

Photostabilization of Polystyrene Films by Schiff base[(Z)-2-((2-aminoethyl)imino)-1,2-diphenylethanol)]Transition Metal Complexes

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ABSTRACT: The photo sensitized degradation of polymer system is occasionally used as a means of solving the problem of environmental pollution, photostabilization of poly styrene films using Schiff base[(z)-2((2-Aminoethyl)imino)-1,2-diphenylethanol)](AIDOH)with Sn^(II), Mn^(II), Ni^(II), Cd^(II), and Zn^(II) complexes was investigated. Poly styrene films with a thickness of 80µm and contains complexes concentration of 0.05% wt were produced by the casting method with chloroform being the solvent The photostabilization activities of these complexes were determined by monitoring changes in carbonyl, (I_{CO}) and hydroxyl, (I_{OH}) indices and calculating the photodecomposition rate constant (k_d) for the studied films The results obtained showed that the photostabilization activity of polystyrene film in the presence of the complexes as additive follows the trends:

Ni (ALDO)₂ > Mn (ALDO)₂ > Sn (ALDO)₂ > Zn (ALDO)₂ > Cd(ALDO)₂ > Pure polystyrene film

KEYWORDS: Photostabilization , Polystyrene, Schiff base complexes.Environment.

I. INTRODUCTION

Many polymeric materials exposure to ultraviolet (UV) radiation cause a significant degradation as it causes photooxidative degradation which results in breaking of the polymer chains, produces free radical and reduces the molecular weight, causing deterioration of mechanical properties and leading to useless materials, after an unpredictable time

Polystyrene (PS) which is one of the most important material in the modern plastic industry, has been used all over the world, due to its excellent physical properties and low-cost. When polystyrene is subjected to UV irradiation in the presence of air, it undergoes a rapid yellowing and a gradual embrittlement. The mechanism of PS photolysis in the solid state (film) depends on the mobility of free radicals in the polymer matrix and their bimolecular recombination.

The UV-photodegradation of PS films has been studied using fluorescence spectroscopy, excitation and dispersed fluorescence spectra were also collected to monitor the chemical changes in the films. These fluorescence gave direct evidence that degradation products indicated to conjugated double bond along the polystyrene backbone named polyene structures-(C(C₆H₅)=CH)_n. Polyene structure is responsible for color change of PS under UV-exposure].

It is well known that the photo sensitized degradation of polymer system is occasionally used as a means of solving the problem of environmental pollution by plastic litter. The attempts to develop plastics with reduced outdoor stability are based on the syntheses of polymers with light-sensitive groups such as aliphatic ketone groups located predominantly in the main chain or independent (side) groups (1-3) and also the modification of polymers by the addition of another polymer (4-5) to do so in addition of using or application of photosensitizers which are added to the polymers or the plastic to photosensitize them against degradation process(6).

A number of research papers have appeared in literature dealing with the photosensitized degradation of polymers by addition of transition-metals salts and complexes (7-11). Preliminary it is found that the photodegradation of the polystyrene film was affected by the type of metal, concentration of the complex in addition to the kind of ligand and film thickness (11-14). It was reported also that the photo-stability of PS was reduced by the addition of bromine containing flame retardant, and appeared to depend upon the chemical structure of the polymeric additives [12]. For PS

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containing carbonyl group, it was found that the photodegradation increased with increasing in irradiation time. The changes in the average molecular weight in photooxidized PS were produced as consequences of chain dissociation by Norrish Type II reaction

The aim of the present investigation is the photostabilization of polystyrene film using Schiff base of [(z)-2((2-Aminoethyl)imino)-1,2-diphenylethanol)]Ni^(II), Mn^(II), Sn^(II), Cd^(II) and Zn^(II) complexes.

