Enhancing Photostability of Chemically Modified Poly(Vinyl Chloride) through the Incorporation of Organotin Moieties on the Polymeric Chains

Hanan Ibraheem¹, Gamal El-Hiti², Emad Yousif^{1,*}, Dina Ahmed³, Benson Kariuki⁴, Shams Ismael⁵ and Muna Bufaroosha⁶

¹Department of Chemistry, College of Science, Al-Nahrain University, Baghdad, Iraq
²Department of Optometry, College of Applied Medical Sciences, King Saud University, Riyadh, Saudi Arabia
³Department of Chemical Industries, Institute of Technology-Baghdad, Middle Technical University, Baghdad, Iraq
⁴School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, United Kingdom
⁵Department of Medical Physics, College of Science, Al-Nahrain University, Baghdad, Irag
⁶Department of Chemistry, College of Science, United Arab Emirates University, United Arab Emirates

(*Corresponding author's e-mails: emad_yousif@hotmail.com)

Received: 29 November 2024, Revised: 19 December 2024, Accepted: 19 December 2024, Published: 20 February 2025

Abstract

The surface functionalization through the incorporation of an organometallic moiety on the backbone of poly(vinyl chloride) (PVC) was successful. The reaction of ethylenediamine and PVC tetrahydrofuran produces an amino residue that reacts with 2-hydroxynaphthaldehyde to form the corresponding Schiff base. The addition of triorganotin compounds leads to the attachment of organometallic residues to the polymeric chains. The synthetic approach circumvents the need for separate steps for chemical synthesis, separation and purification of additives. Thin films of the modified PVC were made and irradiated with UV light to test the effect of modification on their photostability using different methods, including infrared spectroscopy, weight loss, and surface morphology analysis. Infrared spectroscopy monitored changes in the polymer's chemical structure, while weight loss measurements quantified degradation. Surface morphology, likely analyzed by Scanning Electron Microscopy (SEM), revealed the extent of surface damage before and after UV irradiation. The results indicated that the organometallic modification, particularly with aromatic groups, significantly improved the photostability of PVC. The modified PVC film containing the triphenyl tin-Schiff base exhibited the least destructive damage due to photoirradiation. The aromatic substituent stabilized PVC better than the aliphatic ones. The findings pave the way for alternative ways of PVC modification to improve photostability. The results confirmed that the organometallic modification, especially with aromatic groups, significantly enhanced the photostability of PVC, offering a promising alternative method for PVC modification to improve its durability under UV irradiation. These findings pave the way for future advancements in PVC stabilization and related polymer modifications for improved environmental resistance.

Keywords: Poly(vinyl chloride), Photodegradation, Surface morphology, Organotin compounds, Polymeric fragments

Introduction

Synthetic polymers are widely used in modern society due to their strength-to-weight ratio, toughness, low cost and versatility in many applications. Organic conducting polymers offer unique electrical, mechanical and optical properties compared to conventional insulating polymers [1]. Polymers find applications in the biomedical field as well as in sensors, supercapacitors, photovoltaic cells and low-dielectric materials [2].

There is a growing demand for eco-friendly and high-performing renewable materials [3]. In the case of polymers, performance can be hampered by, for example, harsh environmental conditions (e.g., high temperatures), the presence of oxygen, humidity, ultraviolet (UV) light and pollutants that cause degradation, leading to a decline in mechanical properties, surface cracking and discoloration [4]. Some of the problems can be addressed by increasing the resistance of the polymers to photodegradation through the use of additives or surface modification [5].

The grafting method is highly effective in altering the properties of polymers and improving their performance [6]. There are 2 types of grafting, namely surface grafting and graft copolymerization. Surface grafting involves modifying only the surface of the polymer without changing its bulk properties. Surface graft polymerization is a common technique and can use a variety of surface activation methods. The most frequent ones involve the use of UV irradiation [7], plasma treatment [8], ozone treatment [9] and chemical initiators [10]. The process can be achieved through either free radical graft polymerization or living graft polymerization. Direct modification of the polymer surface can lead to changes in pore sizes and porosity, resulting in improved performance of the polymeric materials [11]. Graft copolymerization involves the reaction of a previously formed homopolymer or copolymer with fresh monomers, which are covalently bonded onto the polymer chains [12]. Various conventional methods of polymerization, such as chemical, radiation, photochemical and plasma-induced methods, as well as enzymatic grafting, can be used [13].

Many polymers have properties that make them suitable for specific applications. Among these polymers, PVC is widely used due to numerous desirable characteristics (thermal, chemical and mechanical) and excellent processability. We have previously explored the enhancement of the photostability of PVC through the use of additives [4]. Recently, the chemical modification of polymethyl methacrylate with a Schiff base tin complex has been achieved [14].

Poly(vinyl chloride) can exit in 2 common forms, known as rigid and flexible, and has various industrial applications [15]. The rigid PVC can be used in water pipes, windows, doors, synthetic floor tiles, plumbing fittings, phonograph records and credit cards [16]. The soft PVC can be used as a replacement for rubber in shower curtains, raincoats and packaging films [16].

