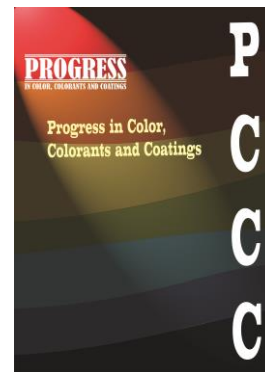


Accepted Manuscript

Title: Enhancing Photostability of PVC Films Using Phenolic Azanylylidene Compounds



Authors: S. H. Mohamed, M. Kadhom, E. Yousif

Manuscript number: **PCCC-2407-1313**

To appear in: Progress in Color, Colorants and Coatings

Received: 21 July 2024

Final Revised: 1 November 2024

Accepted: 4 November 2024

Please cite this article as:

S. H. Mohamed, M. Kadhom, E. Yousif, Enhancing photostability of PVC films using phenolic azanylylidene compounds, Prog. Color, Colorants, Coat., 18 (2025) XX-XXX.

This is a PDF file of the unedited manuscript that has been accepted for publication. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form

Enhancing Photostability of PVC Films Using Phenolic Azanylylidene CompoundsS. H. Mohamed¹, M. Kadhom², E. Yousif^{3,*}¹ Department of Chemistry, College of Basic Education, Tikrit University, Al-Shirqat,

P.O. Box: 3400, Saladin, Iraq

² Department of Environmental Science, College of Energy and Environmental Sciences,

Alkarkh University of Science, P.O. Box: 10081, Baghdad, Iraq

³ Department of Chemistry, College of Science, Al-Nahrain University, P.O. Box: 10072,

Baghdad, Iraq.

* Corresponding Author Email: emad_yousif@hotmail.com,

emad.yousif@nahrainuniv.edu.iq

Abstract

One of the biggest environmental issues with PVC polymer films is UV photodegradation. In this research, three azanylylidene compounds were prepared and filled as homogeneous and heterogeneous aromatic organic in 0.5% concentration within the PVC to investigate their photodegradation effect on the polymer. Infrared spectroscopy and proton nuclear magnetic resonance confirmed the chemical composition of antioxidant phenolic azanylylidene compounds. Concentrated UV radiation was applied to examine the PVC polymer films for 300 h, divided into 100 h intervals. To determine carbonyl, hydroxyl, and polyene group absorption coefficients, the PVC polymer films' infrared spectrum was measured before and after irradiation. The absorption coefficients of these groups decreased by adding those azanylylidene additives. Additionally, the weight loss of blank and embedded PVC films prior to and after irradiation was measured to assess photodegradation. Comparing with the

unmodified PVC film, the modified ones showed less weight loss. SEM images showed that azanylylidene-modified PVC polymer films had significantly less surface damage than plain film, indicating improved stability. X-ray mapping was used to assess azanylylidene compound distribution in PVC polymer films; ratios of some elements were changed, indicating that the additives prevented photo-oxidative decomposition. Energy-dispersive X-ray (EDX) analysis is also applied to detect the elements of PVC film before and after irradiation. The viscosity and molecular weight of all polymeric sheets are measured. The plain polymer's molecular weight decreased significantly with increasing irradiation time, while the modified polymer's molecular weight decreased less. The filled compounds worked as stabilizers that slowed PVC chain degradation.

Keywords: Schiff bases; azanylylidene phenolic; PVC photostability; UV irradiation; Radical scavenging.

1. Introduction

The chemical reactions involving aldehydes or ketones and primary amines, which lead to the substitution of the carbonyl group with an imine group, are commonly known as Schiff bases. These reactions are extensively employed in organic synthesis [1]; these compounds are highly significant because of their extensive range of applications [2]. Schiff bases possess antimicrobial and fungicidal properties [3], and are also utilized for various pharmacological purposes [4].

Plastic is widely utilized globally due to its adaptable characteristics, including its lightweight nature, ease of design, resistance to chemicals, exceptional ability to

withstand relatively high temperatures, and superior electrical insulation properties [5]. UV radiation is one of the factors that cause the highest degradation of plastics due to its high energy content. Photodegradation refers to the process of physical and chemical deterioration in polymers that occurs due to continuous exposure to UV radiation. This degradation process includes the breaking of chemical bonds, alterations in the structure of molecules, a decrease in the size of molecules, and an overall decline in the quality of polymer properties. The degradation is particularly advanced as the material is exposed to UV radiation in the presence of oxygen [6].

Polyvinyl chloride (PVC) is in high demand globally, driven by its unique properties and cost-effective manufacturing process. Its applications span numerous fields, including office supplies, construction, toy manufacturing, furniture, medical equipment, packaging, tubing, and film production. PVC's high chlorine content, making up over fifty percent of its weight, contributes to its value in insulation manufacturing [7, 8]. However, exposure to UV light, sunlight, and high temperatures can lead to photodegradation, impacting PVC's chemical and physical properties unfavorably [9, 10]. The effects of this degradation include mass loss, release of volatile compounds, and the formation of smaller molecular fragments [11–16]. To combat these issues and ensure longer product lifespans, manufacturers incorporate additives into PVC. These additives improve its photostability and maintain its transparency, durability, and color over time [17, 18]. Specific additives, like inorganic salts, heterocycles, and aromatics, are often used in minimal amounts to protect PVC from UV exposure [19].

In this work, we investigate the potential of new photostabilizers, namely azanylylidene phenolic compounds, to reduce PVC photodegradation under UV light

irradiation. The PVC films were investigated using various methods, and the results revealed a notable increase in photoresistivity.

2. Experimental

2.1. Materials and Methods

High-quality solvents and reagents sourced from Fluka A.G., Merck, and BDH, were utilized in this research without any additional purification. A Nicolet 100 Fourier Transform Infrared (FTIR) spectrophotometer was applied to monitor infrared spectra, which spanned between 400 to 4000 cm^{-1} . The FTIR spectra were recorded on a Jasco FT/IR-4200 spectrometer (Tokyo, Japan) using KBr discs, while the reagents and chemicals were bought from Merck of Gillingham, UK. However, the used PVC was purchased from Petkim Petrokimya in Istanbul, Turkey, with a molecular weight (M_v) of around 180,000. The ^1H Nuclear Magnetic Resonance (NMR) spectra were obtained using a Bruker DRX-500 NMR spectrometer (Zürich, Switzerland) operating at a frequency of 500 MHz. The measurements were conducted in dimethyl sulfoxide- d_6 (DMSO- d_6). The scanning electron microscopy (SEM) images were captured using a KYKY-EM3200 digital microscope manufactured by FEI Company in Prague, Czech Republic. An energy-dispersive X-ray (EDX) spectrum was recorded using a Bruker XFlash 6 10 instrument manufactured by Bruker in Tokyo, Japan.

2.2. Q.U.V. Accelerated Weathering Tester

This device was applied to irradiate PVC sheets with UV light of $\lambda_{\text{max}} = 313 \text{ nm}$ and light intensity = $6.43 \times 10^{-9} \text{ ein. dm}^{-3} \cdot \text{s}^{-1}$ at room temperature. The device was from Q-

panel Company (Cleveland, OH, USA). The polymeric sheets were set vertically in a distance of 10 cm from the light source and in line with the UV lamps, while the tester stood on either side of the light with two fluorescent lamps that emit ultraviolet light (UV-B 365, 40 watts). The plastic sheets were rotated regularly to provide even irradiation from all directions. Exposure to UV radiation determined the gel percentage and weight loss as a function of time for the radiated films.

2.3 FTIR Spectrophotometry

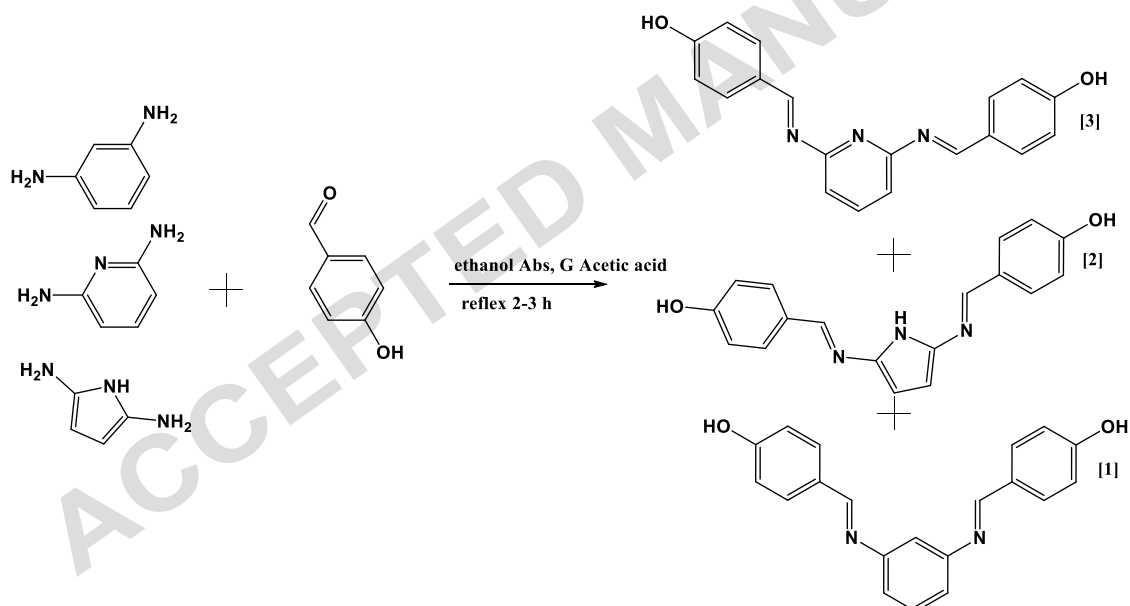
The process of photo-oxidation of PVC resulted in the creation of hydroxyl radicals and conjugated carbon double bonds [11]. The assessment of photodegradation involves the observation of alterations in the intensities of the polyene (1602 cm^{-1}) and carbonyl (1722 cm^{-1}) peaks in the IR spectra of PVC following exposure to irradiation. The C–C bond in PVC chains acts as a benchmark peak at 1328 cm^{-1} [23], and it remains unaltered by exposure to UV radiation. The functional group index (I_s) for each functional group is determined by applying equation 1, in which A represents the peak absorbance of a particular functional group and A_r represents the absorbance of the reference peak.