II. EXPERIMENTAL DETAILS

2-1 Materials and methods

2.1.1 Materials used

The organic chemicals used are Polystyrene, benzoin, glacial acetic acid, ethanol, benzoin, sodium diethyl dithiocarbamate whereas the inorganic one are chromium chloride, CrCl₃.6H₂O; nickel chloride, NiCl₂.6H₂O; manganese chloride, MnCl₂.4H₂O; tin chloride, SnCl₂.2H₂O; cadmium chloride, Cd(NO₃).4H₂O and zinc chloride, ZnCl₂. All these starting materials as well solvents were purchased commercially and used without any further purification except the polystyrene which was re-precipitated from chloroform solution with alcohol several times and finally dried under vacuum at room temperature for 24 hours.

2.1.2 Instruments used

Accelerated weathering Q.U.V tester (Q-panel company, USA), was used for irradiation of polystyrene films at light intensity flux of 1.8×10^{-8} Einstein dm⁻³ sec⁻¹ determined by potassium ferri-oxalate actinometrical technique^[17]. Infrared spectrophotometer 4200-JASCO was used for monitoring the growth of carbonyl and hydroxyl groups at (1730, 3440 cm⁻¹) respectively whereas the ultraviolet-visible spectrophotometer type V-650-JASCO was used to measure the changes in the UV-visible spectrum during irradiation at a wavelength of maximum absorption (λ_{max}). Film thickness was measured by a micrometer type 2610 a, Germany.

2-2 Synthesis of complexes

The synthesis of Schiff base [(z)-2((2-Aminoethyl)imino)-1,2-diphenylethanol] designed (AIDOH) and its metal complexes designed M(AIDO)₂ where M is metal was done via a previously described methods (15,16) in which, a hot ethanolic solution of benzoin (0.02 mol, 4.24 g) and ethylenediamine (0.02 mol, 1.2 g) was added few drops of glacial acetic acid and the mixture refluxed for 3 hours. The hot solution was cooled to room temperature until an orange precipitate of the Schiff's base separated, it was then filtered, washed several times with distilled water, dried and then recrystallized from glacial acetic acid.

The other complexes were prepared by the same manner where a hot ethanolic solution of the ligand (ALDOH) (0.001 mol) in absolute ethanol (10 ml) was prepared and then the metal salt (0.0005 mol) in absolute ethanol also (10 ml) was added to the hot solution of ALDOH ligand. The mixture of ligand and metal salt was refluxed for 2 hours. The produced colored solution was left settled at room temperature to crystallize, then filtered to obtain precipitate which is washed with cooled absolute ethanol and recrystallized from 1:1 methanol: glacial acetic acid mixture and then finally dried.

2-3 Film preparation

Polystyrene and metal complexes were dissolved in CHCl₃ to form polystyrene films which contain 0.05 % w/w of additive and have (80 μm) thickness. The films were prepared by evaporation technique at room temperature for 24 hours in order to remove the possible residual may present.

2-4 Irradiation experiments

The films were located (6 cm) a part from the UV lamps sources [four fluorescent lamps with 40 watt power]. These lamps are of the type UV-B313, giving a spectrum range between 290-360 nm with a maximum being at wavelength 313 nm. The irradiated samples were rotated from time to time to ensure that the intensity of light incident on all samples was the same.

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2-5 Spectrophotometric measurements

For Infrared spectrophotometer and in order to eliminate the effect of sample thickness we adopted the band indexing method [18]. A band index, I_s is defined as $I_s = A_s / A_r$, where A_s is the absorbance of the studied band and A_r , the absorbance of the reference band at 1450cm^{-1} which is the bending mode of $-\text{CH}-$ group in polystyrene [19]. Actual absorbance, the difference between the absorbance of top peak and the base line one ($A_{\text{Top peak}} - A_{\text{Base line}}$), is calculated using the base line method [13,20]. The ultraviolet-visible spectrum was measured during irradiation time for each compound at a wavelength of maximum absorption band (λ_{max}) for calculating the rate photodecomposition constant (k_d).

2-6 Measuring the photodegradation rate of polymer films using Ultraviolet-visible spectrophotometer

Ultraviolet-visible spectrophotometry technique (21) was used to measure the changes in the UV-Visible spectrum during different irradiation times for a polymer film at a wavelength ($\lambda_{\text{max}} = 200\text{-}400\text{ nm}$). The photodegradation rate constant for the Photostabilizer (k_d) was calculated using the first order kinetic equation:

$$\ln(a-x) = \ln a - k_d t \dots\dots\dots (1)$$

where:

a is the additive concentration before irradiation, x is the additive concentration after irradiation time t which is in second.

