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JALEEL R. UKAL

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Improved photostability of PVC films in the presence of 2-thioacetic acid-5-phenyl-1,3,4-oxadiazole complexes

Emad A. YOUSIF^{1,*}, Salah M. ALIWI², Ameer A. AMEER¹,
Jaleel R. UKAL¹

¹*Department of Chemistry, College of Science, AL-Nahrain University, Baghdad-IRAQ*
e-mail: emad_chemistry@yahoo.com

²*Department of Chemistry, College of Science, AL-Mustansiriyah University, Baghdad-IRAQ*

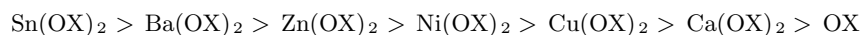
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The photostabilization of poly(vinyl chloride) (PVC) films by 2-thioacetic acid-5-phenyl-1,3,4-oxadiazole with Sn(II), Ba(II), Ni(II), Zn(II), Cu(II), and Ca(II) complexes was investigated. PVC films containing different concentrations of complexes ranging from 0.1% to 0.5% by weight were produced by the same casting method from THF solvent.

The photostabilization activities of these compounds were determined by monitoring the carbonyl and polyene indices with irradiation time. The changes in viscosity average molecular weight of PVC with irradiation time were also tracked (using THF as a solvent).

The quantum yield of the chain scission (Φ_{cs}) of these complexes in PVC films was evaluated and found to range between 4.94×10^{-8} and 1.61×10^{-7} .

The results obtained showed that the rate of photostabilization of PVC in the presence of the additive follows the trend:



Based on the experimental results obtained, several mechanisms were suggested depending on the structure of the additive. HCl scavenging, UV absorption, peroxide decomposer and radical scavenger for photo-stabilizer additives mechanisms were suggested.

Key Words: Photostabilizer, PVC, oxadiazole.

*Corresponding author

Introduction

The low cost and good performance of poly(vinyl chloride) (PVC) products have increased the utilization of this polymer in building, mainly in exterior application, such as window profiles, cladding structures, and siding.¹ However, ultimate user acceptance of PVC products for outdoor building applications depends on their ability to resist photodegradation over long periods of sunlight exposure.² To ensure the weatherability of these materials, the PVC resin needs to be compounded and processed properly using suitable additives, leading to a complex material whose behavior and properties are quite different from the PVC resin by itself.³ On the other hand, it is important to perform reliable accelerated weathering tests.⁴ In this regard, factors that influence the degradation of PVC based materials in the service conditions, like light and temperature, are accelerated.

As part of our program on this subject, the photostabilization of PVC was studied using 2-thioacetic acid-5-phenyl-1, 3, 4-oxadiazole complexes.

Experimental

Materials

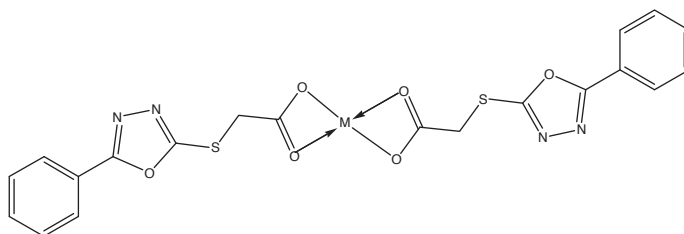
A literature method was used for the preparation of the 2-thioacetic acid-5-phenyl-1,3,4-oxadiazole ligand.^{5,6}

Preparation of complexes

An ethanolic solution of the suitable metal salt (nickel acetate tetrahydrate, tin chloride, copper acetate, cadmium acetate dihydrate, and zinc acetate dihydrate) was added to an ethanolic solution of 2-thioacetic acid-5-phenyl-1,3,4-oxadiazole in 2:1 (ligand:metal) molar ratios. After refluxing the reactants for half an hour, crystalline colored precipitates formed at room temperature. The resulting solids were filtered off, washed with distilled water, dried and recrystallized from ethanol and dried at 50 °C.