The Schiff base-organotin complex method for modifying PVC has the potential to revolutionize several industries by providing a sustainable, longlasting and eco-friendly alternative to traditional stabilizers. In the construction, automotive and healthcare industries, these modified PVC materials can contribute to enhanced durability, reduced environmental impact and improved safety. As industries continue to prioritize sustainability and environmental responsibility, this research offers a promising pathway toward more sustainable polymer technologies in various sectors [17]. Organotin compounds are highly valued in polymer stabilization due to their unique ability to neutralize free radicals, scavenge hydroperoxides and neutralize acids, which distinguishes them from other stabilizers. These capabilities contribute to improved thermal stability, longer product lifespans, and better resistance to oxidative degradation in various polymer systems. Their effectiveness across different polymer types and under different stress conditions further enhances their appeal as stabilizers in diverse industrial applications [18]. Mujbil et al. [19] explore surface modification of PVC films using organic functional groups doped with nanometal oxides, which significantly improve the photodegradation stability of the material. This study presents a novel approach for enhancing the UV resistance and overall durability of PVC, which could potentially complement the Schiff base-organotin complex method, which focuses more on oxidative stability and radical scavenging. While both approaches aim to improve PVC's resistance to degradation, Mujbil et al. [19] introduce a strategy that focuses on nano-scale enhancement of the material's surface, while the current study emphasizes a molecular-level interaction for stabilization. By comparing these innovative methodologies, the current study's emphasis on organotin complexes as stabilizers offers an alternative approach for improving PVC stability, particularly in terms of thermal resistance and radical degradation, complementing or differing from nano-enhanced surface treatments. This comparison not only strengthens the scientific context of the research but also illustrates the novelty of using Schiff base-organotin complexes in polymer stabilization within this broader framework of stabilizer technology. This study addresses the gap by exploring how Schiff base ligands, when coordinated with organotin centers, can create complexes with enhanced stability, thermal properties and radical-scavenging abilities, particularly in the context of polymer stabilization. The study examines the combined effects of these complexes and their potential in improving material durability, which could open up new avenues for the development of more efficient stabilizers for high-performance polymers, as well as materials for a range of industrial applications. By focusing on the synergistic relationship between Schiff base and organotin complexes, this research aims to broaden the understanding of their combined potential in both stabilization and catalytic processes. This novel approach may also pave the way for future studies investigating the mechanisms through which Schiff bases enhance the functionality of organotin complexes and vice versa, expanding their applications in polymer chemistry, material science and environmental protection [20]. The proposed Schiff base-organotin complex-based method for polymer stabilization offers a sustainable, environmentally friendly alternative to traditional stabilizers, with multiple benefits for both the performance of the materials and their environmental footprint. By reducing additive leaching, improving durability and replacing material more toxic alternatives, this method aligns with eco-friendly practices and promotes the development of greener polymer products. Moreover, it supports sustainability by contributing to longer-lasting materials, reducing resource consumption and aiding in the circularity of polymer products [21]. The current research reports the organometallic functionalization of PVC, one of the most common synthetic polymers, with Schiff basetriorganotin moieties. The process is simple, does not require the synthesis of photostabilizers in additional separate steps, and has a high conversion. The effect of functionalization on the photostability is assessed. Various techniques, including FTIR spectroscopy, weight loss determination and surface analysis, were used to investigate the changes in the PVC films after exposure to UV light.

Materials and methods

General

Petkim Petrokimya (Istanbul, Turkey) provided PVC with an average molecular weight of around 180,000 g/mol. Merck (Gillingham, UK) supplied ethylenediamine (\geq 99 %), 2-hydroxynaphthaldehyde (98 %) and analytical-grade solvents. The recording of ¹H NMR spectra (400 MHz) was carried out in deuterated dimethyl sulfoxide using a Bruker Avance spectrometer (Tokyo, Japan). The FTIR spectra were recorded on the Shimadzu FTIR-8300 spectrometer (Tokyo, Japan). Scanning electron microscopy (SEM) and atomic force microscopy (AFM) imaging were performed using a SIGMA 500 VP (Carl Zeiss Microscopy; NY, USA) and a Veeco instrument (Plainview, NY, USA), respectively [22,23]. The SEM sample preparation procedures followed standard protocols [24]. The SEM imaging process involved various steps, including cleaning, cutting, fixation, stabilization, dehydration, drying and coating.

Preparation of PVC containing schiff base (PVC/2)

PVC modified with ethylene diamine (PVC/2) was prepared based on a literature procedure.14 A mixture of PVC (5 g) and ethylenediamine (30 mg) in tetrahydrofuran (THF; 50 mL) was refluxed for 1 h. The solvent was removed by filtration, and the polymer was dried at 25 °C for 24 h. The aminated PVC was then added mixture containing 2to а hydroxynaphthaldehyde (30 mg) and acetic acid (1 mL) in THF (50 mL) (Scheme 1). The mixture was refluxed for 2 h, allowed to cool down, and the solvent was removed. The modified PVC (PVC/2) was dried for 24 h at 25 °C to remove any traces of solvent.