If A_0 represents the absorption intensity of the polymer film containing additive before irradiation, A_∞ is the intensity at infinite irradiation time and A_t is the absorption intensity after irradiation time t , then :

$$a = A_0 - A_\infty \text{ and } x = A_0 - A_t$$

$$a - x = A_0 - A_\infty - A_0 + A_t = A_t - A_\infty \dots\dots\dots (2)$$

Substitution of (a) and (a-x) from equation (2) to equation (1) gives:

$$\ln(A_t - A_\infty) = \ln(A_0 - A_t) - k_d t \dots\dots\dots (3)$$

Thus the plot of $\ln(A_t - A_\infty)$ versus irradiation time (t) gives straight line with a slope equal to (k_d). This indicates that the photodecomposition of the polymer is of first order.

III. RESULTS AND DISCUSSION

[(z)-2((2-Aminoethyl)imino)-1,2-diphenylethanol)] $\text{Ni}^{(11)}$, $\text{Mn}^{(11)}$, $\text{Sn}^{(11)}$, $\text{Cd}^{(11)}$ and $\text{Zn}^{(11)}$ complexes were used as additive for photostabilization of polystyrene films. During UV irradiation polystyrene films intensity of absorption spectrum increased, the initial rates of increase in absorbance are relatively rapid at the beginning, however they gradually decline as the film becomes insoluble (crosslinked) and being slightly yellow in colored (due to formation of diene and triene structures) [10,14]. The irradiation of polystyrene films led to change in the infrared spectra, the growth in absorption bands at 3440 and 1730 cm^{-1} which are belong to hydroxyl and carbonyl groups respectively [14,22], from these absorptions, the carbonyl index (I_{CO}) and hydroxyl index (I_{OH}) were calculated with irradiation time. The effectiveness of these complexes on the rate of photodegradation of polystyrene films was monitored by following the (I_{CO}) and (I_{OH}) with irradiation time. In figures 1 and 2, the (I_{CO}) and (I_{OH}) of complexes shows a lower growth with irradiation time with respect to polystyrene control film without additives. Since the growth of carbonyl and hydroxyl indexes with irradiation time are lower than that of the control, it is safe to conclude that these additives might be considered as photostabilizers of the polymer. An efficient photostabilizer shows a longer induction period. Therefore, the $\text{Ni}(\text{AIDO})_2$ is the most active photostabilizer, followed by $\text{Mn}(\text{AIDO})_2$, $\text{Sn}(\text{ALDO})_2$, $\text{Zn}(\text{ALDO})_2$, and finally the $\text{Cd}(\text{ALDO})_2$ which seem to be the least active one.

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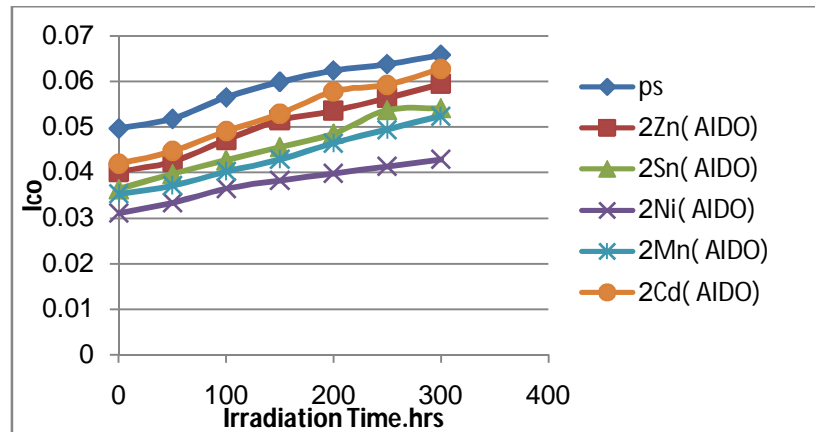


Figure 1: Change of carbonyl index with irradiation time for polystyrene films, 80 μm thickness and containing 0.05% wt of additives.

