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IMPROVEMENT OF THE PHOTOSTABILIZATION OF PVC FILMS IN THE PRESENCE OF THIOACETIC ACID BENZOTHIAZOLE COMPLEXES

(Peningkatan Ciri-ciri Fotokestabilan Filem PVC dengan Kehadiran Kompleks Asid Thioasetik Benzothiazola)

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Abstract

The photostabilization of poly(vinyl chloride) (PVC) films by 2-thioacetic acid benzothiazol with Sn(II), Cd(II), Ni(II), Zn(II) and Cu(II) complexes was investigated. The PVC films containing concentration of complexes 0.5% by weight were produced by the same casting method from tetrahydrofuran (THF) solvent. The photostabilization activities of these compounds were determined by monitoring the carbonyl, polyene and hydroxyl 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 4.71×10^{-8} and 8.98×10^{-8}. Results obtained showed that the rate of photostabilization of PVC in the presence of the additive follows the trend:

$$Sn(L)_2 > Cd(L)_2 > Ni(L)_2 > Zn(L)_2 > Cu(L)_2$$
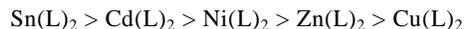
According to the experimental results obtained, several mechanisms were suggested depending on the structure of the additive. Among them HCl scavenging, UV absorption, peroxide decomposer and radical scavenger for photostabilizer additives mechanisms were suggested.

Keywords: Photostabilizer, PVC, 2-Thioacetic benzothiazol acid.

Abstrak

Proses fotokestabilan filem poli(vinil klorida) (PVC) oleh asid 2-thioasetik benzothiazol dengan kompleks Sn(II), Cd (II), Ni(II), Zn(II) dan Cu(II) telah dikaji. Filem PVC yang mengandungi kompleks berkepekatan 0.5% berat telah dihasilkan dengan kaedah acuan yang sama menggunakan pelarut THF. Aktiviti fotokestabilan unsur-unsur ini ditentukan dengan mengkaji indeks karbonil, poliena dan hidroksil dengan masa iradiasi. Perubahan dalam kelikatan berat molekul purata bagi PVC dengan masa iradiasi juga turut dikesan dengan menggunakan THF sebagai pelarut. Hasil kuantum pengguntingan rantai (Φ_{cs}) kompleks-kompleks ini di dalam filem-filem PVC didapati berada dalam julat antara 4.71×10^{-8} and 8.98×10^{-8}. Keputusan yang diperolehi menunjukkan bahawa kadar fotokestabilan PVC dengan kehadiran aditif adalah mengikut turutan berikut:

$$Sn(L)_2 > Cd(L)_2 > Ni(L)_2 > Zn(L)_2 > Cu(L)_2$$
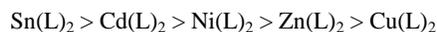
Berdasarkan keputusan eksperimen yang diperolehi, beberapa mekanisme telah dicadangkan bergantung kepada struktur aditif yang digunakan. Empat mekanisme aditif fotokestabilan yang telah dicadangkan termasuklah HCl penguraian, penyerapan UV, pengurai peroksida dan pengautan radikal.

Kata kunci: Fotokestabilan, PVC, Asid 2-thioasetik benzothiazol.

Introduction

Poly(vinyl chloride), better known by its abbreviation PVC, is one of the most versatile plastics. It is the second largest manufactured resin by volume worldwide [1]; currently, its production per annum exceeds 31 million tons. Braun [2] described the most remarkable milestones in PVC history, their importance to the development of macromolecular chemistry, and some PVC research and industrial applications, with respect to polymerization, stabilization, bulk property modification, and chemical and material recycling of PVC waste [3]. The low cost and the good performance of poly(vinyl chloride) products have increased the utilization of this polymer in building, mainly in exterior application, such as window profiles, cladding structure and siding [4]. However, ultimate user acceptance of the PVC products for outdoor building applications will depend on their ability to resist photodegradation over long periods of sunlight exposure. To ensure weather ability, 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 [5]. On the other hand, it is important to perform reliable accelerated weathering test methods. In this regard, factors that influence the degradation of PVC based materials in the service condition, like light and temperature are accelerated. As part of our on-going research in the photostabilization of poly (vinyl chloride), the photostabilization of PVC was studied using 2-thioacetic benzothiazol complexes

Experimental

Materials
The following complexes were all prepared by the method described in reference [6].