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

2.4. Preparation of azanylylidene phenolic compounds

Three azanylylidene phenolic compounds, 4,4'-((1E,1'E)-(1,3-phenylenebis(azanylylidene))bis(methanylylidene))diphenol, 4,4'-((1E,1'E)-((1H-pyrrole-2,5-diyl)bis(azanylylidene))bis(methanylylidene))diphenol, and 4,4'-((1E,1'E)-(pyridine-

2,6-diylbis(azanylylidene))bis(methanylylidene))diphenol, were synthesized through a Schiff base reaction. This involved the reaction of 20 mmol (2.4 g) of 4-hydroxybenzaldehyde with aromatic diamine compounds, namely 3-aminoaniline (1.08 g, 10 mmol), 2,5-diaminopyrrole (0.9 g, 10 mmol), and 2,6-diaminopyridine. The reaction was conducted using 100% ethanol as the solvent and drops of glacial acetic acid as the catalyst, where the reaction is depicted in Scheme 1. The reaction mixture was subjected to heating for a duration of 2-3 h, and the resultant solid material was subjected to drying at a temperature of 50 °C. Table 1 contains a comprehensive list of the physical properties.



Scheme 1. The preparation of azanylylidene phenolic compounds (1, 2, and 3).

Table 1. Physical properties for the azanylylidene phenolic compounds.

Comp. no.	Chemical formula	Color	M.P. (°C)	Yield (%)
1	C ₂₀ H ₁₆ N ₂ O ₂	Yellow	195	85
2	C ₁₈ H ₁₅ N ₃ O ₂	Light brown	215	79
3	C ₁₉ H ₁₅ N ₃ O ₂	Dark brown	223	74

2.5. ¹H NMR Spectroscopy

The ¹H NMR spectra of azanylylidene phenolic compounds, measured in DMSO-d₆ solvent, exhibit a signal at $\delta = 9.81$ - 9.79 ppm. This signal corresponds to two protons originating from the O-H group of carbon [24, 25]. The N=C-H imine group owned two protons that are detected as a signal with a chemical shift of $\delta = 8.77$ - 8.70 ppm. The proton of the N-H pyrrole aromatic group is detected as a signal at a chemical shift of $\delta = 10.74$ ppm. In addition, the spectrum displays the anticipated categories of aromatic protons, as specified in Table 2.

Table 2. ¹H-NMR spectral data for **1–3** azanylylidene compounds.

Compounds	¹ H NMR (500 MHz, DMSO- <i>d</i> ₆)
1	δ : 9.81 (s, 2H), 8.77 – 8.74 (m, 2H), 8.14 – 8.12 (m, 4H), 7.73 (s, 2H), 6.97 (s, 6H).
2	δ : 10.74 – 10.69 (m, 1H), 9.80 (s, 2H), 8.76 – 8.72 (m, 2H), 8.12 (s, 4H), 7.72 (d, <i>J</i> = 9.4 Hz, 4H), 6.97 (s, 2H)
3	δ : 9.79 (s, 2H), 8.74 – 8.70 (m, 2H), 7.75 (d, <i>J</i> = 18.9 Hz, 5H), 6.99 – 6.97 (m, 6H).

2.6. Preparation of PVC Films

The polymeric solution was prepared by mixing 5 g of PVC with 25 mg of the three azanylylidene phenolic compounds in 100 ml of tetrahydrofuran (THF); the mixture was stirred for two hours. The resulting uniform solution was then doped onto a glass tablet with cavities, each measuring approximately 45 μ m in thickness. The tablet was left to dry in air for 24 h at 25 °C. To ensure all traces of solvent were fully terminated, the films underwent an additional drying process for 8 h in a vacuum oven set at 40 °C.

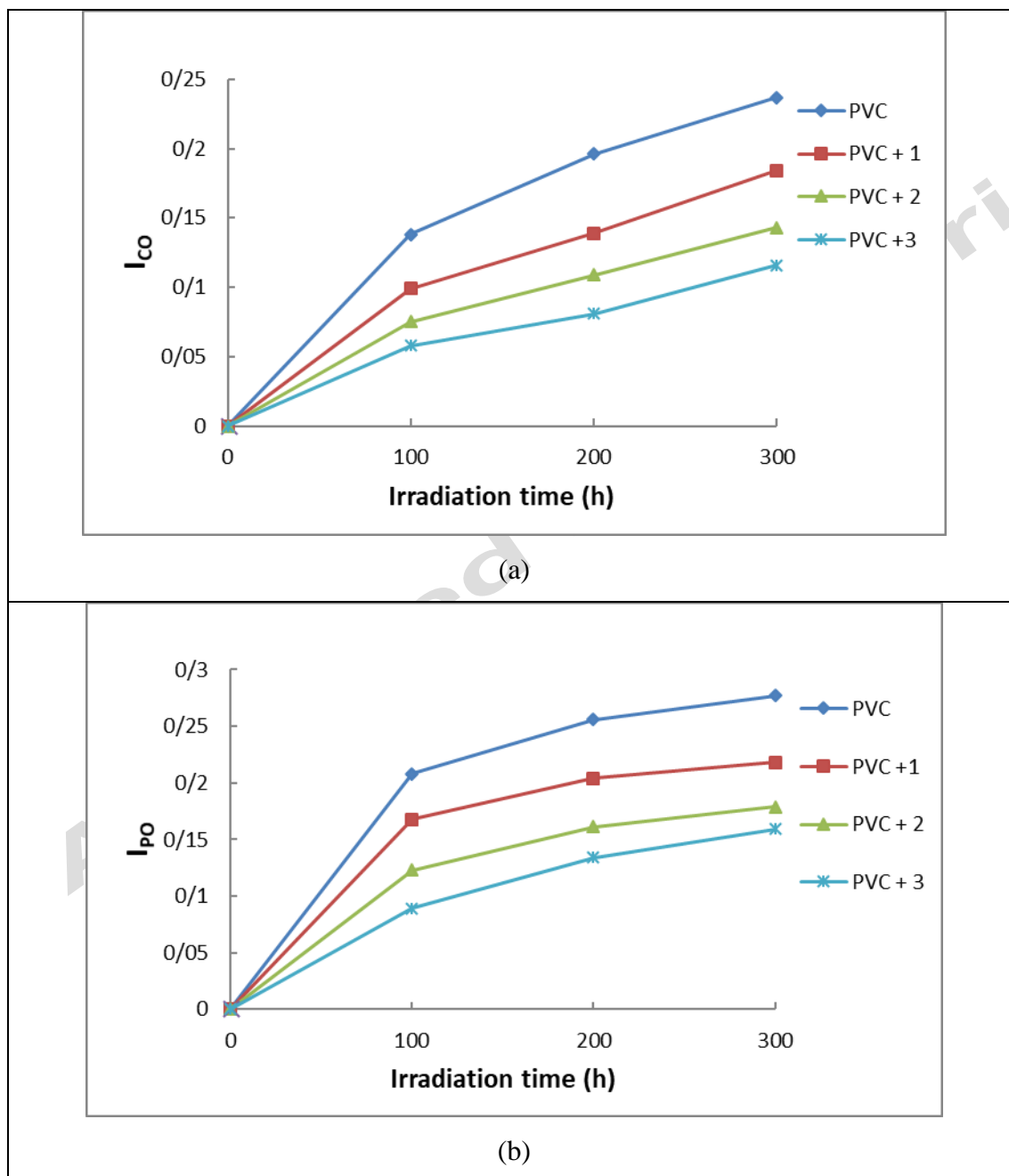
3. Results and Discussion.

3.1 Photodegradation effect of azeynilidene compounds

3.1.1 FTIR Spectroscopy

The FTIR spectra of PVC sheets exhibit characteristic lines at 1725, 1620, and 3450 cm^{-1} , which correspond to aliphatic ketones, double bonds conjugated to the carbonyl group, and alcoholic hydroxyl groups, respectively [26]. The degradation of PVC through exposure to light was investigated by observing variations in the absorption bands of hydroxyl, alkene, and carbonyl groups while being irradiated [27]. The variations in the maximum intensities of these functional groups were compared with the reference peak at 1328 cm^{-1} . The formation indices of the functional groups $I_{\text{C=O}}$, $I_{\text{C=C}}$, and I_{OH} were computed and graphed in Figure 1 a, b, and c, respectively. The indices of C=O, C=C, and OH in PVC sheets containing azanylylidene compounds were reduced and compared to the indices in the blank PVC film. Compounds 1, 2, and 3 have been shown to greatly decrease photodegradation, making them effective additions for providing long-term protection to PVC films versus radiation. Out of the prepared compounds, compound 3 had the highest efficacy in preventing photodegradation. Prior research in our group showed that the most effective concentration of azanylylidene phenolic compounds, synthesized by Schiff base reactions and applied to improve the durability of PVC, is 0.5 wt.% [25]. Therefore, this ratio was applied to fill the azanylylidene phenolic compounds within the PVC films and ultimately enhance the resistance of PVC materials to degradation caused by light exposure. The carbonyl (I_{CO}), polyene (I_{PO}), and hydroxyl (I_{OH}) indices were computed and graphed as a function of irradiation time as illustrated in Figure 1. Indices of PVC films containing azanylylidene

compounds showed lower values than those without these compounds. Hence, the results clearly indicate that azanylylidene phenolic compounds, particularly compound 3, can effectively act as photostabilizers for PVC films.