The following ligand and complexes were all prepared by the method described by Yousif.⁵

2-thioacetic acid-5-phenyl-1,3,4-oxadiazole	(OX)
Bis [2-thioacetic acid-5-phenyl-1,3,4-oxadiazole]tin(II)	Sn(OX) ₂
Bis[2-thioacetic acid-5-phenyl-1,3,4-oxadiazole]barium(II)	Ba(OX) ₂
Bis [2-thioacetic acid-5-phenyl-1,3,4-oxadiazole]nickel(II)	Ni(OX) ₂
Bis [2-thioacetic acid-5-phenyl-1,3,4-oxadiazole]zinc(II),	Zn(OX) ₂ .
Bis[2-thioacetic acid-5-phenyl-1,3,4-oxadiazole]copper(II)	Cu(OX) ₂
Bis[2-thioacetic acid-5-phenyl-1,3,4-oxadiazole]calcium(II)	Ca(OX) ₂



where M = Sn(II), Ba(II), Ni(II), Zn(II), Cu(II), and Ca(II)

Experimental techniques

I) Film preparations

Commercial PVC supplied from Petkim company (Turkey) was re-precipitated from THF solution by alcohol several times and finally dried under vacuum at room temperature for 24 h. Different concentrations of PVC solution (g/mL) in tetrahydrofuran (THF) were used to prepare different polymer films of varying thickness (measured by a micrometer type 2610 A, Germany). Various concentrations of the prepared complexes were added to these films starting at zero. The films were prepared by evaporation technique at room temperature for 24 h. To remove the possible residual tetrahydrofuran solvent, film samples were further dried at room temperature for 3 h under reduced pressure. The films were fixed on a stand especially used for irradiation. The stand has an aluminum plate 0.6 mm in thickness supplied by Q-panel company.

II) Irradiation experiments

Accelerated testing technique

Accelerated weatherometer Q.U.V. tester (Q-panel company, USA), was used for irradiation of polymers films. The accelerated weathering tester contains a stainless steel plate that has 2 holes in the front side and a third one behind. Each side contains a lamp (type Fluorescent Ultraviolet Lights) 40 W each. These lamps are of the type UV-B 313, giving a spectrum range between 290 and 360 nm with a maximum at wavelength 313 nm.

The polymer film samples were vertically fixed parallel to the lamps to make sure that UV incident radiation was perpendicular on the samples. The irradiated samples were rotated from time to time to ensure that the intensity of light incident on all samples was the same.

III) Photodegradation measuring methods

A. Measuring the photodegradation rate of polymer films using infrared spectrophotometry

The degree of photodegradation of polymer film samples was followed by monitoring FTIR spectra in the range 4000-400 cm^{-1} using a FTIR 8300 Shimadzu spectrophotometer.

The position of carbonyl absorption is specified at 1722 cm^{-1} and that of polyene group at 1602 cm^{-1} .⁷

The progress of photodegradation during different irradiation times was followed by observing the changes in carbonyl and polyene peaks. Then carbonyl (I_{co}) and polyene (I_{po}) indices were calculated by comparison of the FTIR absorption peak at 1722 cm^{-1} and 1602 cm^{-1} with a reference peak at 1328 cm^{-1} , respectively. This method is called the band index method,⁷ which includes:

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

A_s = Absorbance of peak under study.

A_r = Absorbance of reference peak.

I_s = Index of group under study.

Actual absorbance, the difference between the absorbance of top peak and base line (A Top Peak – A Base Line), is calculated using the base line method.⁸

B. Determination of viscosity average molecular weight (\bar{M}_v) using viscometry

The viscosity property was used to determine the molecular weight of polymer, using the Mark-Houwink relation.⁹

$$[\eta] = K\bar{M}_v^\alpha \quad (2)$$

$[\eta]$ = is the intrinsic viscosity.

K, α = are constants dependent upon the polymer-solvent system at a particular temperature.

The single-point measurements were converted to intrinsic viscosities by Eq. (3):¹⁰

$$[\eta] = \left(\sqrt{2}/c\right) (\eta_{sp} - l\eta_{re})^{1/2} \quad (3)$$

c = Concentration of polymer solution (g/100 mL).

By applying Eq. (3), the molecular weight of degraded and undegraded polymer can be calculated.

Molecular weights of PVC with and without additives were calculated from intrinsic viscosities measured in THF solution using the following equation:⁹

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

The quantum yield of main chain scission (ϕ_{cs}) was calculated from viscosity measurement using the following equation:¹⁰

$$\phi_{cs} = (CA/\bar{M}_{v,o}) \left[([\eta_o]/[\eta])^{1/\alpha} - 1 \right] / I_o t \quad (5)$$

where C = concentration, A = Avogadro's number, $(\bar{M}_{v,o})$ = the initial viscosity-average molecular weight, $[\eta_o]$ = intrinsic viscosity of polymer before irradiation, $[\eta]$ = intrinsic viscosity of polymer after irradiation; α = exponent in the relation: $[\eta] = KM^\alpha$, I_o = incident intensity, and t = irradiation time in seconds.