Bis(2-thioacetic acid benzothiazol) tin(II)	$Sn(L)_2$
Bis(2-thioacetic acid benzothiazol) cadmium(II)	$Cd(L)_2$
Bis(2-thioacetic acid benzothiazol) nickel(II)	$Ni(L)_2$
Bis(2-thioacetic acid benzothiazol) zinc(II)	$Zn(L)_2.$
Bis(2-thioacetic acid benzothiazol) copper(II)	$Cu(L)_2$
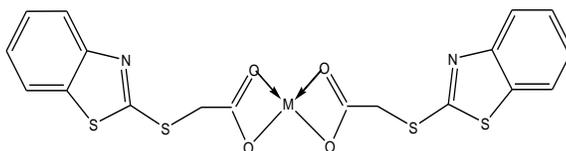
where M = Sn(II), Cd(II), Ni(II), Zn(II) or Cu(II)

Experimental techniques
Films preparation:
Commercial poly(vinyl chloride) supplied by Petkim company (Turkey) was re-precipitated from THF solution by alcohol several times and finally dried under vacuum at room temperature for 24 hours. Fixed concentrations of poly(vinyl chloride) solution (5 g/100 ml) in tetrahydrofuran were used to prepare polymer films with 30 μm thickness (measured by a micrometer type 2610 A, Germany). The prepared complexes (0.5% concentrations) were added to the films starting at 0 concentrations (control). The films were prepared by evaporation technique at room temperature for 24 hours. To remove the possible residual tetrahydrofuran solvent, film samples were further dried at room temperature for three hours under reduced pressure. The films were fixed on stands especially used for irradiation. The stand is provided with an aluminum plate (0.6 mm in thickness) supplied by Q-panel company.

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 stainless steel plate, which has two holes in the front side and a third one behind. Each side contains a lamp (type Fluorescent Ultraviolet Lights) 40 Watt each. These lamps are of the type UV-B 313 giving spectrum range between 290-360 nm with a maximum at wavelength 313 nm. The polymer film samples were vertically fixed parallel to the lamps to make sure that the UV incident radiation is perpendicular on the samples. The irradiated samples are rotated from time to time to ensure that the intensity of light incident on all samples is the same.

Photodegradation measuring methods
Measuring the photodegradation rate of polymer films using infrared spectrophotometery:
The degree of photodegradation of polymer film samples was followed by monitoring FTIR spectra in the range 4000-400 cm^{-1} using FTIR 8300 Shimadzu Spectrophotometer. The position of carbonyl absorption is specified at 1722 cm^{-1}, polyene group at 1602 cm^{-1} and the hydroxyl group at 3500 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}), polyene (I_{po}) and hydroxyl (I_{OH}) indices were calculated by comparison of the FTIR absorption peak at 1722, 1602 and 3500 cm^{-1} with reference peak at 1328 cm^{-1} attributed to osicissoring and bending of CH_2 group, respectively. This method is called band index method which includes [7]:

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

As = Absorbance of peak under study
Ar = Absorbance of reference peak
Is = 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].

Determination of average molecular weight $(\overline{M}_v)$ ***using viscometry method:***

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

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

$[\eta]$ = the intrinsic viscosity

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

The intrinsic viscosity of a polymer solution was measured with an Ostwald U-tube viscometer. Solutions were made by dissolving the polymer in a solvent (gm/100ml) and the flow times of polymer solution and pure solvent are t and t_0 respectively. Specific viscosity (η_{sp}) was calculated as follows:

$$\eta_{re} = \frac{t}{t_o} \qquad (3)$$

η_{re} = Relative viscosity

$$\eta_{sp} = \eta_{re} - 1 \tag{4}$$

The single – point measurements were converted to intrinsic viscosities by the relation 2.

$$[\eta] = (\sqrt{2}/c)(\eta_{sp} - ln\eta_{re})^{1/2} \tag{5}$$

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

By applying Equation 5, the molecular weight of degraded and the virgin polymer 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:

$$[\eta] = 1.38 \times 10^{-4} Mv^{0.77} \tag{6}$$

The quantum yield of main chain scission (ϕ_{cs}) [10] was calculated from viscosity measurement using the following relation 7.

$$\phi_{cs} = (CA/\bar{M}_{v,0})\left[([\eta_0]/[\eta])^{1/\alpha} - 1\right]/I_0 t \tag{7}$$

where: C = concentration; A = Avogadro's number; $(\overline{M}_{v,o})$ = the initial viscosity–average molecular weight; $[\eta_o]$ = Intrinsic viscosity of PVC before irradiation; I_o = Incident intensity and t = Irradiation time in second.

