SOME METAL COORDINATION COMPLEXES AS POLYVINYL CHLORIDE FILMS PHOTOSTABILIZER

[1]SALAM A. MOHAMMED, [2]RAGHAD A. HADDAD, [3]EMAD A.YOUSIF

[1]Department of Chemical and Petrochemical Engineering, College of Engineering, University of Nizwa, Sultanate of Oman
[2]Department of Chemistry, College of Science, Al-Nahrain University, Baghdad-IRAQ
Email: salam.mohammed@unizwa.edu.om, raghadhaddad89@yahoo.com

Abstract: Some coordination complexes of Ni(II), Cu(II), Zn(II), Cd(II) and Sn (II) metal with [2-thioacetic acid-5-phenyl-1,3,4-oxadiazole] has been prepared in alcoholic solvent and used as photostabilizer for poly(vinyl chloride) films against degradation. Poly (vinyl chloride) has been mixed with these complexes in tetrahydrofuran solvent to form modified PVC, which containing 0.5% by weight concentration of complex and was produced by the casting method from the solvent. The light intensity is ($1.052*10^{-8}$Ein Dm^{-3} S^{-1}) with wavelength λ=313 nm was used for irradiation of the films at room temperature. The photostabilization activity of these compounds was determined by calculating the photodecomposition rate constant for PVC films with and without additive.

Keywords: PVC; UV light; Photostabilizer; Photodegradation

I. INTRODUCTION

Poly(vinyl chloride), or as it is known by PVC, is a thermoplastic and the third largest production polymer in the world.Pure Poly(vinyl chloride) is a white, brittle solid. It is insoluble in alcohol but slightly soluble in tetrahydrofuran[1]. It undergoes rapid autocatalytic dehydrochlorinationwhen exposures to heat and lightduring its molding and use [2]. Conjugatedpolyene sequences are formed from the beginning of the reaction, and they give rise to discoloration of the polymer and change its physical properties [3]. The low cost and good performance of PVC products have increased the utilization of this polymer in building, exterior application, such as window profiles, cladding structure, and siding [4]. One of the disadvantages of using polymers is that they degrade when they are usedfor outdoor applications [5-6].It is well known that all used plastics degrade under the influence of sunlight. All synthetic polymers require stabilization against the adverse effects; it became necessary to find ways to prevent, or at least reduce, the damage caused by the environmental parameters such as light, air and heat. Therefor the polymersphotostabilizer is one of the most important methodsto resolve the mentioned disadvantages for PVC applications and to improve the polymer resistance property. The photostabilization of polymers involves the retardation or elimination of photochemical process in polymers and plastics that occur during irradiation [7]. Generally speaking, there are five types of photostabilizersbased on the nature of stabilizer function: (a) light screeners, (b) UV absorbers, (c) excited state quenchers, (d) peroxide decomposers and (e) radical scavengers[8-11]. The purpose of this work was to investigate photodegradation constant (K_d)valuesforthe prepared PVC films mixed with different photostabilizerscomplexesand compared them with PVC (blank) films.

II. MATERIALS AND METHODOLOGY

All the reagents, starting materials and solvents were purchased commercially and used without any further purification. The ultraviolet-visible (UV-VIS) spectra were recorded by using Shimadzu UV-VIS. 160 A-Ultra-violet spectrophotometer in the range of 200-1100 nm. The thickness of films was measuredusing a micrometermodel 2610 A, Germany.

2.1 Synthesis of complexes

The steps of the synthesisof 2-thioacetic acid-5-phenyl-1,3,4-oxadiazole can be summerized in figure 1 [12].

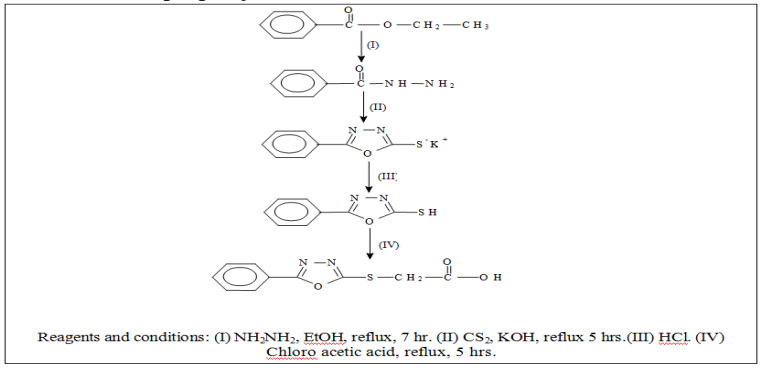


Figure 1:synthesis of 2-thioacetic acid-5-phenyl-1,3,4-oxadiazole

2.2 Experimental techniques

2.2.1 Films preparation:

A solution of polyvinyl chloride (5% w/v) in tetrahydrofuran (THF) was used to prepare polymer films. The films were prepared by evaporation technique for 24 hours, to remove the possible residual solvent at room temperature. After the evaporation of solvent, thePVC films were formed. The thickness of these films was about (30μm). Modified PVCcould be prepared by mixing of (0.5%) by weight from 2-thioacetic acid-5-phenyl-1,3,4-oxadiazole complexes to the solution containing PVC[13-14].