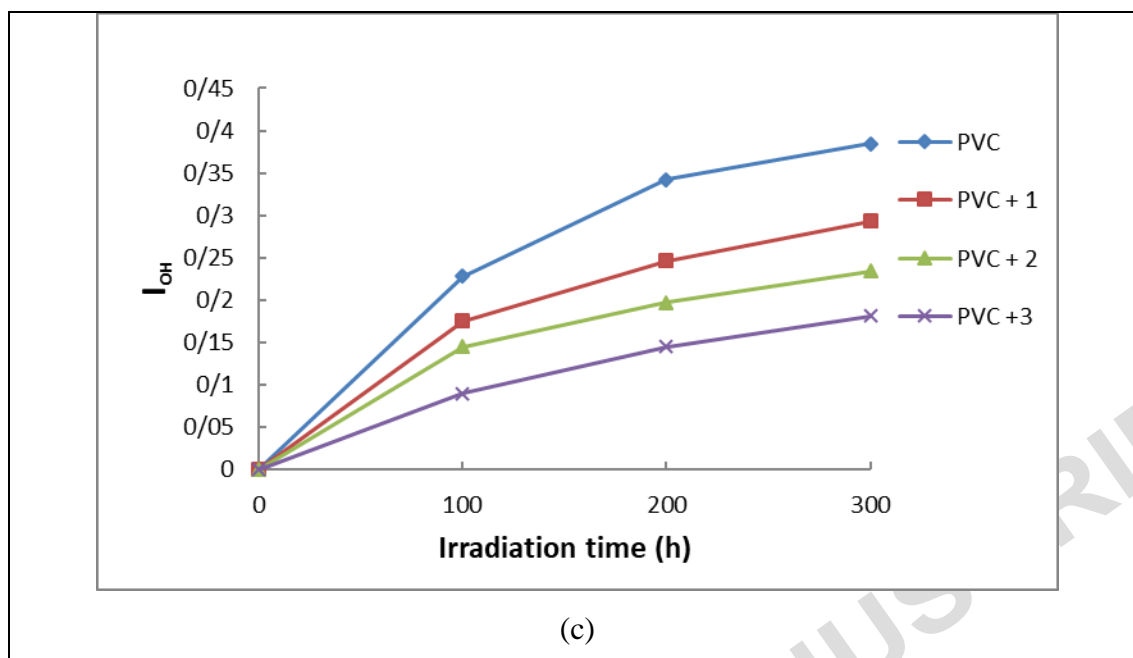


Figure 1. Influence of irradiation time on (a) $I_{C=O}$, (b) $I_{C=C}$, and (c) I_{O-H} of the PVC films.

3.1.2. Weight Loss Estimation

Weight loss results from dehydrochlorination, which involves the removal of hydrochloric acid (HCl) and is a primary source of PVC photodegradation [28]. The proportion of PVC weight lost following radiation exposure can be used to calculate the extent of PVC photodegradation. Figure 2 illustrates the impact of the irradiation period on the rate of weight loss in PVC film. Compared to plain PVC film, there was a significant reduction in weight loss when azanylylidene phenolic compounds were added. The most effective addition was compound 3, which likely acted as a powerful radical scavenger due to its dihydroxy group and nitrogen atoms in the pyridine aromatic ring, enhancing stability through resonance. PVC films containing azanylylidene phenolic compounds exhibited decreased weight loss upon radiation exposure, attributed to the reduction in hydrogen chloride release and the inhibition of polymer chain breakdown [29].

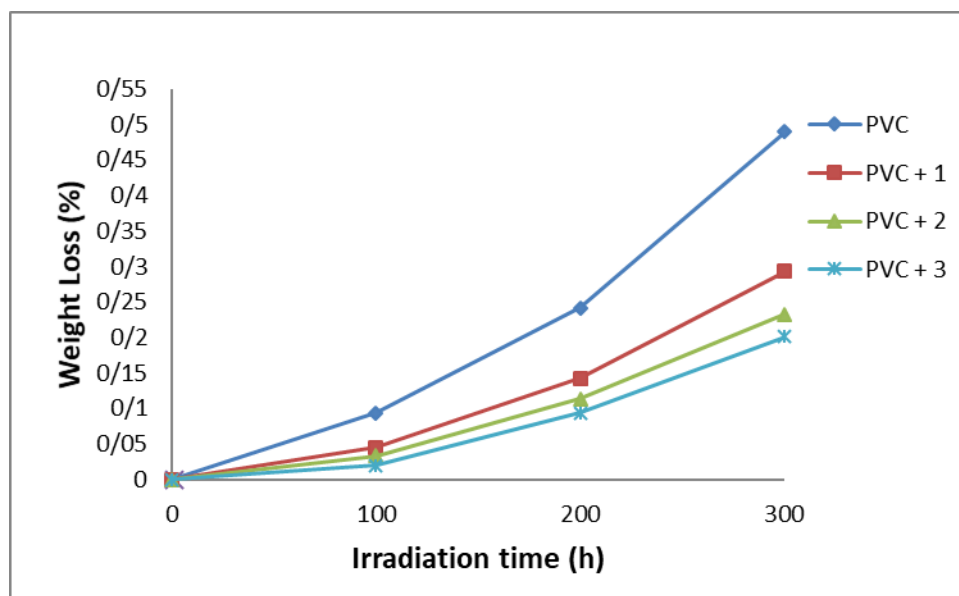


Figure 2. Influence of irradiation time on weight loss (%) for the PVC films.

3.1.3. Molecular weight variation

The alteration molecular weight (M_v) of PVC sheets containing azanylylidene phenolic compounds at a concentration of 0.5 wt.% was determined as a function of irradiation time. This measurement is depicted in Figure 3. The PVC film without any additives exhibited a more significant reduction in M_v compared to the films containing them. Among the fillers, Schiff base 3 showed the most effectiveness. The decrease in M_v seen during irradiation is most likely a result of the deterioration of PVC chains, which leads to the creation of polymeric chains with lower molecular weights [30, 31].

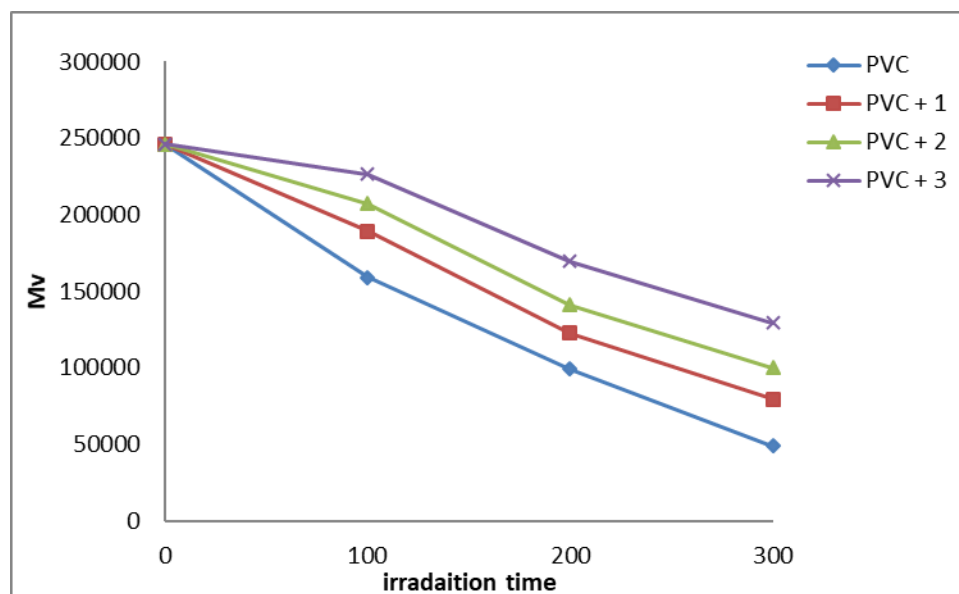


Figure 3. Impact of irradiation time on M_v of PVC films.

The process of photodegradation of PVC results in the breaking of chemical bonds in the polymeric chains and the creation of smaller pieces of the polymer. This results in a reduction in the average size of the polymer molecules, as measured by the M_v [32]. Several PVC films underwent irradiation for durations ranging from 100 to 300 h. After irradiation, THF was introduced to the membranes while agitated and subsequently filtered to eliminate insoluble residues [33]. The solutions' intrinsic viscosity $[\eta]$ was determined employing a viscometer and estimated using equation 2 [34]. Figure 3 demonstrates the reduction in molecular weight of the PVC sheets that were exposed to radiation.

$$[\eta] = 1.38 \times 10^{-4} M_v^{0.77} \quad (2)$$

The molecular weight of PVC is significantly lower when it does not contain additives, as opposed to PVC which contains azanylylidene phenolic compounds. The molecular weight of the plain PVC declined from 246K to 159K after 100 h of irradiation, and further lowered to 49,021 after 300 h. The addition of azanylylidene compounds

significantly mitigated the decrease, providing compelling evidence of their efficacy as photostabilizers for PVC. Following 300 h of exposure to radiation, the molecular weights of the PVC + 1, PVC + 2, and PVC + 3 composites were determined to be 79,336, 99,867, and 129,341, respectively. The blank film experienced a reduction of almost 80%, while the film containing PVC with azanylylidene phenolic compound 3 only experienced a reduction of 47%. The results, supported by FTIR spectroscopy, demonstrate that the reduction in weight and average molecular weight were constant, demonstrating that azanylylidene phenolic compounds, particularly Compound 3, efficiently protect PVC from UV radiation.