Results and Discussion

The 2-thioacetic acid benzothiazol complexes with Sn(II), Cd(II), Ni(II), Zn(II) and Cu(II) were used as additives 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 UV light of wavelength, λ = 313 nm led to a clear change in the FTIR spectrum, as shown in Figure 1. Appearance of bands in 1772 cm^{-1} and 1724 cm^{-1}, were attributed to the formation of carbonyl groups related to chloroketone and to aliphatic ketone, respectively. A third band was observed at 1604 cm^{-1}, related to polyene group. The hydroxyl band appeared at 3500 cm^{-1} was annotated to the hydroxyl group [11].

The absorption of the carbonyl, polyene and hydroxyl groups was used to follow the extent of polymer degradation during irradiation. This absorption was calculated as carbonyl index (I_{co}), polyene index (I_{PO}) and hydroxyl index (I_{OH}). It is reasonable to assume that the growth of carbonyl index is a measure to the extent of degradation. However, in Figure 2,   the I_{co} of Cu(L)$_2$ Zn(L)$_2$, Ni(L)$_2$, Cd(L)$_2$ and Sn(L)$_2$ showed lower growth rate with irradiation time with respect to the PVC control film without additives. Since the growth of carbonyl index with irradiation time is lower than PVC control, as seen in Figure 2, it is suitable to conclude that these additives might be considered as photostabilizers of PVC polymer. Efficient photostabilizer shows a longer induction period. Therefore, the Sn(L)$_2$ is the most active photostabilizer, followed by Cd(L)$_2$, Ni(L)$_2$, Zn(L)$_2$ and Cu(L)$_2$ which is the least active. Just like carbonyl, polyene compounds are also produced during photodegradation of PVC. Therefore, polyene index (I_{PO}) could also be monitored with irradiation time in the presence and absence of these additives. Results are shown in Figure 3.
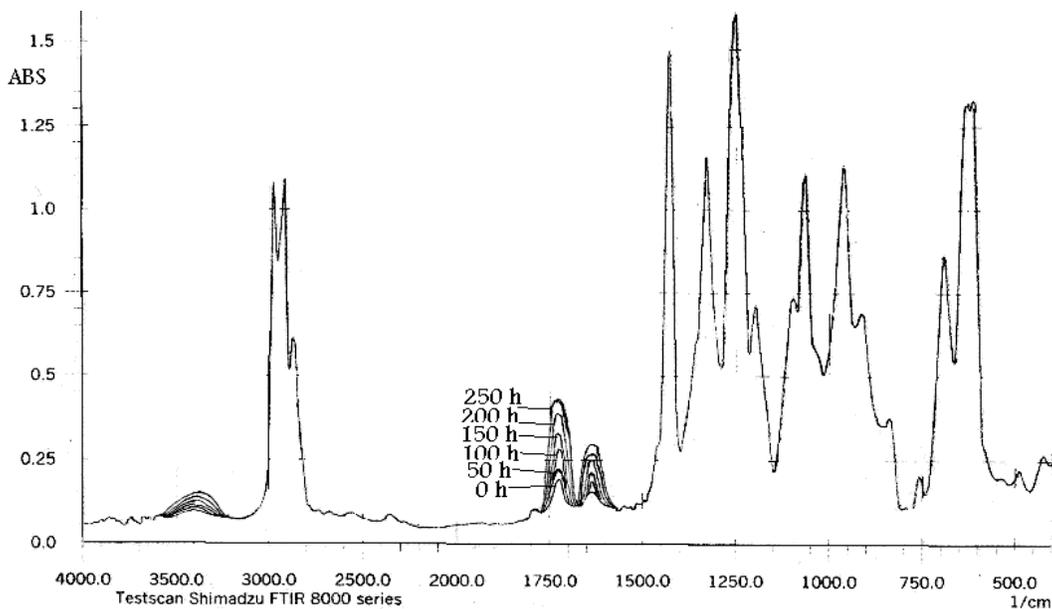
Fig. 1: Change in IR spectrum of PVC film (30 µm) in the presence of Cd(L)$_2$ complex.
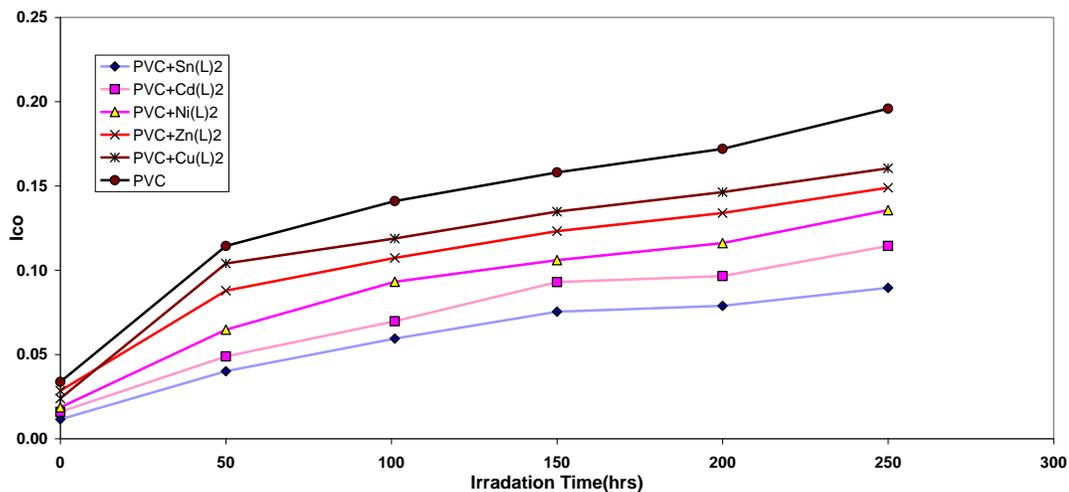

