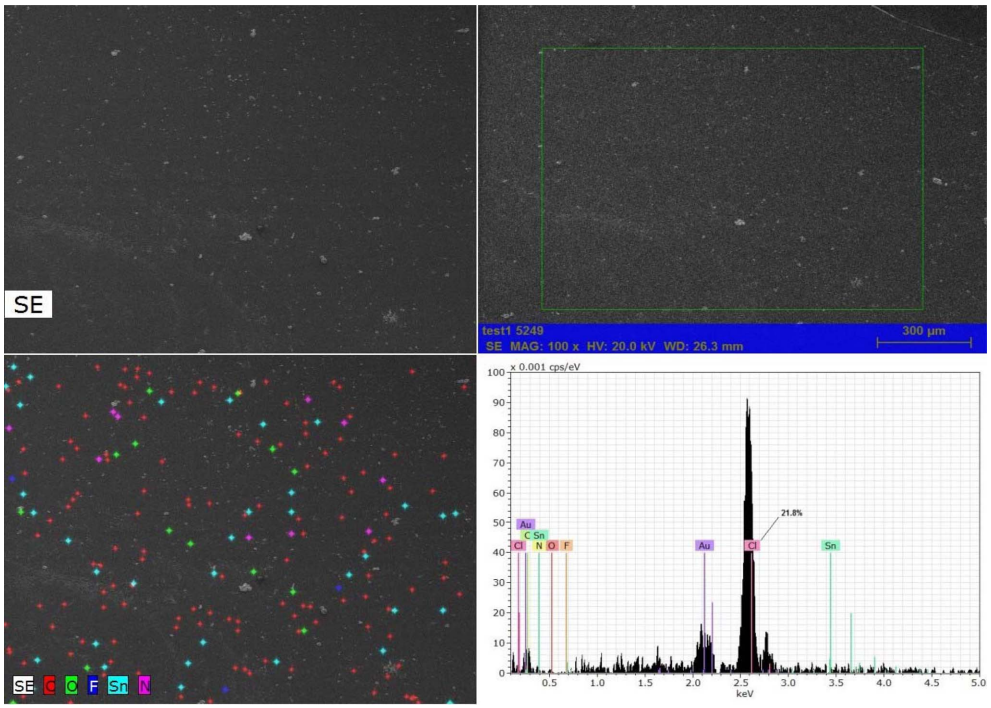


Fig. 11. Energy dispersive X-ray mapping of PVC-Me_2SnL_2 film.