3.2. Scanning electrons microscopy analysis

Field scanning electron microscopy (FSEM) techniques are frequently used to study the impact of irradiation on plastics, including PVC. The impact of ultraviolet radiation on the PVC surface was evaluated [35]. The non-irradiated PVC surface exhibited high smoothness and regularity, whereas the irradiated PVC surface appeared irregular, with white spots and cracks [34]. The omission of hydrochloric acid from PVC resulted in the process of crosslinking and the subsequent development of cracks and spots with diverse forms and sizes as shown in Figure 4a and b. The existence of azanylylidene phenolic compounds in PVC reduces the extent of surface damage compared to PVC without these compounds, where the morphology of PVC films filled with components 1, 2, and 3 is illustrated in Figure 4a, b, and c, respectively. Azanylylidene phenolic compound 3 exhibited minimal surface damage. This investigation provides evidence that UV irradiation has a substantial impact on the characteristics of PVC. UV rays can lead to the

deterioration of the surface and the loss of chlorine in PVC, which ultimately leads to a decrease in the material's physical and chemical characteristics. Azanylylidene phenolic compounds have the ability to reduce these detrimental effects, hence improving the acceptability of PVC for outdoor applications.

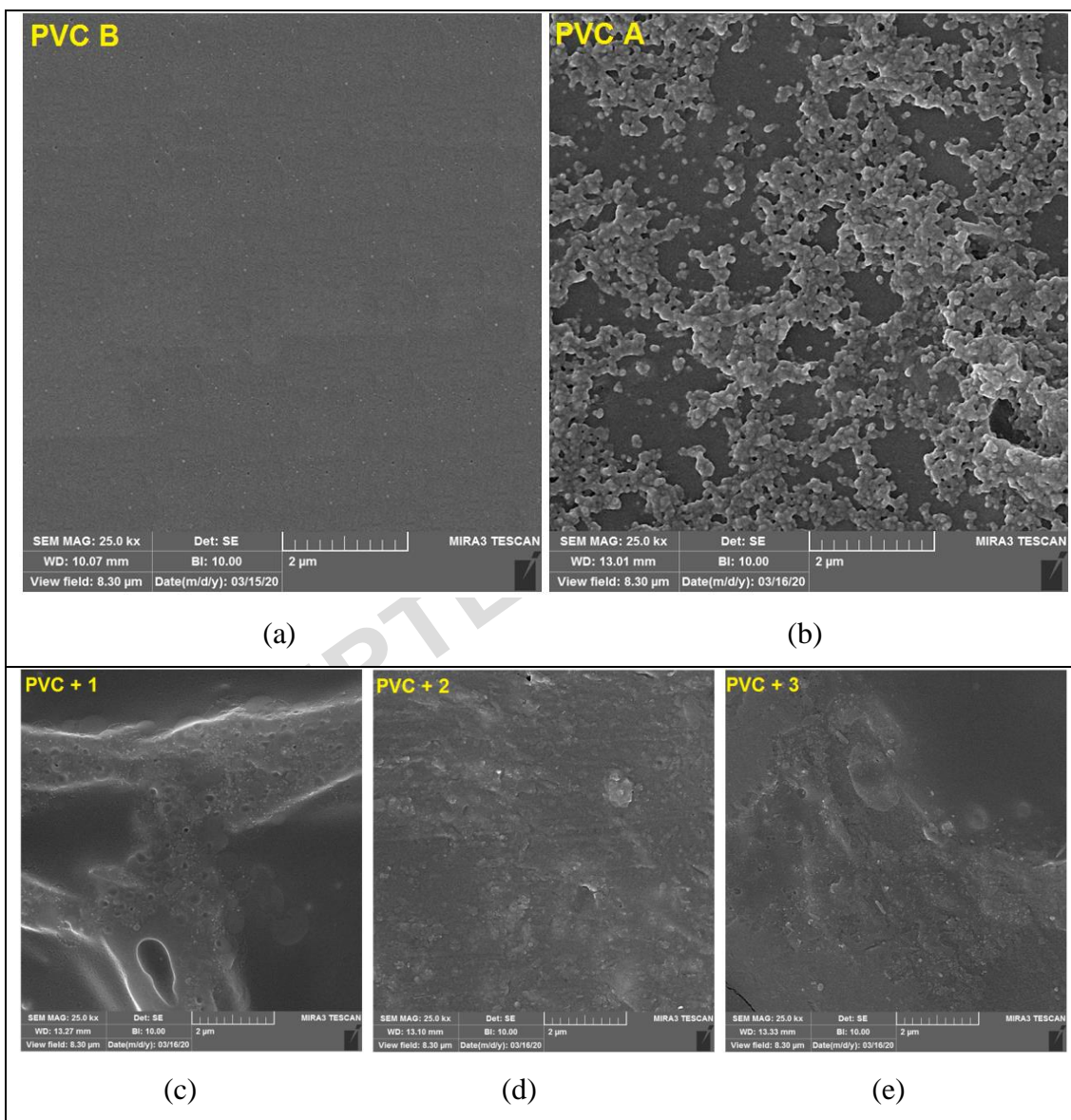
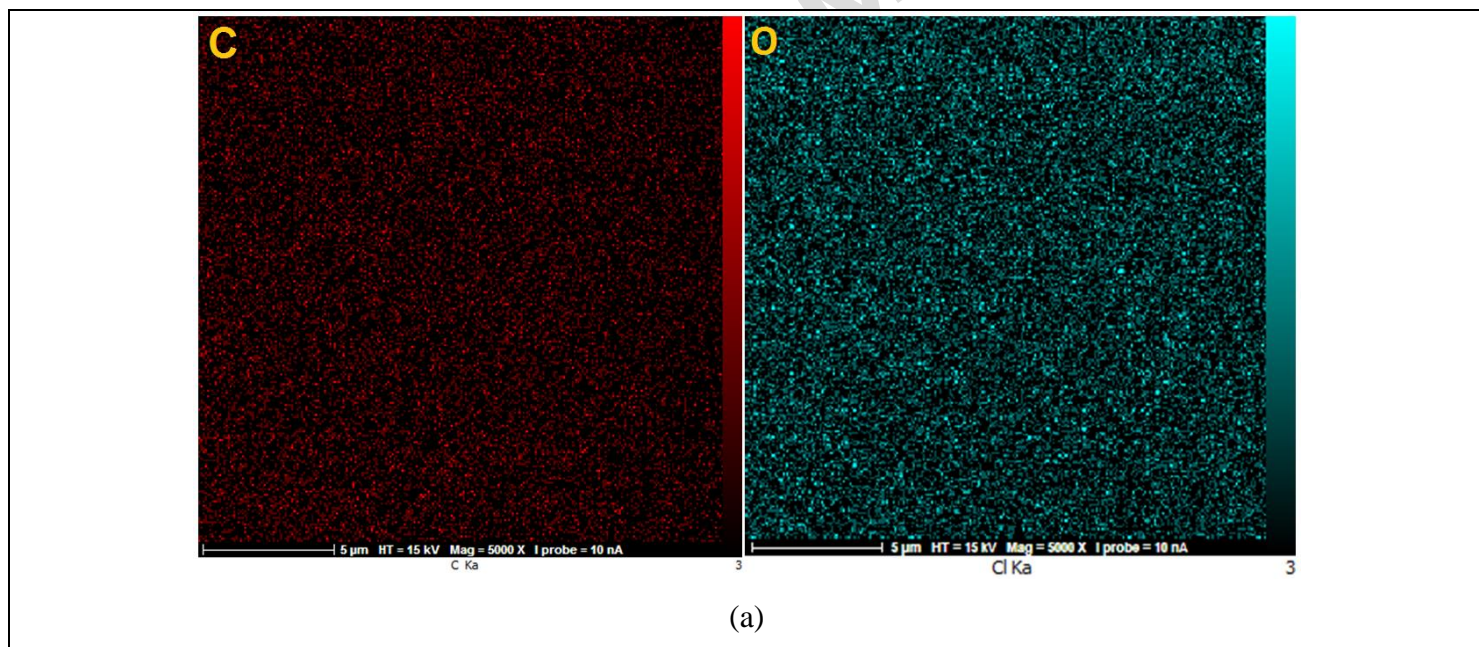


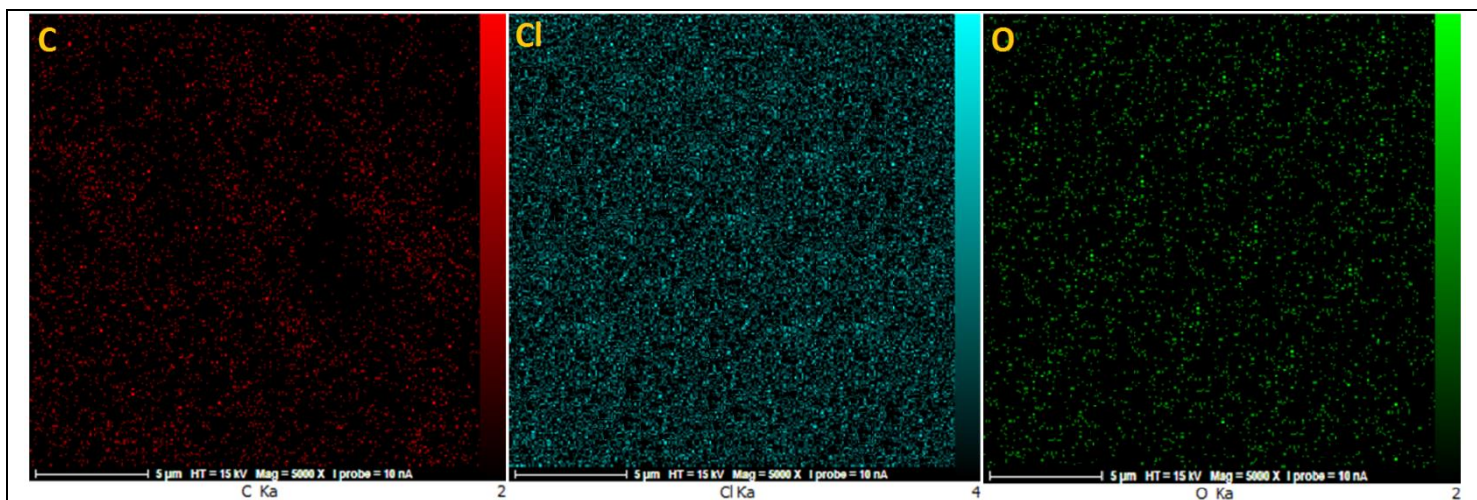
Figure 4. SEM pictures of the PVC films: (a) blank before irradiation, and after irradiation of (b) blank, (c) PVC + 1, (d) PVC + 2, and (e) PVC + 3.