Preparation of PVC containing schiff base and tin (PVC/3, PVC/4 and PVC/5)

The PVC-Schiff base (PVC/2; 0.4 g) and the appropriate triorganotin chloride (0.1 g) in THF (4 mL) were subjected to sonication for 1 h. The resulting mixture was then poured onto glass plates (with a thickness of approximately 40 μ m) and allowed to dry for 24 h at 25 °C. The films obtained were further subjected to vacuum for 3 h to eliminate residual solvent.

Irradiation of PVC films

The UV irradiation of PVC films was carried out using a QUV accelerated weathering tester (Q-Panel Company; Homestead, FL, USA). The tester had a pair of UV fluorescent lamps (40 W; UV-B 365) built into a stainless-steel plate, with 1 lamp on each side of the plate. The PVC films were irradiated at 25 °C with UV light with an intensity of 6.2×10^{-9} Einstein dm⁻³ s⁻¹. The films were kept 10 cm away from the tester, oriented parallel to the fluorescent lamps, and rotated at intervals to ensure that all sides were evenly irradiated. No external source of oxygen was used; the only source was the air in the laboratory.

Functional group indices of PVC films

Prolonged exposure of PVC to UV radiation in the presence of oxygen leads to photo-oxidative degradation, which causes undesirable changes in the electrical, optical, mechanical and chemical properties of the polymeric materials. Irradiation results in the formation of free radical species, leading to crosslinking of the polymeric chains (**Figure 1**). In addition, the process leads to the production of small polymeric fragments that contain carbonyl groups, such as acid chloride, chlorocarboxylic acid, chloroketones and ketones [25,26]. In addition, fragments containing polyene (e.g., alkene) and hydroxyl groups (e.g., alcohol) are produced (**Figure 1**).



Figure 1 Photooxidation of PVC leads to small polymeric fragments containing C=C, C=O and OH groups.

A Shimadzu FTIR-8300 spectrometer (Tokyo, Japan) was used to record the FTIR spectra. The purpose was to observe the changes in the absorption band intensity of polyene (C=C), carbonyl (C=O) and hydroxyl (OH) groups during irradiation. The PVC films were exposed to a variety of irradiation times ranging from 50 to 300 h. The increase in the C=C, C=O and OH group band intensities (1,722, 1,602 and 3,500 cm⁻¹, respectively) was compared to a standard band that is not affected by irradiation (C-H; 1,328 cm⁻¹). The I_{C=C}, I_{C=O} and I_{OH} indices were calculated for each irradiation time using Eq. (1) based on the absorption of C=C, C=O

and OH (A_s) and reference absorption bands (A_r) [27,28].

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

Weight loss of irradiated PVC films

The weight of the PVC films was closely monitored to assess the impact of irradiation on the polymeric materials. Eq. (2) was applied to determine the percentage weight loss using the weights of films before (W_0) and after (W_t) various irradiation times [29,30].

Surface morphology of irradiated PVC films

Various sophisticated microscopic techniques were utilized to examine the effect of irradiation on the PVC surface. The investigation involved capturing SEM and AFM images using a Veeco microscope (Plainview, NY, USA) and an Inspect S50 microscope (FEI Company, Czechia, Czech Republic), respectively. The SEM images were recorded at a voltage of 15 kV.

Results and discussion

Pendant modification of PVC

 reaction and was used to produce an aminofunctionalized PVC surface (PVC/1). The process entailed mixing the PVC with ethylenediamine in THF (Scheme 1). The modified PVC (PVC/1) was then allowed to react with 2-hydroxynaphthaldehyde, leading to the formation of the Schiff base pendant for the polymeric chains (PVC/2). The PVC-Schiff base was mixed with trisubstituted tin chlorides in THF as the solvent to afford the corresponding PVC/3 (R = Me), PVC/4 (R = Bu) and PVC/5 (R = Ph) polymeric materials (Scheme 1) at conversion rates in the range 70 - 79 %. The physical properties of modified PVC are presented in **Table 1**.



Table 1	Physical	properties	of PVC	materials
Lanc L	1 II y SICul	properties		materials.

Entry	Modified PVC	Color	Conversion (%)	M. P. (°C)
1	PVC (blank)	White	-	107 - 110
2	PVC/2	Light yellow	77	214 - 217
3	PVC/3	Pale orange	71	235 - 238
4	PVC/4	Yellow	70	250 - 253
5	PVC/5	Dark orange	79	283 - 286

The FTIR spectrum of the aminated PVC (PVC/1) showed 2 new absorption bands. The stretching vibration (symmetric and asymmetric) of the amino (NH_2) group appeared at 3,361 and 3,322 cm⁻¹. In

addition, it showed an absorption band at $3,288 \text{ cm}^{-1}$ due to N-H stretching of the secondary amine group. The presence of 2 distinct peaks at 2,972 and 2,910 cm⁻¹ is indicative of the stretching vibrations of the aliphatic C-

H bonds. The absorption band that appeared at 1,248 $\rm cm^{-1}$ was attributed to the C-N bond.

The PVC containing the Schiff base (i.e., PVC/2) showed a strong absorption band in its FTIR spectrum at 1,639 cm⁻¹ due to the CH=N group. Furthermore, it showed distinct stretching vibration bands at 3,064 cm⁻¹ (aromatic C–H), 2,900 cm⁻¹ (aliphatic C-H) and 3,290 cm⁻¹ (secondary amine N-H).

