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ORIGINAL ARTICLE

Mechanism of photostabilization of poly(methy methacrylate) films by 2-thioacetic acid benzothiazol complexes

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Abstract The photostabilization of poly(methy methacrylate) (PMMA) films by 2-thioacetic acid benzothiazol with Sn(II), Cd(II), Ni(II), Zn(II) and Cu(II) complexes was investigated. The PMMA films containing concentration of complexes 0.5% by weight were produced by the casting method from chloroform solvent. The photostabilization activities of these compounds were determined by monitoring the hydroxyl index with irradiation time. The changes in viscosity-average molecular weight of PMMA with irradiation time were also tracked (using benzene as a solvent). The quantum yield of the chain scission (Φ_{cs}) of these complexes in PMMA films was evaluated and found to range between 3.64×10^{-5} and 7.44×10^{-5}. Results obtained showed that the rate of photostabilization of PMMA in the presence of the additive followed the trend:

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

According to the experimental results obtained, several mechanisms were suggested depending on the structure of the additive. Among them UV absorption, peroxide decomposer and radical scavenger for photostabilizer additives mechanisms were suggested.

1. Introduction

Many polymers undergo thermal oxidative degradation during processing. Over longer periods at ambient temperature polymers also deteriorate in the solid state through autooxidation and photooxidation. In outdoor applications where the materials are exposed to UV solar radiation, the energy of this radiation is sufficient to initiate photochemical reaction leading to degradation. Plastics are commonly protected

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against such deterioration by the addition of antioxidants, light and heat stabilizers (Chmela et al., 2001; Yousif et al., 2010).

There is a great interest at present in the photo-oxidative degradation of polymeric materials because macromolecules have increasingly widespread commercial applications. Polymeric synthetic, semi synthetic and natural are degraded when exposed to the environment (Grassie and Scott, 1985). All commercial organic polymers degrade in air when exposed to sunlight as the energy of sunlight is sufficient to cause the breakdown of polymeric C–C bonds as a consequence of degradation. The resulting smaller fragments do not contribute effectively to the mechanical properties and the polymeric article because brittle. Thus the life of thermoplastics for outdoor applications becomes limited due to weathering (Andrady et al., 1988).

Almost all synthetic polymers require stabilization against the adverse effect with the development of synthetic resins it became necessary to look for ways and means to prevent, or at least reduce, the damage caused by the environmental parameters such as light, air and heat. This can be achieved through addition of special chemicals, light stabilizers or UV stabilizers, that have to be adjusted to the nature of the resin and the specific application considered. The photostabilization of polymers may be achieved in many ways. The following stabilizing systems have been developed, which depend on the action of stabilizer: (a) light screeners, (b) UV absorbers, (c) excited state quenchers, (d) peroxide decomposers and (e) free radical scavengers, of these it is generally believed that types (c)–(e) are the most effective.

Most of stabilizers are believed to be multifunctional in their mode of operation. This view is complicated by the fact that mechanisms involved in photo-oxidation and these, in turn depend on the polymer structure and other variables, such as manufacturing, operation, processing and conditions (Harper et al., 1974).

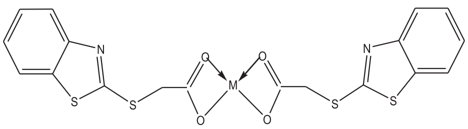
As part of our on-going research on the photostabilization of polymers, the photostabilization of PMMA was studied using 2-thioacetic benzothiazol complexes.

2. Experimental

2.1. Materials

The following complexes were all prepared by the method described by Yousif et al. (2010):

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)

2.2. Experimental techniques

2.2.1. Films preparation

Commercial PMMA supplied by Petkim Company (Turkey) was re-precipitated from chloroform solution by alcohol several times and finally dried under vacuum at room temperature for 24 h. Fixed concentrations of PMMA solution (5 g/100 ml) in chloroform were used to prepare polymer films with 40 μm thickness (measured by a micrometer type 2610 A, Germany). The prepared complexes (0.5% concentrations) were added to the films (blank). The films were prepared by evaporation technique at room temperature for 24 h. To remove the possible residual chloroform solvent, film samples were further dried at room temperature for 3 h 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.