Fig. 2: The relationship between the carbonyl index and irradiation time for PVC films (30 μm thickness) containing different additives. Concentration of additives is fixed at 0.5% by weight.
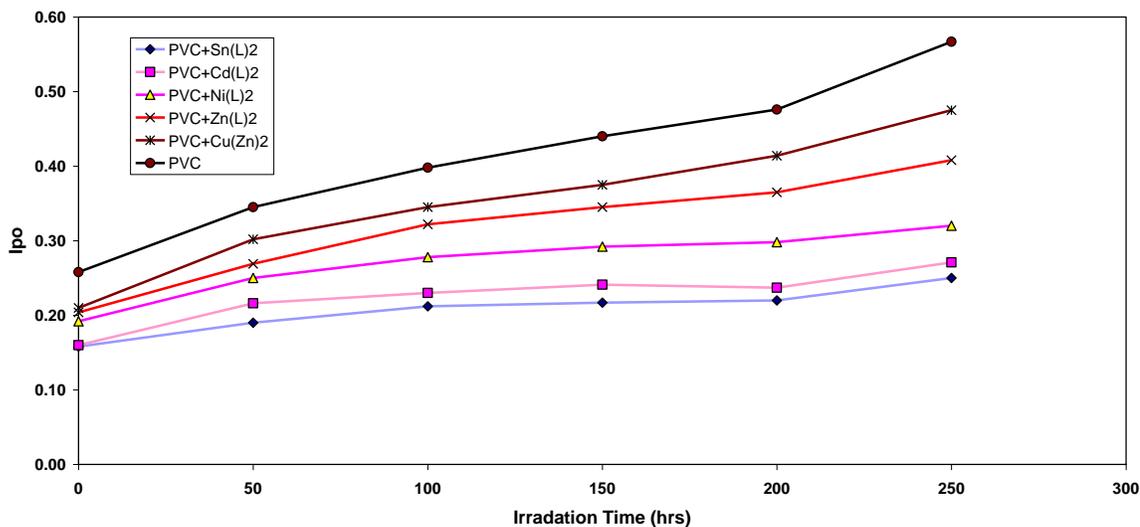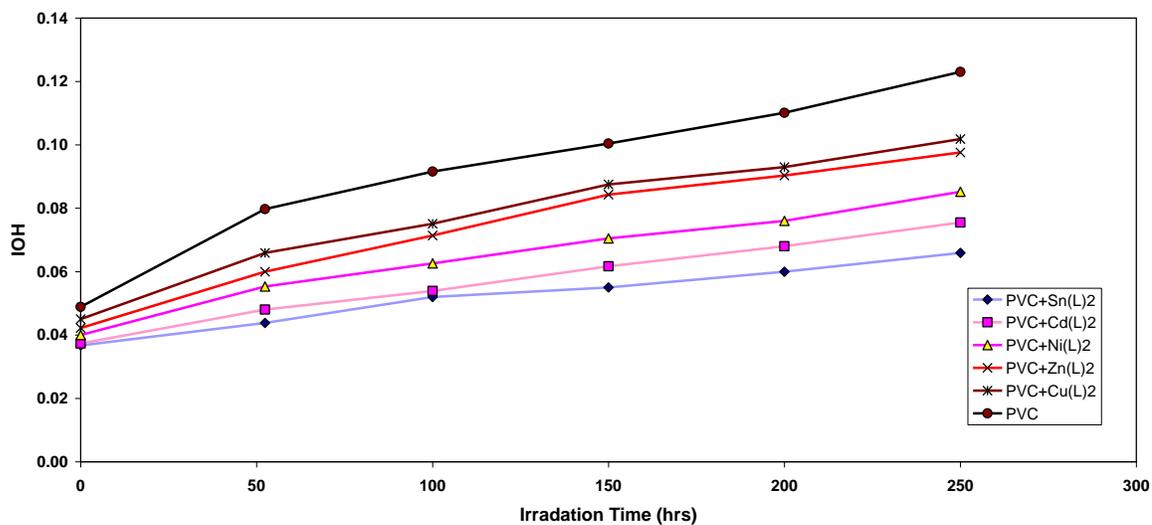
Fig. 3: The relationship between the polyene index and irradiation time for PVC films (30 μm thickness). Containing different additives, concentration of additives are fixed at 0.5% by weight.