3.3. X-ray mapping

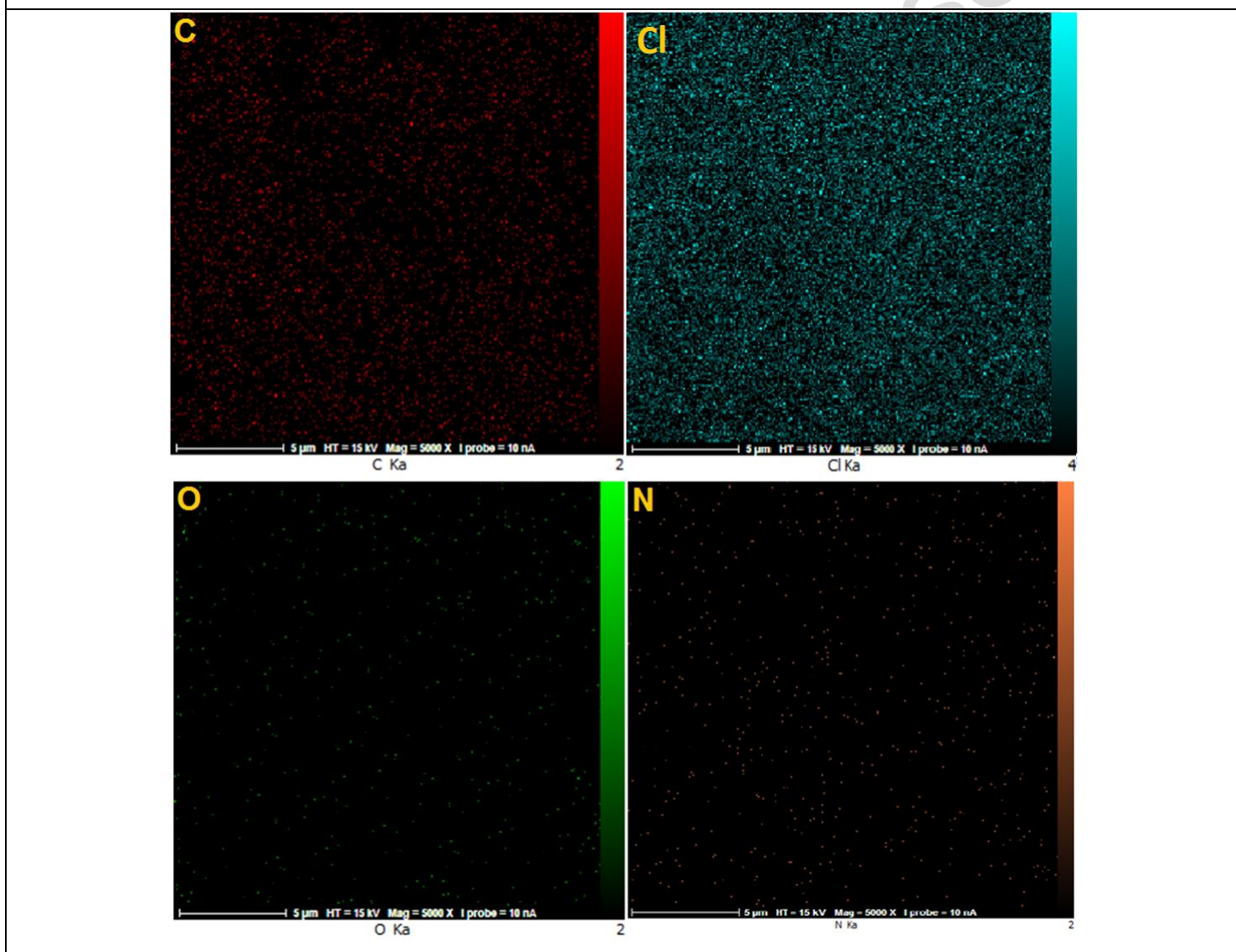
X-ray mapping is used to show images of the distributions and relative

abundances of elements in different colors of a sample [36]. This technique relies on the analysis of X-ray scattering from a film sample, where each atomic element produces a unique scattering pattern [25, 34]. After exposure of PVC to ultraviolet radiation, significant dechlorination of the plain PVC sheet occurs, releasing HCl and decreasing the abundance of chlorine, as illustrated in Figure 5a and b. The distribution of elements and the abundance of phenolic azanylylidene compounds on the PVC surface reduce photodegradation, as presented in Figure 5c. In contrast, the presence of phenolic azanylylidene compounds works to reduce or prevent the autolysis of HCl and also reduces the formation of peroxides, the main source of photodegradation. This is inferred from the decrease in the atomic abundance of oxygen after irradiation of the PVC film in the existence of phenolic azanylylidene compounds compared to the virgin PVC film after irradiation for 300 h, as shown in Figure 5c. Compound 3 shows greater efficiency as a stabilizer against photodegradation compared to other additive compounds.





(b)

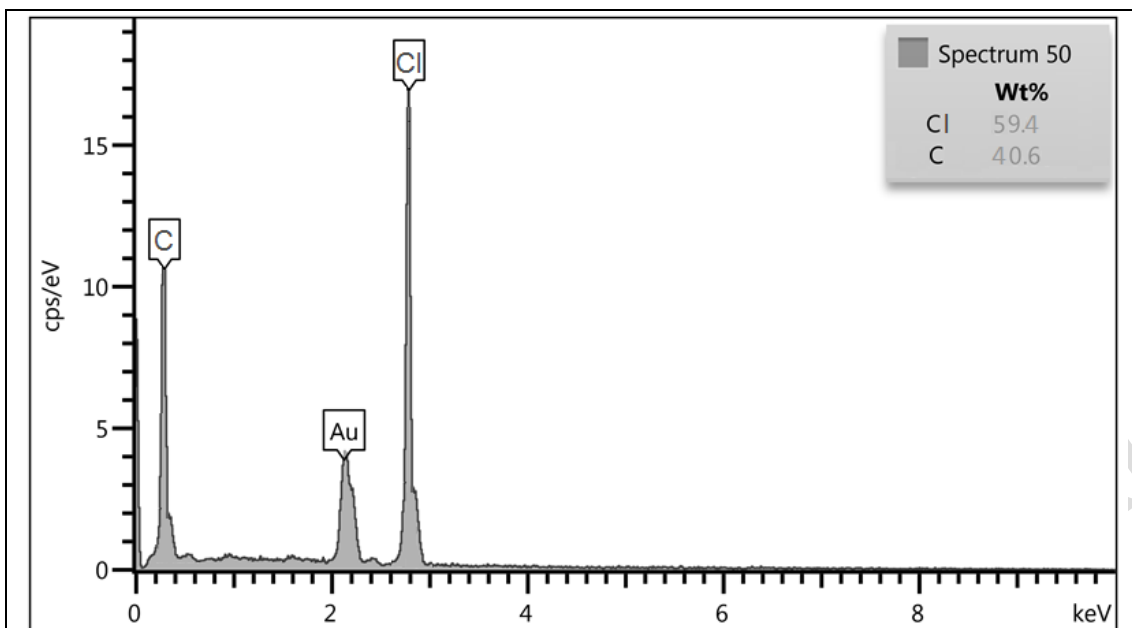


(c)

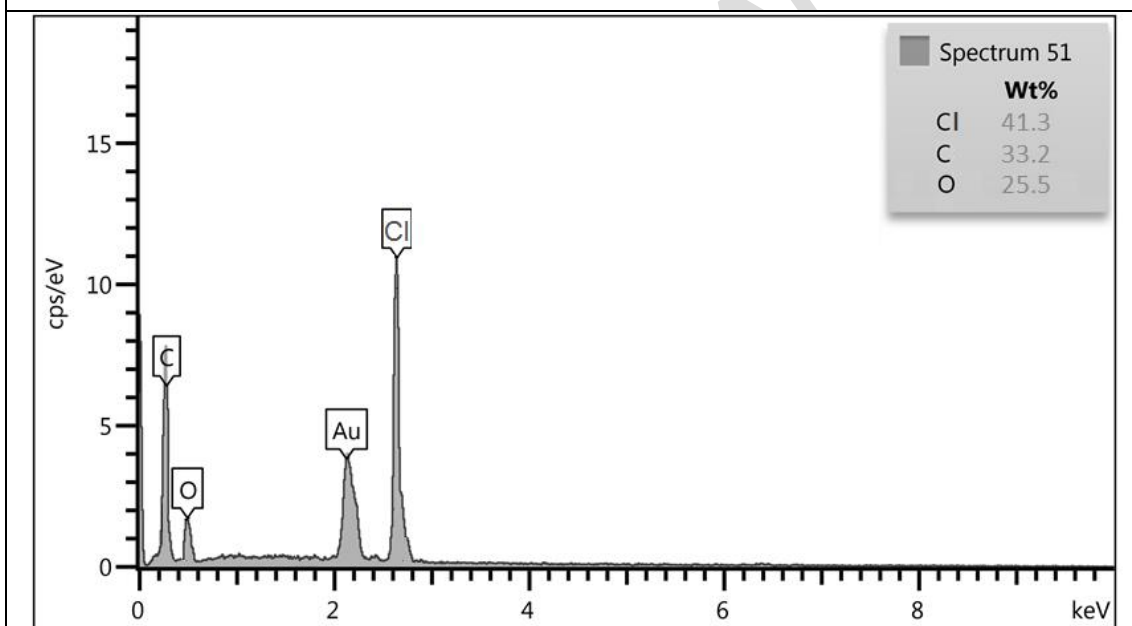
Figure 5. X-ray mapping images of PVC films (a) before irradiation, (b) after 300 h irradiation, and (c) PVC + 3 after irradiation.