2.2.2. Irradiation experiments

2.2.2.1. 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, which has two 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 the UV incident radiation is perpendicular on the samples. The irradiated samples were rotated from time to time to ensure that the intensity of light incident on all samples is the same.

2.2.3. Photodegradation measuring methods

2.2.3.1. 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 FTIR 8300 Shimadzu Spectrophotometer. The position of hydroxyl absorption is specified at 3430 cm^{-1} (Rabek and Ranby, 1975). The progress of photodegradation during different irradiation times was followed by observing the changes in hydroxyl peak. Then hydroxyl (I_{OH}) index was calculated by comparison of the FTIR absorption peak at 3430 cm^{-1} with reference peak at 1450 cm $^{-1}$, respectively. This method is called band index method which includes (Rabek and Ranby, 1975):

$$\mathrm{Is} = \frac{\mathrm{As}}{\mathrm{Ar}} \tag{1}$$

where As is the absorbance of peak under study; Ar the Absorbance of reference peak; Is is the 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 (Rabek and Ranby, 1975).

2.2.3.2. 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 (Mark, 2007):

$$[\eta] = K\overline{M}_v^{\alpha} \tag{2}$$

where $[\eta]$ is the intrinsic viscosity; K and 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 (g/100 ml) and the flow times of polymer solution and pure solvent are t and t_0. Specific viscosity (η_{sp}) was calculated as follows:

$$\eta_{re} = \frac{t}{t_0} \tag{3}$$

where η_{re} is the relative viscosity:

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

The single-point measurements were converted to intrinsic viscosities by the relation (2):

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

where C is the concentration of polymer solution (g/100 ml).

By applying Eq. (5), the molecular weight of degraded and undegraded polymer can be calculated. Molecular weights of PMMA with and without additives were calculated from intrinsic viscosities measured in benzene solution using Eq. (2).

The quantum yield of main chain scission (Φ_{cs}) (Nakajima et al., 1990) was calculated from viscosity measurement using the following relation:

$$\Phi_{cs} = (CA/\overline{M}_{v,o})[([\eta_o]/[\eta])^{1/\alpha} - 1]/I_o t \tag{6}$$

where C is the concentration; A the Avogadro's number; ($\overline{M}_{v,o}$) the initial viscosity-average molecular weight; $[\eta_o]$ the intrinsic viscosity of PMMA before irradiation; I_o the incident intensity and t is the irradiation time in second.

3. 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 PMMA films. In order to study the photochemical activity of these additives for the photostabilization of PMMA films, the hydroxyl index was monitored with irradiation time using IR spectrophotometry. The irradiation of PMMA films with UV light of wavelength, λ = 313 nm led to a clear change in the FTIR spectrum. Appearance of bands in 3430 cm^{-1} were attributed to the formation of the hydroxyl group (Andrady and Searle, 1989).

The absorption of the hydroxyl group was used to follow the extent of polymer degradation during irradiation. This absorption was calculated as hydroxyl index (I_{OH}). It is reasonable to assume that the growth of hydroxyl index is a measure to the extent of degradation. However, in Fig. 1, the I_{OH} of $Sn(L)_2$, $Cd(L)_2$, $Zn(L)_2$, $Cu(L)_2$ and $Ni(L)_2$ showed lower growth rate with irradiation time with respect to the PMMA control film without additives. Since the growth of hydroxyl index with irradiation time is lower than PMMA control, as seen in Fig. 1, it is suitable to conclude that these additives might be considered as photostabilizers of PMMA polymer. Efficient photostabilizer shows a longer induction period. Therefore, the $Ni(L)_2$ is the most active photostabilizer, followed by $Cu(L)_2$, $Zn(L)_2$, $Cd(L)_2$ and $Sn(L)_2$, which is the least active.

3.1. *Variation of PMMA 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. Fig. 2 shows the plot of ($\overline{M}_v$) versus irradiation time for PMMA film with and without 0.5% (wt/wt) of the selected additives, with absorbed light intensity of 1.052×10^{-8} ein dm^{-3} s^{-1}. ($\overline{M}_v$) is measured using Eq. (3) with benzene as a solvent at 25 °C.