Hydroxyl species were produced during photodegradation of PVC. Therefore, hydroxyl index (I_{OH}) was monitored with irradiation time for PVC and with additives. From Figure 4, the $Cu(L)_2$, $Zn(L)_2$, $Ni(L)_2$, $Cd(L)_2$ and $Sn(L)_2$ showed lower growth rate of hydroxyl index with irradiation time compare to PVC film without modification.

Fig. 4: The relationship between the hydroxyl index and irradiation time for PVC films (30 μm thickness). Containing different additives, concentration of additives are fixed at 0.5% by weight.

Variation of PVC molecular weight during photolysis in the presence of by 2-thioacetic acid benzothiazol complexes

Analysis of the relative changes in viscosity average molecular weight $(\overline{M}_v)$ **,** has been shown to provide a versatile test for random chain scission. Figure 5 shows the plot of $\overline{M}v$ versus irradiation time for PVC film with and without 0.5% (wt/wt) of the selected additives, with absorbed light intensity of 1.052 x 10^{-8} ein. dm^{-3}. s^{-1} . $\overline{M}v$ is measured using Equation 4 with THF as a solvent at 25 ^{o}C .
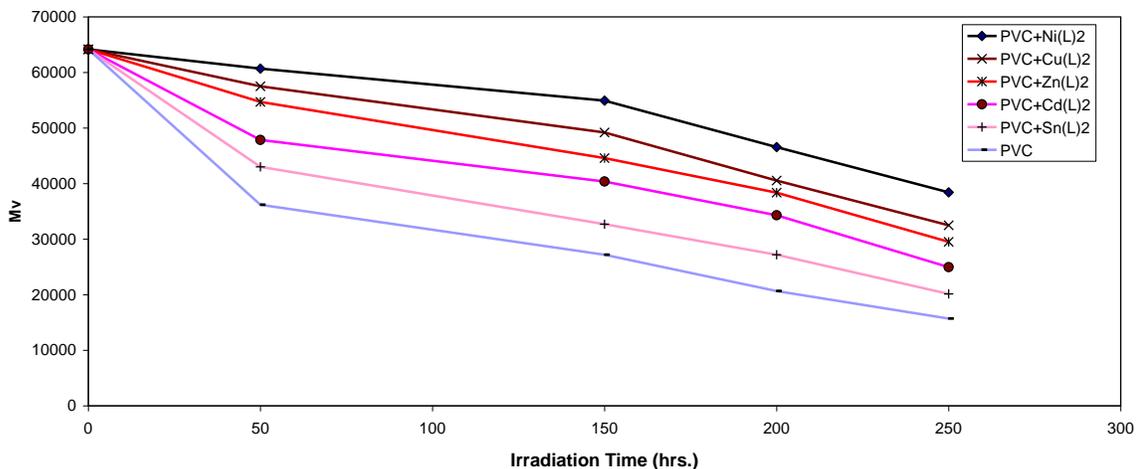

Fig. 5: Changes in the viscosity-average molecular weight $(\overline{M}_v)$ during irradiation of PVC films (30 μm) (control) and with 0.5 wt% of additives.