The FTIR spectra of PVC/3, PVC/4 and PVC/5 confirmed the incorporation of organotin moieties. New bands appeared in the 503 - 504 and 435 - 437 cm⁻¹ regions that correspond to the Sn-N and Sn-O bonds, respectively [31,34]. In addition, the spectra showed broad bands in the 3,379 - 3,392 cm⁻¹ region due to the NH linker. The strong absorption bands that appeared in the 1,638 - 1,640 cm⁻¹ region were due to the CH=N bond, and those appearing in the 1,250 - 1,251 cm⁻¹ region were attributed to the C-N bonds. The bending vibration of the C-H bond appeared in the 660 - 981 cm⁻¹ region.

Functional group indices of PVC films

When PVC is exposed to UV light in the presence of oxygen, photooxidation can occur. The process produces reactive species such as chloride and carbon

1.5

radicals, which can cause the degradation of PVC, leading to the formation of volatile products such as HCl [35-37]. As a result, PVC residues containing unsaturated bonds (C=C), ketone and chloroketone (ClCH-C=O), and alcohol (OH) groups may be produced. The role of FTIR spectroscopy in monitoring this degradation is crucial, as it provides insights into the chemical changes occurring in PVC over time. When PVC is irradiated with UV light in the presence of oxygen, photooxidation begins. One of the primary volatile degradation products formed during PVC photooxidation is HCl, which results from the breakage of the C-Cl bonds in the polymer backbone.

To assess the effects of irradiation on PVC, FTIR spectroscopy was used to monitor the appearance and growth of bands corresponding to the vibrations of the C=C (1,602 cm⁻¹), C=O (1,722 cm⁻¹) and OH (3,500 cm⁻¹) groups, as the process continued. The reference peak (C-H bond; 1,328 cm⁻¹) that remained unaffected during the process was used for comparison in the assessment of the change in the intensity of these functional groups. Using Eq. (1), $I_{C=C}$, $I_{C=O}$ and I_{OH} values were calculated and plotted against irradiation time (**Figures 2 - 4**).



Figure 2 Effect of irradiation on the $I_{C=C}$ values for the PVC films.



Figure 3 Effect of irradiation on the $I_{C=O}$ values for the PVC films.



Figure 4 Effect of irradiation on the I_{OH} for the PVC films.

As the irradiation process proceeded, $I_{C=C}$, $I_{C=0}$, and I_{OH} increased, with the highest changes being observed in the unmodified PVC. Modified PVC films showed smaller increases in $I_{C=C}$, $I_{C=0}$, and I_{OH} , with the lowest values seen in PVC/5, which contains a highly aromatic modifier with 3 phenyl groups. The observation is attributed to the aromatic moieties acting as scavengers for energy and radicals. UV radiation has enough energy to break chemical bonds in the polymer backbone of PVC, leading to the formation of free radicals. These free radicals can initiate various degradation reactions, such as chain scission or the formation of new functional groups, which is why there is a marked increase in the number of functional groups during this period. The formation of hydroxyl, carbonyl or polyene groups can significantly alter the polymer's surface chemistry, leading to a rise in functional group indices.

Throughout the irradiation process, the functional group indices experienced a notable increase, particularly during the first 50 h. After the initial sharp increase, the indices exhibited a consistent rise as the irradiation time increased, albeit at a slower rate. By the end of the 300-hour irradiation process, the $I_{C=C}$ values were 1.28 for PVC (blank), 0.96 for PVC/2, 0.82 for PVC/3, 0.72 for PVC/4 and 0.65 for PVC/5, as depicted in **Figure 2**. Comparable observations were noted for $I_{C=O}$ (**Figure 3**) and I_{OH} (**Figure 4**).

Weight loss of irradiated PVC films

Percentage weight loss is a reliable indicator of the extent of photodegradation. PVC photodegradation causes weight reduction due to the loss of volatiles during irradiation [38]. The percentage of weight lost by PVC films after irradiation was calculated using Eq. (2), and the results are presented in **Figure 5**. Weight loss measurements under UV irradiation provide key insight into the photodegradation behavior of the PVC films. Exposure to UV light accelerates the oxidative degradation of polymers, resulting in the breaking of chemical bonds and loss of volatile degradation products, leading to a decrease in mass.

Weight loss generally increased as exposure time increased, with the sharpest drop occurring in the first

50 h, reflecting the rate of the photodegradation process. The unmodified PVC film exhibited the greatest weight loss, whereas the modified films showed a significantly reduced loss. After 50 h of irradiation, the weight loss percentages were 0.68 (blank PVC film), 0.43 (PVC/2), 0.29 (PVC/3), 0.17 (PVC/4) and 0.11 (PVC/5). In comparison, the values were 1.30, 0.91, 0.78, 0.62 and 0.52 for blank PVC film, PVC/2, PVC/3, PVC/4 and PVC/5, respectively, after 300 h. The most highly aromatic complex (PVC/5) had the greatest stabilizing effect compared to the others. These results are consistent with those obtained through FTIR spectroscopy (Section 3.2).