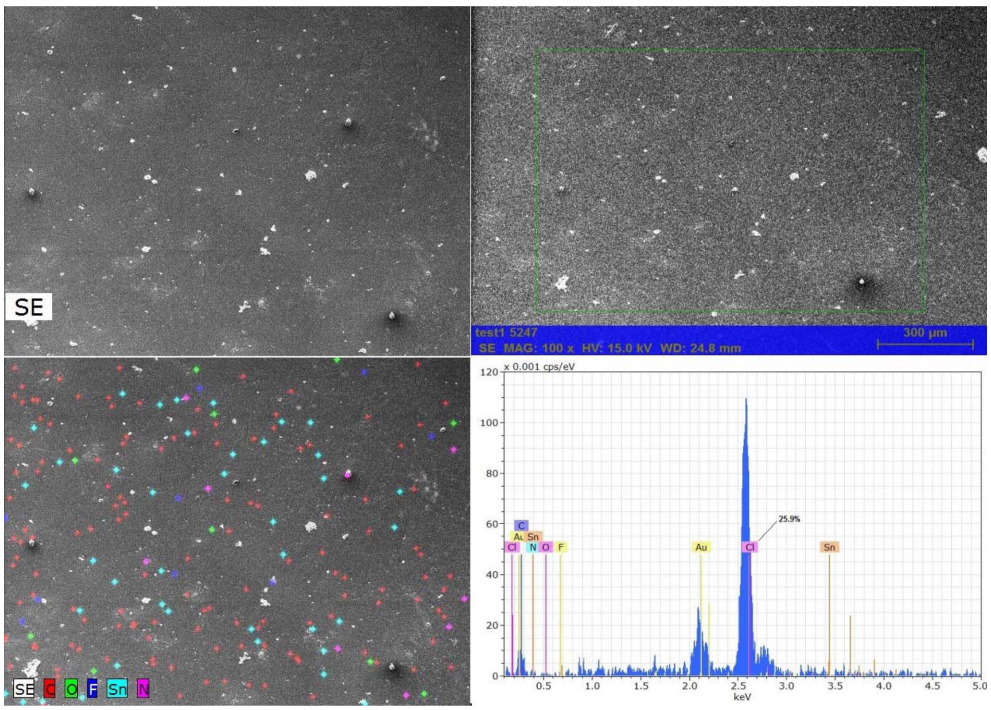


Fig. 12. Energy dispersive X-ray mapping of PVC-Bu_2SnL_2 film.

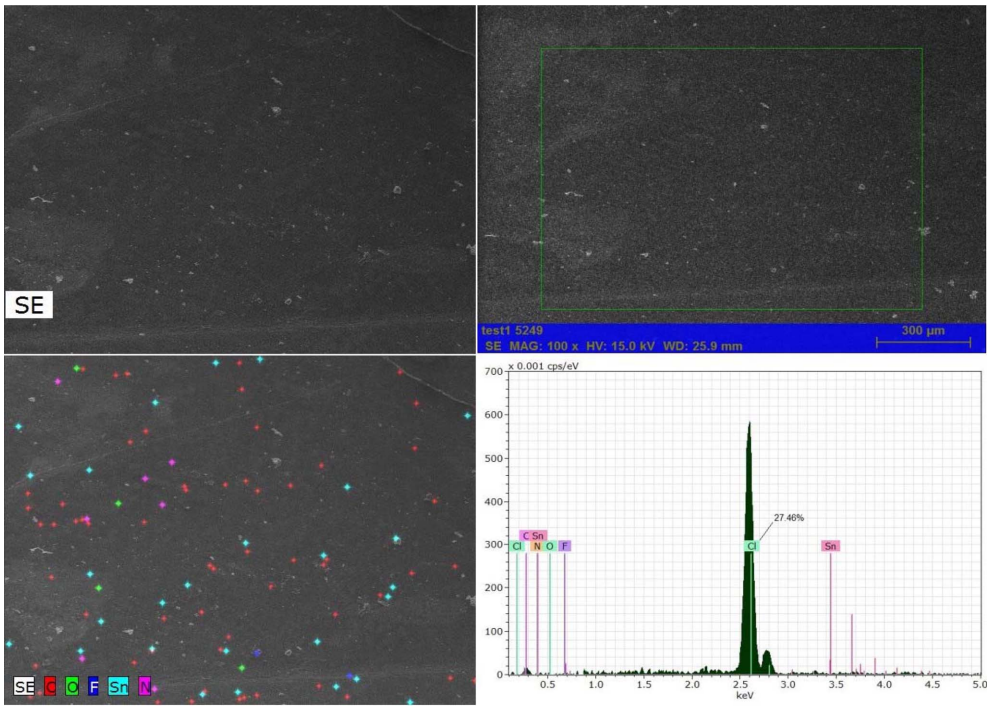


Fig. 13. Energy dispersive X-ray mapping of PVC-Bu_3SnL film.