Results and discussion

2-Thioacetic acid-5-phenyl-1,3,4-oxadiazole with Sn(II), Ba(II), Ni(II), Zn(II), Cu(II), and Ca(II) complexes were used as additive for the photostabilization of PVC films. In order to study the photochemical activity of these additives for the photostabilization of PVC films, the carbonyl and polyene indices were monitored with irradiation time using IR spectrophotometry.

The irradiation of PVC films with light of wavelength, $\lambda = 313$ nm led to a clear change in their FTIR spectrum, as shown in Figure 1. Appearance of bands in 1772 cm^{-1} and 1724 cm^{-1} was attributed to the formation of carbonyl groups related to chloroketone and to aliphatic ketone, respectively. A third band was observed at 1604 cm^{-1} and was related to polyene group.¹¹ The hydroxyl band was too weak to allow accurate quantitative determination of hydroperoxide and alcohol functions.¹²

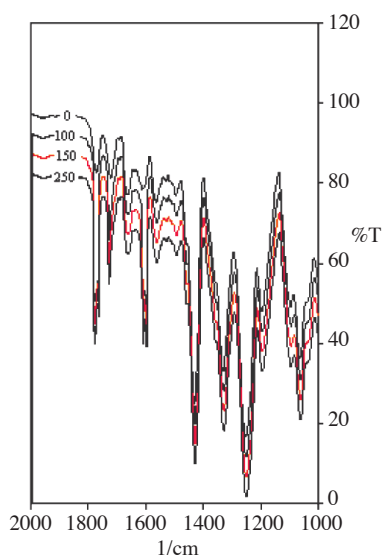


Figure 1. Change in IR spectrum of PVC film ($30 \mu\text{m}$) in the presence of $\text{Ni}(\text{OX})_2$ complex. (Numbers in spectra are irradiation time in hours).

The absorption of the carbonyl and polyene group is used to follow the extent of polymer degradation during irradiation. This absorption was calculated as carbonyl index (I_{co}) and polyene index (I_{PO}). It is reasonable to assume that the growth of carbonyl index is a measure of the extent of degradation. However, in Figure 2, the I_{co} of OX, $\text{Ca}(\text{OX})_2$, $\text{Cu}(\text{OX})_2$, $\text{Ni}(\text{OX})_2$, $\text{Zn}(\text{OX})_2$, $\text{Ba}(\text{OX})_2$, and $\text{Sn}(\text{OX})_2$ shows a lower growth rate with irradiation time with respect to PVC control film without additives.

Since the growth of carbonyl index with irradiation time is lower than in the PVC control, as seen in Figure 2, it is safe to conclude that these additives might be considered as photostabilizers of PVC polymer. An efficient photostabilizer shows a longer induction period. Therefore, the $\text{Sn}(\text{OX})_2$ is the most active photostabilizer, followed by $\text{Ba}(\text{OX})_2$, $\text{Zn}(\text{OX})_2$, $\text{Ni}(\text{OX})_2$, $\text{Ca}(\text{OX})_2$, and OX, which is the least active.

Just like carbonyl, polyene compounds are also produced during the photodegradation of PVC. Therefore, polyene index (I_{PO}) could also be monitored with irradiation time in the presence and absence of these additives. The results are shown in Figure 3.

Effect of the concentration of 2-thioacetic acid-5-phenyl-1,3,4-oxadiazole complexes as additives in the photostabilization of PVC films

The concentration of additive plays an important role in photostabilization and photodegradation of polymers. Many investigators have studied the effect of additive concentrations on photostabilization and photodegradation of polymers. In the present work the effect of additive concentrations in the photostabilization of PVC films at constant thickness ($30 \mu\text{m}$) was examined. Figures 4-7 show that the calculated values of carbonyl index (I_{co}) and polyene index (I_{po}) with different irradiation times using different concentrations of additive ranging from PVC (control), 0.1, 0.2, 0.3, 0.4, and 0.5 (wt%).