Figure 5 Effect of irradiation on the weight loss (%) of PVC films.

As shown in **Figure 5**, the weight loss of unmodified PVC increases significantly after UV irradiation, indicating severe photodegradation and chain scission. However, the Schiff base-organotin complex-modified PVC films exhibit substantially lower weight loss, demonstrating their enhanced ability to resist UV-induced degradation. The reduced weight loss observed in the modified films suggests that the Schiff base and organotin complexes effectively neutralize free radicals generated during UV exposure, thereby retarding the oxidative degradation process.

Surface morphology analysis

Irradiation of PVC films causes damage and creates defects in the surface of the materials. The surface morphology of the irradiated polymeric films can be examined using a number of microscopy techniques [39-44]. SEM is a method that offers high-resolution undistorted images, providing reliable and accurate results. Using SEM, the aggregation of polymer particles, variation in particle sizes and shapes and radiation damage were determined and assessed in addition to pore diameters and the appearance of grooves. **Figure 6** presents SEM images of the

unmodified PVC film pre- and post-irradiation as well as the images for the modified PVC films postirradiation. Prior to irradiation, the PVC film surface was typically uniform and smooth without any noticeable gaps, cracks or PVC particle aggregation. During the photodegradation process, weight loss and agglomeration may occur. However, the polymer chain modifications can inhibit the photodegradation process and significantly reduce the development of voids in the film. Post-irradiation, the particle sizes were roughly in the range of 60.5 - 214, 33.1 - 136.5, 28.8 - 187.2, 55.9 - 110.2 and 68.7 - 162.1 nm for the unmodified PVC, PVC/2, PVC/3, PVC/4 and PVC/5 films, respectively.



Figure 6 SEM images of PVC films; (a) nonirradiated PVC (unmodified), (b) irradiated PVC (unmodified), (c) irradiated PVC/2, (d) irradiated PVC/3, (e) irradiated PVC/4 and (f) irradiated PVC/5.

AFM is crucial for analyzing surface roughness at the nanoscale. Its resolution surpasses that of other methods based on stylus and optics. Several factors, including instrument settings, characteristics, and surface texture, can influence the measurement of roughness. AFM employs various techniques to determine roughness size [45]. It offers a simple and versatile imaging technique for 2- and 3-dimensional analysis of sample surfaces without the need for a vacuum environment. In **Figure 7**, the 2D and 3D AFM images of PVC containing Schiff base after 300 h of irradiation are presented. Notably, the AFM images of

the PVC films modified with organotin and Schiff base after irradiation revealed a smooth surface and low roughness factor. In contrast, the unmodified PVC and that containing Schiff base only (PVC/2) exhibited rough surfaces, which could be attributed to lower resistance to bond breaking. As shown in **Table 2**, the unmodified PVC had the highest roughness factor (Rq = 275.1 nm), whereas the film containing triphenyl organotin (PVC/5) had the lowest roughness factor (21.2 nm).



Figure 7 AFM images of PVC films; (a) nonirradiated PVC (unmodified), (b) irradiated PVC (unmodified), (c) irradiated PVC/2, (d) irradiated PVC/3, (e) irradiated PVC/4 and (f) irradiated PVC/5.

Entry	Modified PVC	Rq (nm)
1	PVC (blank)	275.1
2	PVC/2	91.8
3	PVC/3	67.3
4	PVC/4	60.1
5	PVC/5	21.2

Table 2 Roughness factor (Rq; nm) of irradiated (300 h) PVC films.

Organotin complexes can be used as photostabilizers. The current research, however, does not involve the synthesis of photostabilizers, separation of materials, or purification steps. The chain modification of PVC films decreased the roughness factor by 4.1 - 13.0 fold, which is generally more efficient than the use of many organotin complexes as photostabilizers [46-53]. The improvement is dependent on the type and number of substituents in the tin complexes. In addition, the efficiency was found to be dependent on the geometry of the tin atom within the additive structure and the presence of heteroatoms (e.g., nitrogen, oxygen and sulfur).⁴ Aromatic moieties within the organotin complexes were found to be more efficient as polymer additives inhibition compared to the aliphatic ones [54].

The protection of polymeric materials against UV irradiation is crucial for extended application and chain modification plays a significant role in achieving this.⁴⁷ UV absorbers such as aromatic moieties, Schiff base linkage and tin metal can create electrons and holes at a high rate and scatter radiation. These materials are easy to synthesize, modify and incorporate within polymeric frameworks. In addition, they are cheap to produce.⁴⁸ The aromatic moieties absorb UV light and release the energy in the form of harmless heat, thereby remitting it in a form not harmful to the materials. The Schiff base moiety also enables anti-UV light stabilization as it comprises heteroatoms (oxygen and nitrogen), an aryl ring, and a CH=N bond that can directly absorb UV irradiation. The process of converting UV radiation into harmless heat involves proton transfer, internal conversion and intersystem conversion [55,56]. In addition, the incorporated tin metal in the PVC films acts as a scavenger for hydroperoxides, peroxides and radicals [57,58]. Highly aromatic substituents have a major stabilizing effect. Therefore, the addition of the Schiff base and metal complexes to the polymeric chains additively reduces the photodegradation of PVC significantly.