3.4. Energy-dispersive X-ray spectroscopy

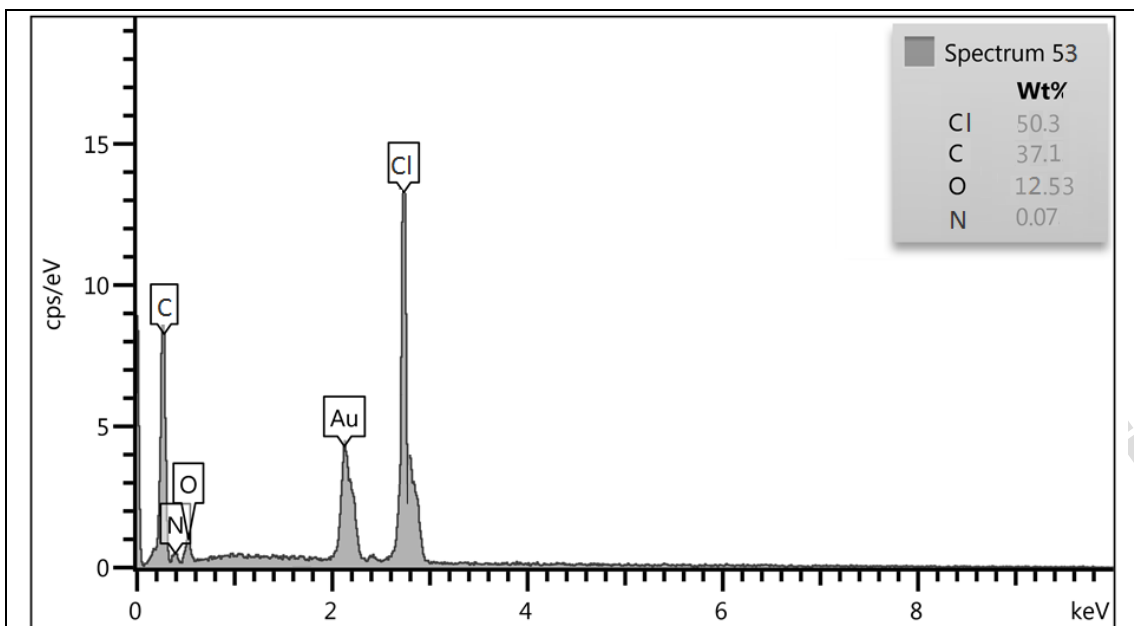
EDX spectroscopy is a method of analysis that is employed to conduct chemical characterization or elemental analysis of a given sample. The process involves examining the interaction between a source of X-ray excitation and the sample. The technique's characterization capabilities arise from the idea that each element possesses a distinct atomic structure, resulting in a special pattern of peaks on its electromagnetic emission spectrum [37]. The X-ray energies are directly related to the variations in energy levels between the atomic structure and the shells of the element that is releasing them. This allows EDX to accurately define the elemental composition of the specimen [38]. The percentage distribution of the elements in each sample was determined by EDX spectroscopy of PVC films with additions of phenolic azanylylidene compounds. The findings are displayed in the pictures illustrated in Figure 6.



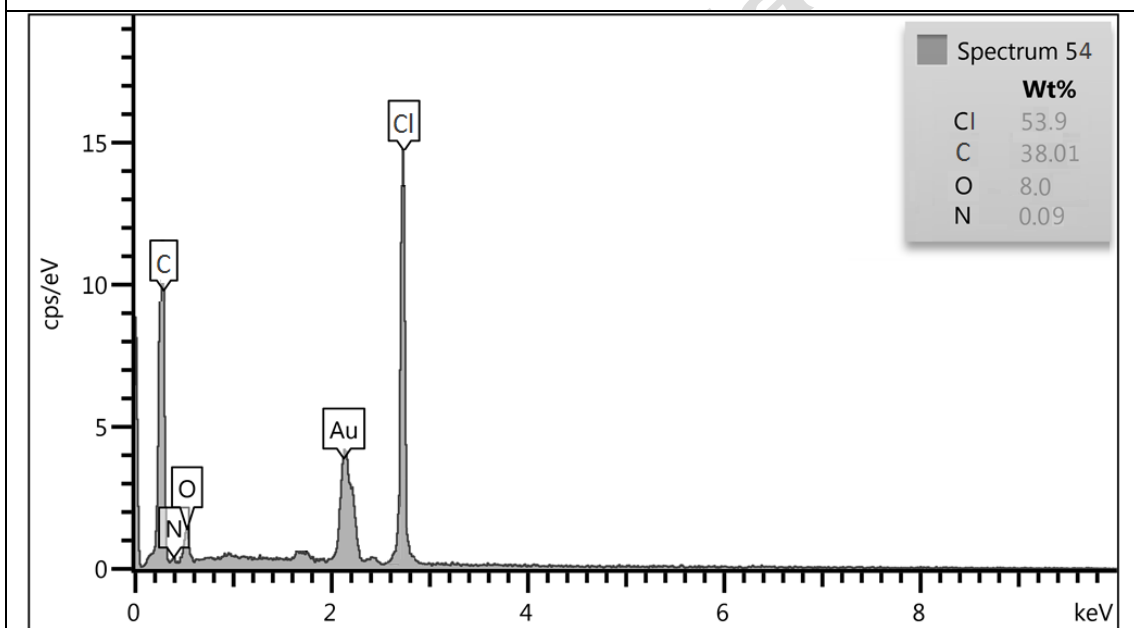
(a)



(b)



(c)



(d)

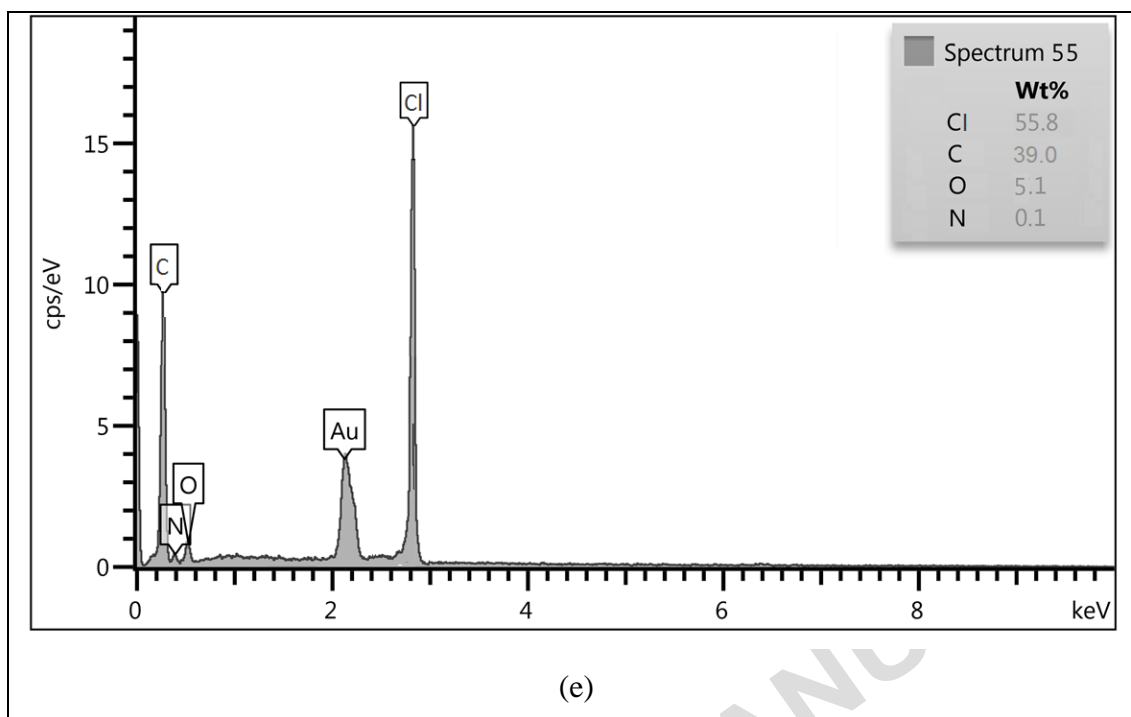


Figure 6. EDX test of PVC (a) plain before irradiation, (b) plain after irradiation, (c) filled with component 1 after irradiation, (d) filled with component 2 after irradiation, and (e) filled with component 3 after irradiation.

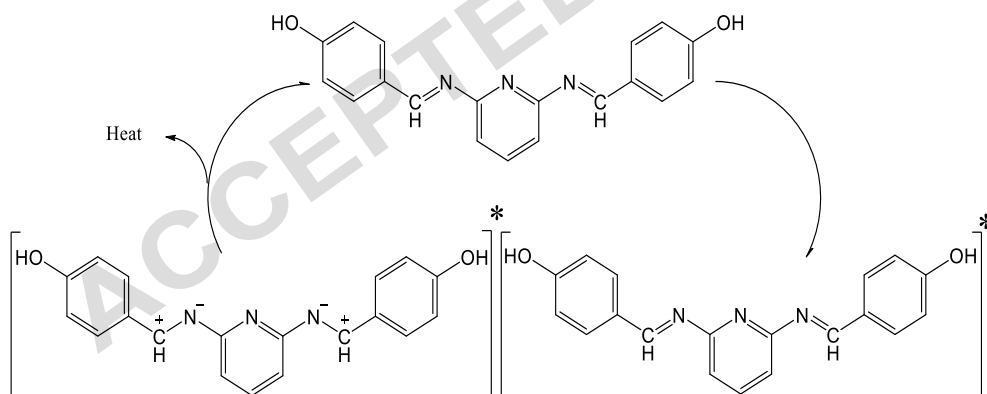
The EDX spectra of the polymeric sheets presented strong absorption bands for atomic chlorine and carbon at 59.4 % and 40.6 %, respectively, before exposure to focused UV radiation. After the 300 h irradiation, the PVC sheet showed lower absorption bands for atomic chlorine (41.3 %) and carbon (33.2 %), with decreases of 30% and 18%, respectively, and the appearance of an average absorption band for atomic oxygen with a percentage higher than 25% compared to the PVC film before irradiation. This means that photo-oxidation and degradation of the polymer films occur, leading to weight loss. Additionally, PVC that contains phenolic azanylylidene compounds presented new bands that refer to nitrogen and oxygen atoms. The band corresponding to atomic nitrogen was more abundant in the blends of PVC + 2 and PVC + 3 than in PVC + 1. The plot of the EDX peaks is consistent with those reported previously [39]. The