The results in Figures 4 to 7 show that the carbonyl index and polyene index decrease with increasing

wt% concentration of 2-thioacetic acid-5-phenyl-1,3,4-oxadiazole with Sn(II), Ba(II), Ni(II), Zn(II), Cu(II), and Ca(II) complexes as additives in films.

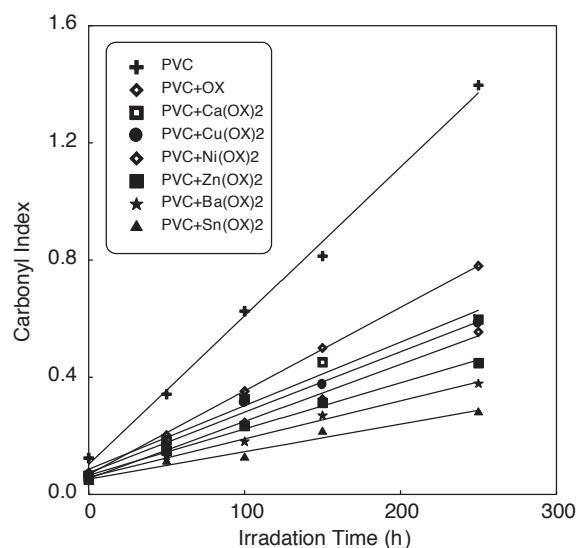


Figure 2. The relationship between the carbonyl index and irradiation time for PVC films 30 μm in thickness containing different additives, concentration of additives are fixed at 0.5% by weight.

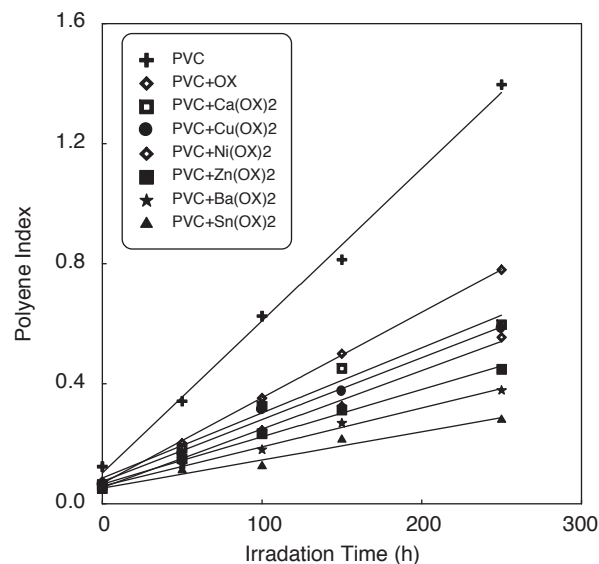


Figure 3. The relationship between the polyene index and irradiation time for PVC films 30 μm in thickness containing different additives, concentration of additives are fixed at 0.5% by weight.

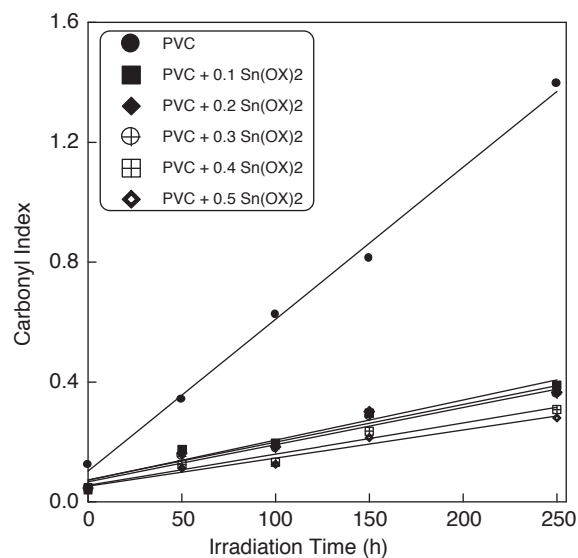


Figure 4. Change in carbonyl index with irradiation time for PVC films 30 μm in thickness containing different concentrations of Sn(OX)₂ complex.