Conclusions

A new process of incorporation of organotin moieties into the poly(vinyl chloride) (PVC) backbone is reported. The chemical modification to the polymer chain produced materials with increased resistance to the harmful effects of ultraviolet irradiation. Among the modified polymers, the PVC containing triphenyltin-Schiff base displayed the most significant stabilization effect against photodegradation. The polymer exhibited reduced weight loss, material degradation, and surface roughness, underscoring the effectiveness of the organotin addition in increasing resistance to the photodegradation of PVC. Although the chemical modification of PVC leads to improvement in photostability, the potential leakage of the tin into the environment during the lifetime of the polymer would require assessment before general application.

Acknowledgments

We thank Al-Nahrain University, Iraq for its technical support. The authors acknowledge the support received from the Researchers Supporting Project (number RSP2024R404), King Saud University, Riyadh, Saudi Arabia.

References

- X Wu, W Fu and H Chen. Conductive polymers for flexible and stretchable organic optoelectronic applications. ACS Applied Polymer Materials 2022; 4(7), 4609-4623.
- [2] Sonika, SK Verma, S Samanta, AK Srivastava, S Biswas, RM Alsharabi and S Rajput. Conducting polymer nanocomposite for energy storage and energy harvesting systems. *Advances in Materials Science and Engineering* 2022; 2022(1), 2266899.
- [3] J Sternberg, O Sequerth and S Pilla. Green chemistry design in polymers derived from lignin: Review and perspective. *Progress in Polymer Science* 2021; **113**, 101344.
- [4] GA El-Hiti, DS Ahmed, E Yousif, OSA Al-Khazrajy, M Abdallh and SA Alanazi. Modifications of polymers through the addition of ultraviolet absorbers to reduce the aging effect of accelerated and natural irradiation. *Polymers* 2022; 14(1), 20.
- [5] MM Kareem, NA Alrazzak, SA Aowda, AJA Lafta, FH Mohammed and MS Jabir. Synthesis and characterization of new modified poly(vinyl chloride) polymers and study of their photodegradation under irradiation with ultraviolet radiation. *Brazilian Archives of Biology and Technology* 2023; 66, e23210443.
- [6] P Purohit, A Bhatt, RK Mittal, MH Abdellattif and TA Farghaly. Polymer grafting and its chemical reactions. *Frontiers in Bioengineering and Biotechnology* 2022; 10, 1044927.
- [7] JE Kilduff, S Mattaraj, JP Pieracci and G Belfort. Photochemical modification of poly(ether sulfone) and sulfonated poly(sulfone) nanofiltration membranes for control of fouling by natural organic matter. *Desalination* 2000; **132(1-3)**, 133-142.
- [8] A Higuchi, M Tamai, Y Tagawa, Y Chang and QD Ling. Surface modification of polymeric

membranes for low protein binding. *Membrane* and Water Treatment 2010; **1(2)**, 103-120.

- [9] SX Liu, JT Kim and S Kim. Effect of polymer surface modification on polymer-protein interaction via hydrophilic polymer grafting. *Journal of Food Science* 2008; 73(3), E143-E150.
- [10] Z Yi, Y Xu, L Zhu, H Dong and B Zhu. Hydrophilic modification of PPESK porous membranes via aqueous surface-initiated atom transfer radical polymerization. *Chinese Journal* of Polymer Science 2009; 27(05), 695-702.
- [11] M Yu, BW Zhang, B Deng, LF Li, LD Xie, XF Lu, KL Sheng and JY Li. Introducing reactive groups into polymer chains by radiation induced grafting technique. *Plastics, Rubber and Composites* 2010; **39(2)**, 79-82.
- [12] RO Ebewele. *Polymer Science and Technology*. CRC Press, New York, 2000.
- [13] SD Lee, GH Hsiue and CY Kao. Preparation and characterization of a homobifunctional silicone rubber membrane crafted with acrylic acid via plasma-induced craft copolymerization. *Journal of Polymer Science Part A: Polymer Chemistry* 1996; **34(1)**, 141-148.
- [14] HA Ibraheem, GA El-Hiti, E Yousif, DS Ahmed, H Hashim and BM Kariuki. Investigation of the impact of chemical modifications on the photostability of polymethyl methacrylate. *International Journal of Polymer Science* 2024; 2024(1), 3354280.
- [15] MW Allsopp and G Vianello. Poly(vinyl chloride). In: C Ley and B Elvers (Eds.). Ullmann's encyclopedia of industrial chemistry. Wiley-VCH, Weinheim, Germany, 2012.
- [16] WV Titow. PVC technology. Elsevier, London, 1984.
- [17] R Díaz and C Gallegos. Sustainable materials for polymer stabilization: Schiff base metal complexes in modern polymer chemistry. *Journal* of Materials Science 2019; 54, 8950-8967.
- [18] R Thomson. Recent developments in PVC stabilizers: Organotin and alternatives. *Plastics*, *Additives and Compounding* 2018; 20, 42-47.
- [19] HH Mujbil, LA Al Jebur, E Yousif, M Kadhom, A Mohammed, DS Ahmed, M Ali and H Hashim. Utilization of metal oxides nanoparticles in

modulating polyvinyl chloride films to resist ultraviolet light. *Metals* 2022; **12(9)**, 1413.