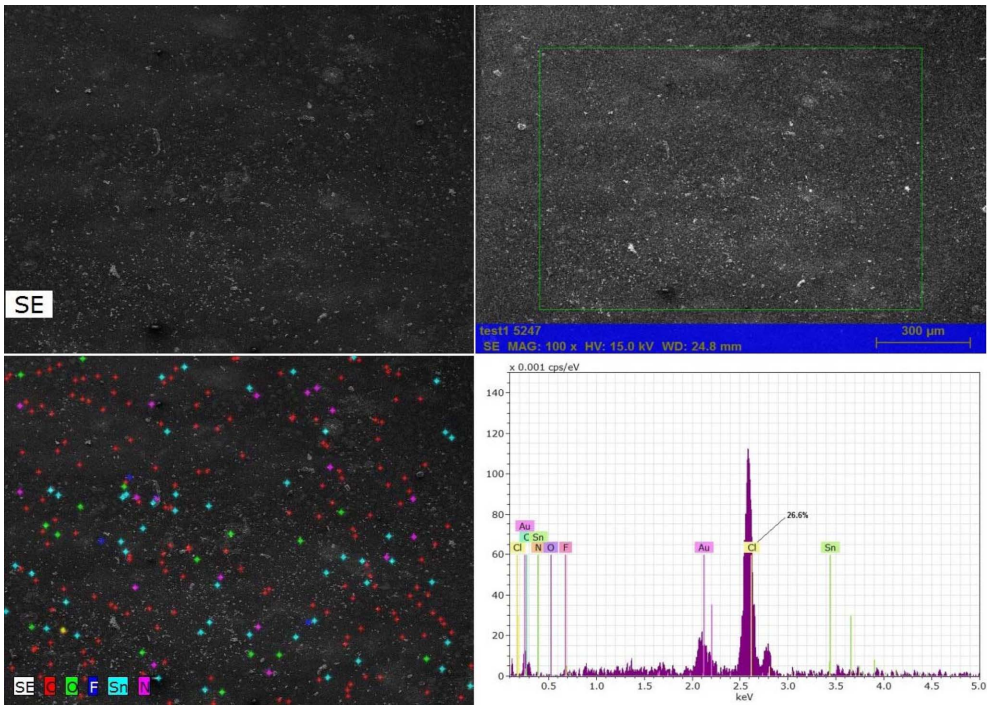


Fig. 14. Energy dispersive X-ray mapping of PVC-Ph_2SnL_2 film.

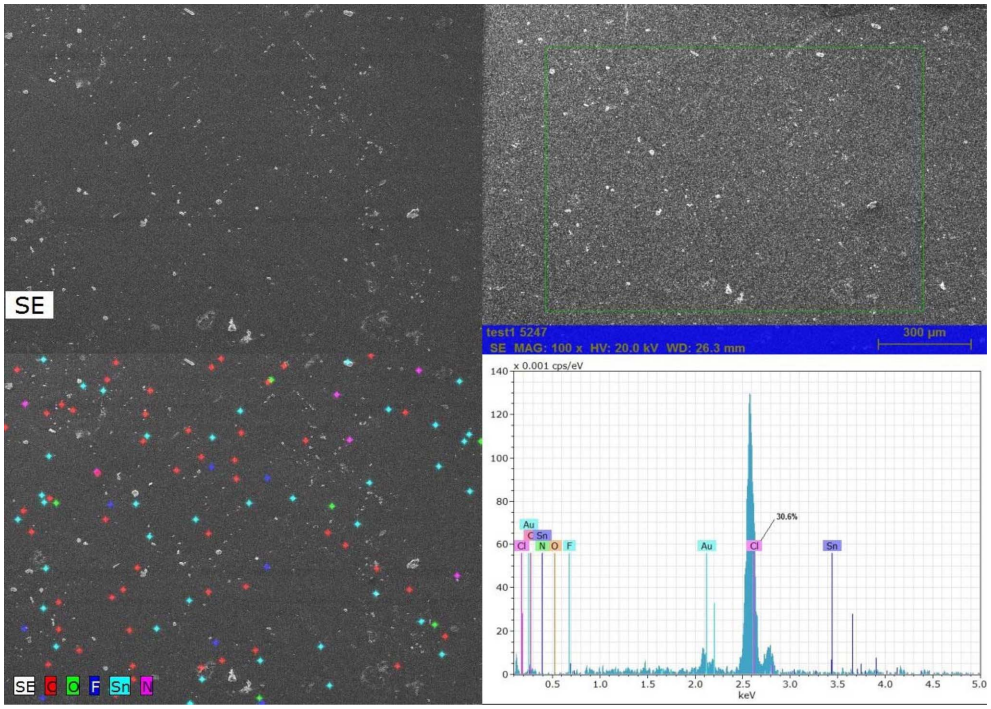


Fig. 15. Energy dispersive X-ray mapping of PVC-Ph_3SnL film.