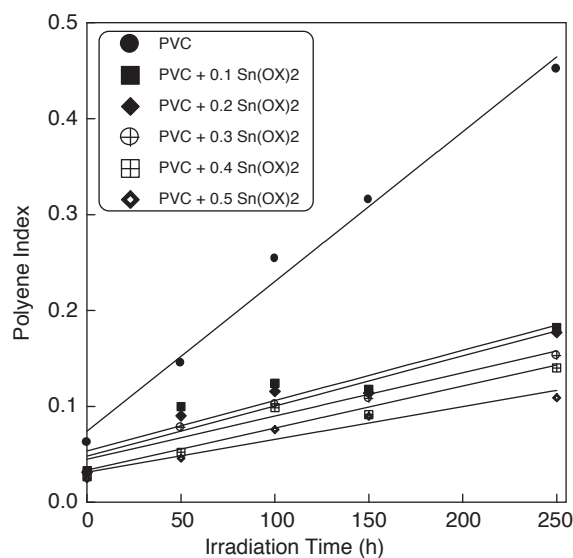


Figure 5. Change in polyene index with irradiation time for PVC films 30 μm in thickness containing different concentrations of Sn(OX)₂ complex.

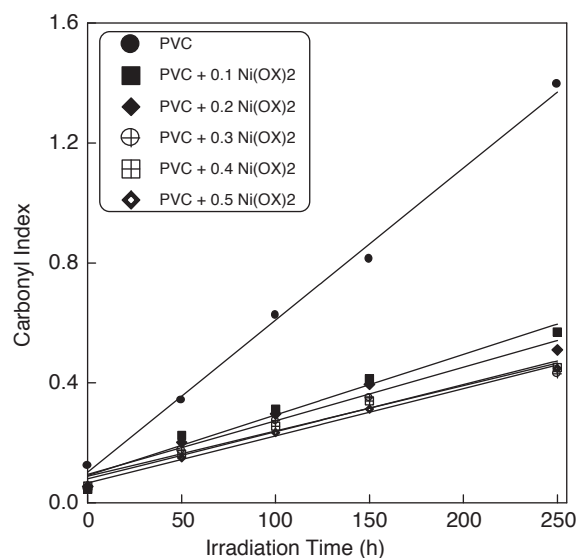


Figure 6. Change in carbonyl index with irradiation time for PVC films 30 μm in thickness containing different concentrations of $\text{Ni}(\text{OX})_2$ complex.

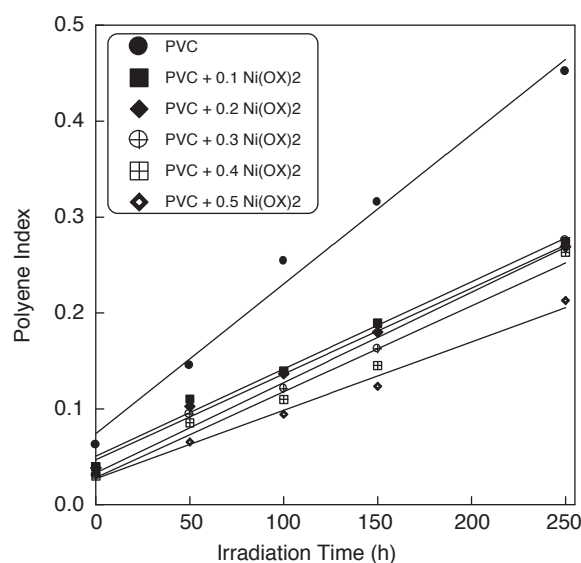


Figure 7. Change in polyene index with irradiation time for PVC films 30 μm in thickness containing different concentrations of $\text{Ni}(\text{OX})_2$ complex.

Variation in PVC molecular weight during photolysis in presence of 2-thioacetic acid-5-phenyl-1,3,4-oxadiazole complexes

Analysis of the relative changes in viscosity average molecular weight (\bar{M}_v), described by Scott,¹³ has been shown to provide a versatile test for random chain scission. Figure 8 shows the plot of (\bar{M}_v) versus irradiation time for PVC film with and without 0.5% (wt/wt) of 4 selected additives, with absorbed light intensity of $1.052 \times 10^{-8} \text{ ein. dm}^{-3} \cdot \text{s}^{-1}$. (\bar{M}_v) is measured using Eq. (4) with THF as a solvent at 25 °C.