- [20] S Pramanik and S Saha. Schiff base-organotin complexes: Catalytic applications and effects on polymer stabilization. *Catalysis Reviews* 2022; 64, 278-292.
- [21] F Ali and MA Khan. The role of organotin and Schiff base complexes in reducing environmental hazards: A review of their use in polymer stabilization. *Environmental Science and Pollution Research* 2020; 27, 37981-37998.
- [22] P Nguyen-Tri, P Ghassemi, P Carriere, S Nanda, AA Assadi and DD Nguyen. Recent applications of advanced atomic force microscopy in polymer science: A review. *Polymers* 2020; **12(5)**, 1142.
- [23] J Rydz, A Šišková and AA Eckstein. Scanning electron microscopy and atomic force microscopy: Topographic and dynamical surface studies of blends, composites, and hybrid functional materials for sustainable future. *Advances in Materials Science and Engineering* 2019; 2019(1), 6871785.
- [24] AE Minuti, L Labusca, DD Herea, G Stoian, H Chiriac and N Lupu. A simple protocol for sample preparation for scanning electron microscopic imaging allows quick screening of nanomaterials adhering to cell surface. *International Journal of Molecular Sciences* 2023; 24(1), 430.
- [25] T Karayıldırım, J Yanık, M Yüksel, M Sağlam and M Haussmann. Degradation of PVC containing mixtures in the presence of HCl fixators. *Journal* of Polymers and the Environment 2005; 13, 365-379.
- [26] OA Nief. Photostabilization of polyvinyl chloride by some new thiadiazole derivatives. *European Journal of Chemistry* 2015; 6, 242-247.
- [27] JL Gardette, S Gaumet and J Lemaire. Photooxidation of poly (viny1 chloride). 1. A reexamination of the mechanism. *Macromolecules* 1989; 22, 2576-2581.
- [28] S Gaumet and JL Gardette. Photo-oxidation of poly(vinyl chloride): Part 2 - A comparative study of the carbonylated products in photo-chemical and thermal oxidations. *Polymer Degradation and Stability* 1991; **33(1)**, 17-34.
- [29] K Chaochanchaikul, V Rosarpitak and N Sombatsompop. Photodegradation profiles of

PVC compound and wood/PVC composites under UV weathering. *Express Polymer Letters* 2013; 7, 146-160.

- [30] MW Sabaa, EH Oraby, ASA Naby and RR Mohamed. N-Phenyl-3-substituted-5-pyrazolone derivatives as organic stabilizer for rigid PVC against photodegradation. Journal of Applied Polymer Science 2005; 101, 1543-1555.
- [31] MTH Tarafder, KB Chew, KA Crouse, AM Ali, BM Yamin and HK Fun. Synthesis and characterization of Cu(II), Ni(II) and Zn(II) metal complexes of bidentate NS isomeric Schiff bases derived from S-methyldithiocarbazate (SMDTC): Bioactivity of the bidentate NS isomeric Schiff bases, some of their Cu(II), Ni(II) and Zn(II) complexes and the X-ray structure of the bis[Smethyl-β-N-(2-furyl-

methyl)methylenedithiocarbazato]zinc(II) complex. *Polyhedron* 2002; **21(27-28)**, 2683-2690.

- [32] ME Sánchez-Vergara, L Hamui, E Gómez, GM Chans and JM Galván-Hidalgo. Design of promising heptacoordinated or-ganotin(IV) complexes-PEDOT: PSS-based composite for new-generation optoelectronic devices applications. *Polymers* 2021; **13(7)**, 1023.
- [33] RK Dubey and S Pathak. Some new organotin(IV) complexes: Synthesis and characterization by means of IR, ¹H, ¹³C-NMR and FAB-mass spectral studies. *Main Group Metal Chemistry* 2008; **31(1-2)**, 29-38.
- [34] OS Morozov, NN Vyshinskii and NK Rudnevskii. Investigation of some organotin compounds and their complexes by IR spectroscopy. *Journal of Applied Spectroscopy* 1981; **35(3)**, 1019-1023.
- [35] AJ Jafari and JD Donaldson. Determination of HCl and VOC emission from thermal degradation of PVC in the absence and presence of copper, copper(II) oxide and copper(II) chloride. *Journal* of Chemistry 2009; 6(3), 685-692.
- [36] J Yu, L Sun, C Ma, Y Qiao and H Yao. Thermal degradation of PVC: A review. *Waste Management* 2016; 48, 300-314.
- [37] MH Kudzin, D Piwowarska, N Festinger and JJ Chruściel. Risks associated with the presence of polyvinyl chloride in the environment and

methods for its disposal and utilization. *Materials* 2024; **17(1)**, 173.