the role of organotin (IV) complexes as PVC photo-stabilizers. Tin (IV) functions as a strong Lewis acid, acting as an HCl scavenger by substituting the chlorine atom in the reactive region of PVC with the ligand of the PVC stabilizers. This prevents the dehydrochlorination reaction, also known as a secondary stabilizer of PVC. Additionally, organotin (IV) complexes act as hydro-peroxide (POOH) decomposers, potentially decom-posing peroxides and inhibiting the photo-degradation of PVC. They also serve as radical (POO·) quenchers by complexing with radicals and additives containing a π-system.[26-28]

It is good to mention that these organotin(IV) complexes persist in the environment and may poison aquatic organisms and mammals, act as endocrine disruptors, bioaccumulate within organisms, and are subject to regulatory restrictions and bans in certain applications. Their toxic effects can disrupt hormonal systems and reproductive functions, and their bioaccu-mulation in aquatic organisms can disrupt ecosystems and food chains. Their endocrine-disrupting properties can also harm human and animal growth, development, and reproduction.[29]

4. Conclusions

This study examined organotin(IV) complex derivative-induced photohydrolysis of PVC films based on novel complexes. Several key findings were obtained by radiation-exposing PVC films with and without these additives. Ph_3SnL and other organotin(IV) complex derivatives reduced UV light absorbance and gel content in PVC sheets, indicating greater stability than untreated PVC. EDX analysis also showed that the PVC-Ph_3SnL blend had the highest chlorine content, 30 %, presenting better polymeric material stabilization. These findings suggest that organotin(IV) complex derivatives, particularly Ph_3SnL, can improve PVC film radiation stability, which could benefit industrial applications. This research helps develop strategies to improve PVC material durability and performance in harsh environments. Further research could lead to novel additives that stabilize polymeric materials better, meeting critical needs in PVC-dependent industries. EDX microscope the organotin (IV) complexes prove their activity to retard the photo-degradation of PVC in the trend following: $Ph_3SnL > Ph_2SnL_2 > Bu_3SnL > Bu_2SnL_2 > Me_2SnL_2$.

Acknowledgments

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References

1. R. Chen, Q. Li, X. Xu, and D. Zhang, *Fuel*, **246**, 212-221 (2019). https://doi.org/10.1016/j.fuel.2019.02.129
2. W. V. Titow, 'PVC Plastics Properties, Processing, and Applications' Elsevier, 1990.
3. PVC Piping Systems for Commercial and Industrial Applications, 2012 Plastic Pipe and Fittings Association (PPFA).
4. W. V. Titow, 'PVC Technology' 4th Ed., Elsevier, 1984.
5. Y. Lu, B. Wang, M. Xue, and Y. Lu, *Waste Management*, **121**, 52-58 (2021). https://doi.org/10.1016/j.wasman.2020.11.019
6. A. S. Elgharbawy, *International Journal of Smart Grid*, **2**(4), 218-220 (2018). https://doi.org/10.20508/ijsmartgrid.v2i4.31.g29
7. A. Elgharbawy and A. Sayed, *J. Pet. Min. Eng.*, **22**(2), 92-99 (2020). https://doi.org/10.21608/JPME.2020.39252.1044.
8. X. Xia, S. Menghan, Z. Miao, C. Zhongjie, and L. Li, *Sci. Total Environ.*, **716**, 136479 (2020). https://doi.org/10.1016/j.scitotenv.2019.136479.
9. M. Gao, M. Wan, and X. Zhou, *J. Therm. Anal. Calorim.*, **138**(1), 387-396 (2019). https://doi.org/10.1007/s10973-019-08219-3
10. D. Li, K. Panchal, N. K. Vasudevan, R. Mafi, and L. Xi, *Chem. Eng. Sci.*, **249**, 117334 (2022). https://doi.org/10.33774/chemrxiv-2021-4j8z6
11. H. Zhang and J. Zhang, *J. Appl. Polym. Sci.*, **139**, 52186 (2022). https://doi.org/10.1002/app.52186
12. C. Jubsilp, A. Asawakosinchai, P. Mora, D. Saramas, and S. Rimdusit, *Polymers*, **14**(1), 133 (2021). https://doi.org/10.3390/polym14010133