It is worth mentioning that traces of the films with additives are not soluble in chloroform indicating that cross-linking or branching in the PMMA chain does occur during the course of photolysis (Mori et al., 1997). For better support of this view, the number of average chain scission (average number cut per single chain) (S) (Shyichuk and White, 2000) was calculated using the following relation:

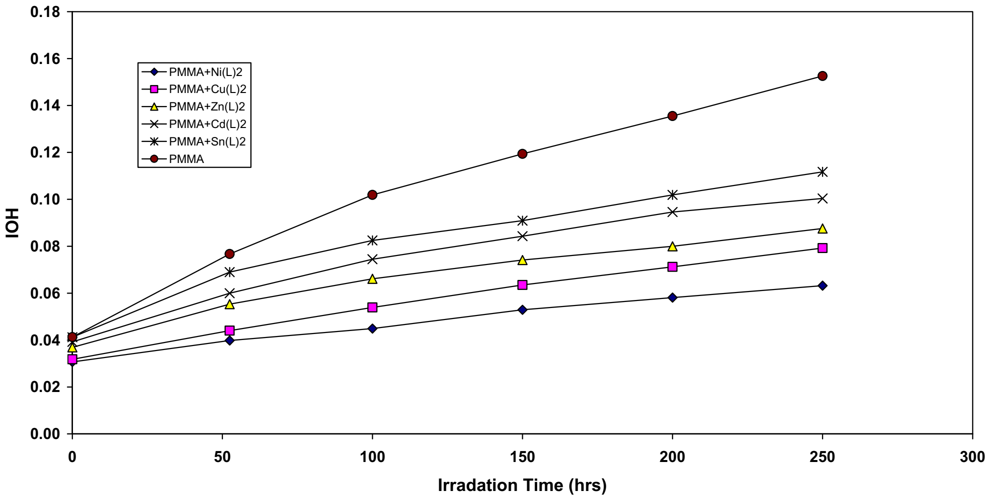


Figure 1 The relationship between the hydroxyl index and irradiation time for PMMA films (40 µm thickness). Containing different additives, concentration of additives are fixed at 0.5% by weight.

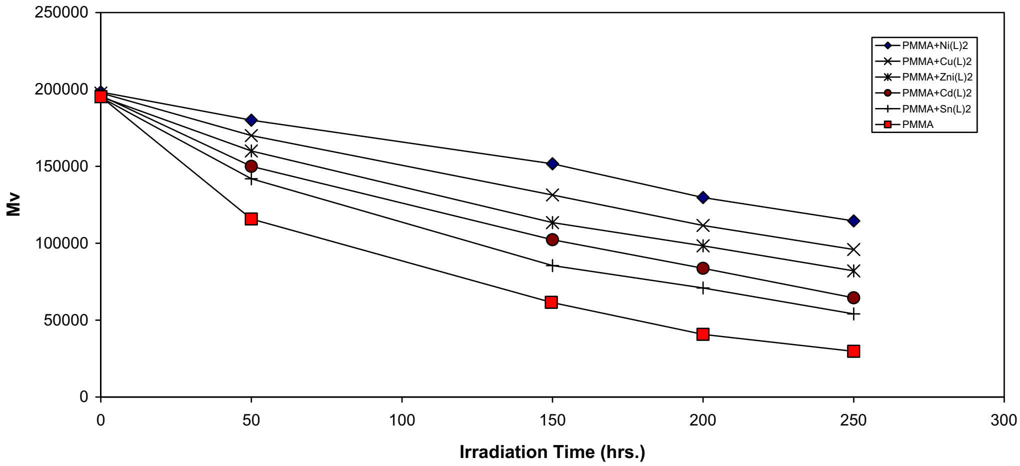


Figure 2 Changes in the viscosity-average molecular weight ($\overline{M}_{\mathrm{v}}$) during irradiation of PMMA films (40 μm) (control) and with 0.5 wt% of additives.

$$S = \frac{\overline{M}_{\mathrm{v,o}}}{\overline{M}_{\mathrm{v},t}} - 1 \tag{7}$$

where $\overline{M}_{\mathrm{v,o}}$ and $\overline{M}_{\mathrm{v},t}$ are viscosity-average molecular weight at initial (o) and t irradiation time, respectively. The plot of S versus time is shown in Fig. 3. 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 evidence to the idea that cross-linking does occur.