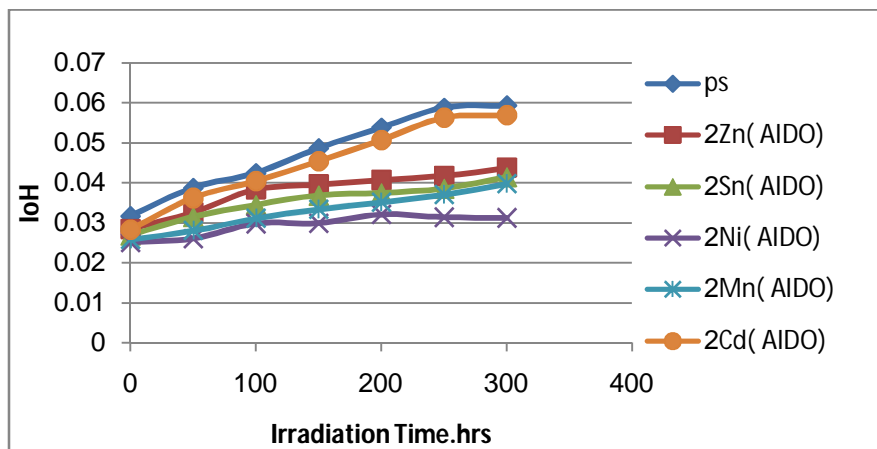


Figure 2: The relationship between the hydroxyl index and irradiation time for polystyrene films of 80 μm thickness and those containing additives with a concentration of 0.05% wt.

The change of $\ln(A_t - A_\infty)$ versus irradiation time, t for Ni(AIDO)_2 additive in polymer as example is a straight line and is shown in (fig 3). This indicates that the rate is first order for the decomposition of polymer, the slope is equal to the value $(-k_d)$. The values of the all first order constants of all additives used calculated by the same way are shown in table 1.

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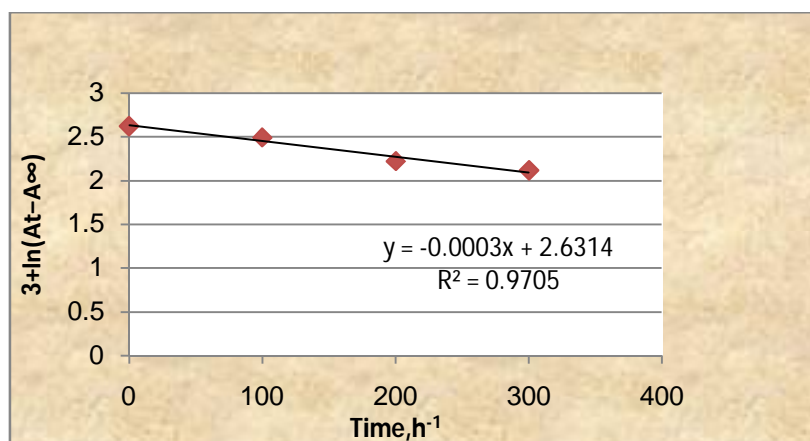


Figure3: Variation $\ln(A_t - A_\infty)$ with time for polystyrene films of (80 μ m) thickness and containing 0.05% wt of Ni(AIDO)₂ as additive.

Table 1: photodecomposition rate constant (k_d) of polystyrene films of (80 μ m) thickness and containing 0.05 % wt additives.

$K_d(h^{-1})$	Film used
0.0026	Polystyrene
0.0013	Polystyrene + Cd(AIDO) ₂
0.0009	Polystyrene + Zn(AIDO) ₂
0.0008	Polystyrene + Sn(AIDO) ₂
0.0003	Polystyrene + Ni(AIDO) ₂
0.0006	Polystyrene + Mn(AIDO) ₂

The photostabilizers always possess low k_d values, which mean that these modified polymer films are stable towards UV light more than polystyrene without additive. Absorption in polystyrene film at 241, 260 and 305nm have been attributed to acetophenone, dicarbonyl structures and benzalacetophenone respectively[22].

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