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 does occur during the course of photolysis [12]. For better support of this view, the number of average chain scission (average number cut per single chain) (S) [13] was calculated using the relation 8:

$$S = \frac{\overline{M}_{v,o}}{M_{v,t}} - 1 \tag{8}$$

where $\overline{M}_{v,o}$ and $\overline{M}_{v,t}$ are viscosity average molecular weights at initial (o) and t irradiation time respectively.

The plot of S versus time is shown in Figure 6. The curve indicates an increase in the degree of branching such as that might arise from cross-linking occurrence. It is observed that insoluble material was formed during irradiation which provided an additional evidences to the idea that cross-linking does occur.

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

$$\alpha = \frac{m.s}{\overline{M}_v} \tag{9}$$

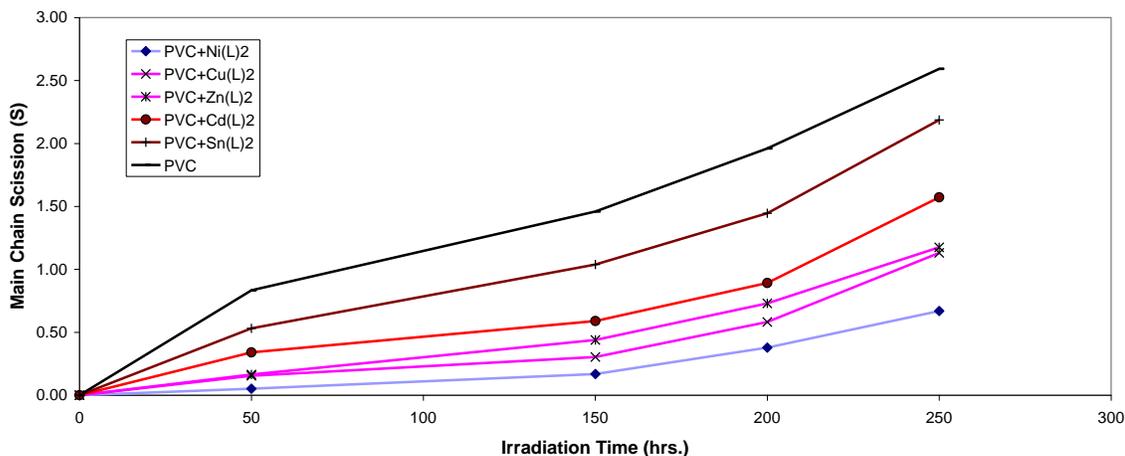where m is the initial molecular weight.

Fig. 6: Changes in the main chain scission (S) during irradiation of PVC films (30 μm) (control) and with 0.5 wt% of additives.

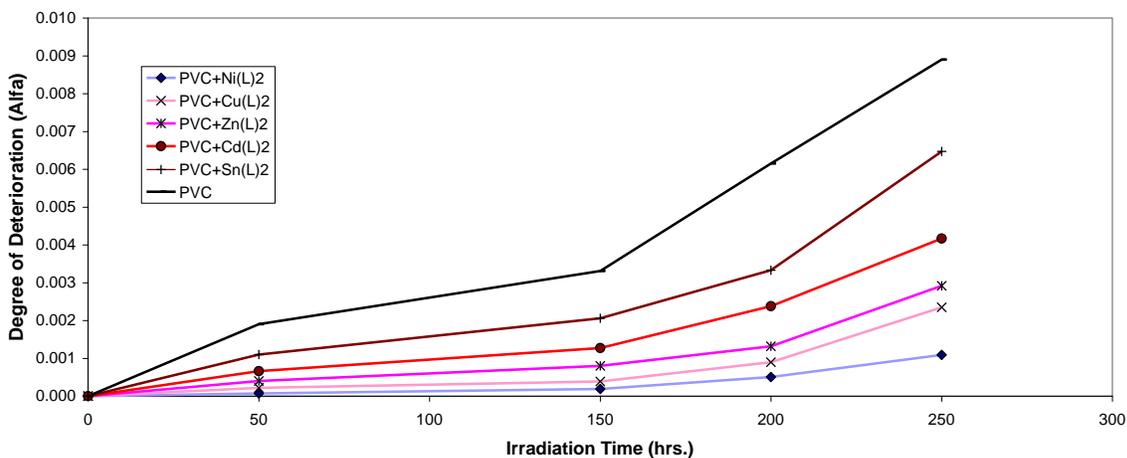The plot of α as a function of irradiation time is shown in Figure 7.