2.2.2 Irradiation experiments

2.2.2.1 Accelerated Testing Technique:

UV- Light was used for irradiation of produced PVC films, giving wavelength range between (250 to 380 nm) and the maximum wavelength light intensity is at 1.052×10^{-8}Ein Dm^{-3} S^{-1}. The polymer film samples were fixed parallel to each other and the lamp of the UV. radiation is vertically incident on the samples. The distance between the polymer films and the source was fixed to be 10 cm [15].

2.2.3 Photodegradation measuring methods

2.2.3.1 Measuring the photodegradation rate of PVC films using ultraviolet-visible spectrophotometer:

The ultraviolet-visible spectrophotometer type Shimadzu UV-VIS. 160 was used to measure the changes in the Uv-visible spectrum during irradiation time for each compound at maximum absorption band (λ_{max}). The absorption spectrum was measured in the range of (200-400nm), and the (λ_{max}) at each absorption was also recorded for different irradiation times.

The infinite irradiation time was considered and the infinite absorption (A_∞) was assumed to be after the infinite irradiation time.

To determine the photodegradation rate constant for photostabilizer (K_d), the first order equation was implemented as shown in equation 1:

$$\ln(a-x) = \ln a - K_d t \quad \text{……..(1)}$$

Where a, represent the stabilizer concentration before irradiation, x represents the change in stabilizer concentration after irradiation time (t).

AssumingA_o represents the absorption intensity of the polymer film containing stabilizer before irradiation, A_t represents the absorption intensity after t time of irradiation, then:

$$a = A_o - A_\infty$$

$$x = A_o - A_t$$

$$a - x = A_o - A_\infty - A_o + A_t = A_t - A_\infty \quad \text{……. (2)}$$

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

$$\ln(A_t - A_\infty) = \ln(A_o - A_\infty) - K_d t \quad \text{……. (3)}$$

Thus a plot of $\ln(A_t - A_\infty)$ versus irradiation time (t) expected to form straight line with a slope equal (K_d) which indicates that additivesphotodecomposition is a first orderrelation [15-17].

RESULTS AND DISCUSSION

3.1 Study of the efficiency of prepared complexes as photostabilizers of PVC films by ultraviolet spectroscopy

The complexes2-thioacetic acid-5-phenyl-1,3,4-oxadiazole was used as additives for the photodegradation of PVC films in 5% by weight thickness with (0.5%) by weight concentration from complex. The irradiation of PVC films with UV light of wavelength, λ= 313 nm led to a clear change in the FTIR spectrum[18-19]. Ultraviolet radiations are known to have deleterious effects on most industrial polymers inducing chemical modification and scission of polymer chain, which ultimately lead to an undesirable loss of the mechanical and surface properties of the irradiated material. The PVC contains only C-C, C-H and C-Cl bonds, therefore not expected to absorb light of wavelength longer than 190-220 nm[20].The carbonyl andpolyene groups generated during the photo-oxidation process of polymer extend the PVC film absorption to longer wavelengths and most probably are responsible for the yellow coloration of the polymer[20].These groups absorb light when they irradiated with light of wavelength between (200-700 nm) and activated to the singlet and triplet excited states which enhances various successive photo-oxidation reactions[21-22].The general process for photodegradation of PVC [10, 23] is shown in Figure(2).