13. J. Yu, L. Sun, C. Ma, Y. Qiao, and H. Yao, *Waste Management*, **48**, 300-314 (2016). https://doi.org/10.1016/j.wasman.2015.11.041
14. N. Dutta, S. Hazarika, and T. K. Maji, *Polym. Eng. Sci.*, **61**(9), 2339-2348 (2021). https://doi.org/10.1002/pen.25761
15. X. Deng, C. Zhang, Y. Chen, Y. Yan, Y. Liu, and X. Chen, *Compos. Struct.*, **189**, 428-434 (2018). https://doi.org/10.1016/j.compstruct.2018.01.103
16. N. Mahmood, E. Yousif, M. Alias, G. A. El-Hiti, and D. S. Ahmed, *J. Polym. Res.*, **27**(9), 267 (2020). https://doi.org/10.1007/s10965-020-02245-8
17. M. Fadhil, E. Yousif, D. S. Ahmed, B. M. Kariuki, and G. A. El-Hiti, *Polymers,* **14**(18), 3720 (2022). https://doi.10.3390/polym14183720
18. A. Mohammed, G. A. El-Hiti, E. Yousif, A. A. Ahmed, D. S. Ahmed, and M. H. Alotaibi, *Polymers*, **12**(4), 969 (2020). https://doi.org/10.3390/polym 12040969
19. M. W. Sabaa, E. H. Oraby, A. S. A. Naby, and R. R. Mohamed, *J. Appl. Polym. Sci.*, **101**, 1543-1555 (2005). https://doi.org/10.1002/app.23402
20. M. Bufaroosha, N. Salih, A. Hadi, D. Ahmed, M. Al-mashhadani, and E. Yousif, *ANJS*, **23**, 57-61 (2020). https://doi.org/10.22401/anjs.23.1.08
21. E. Yousif and R. Haddad, *Springer Plus*, **2** (398), 1-32 (2013). https://doi.org/10.1186/2193-1801-2-398
22. D. Braun, S. T. Rabie, N. Y. Khaireldin, and M. A. Abd El-Ghaffar, *J. Vinyl Addit. Technol.*, **17**, 47-155 (2011). https://doi.org/10.1002/vnl.20278
23. K. Saranya, Md. Rameez, and A. Subramania, *Eur. Polym. J.*, **66**, 207-227 (2015). https://doi.org/10.1016/j.eurpolymj.2015.01.049
24. R. Allcock, W. Lampe, and P. Mark, 'Contemporary Polymer Chemistry (3rd ed.). Pearson Prentice-Hall, 2003.
25. C. Lu, H. Bai, F. Su, W. Chen, J. F. Hwang, and H. Lee, *J. Air Waste Manag. Assoc.*, **60**, 489-496 (2010). https://doi.org/10.3155/1047-3289.60.4.489
26. R. N. Abed, E. Yousif, M. H. Rahman, M. Kadhom, A. Basem, and H. Hashim, *Prog. Color Colorants Coat.*, **17**, 1-48 (2024). https://doi.org/10.30509/pccc.2024.167313.1300
27. D. Astruc, Organometallic Chemistry and Catalysis. Springer, 2007.
28. I. Omae, Applications of Organometallic Compounds. John Wiley, 1998.
29. M. Hoch, *Appl. Geochem.*, **16**(7-8), 719-743(2001). https://doi.org/10.1016/S0883-2927(00)00067-6

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