It is worth mentioning that traces of the films with additives are not soluble in THF, indicating that cross-linking or branching in the PVC chain occurs during the course of photolysis.¹⁴

For better support of this view, the average chain scission number (average number cut per single chain) (S) was calculated using Eq. (6):

$$S = \frac{\bar{M}_{v,o}}{\bar{M}_{v,t}} - 1 \quad (6)$$

where $\bar{M}_{v,o}$ and $\bar{M}_{v,t}$ are viscosity average molecular weight at (zero) and (t) irradiation time, respectively.

The plot of S versus time is shown in Figure 9. The curve indicates an increase in the degree of branching such as might arise from cross-linking.

It is observed that insoluble material was formed during irradiation, which provides additional evidence for the idea that cross-linking does occur.

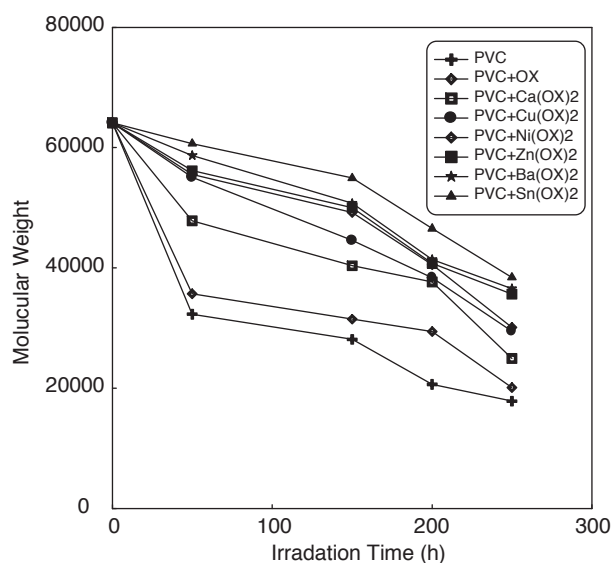


Figure 8. Changes in the viscosity average molecular weight (\bar{M}_v) during irradiation of PVC films ($30 \mu\text{m}$) (control) and with 0.5 wt% of additives.

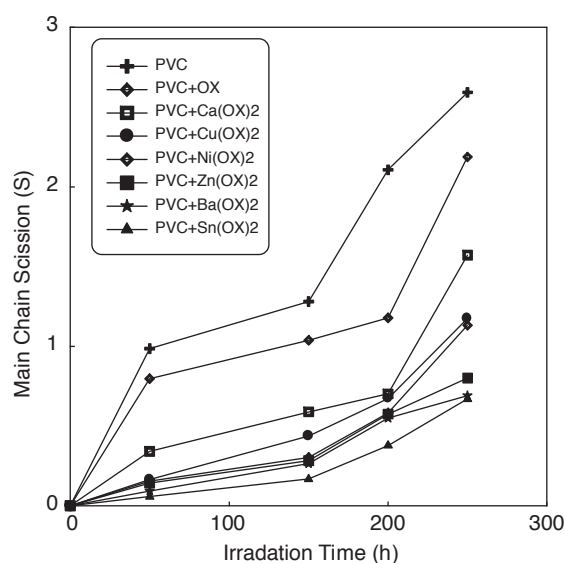


Figure 9. Changes in the number of average chains during irradiation of PVC films ($30 \mu\text{m}$) (control) and with 0.5 wt% of additives.

For randomly distributed weak bond links, which break rapidly in the initial stages of photodegradation, the degree of deterioration α is given as:

$$\alpha = \frac{m.s}{\bar{M}_v} \quad (7)$$

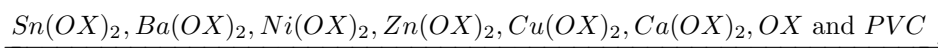
where m and M_{v0} are the molecular weight at 0 time and at t of irradiation time, respectively.

The plot of α as a function of irradiation time is shown in Figure 10. The curves indicate that the degradation takes place by random breaking of one type of bond.

The values of α of the irradiated samples are higher when additives are absent and lower in presence of additives compared to the corresponding values of the additive free PVC. In the initial stages of photodegradation of PVC, the value of α increases rapidly with time; this indicates a random breaking of bonds in the polymer chain.

Another way of degradation reaction characterization is the measurement of the quantum yield of the chain scission (Φ_{cs}). The quantum yield for chain scission was calculated¹⁵ for PVC films with and without 0.5% (wt/wt) of additive mentioned above using Eq. (5). The Φ_{cs} values for complexes are tabulated in Table 1.