oxygen atomic percentage increases as irradiation progresses. Thereby, the enhanced photo-oxidation rate of PVC led to a decline in the atomic chlorine content due to the removal of hydrochloric acid. Furthermore, there was a decrease in atomic carbon due to the crosslinking and the generation of short-chains fragments. After irradiating the plain PVC film, EDX measurements presented that the ratios of both atomic chlorine and carbon diminished. In contrast, the reduction in both atomic chlorine and carbon in the PVC/phenolic azanylylidene compounds mixtures was less pronounced due to the reduced release of hydrochloric acid vapors produced during irradiation processes [40]. Stabilizer 3 showed the highest activity towards photodegradation among the other stabilizers, with a lower reduction rate of 6.1% for atomic chlorine and 3.9% for carbon, and an increase of 8% for oxygen, which is a small amount compared to blank PVC film. Once again, phenolic azanylylidene compounds were shown to act as effective optical stabilizers for PVC.

3.5. Mechanisms of photostabilization proposed

The PVC polymer undergoes photodegradation when exposed to UV rays found in sunlight, resulting in a loss of mechanical properties and discoloration. Therefore, optical stabilizers are used to prevent or slow down the photodegradation process. Phenolic derivatives are among the most common optical stabilizers for PVC polymer. These compounds work by absorbing ultraviolet rays and converting them into thermal energy, thus protecting polymer chains from damage. They prevent the breaking of bonds within the polymer chains. Phenolic azanylylidene compounds has the ability to stabilize PVC versus photodegradation through various mechanisms. These chemicals enhance the

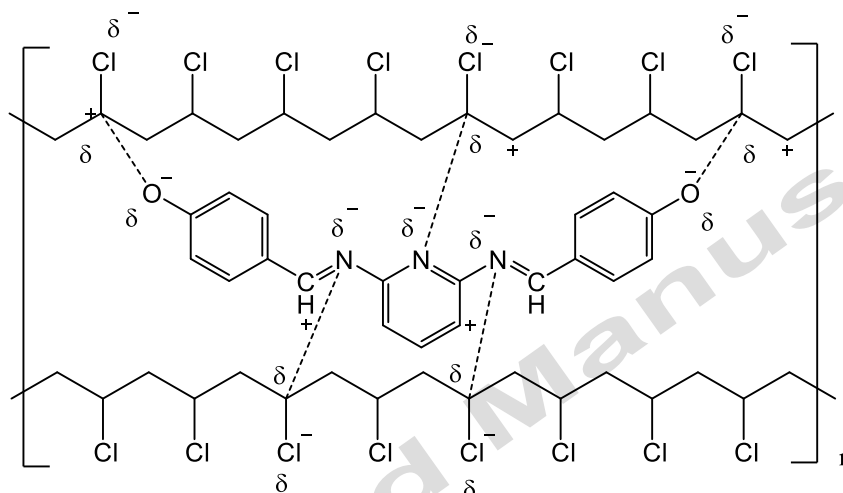
stability of PVC by absorbing UV radiation. Organosilanes' aromatic components (phenyl and aryl groups) serve as ultraviolet (UV) absorbers. These groups emit the received energy as heat without causing any damage to the PVC material [41]. Phenolic azanylylidene has varied performance outcomes due to the strong electron-donating nature of hydroxyl groups. The higher resonance of aryl groups makes hydroxyl groups the most effective in stabilizing PVC. The presence of nitrogen atoms in the heteroaromatic rings of pyrrole and pyridine contributes to the enhancement of photostabilization by donating electrons. This electron donation helps in connecting polymer chains and inhibiting chlorine auto-decomposition. In addition, the $-\text{CH}=\text{N}$ bond can absorb UV light and create a stable excited species with separated charges as shown in Scheme 2. This arrangement dissipates absorbed light energy in the form of heat through rotational and vibrational motion without causing harm to the PVC material.



Scheme 2. PVC photostabilization of phenolic azanylylidene **3** via direct absorption of UV radiation.

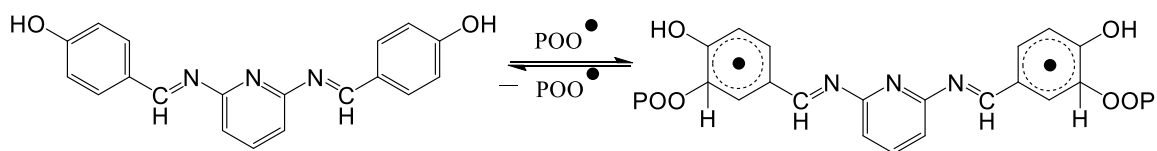
Azanylylidene phenolic compounds improve the resistance of PVC to degradation caused by light by forming a coordination link between the polarized atoms of the $-\text{CH}=\text{N}$ group in Schiff bases and the C-Cl bonds in the polymer chains (Scheme 3). In addition, the alignment of the polarized oxygen atoms in phenolic azanylylidene compounds with the

carbon atoms of the C–Cl bonds contributes to the stabilization of the polymer [25, 34]. The coordination bonds enable the transfer of excited state energy from PVC to phenolic azanylylidene without detrimental effects on the polymer. However, the likelihood of forming strong coordination bonds inside macromolecules is rather restricted.



Scheme 3. PVC photostabilization *via* interaction between PVC chains and phenolic azanylylidene 3.

Azanylylidene phenolic compounds can function as radical scavengers while the existence of a chromophore (POO) [42]. These chemicals react with chromophores (polymeric proxy radicals; POO•) [6] to create steady complexes as presented in Scheme 4. The absorbed energy is counteracted and made stable through the resonance of aryl groups, enabling its transfer across a significant number of atoms.



Scheme 4. PVC photostabilization by phenolic azanylylidene 3 as a radical scavenger.

4. Conclusion.

Phenolic azanylylidene compounds show promise as additives for extending the lifespan of PVC products used in exposed environments, such as pipes and membranes. Acting as antioxidants, these compounds absorb UV radiation and neutralize free radicals formed from reactions with oxygen, thereby preventing polymer degradation. After 300 h of irradiation, our findings revealed that the addition of phenolic azanylylidene compounds to PVC films significantly reduced the growth of absorption coefficients for carbonyl, hydroxyl, and polyene groups by 51 %, 52 %, and 42 %, respectively, compared to untreated PVC films. Weight loss measurements indicated greater stability for PVC films treated with phenolic azanylylidene compounds. Remarkably, the weight loss after irradiation of the film filled with compound 3 was reduced to 59 % compared to plain PVC. Moreover, the molecular weight of the untreated polymer decreased significantly with increasing irradiation time, whereas the polymer treated with phenolic azanylylidene exhibited a much lower reduction in molecular weight. Specifically, the untreated film showed a molecular weight reduction of over 80 %, while the PVC film containing compound 3 showed only a 47 % decrease. The other compounds also minimized surface changes in the polymer upon UV exposure in different degrees. Hence, it can be concluded that incorporating phenolic azanylylidene compounds into PVC films enhances their resistance to UV degradation.

Acknowledgment

The authors like to thank the Department of Chemistry at Al-Nahrain University for providing access to labs.

5. References

- [1] Usharani M, Akila E, Rajavel R. Pharmacological properties of Schiff base metal complexes derived from substituted pyridine and aromatic amine: A review. *Int J Adv Sci Tech Res.* 2013; 5:198-206. <https://doi.org/10.4236/ns.2012.43025>.
- [2] Al Zoubi W. Biological activities of Schiff bases and their complexes: A review of recent works. *Int J Org Chem.* 2013. <https://doi.org/10.4236/ijoc.2013.33A008>.
- [3] Naser AW, Majeed AM. Synthesis of some new sulfonamide derivatives based on 1,3,4-oxadiazole. *J Chem Pharm Res.* 2015; 7(3):300-306. <https://doi.org/10.7598/cst2015.1029>.
- [4] Mohammed MY, Abd AN, Ali AS. Synthesis and characterization of some metals (II) complexes with mixed ligands of saccharinate and isatin Schiff base. *Tikrit J Pure Sci.* 2018; 22(6):56-64. <https://doi.org/10.25130/tjps.v22i6.791>.
- [5] Lee QY, Li H. Photocatalytic degradation of plastic waste: A mini review. *Micromachines.* 2021; 12(8):907. <https://doi.org/10.3390/mi12080907>.
- [6] Yousif E, Haddad R. Photodegradation and photostabilization of polymers, especially polystyrene. *SpringerPlus.* 2013; 2:1-32. <https://doi.org/10.1186/2193-1801-2-398>.
- [7] Keane MA. Catalytic conversion of waste plastics: Focus on waste PVC. *J Chem Technol Biotechnol.* 2007; 82(9):787-795. <https://doi.org/10.1002/jctb.1757>.
- [8] Ma Y, Liao S, Li Q, Guan Q, Jia P, Zhou Y. Physical and chemical modifications of

poly(vinyl chloride) materials to prevent plasticizer migration—Still on the run. *React Funct Polym.* 2020; 147:104458. <https://doi.org/10.1016/j.reactfunctpolym.2019.104458>.

[9] Starnes WH Jr. Structural and mechanistic aspects of the thermal degradation of poly(vinyl chloride). *Prog Polym Sci.* 2002; 27(10):2133-2170. [https://doi.org/10.1016/S0079-6700\(02\)00063-1](https://doi.org/10.1016/S0079-6700(02)00063-1).