For randomly distributed weak bond links (Gugumus, 1990), which break rapidly in the initial stages of photodegradation, the degree of deterioration α is given as:

$$\alpha = \frac{m \cdot s}{\overline{M}_{\mathrm{v}}} \tag{8}$$

where m is the initial molecular weight.

The plot of α as a function of irradiation time is shown in Fig. 4.

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 PMMA. In the initial stages of photodegradation of PMMA, the value of α increases rapidly with time, these indicators indicates a random breaking of bonds in the polymer chain (Yousif et al., 2010).

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 PMMA films with and without 0.5% (wt/wt) of additive mentioned above using relation (6). The Φ_{cs} values for complexes are tabulated in Table 1.

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

$$\mathrm{Ni(L)_2,\ Cu(L)_2,\ Zn(L)_2,\ \underset{\rightarrow}{Cd(L)_2},\ Sn(L)_2\ and\ PMMA}$$

3.2. Suggested mechanisms of photostabilization of PMMA by 2-thioacetic acid benzothiazol complexes

Depending on the overall results obtained, the efficiency of 2-thioacetic acid benzothiazol complexes as stabilizer for

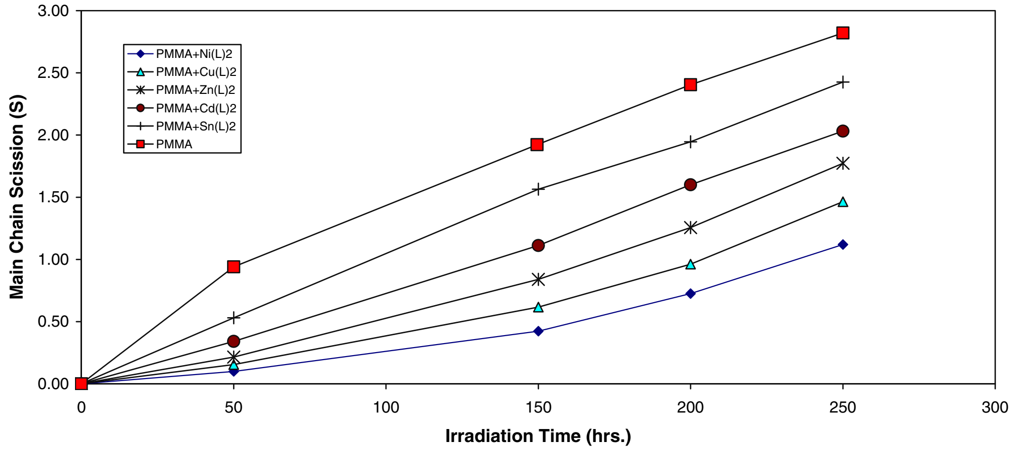


Figure 3 Changes in the main chain scission (S) during irradiation of PMMA films (40 μm) (control) and with 0.5 wt% of additives.

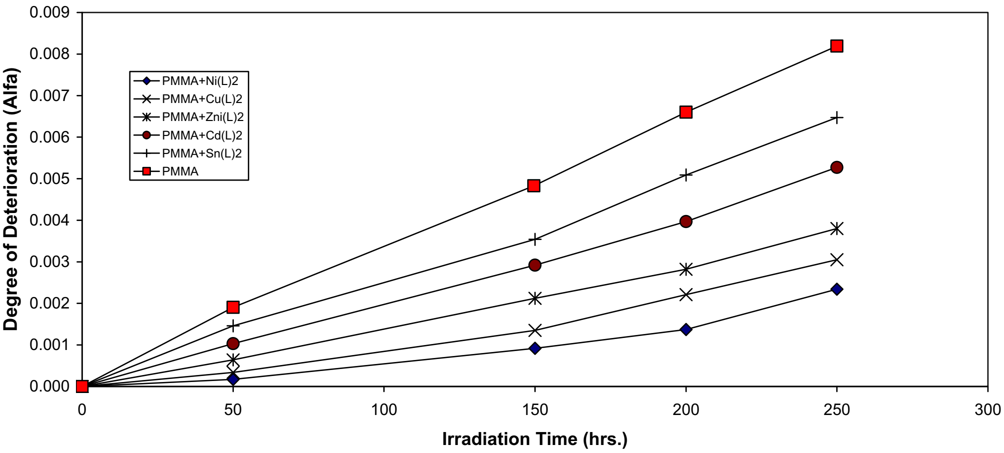


Figure 4 Changes in the degree of deterioration (α) during irradiation of PMMA films (40 μm) (control) and with 0.5 wt% of additives.