The Φ_{cs} values for PVC films in the presence of additive are less than those of additive-free PVC (control), which increase in the order:



The explanation for the low values of Φ_{cs} is that in large molecule of PVC the energy is absorbed at one site, and then the electronic excitation is distributed over many bonds so that the probability of a single bond breaking is small, or the absorbed energy is dissipated by non-reactive processes.¹⁶

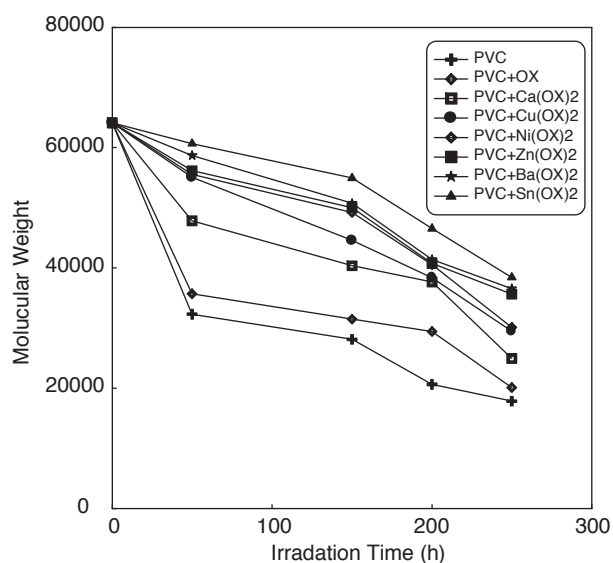


Figure 10. Changes in the degree of deterioration (α) during irradiation of PVC films ($30 \mu\text{m}$) (control) and with 0.5 wt% of additives.

Table 1. With and without 0.5 (wt/wt) additive after 250 h irradiation time.

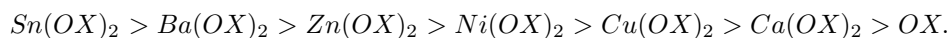
Additive (0.5%wt)	Quantum yield of main chain scission (Φ_{cs})
PVC+Sn(OX) ₂	4.94E-08
PVC+Ba(OX) ₂	5.10E-08
PVC+Ni(OX) ₂	5.91E-08
PVC+Zn(OX) ₂	8.35E-08
PVC+Cu(OX) ₂	8.67E-08
PVC+Ca(OX) ₂	1.16E-07
OX	1.61E-07
PVC (control)	4.89E-05

It is well established that the quantum yield (Φ_{cs}) increases with increasing temperature¹⁷ around the glass transition temperature (T_g) of the amorphous polymer, and around the melting temperature of crystalline polymers. In the present study, the photolysis of PVC film is carried out at a temperature (35-45 °C) well below the glass transition temperature (T_g of PVC = 80 °C). Therefore, the Φ_{cs} dependency on temperature is not expected to be observed.

III) Suggested mechanisms of photostabilization of PVC by the 2-thioacetic acid-5-phenyl-1,3,4-oxadiazole complexes

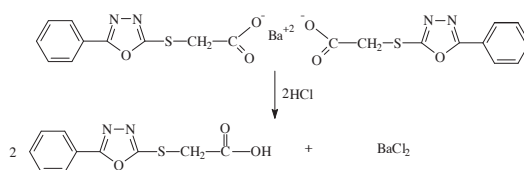
Depending on the overall results obtained, the efficiency of 2-thioacetic acid-5-phenyl-1,3,4-oxadiazole complexes as stabilizers for PVC films can be arranged according to the change in the carbonyl and polyene concentration

as a reference for comparison, as shown in Figures 2 and 3, as follows:

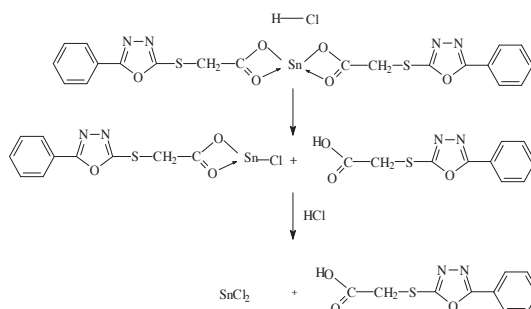


Metal carboxylates stabilize PVC by 2 mechanisms, depending on the metal. Strongly basic carboxylates derived from metals such as Ca and Ba, which have little or no Lewis acidity are mostly HCl scavengers (Scheme 1). Metals such as Sn, Zn, Ni, and Cu, which are stronger Lewis acids and form covalent carboxylates, not only scavenge HCl, but also substitute carboxylate for the allylic chlorine atoms.¹⁸

These stabilizers provide very good long-term stability and are usually referred to as secondary stabilizers (Scheme 2).