Fig. 7: Changes in the degree of deterioration (α) during irradiation of PVC films (30 μm) (control) and with 0.5 wt% of additives.

The values of α of the irradiated samples are higher when additives are absent and lower in the 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, these indicators 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 calculated for PVC films with and without 0.5% (wt/wt) of additive mentioned above using relation 5. The Φ_{cs} values for complexes are tabulated in Table 1.

Table 1: Quantum yield (Φcs) for the chain scission for PVC films (30μm) thickness with and without 0.5 (wt/wt) additive after 250 hrs. irradiation time.

Additive (0.5%wt)	Quantum yield of main chain scission (Φ_{cs})
PVC+Sn(L)$_2$	4.71E-08
PVC+Cd(L)$_2$	5.23E-08
PVC+Ni(L)$_2$	6.63E-08
PVC+Zn(L)$_2$	7.54E-08
PVC+Cu(L)$_2$	8.98E-08
PVC(control)	8.54E-05

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

$$Sn(L)_2, \ Cd(L)_2, \ Ni(L)_2, \ Zn(L)_2, \ Cu(L)_2 \ and \ PVC$$

$$\longrightarrow$$
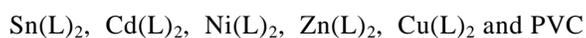
It is well established that the quantum yield ($\Phi_{cs.}$) increases with increasing temperature [14] around the glass transition temperature, (T_g) of the amorphous polymer, and around the melting temperature of crystalline polymers. In the study presented in this work, the photolysis of PVC film 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.
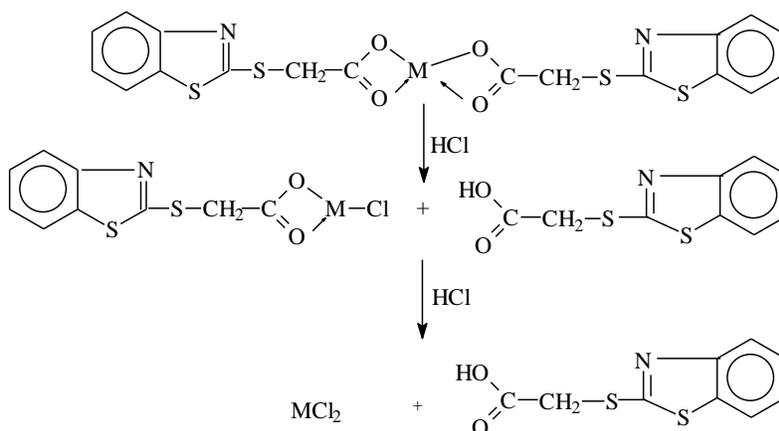
Suggested mechanisms of photostabilization of PVC by 2-thioacetic acid benzothiazol complexes
Depending on the overall results obtained, the efficiency of 2-thioacetic acid benzothiazol complexes as stabilizer for PVC films can be arranged according to the change in the carbonyl, polyene and hydroxyl concentration as a reference for comparison as shown in Figures 2 to 4, as follows:

$$Sn(L)_2 > Cd(L)_2 > Ni(L)_2 > Zn(L)_2 > Cu(L)_2$$

Metal carboxylates stabilize PVC by two 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, Cd and Cu which are stronger Lewis acids and form covalent carboxylates, not only scavenge HCl, but also substitute carboxylate for the allylic chlorine atoms. These stabilizers provide very good long-term stability and are usually referred to as secondary stabilizers, Scheme 1. Similar mechanism was suggested by Yousif et.al (2009) for photostabilizing of PVC using of 2-thioacetic acid -5-phenyl-1,3,4-oxadiazole complexes [15].