Table 1 Quantum yield (Φ_{cs}) for the chain scission for PMMA films (40 μm) thickness 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})
PMMA + $Sn(L)_2$	3.64E−05
PMMA + $Cd(L)_2$	4.31E−05
PMMA + $Ni(L)_2$	5.01E−05
PMMA + $Zn(L)_2$	6.54E−05
PMMA + $Cu(L)_2$	7.44E−05
PMMA (control)	4.53E−04

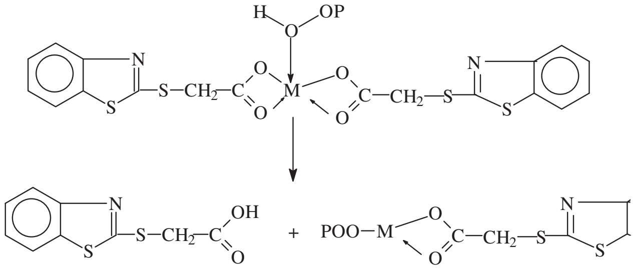
PMMA films can be arranged according to the change in the hydroxyl concentration as a reference for comparison as shown in Figs. 1–4, as follows:

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

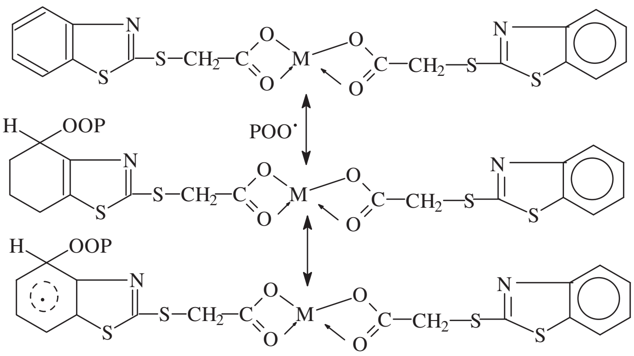
Metal chelate complexes generally known as photostabilizers for PMMA through both peroxide decomposer and excited state quencher. Therefore, it is expected that these complexes act as peroxide decomposer through the following proposed mechanism (Yousif et al., 2009a,b) (Scheme 1).

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$^{\bullet}$) and stabilize through resonating structures as shown in Scheme 2.

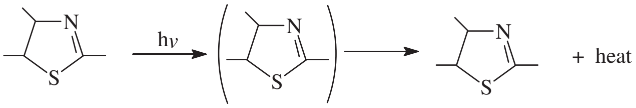
The ring of benzothiazol in this compound plays an important role in the mechanism of stabilizing process by acting as UV absorber. The UV light absorption by these additives containing benzothiazol dissipates the UV energy to harmless heat energy, Scheme 3. Further more this ring plays a role in resonating structures conjugation of radical in peroxide decomposer, Scheme 3, which supports this compound as a photostabilizer (Rasheed et al., 2009).



Scheme 1 Suggested mechanism of photostabilization of complexes as peroxide decomposer.



Scheme 2 Suggested mechanism of photostabilization of carboxylates complexes as radical scavengers through energy transfer and forming un-reactive charge transfer and stabilize through resonating structure.



Scheme 3 Suggested mechanism of photostabilization of benzothiazole as UV absorber.

4. Conclusions

In the work described in this paper, the photostabilization of PMMA films using 2-thioacetic acid benzothiazol complexes were studied. These additives behave successfully as photostabilizer for PMMA films. The additives take the following order in photostabilization activity according to their decrease in hydroxyl index for PMMA films:

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

These additives stabilize the PMMA films through UV absorption or screening, peroxide decomposer and radical scavenger mechanisms. The nickel complex was found to be the more efficient in the photostabilization process according to the photostability and mechanisms mentioned above. These mechanisms support the idea of using Ni(II) complexes as commercial stabilizer for PMMA.

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