[10] Lu T, Solis-Ramos E, Yi YB, Kumosa M. Particle removal mechanisms in synergistic aging of polymers and glass reinforced polymer composites under combined UV and water. *Compo Sci Technol.* 2017; 153:273-281. <https://doi.org/10.1016/j.compscitech.2017.10.028>.

[11] Ibrahiem H, El-Hiti GA, Al-Mashhadani MH, Ahmed DS, Bufaroosha M. Impact of ultraviolet radiation on the aging properties of PVC films doped by tin (IV) complexes. *Baghdad Sci J.* 2024. <https://doi.org/10.21123/bsj.2024.10430>.

[12] Valko L, Klein E, Kovařík P, Bleha T, Šimon P. Kinetic study of thermal dehydrochlorination of poly(vinyl chloride) in the presence of oxygen: III. Statistical thermodynamic interpretation of the oxygen catalytic activity. *Eur Polym J.* 2001; 37(6):1123-1132. [https://doi.org/10.1016/S0014-3057\(00\)00239-1](https://doi.org/10.1016/S0014-3057(00)00239-1).

[13] Zheng XG, Tang LH, Zhang N, Gao QH, Zhang CF, Zhu ZB. Dehydrochlorination of PVC materials at high temperature. *Energy Fuels.* 2003; 17(4):896-900. <https://doi.org/10.1021/ef020131g>.

[14] Liu J, Lv Y, Luo Z, Wang H, Wei Z. Molecular chain model construction, thermo-stability, and thermo-oxidative degradation mechanism of poly(vinyl chloride). *RSC Adv.* 2016; 6(38):31898-31905. <https://doi.org/10.1039/C6RA02354A>.

[15] Lu T, Solis-Ramos E, Yi Y, Kumosa M. UV degradation model for polymers and

polymer matrix composites. *Polym Degrad Stab.* 2018; 154:203-210.

<https://doi.org/10.1016/j.polymdegradstab.2018.06.004>.

[16] Folarin OM, Sadiku ER. Thermal stabilizers for poly(vinyl chloride): A review. *Int J Phys Sci.* 2011; 6(18):4323-4330. <https://doi.org/10.5897/IJPS11.654>.

[17] Jirjees VY, Al-Hamdani AAS, Wannas NM, AR F, Dib A, Al Zoubi W. Spectroscopic characterization for new model from Schiff base and its complexes. *J Phys Org Chem.* 2021; 34(4). <https://doi.org/10.1002/poc.4169>.

[18] Ahmed DS, Mohammed A, Husain AA, El-Hiti GA, Kadhom M, Kariuki BM, Yousif E. Fabrication of highly photostable polystyrene films embedded with organometallic complexes. *Polymers.* 2022; 14(5):1024. <https://doi.org/10.3390/polym14051024>.

[19] Ahmed A, Abdallah M, Al-Mashhadani MH, Ahmed DS, Bufaroosha M, Jawad AH, Yousif E. Environmental stability of poly(vinyl chloride) modified by Schiff's base under exposure to UV. *Biointerface Res Appl Chem.* 2021; 11(5):13465-13473. <https://doi.org/10.33263/BRIAC115.1346513473>.

[20] Yaseen AA, Yousif E, Al-Tikrity ET, El-Hiti GA, Kariuki BM, Ahmed DS, Bufaroosha M. FTIR, weight, and surface morphology of poly(vinyl chloride) doped with tin complexes containing aromatic and heterocyclic moieties. *Polymers.* 2021; 13(19):3264. <https://doi.org/10.3390/polym13193264>.

[21] Ahmed AA, Al-Mashhadani MH, Hashim H, Ahmed DS, Yousif E. Morphological, color impact, and spectroscopic studies of new Schiff base derived from 1,2,4-triazole ring. *Prog Color Colorants Coat.* 2021; 14(1):27-34. <https://doi.org/10.30509/PCCC.2021.81664>.

[22] Mousa OG, El-Hiti GA, Baashen MA, Bufaroosha M, Ahmed A, Ahmed AA, et al. Synthesis of carvedilol–organotin complexes and their effects on reducing photodegradation of poly(vinyl chloride). *Polymers*. 2021; 13(4):500. <https://doi.org/10.3390/polym13040500>.

[23] Mohamed SH, Hameed AS, Yousif E, Alotaibi MH, Ahmed DS, El-Hiti GA. New porous silicon-containing organic polymers: Synthesis and carbon dioxide uptake. *Processes*. 2020; 8(11):1488. <https://doi.org/10.3390/pr8111488>.

[24] Mohammed HA, Taha NI. Microwave preparation and spectroscopic investigation of binuclear Schiff base metal complexes derived from 2,6-diaminopyridine with salicylaldehyde. *Int J Org Chem*. 2017; 7(4):412-419. <https://doi.org/10.4236/ijoc.2017.74033>.

[25] Mohamed SH, Yousif E, Hameed AS, Ahmed DS, Zainulabdeen K, Saleh HM, et al. Morphology and performance of poly(vinyl chloride) thin films doped with polyorganosilanes against photodegradation. *Silicon*. 2023; 15(9):4027-4038. <https://doi.org/10.21203/rs.3.rs-2144338/v1>.

[26] Shi X, Chen Z, Liu X, Wei W, Ni BJ. The photochemical behaviors of microplastics through the lens of reactive oxygen species: Photolysis mechanisms and enhancing photo-transformation of pollutants. *Sci. Total Environ*. 2022; 846:157498. <https://doi.org/10.1016/j.scitotenv.2022.157498>.

[27] Mousa OG, El-Hiti GA, Baashen MA, Bufaroosha M, Ahmed A, Ahmed AA, et al. Synthesis of carvedilol–organotin complexes and their effects on reducing photodegradation of poly(vinyl chloride). *Polymers*. 2021; 13(4):500. <https://doi.org/10.3390/polym13040500>.

- [28] Jafari AJ, Donaldson JD. 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. *J Chem.* 2009; 6(3):685-692. <https://doi.org/10.1155/2009/753835>.
- [29] Mohamed S, Yousif E, Kadhom M, Bufaroosha M. Enhanced photostability of polyvinyl chloride films through antipyrine derivatives: A comprehensive study on UV resistance and degradation inhibition. *Macromol Res.* 2024; 1-19. <https://doi.org/10.1007/s13233-024-00310-5>.
- [30] Mark JE, editor. *Physical properties of polymers handbook*. Vol. 1076. New York: Springer; 2007. p. 825. <https://doi.org/10.1007/978-0-387-69002-5>.
- [31] Dadoosh RM, Alwan AF, Farhan SA, Jassim BE, Mahmood A, Al-Saadi LG, Abed RN. Study of physicochemical properties of PVC thin films affected by carbon nanotubes to prevent photodegradation during UV light exposure. *Prog Color Colorants Coat.* 2024; 17(3):307-324. <https://doi.org/10.30509/pccc.2024.167260.1275>.
- [32] Salman H, Ahmed DS, Hassan AA, Shnein J, Kadhom M, Kareem R, et al. Innovative metal complexes as photostabilizers to improve the functional longevity of polyvinyl chloride. *Kimya Problemleri.* 2024; 22(2):221-230. <https://doi.org/10.32737/2221-8688-2024-2-221-230>.
- [33] Ali A, Zhang N, Santos RM. Mineral characterization using scanning electron microscopy (SEM): A review of the fundamentals, advancements, and research directions. *Appl Sci.* 2023; 13(23):12600. <https://doi.org/10.3390/app132312600>.
- [34] Mohamed SH, Hameed AS, El-Hiti GA, Ahmed DS, Kadhom M, Baashen MA, et al. A process for the synthesis and use of highly aromatic organosilanes as additives for poly(vinyl chloride) films. *Processes.* 2021; 9(1):91. <https://doi.org/10.3390/pr9010091>.

- [35] Liu B, Xin YN, Zou J, Khoso FM, Liu YP, Jiang XY, et al. Removal of chromium species by adsorption: Fundamental principles, newly developed adsorbents, and future perspectives. *Molecules*. 2023; 28(2):639. <https://doi.org/10.3390/molecules28020639>.
- [36] Sabaa MW, Oraby EH, Naby ASA, Mohamed RR. Anthraquinone derivatives as organic stabilizers for rigid poly(vinyl chloride) against photo-degradation. *Eur Polym J*. 2005; 41(11):2530-2543. <https://doi.org/10.1016/j.eurpolymj.2005.05.015>.
- [37] Goldstein JI, Newbury DE, Michael JR, Ritchie NW, Scott JHJ, Joy DC. *Scanning electron microscopy and X-ray microanalysis*. Springer; 2017. <https://doi.org/10.1007/978-1-4939-6676-9>.
- [38] Bates S, Zografu G, Engers D, Morris K, Crowley K, Newman A. Analysis of amorphous and nanocrystalline solids from their X-ray diffraction patterns. *Pharm Res*. 2006; 23:2333-2349. <https://doi.org/10.1007/s11095-006-9086-2>.
- [39] Newbury DE. The new X-ray mapping: X-ray spectrum imaging above 100 kHz output count rate with the silicon drift detector. *Microsc Microanal*. 2006; 12(1):26-35. <https://doi.org/10.1017/S143192760606020X>.
- [40] Jafari AJ, Donaldson JD. 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. *J Chem*. 2009; 6(3):685-692. <https://doi.org/10.1155/2009/753835>.
- [41] Balakit AA, Ahmed A, El-Hiti GA, Smith K, Yousif E. Synthesis of new thiophene derivatives and their use as photostabilizers for rigid poly(vinyl chloride). *Int J Polym Sci*. 2015; 2015(1):510390. <https://doi.org/10.1155/2015/510390>.
- [42] Ibrahiem H, El-Hiti GA, Al-Mashhadani MH, Ahmed DS, Bufaroosha M. Impact of ultraviolet radiation on the aging properties of PVC films doped by tin(IV) complexes.

Accepted Manuscript