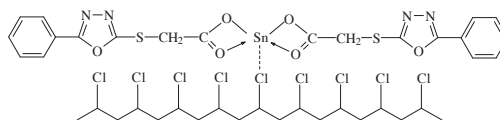


Scheme 1. Suggested mechanism of photostabilization of $Ba(OX)_2$ and $Ca(OX)_2$ complexes as HCl scavengers.



Scheme 2. Suggested mechanism of photostabilization of $Sn(OX)_2$, $Zn(OX)_2$, $Ni(OX)_2$, and $Cu(OX)_2$ complexes as HCl scavengers.

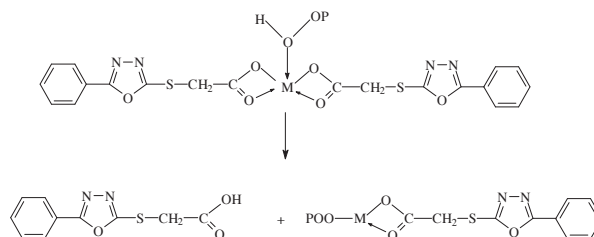
IR spectroscopy has shown that metals carboxylates associate with PVC molecules at the surface of primary particles¹⁹ and are, consequently, very effective in the substitution of allylic chlorine. In this mechanism, the stabilizer is classified as a primary stabilizer.



Scheme 3. Suggested mechanism of photostabilization of $Sn(OX)_2$, $Zn(OX)_2$, $Ni(OX)_2$, and $Cu(OX)_2$ complexes as primary stabilizers.

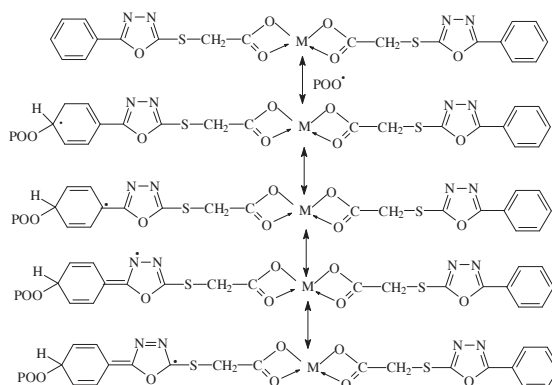
It has been postulated that metal stabilizers associate with chlorine atoms at the surface of PVC primary particles, which explains their high efficiency in PVC stabilization²⁰ (Scheme 3).

Metal chelate complexes are generally known as photostabilizers for poly olefins²⁰ through both peroxide decomposer and excited state quencher. Therefore, it is expected that these complexes act as peroxide decomposers through the following proposed mechanism, Scheme 4, below.



Scheme 4. Suggested mechanism of photostabilization of Sn((OX)₂, Zn((OX)₂, Ni((OX)₂, and Cu(OX)₂ complexes as peroxide decomposers through antioxidant action.

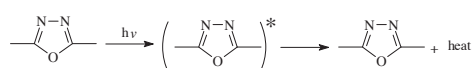
These metal chelate complexes also function as radical scavengers through energy transfer and by forming un-reactive charge transfer complexes between the metal chelate and excited state of the chromophore (POO·) and stabilize through resonating structures as shown in Scheme 5.



Scheme 5. Suggested mechanism of photostabilization of carboxylates complexes as radical scavengers through energy transfer and forming unreactive charge transfer and stabilizing through resonating structure.

The ring of 1, 3, 4-oxadiazole in this compound plays an important role in the mechanism of stabilizing process by acting as a UV absorber.

The UV light absorption by these additives containing 1, 3, 4-oxadiazole dissipates the UV energy to harmless heat energy (Scheme 6). Furthermore, this ring plays a role in resonating structures' conjugation of radical in peroxide decomposer (Scheme 5), which supports this compound as a photostabilizer.



Scheme 6. Suggested mechanism of photostabilization of 1,3,4-oxadiazole carboxylates compounds as UV absorber.

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