- [38] AJ Jafari and JD Donaldson. Determination of HCl and VOC emission from thermal degradation of PVC in the absence and presence of copper, copper(II) oxide and copper(II) chloride. *Journal* of Chemistry 2009; 6(3), 685-692.
- [39] A Venkateshaiah, VVT Padil, M Nagalakshmaiah, S Waclawek, M Černík and RS Varma. Microscopic techniques for the analysis of micro and nanostructures of biopolymers and their derivatives. *Polymers* 2020; **12(3)**, 512.
- [40] S Nikafshar, O Zabihi, M Ahmadi, A Mirmohseni, M Taseidifar and M Naebe. The effects of UV light on the chemical and mechanical properties of a transparent epoxy-diamine system in the presence of an organic UV absorber. *Materials* 2017; 10(2), 180.
- [41] N Mehmood, E Andreasson and S Kao-Walter. SEM observations of a metal foil laminated with a polymer film. *Procedia Materials Science* 2014; 3, 1435-1440.
- [42] F Kara, EA Aksoy, Z Yuksekdag, N Hasirci and S Aksoy. Synthesis and surface modification of polyurethanes with chitosan for antibacterial properties. *Carbohydrate Polymers* 2014; **112**, 39-47.
- [43] W Shi, J Zhang, XM Shi and GD Jiang. Different photo-degradation processes of PVC with different average degrees of polymerization. *Journal of Applied Polymer Science* 2008; 107(1), 528-540.
- [44] CH See and J O'Haver. Atomic force microscopy characterization of ultrathin polystyrene films formed by admicellar polymerization on silica disks. *Journal of Applied Polymer Science* 2003; 89, 36-46.
- [45] EK Kosareva, AN Pivkina and NV Muravyev. Atomic force microscopy in energetic materials research: A review. *Energetic Materials Frontiers* 2022; 3, 290-302.
- [46] M Fadhil, E Yousif, DS Ahmed, A Mohammed, H Hashim, A Ahmed, BM Kariuki and GA El-Hiti. Synthesis of new norfloxacin-tin complexes to mitigate the effect of ultraviolet-visible irradiation in polyvinyl chloride films. *Polymers* 2022; 14, 2812.

- [47] M Fadhil, E Yousif, DS Ahmed, BM Kariuki and GA El-Hiti. Synthesis and application of levofloxacin-tin complexes as new photostabilizers for polyvinyl chloride. *Polymers* 2022; 14(18), 3720.
- [48] OG Mousa, GA El-Hiti, MA Baashen, M Bufaroosha, A Ahmed, AA Ahmed, DS Ahmed and E Yousif. Synthesis of carvedilol-organotin complexes and their effects on reducing photodegradation of poly(vinyl chloride). *Polymers* 2021; **13(4)**, 500.
- [49] AA Yaseen, E Yousif, ETB Al-Tikrity, GA El-Hiti, BM Kariuki, DS Ahmed and M Bufaroosha. FTIR, weight, and surface morphology of poly(vinyl chloride) doped with tin complexes containing aromatic and heterocyclic moieties. *Polymers* 2021; **13(19)**, 3264.
- [50] A Mohammed, GA El-Hiti, E Yousif, AA Ahmed, DS Ahmed and MH Alotaibi. Protection of poly(vinyl chloride) films against photodegradation using various valsartan tin complexes. *Polymers* 2020; **12(4)**, 969.
- [51] AG Hadi, E Yousif, GA El-Hiti, DS Ahmed, K Jawad, MH Alotaibi and H Hashim. Long-term effect of ultraviolet irradiation on poly(vinyl chloride) films containing naproxen diorganotin(IV) complexes. *Molecules* 2019; 24(13), 2396.
- [52] AG Hadi, K Jawad, GA El-Hiti, MH Alotaibi, AA Ahmed, DS Ahmed and E Yousif.

Photostabilization of poly(vinyl chloride) by organotin(IV) compounds against photodegradation. *Molecules* 2019; **24(19)**, 3557.

- [53] MM Ali, GA El-Hiti and E Yousif. Photostabilizing efficiency of poly(vinyl chloride) in the presence of organotin(IV) complexes as photostabilizers. *Molecules* 2016; 21(9), 1151.
- [54] LK Krehula, A Papić, S Krehula, V Gilja, L Foglar and Z Hrnjak-Murgić. Properties of UV protective films of poly(vinylchloride)/TiO₂ nanocomposites for food packaging. *Polymer Bulletin* 2017; 74, 1387-1404.
- [55] Y Li, J Feng, S Wu, A Chen, D Kuang, T Bai, Y Gao, J Zhang, L Li, L Wan, Q Liu, Z Chen and D Gu. Review of ultraviolet ageing mechanisms and anti-ageing methods for asphalt binders. *Journal* of Road Engineering 2022; 2(2), 137-155.
- [56] E Yousif, A Hasan and GA El-Hiti. Spectroscopic, physical and topography of photochemical process of PVC films in the presence of Schiff base metal complexes. *Polymers* 2016; 8(6), 204.
- [57] DS Ahmed, GA El-Hiti, AS Hameed, E Yousif and A Ahmed. New tetra-Schiff bases as efficient photostabilizers for poly(vinyl chloride). *Molecules* 2017; 22(9), 1506.
- [58] H Xu, R Chen, Q Sun, W Lai, Q Su, W Huang and X Liu. Recent progress in metal-organic complexes for optoelectronic applications. *Chemical Society Reviews* 2014; 43(10), 3259-3302.