IR spectroscopy has shown that metals carboxylates associate with PVC molecules at the surface of primary particles and are, consequently, very effective in the substitution of allylic chlorine. In this mechanism, the stabilizer is classified as a primary stabilizer. It has been postulated that metals stabilizers associate with chlorine atoms at the surface of PVC primary particles which explains their high efficiency in PVC stabilization [16], Scheme 2.
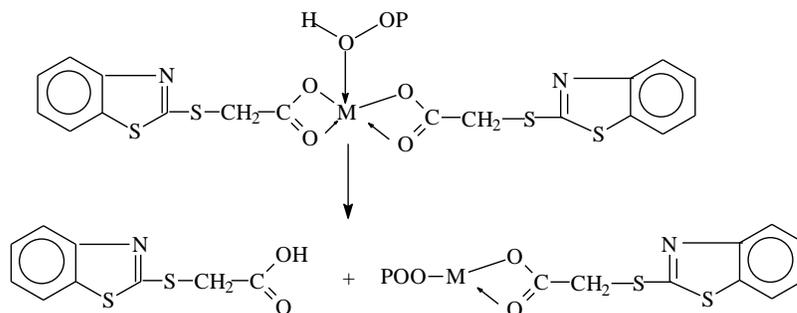
Scheme 1: Suggested mechanism of photostabilization of complexes as HCl scavengers.
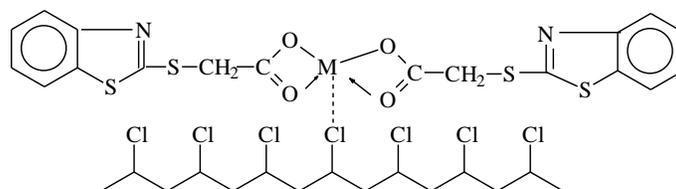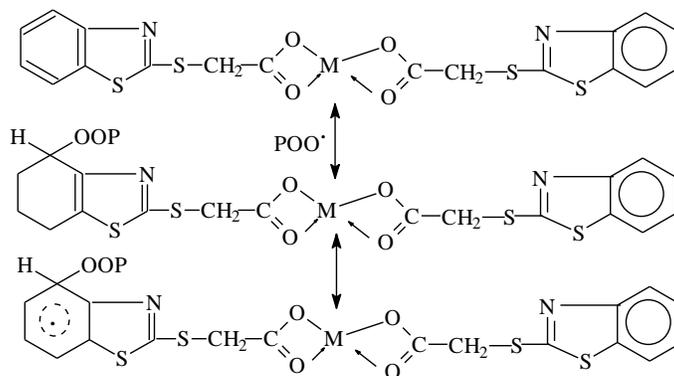

Scheme 2: Suggested mechanism of photostabilization of complexes as primary stabilizers.

Metal chelate complexes generally known as photostabilizers for PVC through both peroxide decomposer and excited state quencher. Therefore, it is expected that these complexes act as peroxide decomposer through the following proposed mechanism, Scheme 3 below. This mechanism is in agreement with that reported by Adil [17].
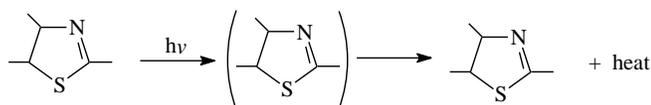

Scheme 3: Suggested mechanism of photostabilization of complexes as peroxide decomposer.

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 4. This mechanism is adopted by Adil [17].

Scheme 4:   Suggested mechanism of photostabilization of carboxylates complexes as radical scavengers through energy transfer and forming unreactive charge transfer and stabilize through resonating structure.

The ring of benzothiazol in this compound plays an important role in the mechanism of stabilizing process by acting as UV absorber. The UV light absorption by these additives containing benzothiazol dissipates the UV energy to harmless heat energy, Scheme 5. Further more this ring plays a role in resonating structures conjugation of radical in peroxide decomposer, Scheme 5, which supports this compound as a photostabilizer [18].

Scheme 5: Suggested mechanism of photostabilization of benzothiazole as UV absorber.

Conclusion

In the work described in this paper, the photostabilization of poly(vinyl chloride) (PVC) films using 2-thioacetic acid benzothiozol complexes were studied. These additives behave successfully as photostabilizer for PVC films. The additives take the following order in photostabilization activity according to their decrease in carbonyl, polyene and hydroxyl indices for PVC films.

$$Sn(L)_2 > Cd(L)_2 > Ni(L)_2 > Zn(L)_2 > Cu(L)_2$$

These additives stabilize the PVC films through HCl scavenging, UV absorption or screening, peroxide decomposer and radical scavenger mechanisms. The tin complexes were found to be the more efficient in photostabilization process according to the photostability and mechanisms mentioned above. These mechanisms support the idea of using tin complexes as commercial stabilizer for PVC.

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