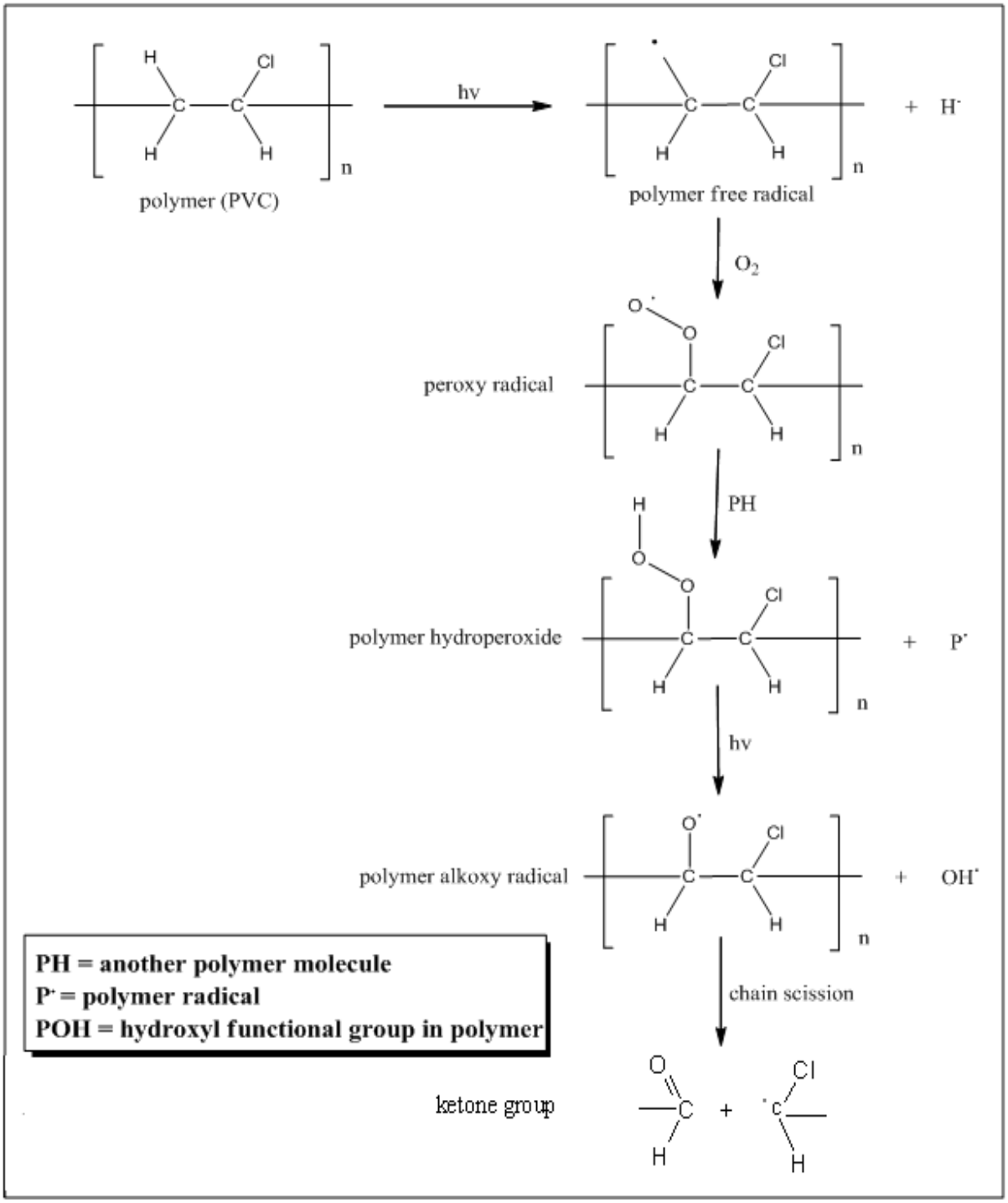


Figure 2: The general process for photodegradation of polyvinyl chloride

UV light induces the production of radicals by the oxidation. The prepared complexes were used as photostabilizers to PVC films comparing with PVC blank. The additives used in this study were chosen to be completely soluble in polymer solvent, (THF). It has been notice that the additives used in the present work are photodecomposed during the photolysis. Thus the photo decomposition rate constant (K_d) was possible to be estimated. The $K_d$values were computed using the UV (as in 2.2.3). Spectra changes of PVC films thickness 30μm containing 0.5% w/w from additives. The plot of irradiation time versus ln (A_t-A_∞), gave a straight line which indicate primarily the first order reaction. The slope equal to thedecomposition rate constant K_d(equation 3). Figure 3 to 9presnt the variation of ln (A_t - A_∞) with irradiation time foradditives in PVC films at λ=313 nm. The photostabilizers always posses low K_d values, as been listed in table 1indicating that these additives are intended to be stable towards UV light. In other hand, $K_d$valueswrer sensitive to the type of additive added in PVC films, which decrease in order bellow. The conducted results point out to increasing the photostabilityof this additive in this term.

PVC >$Ca(OX)_2$ > $Cu(OX)_2$ > $Zn(OX)_2$ > $Ni(OX)_2$ > $Ba(OX)_2$ > $Sn(OX)_2$

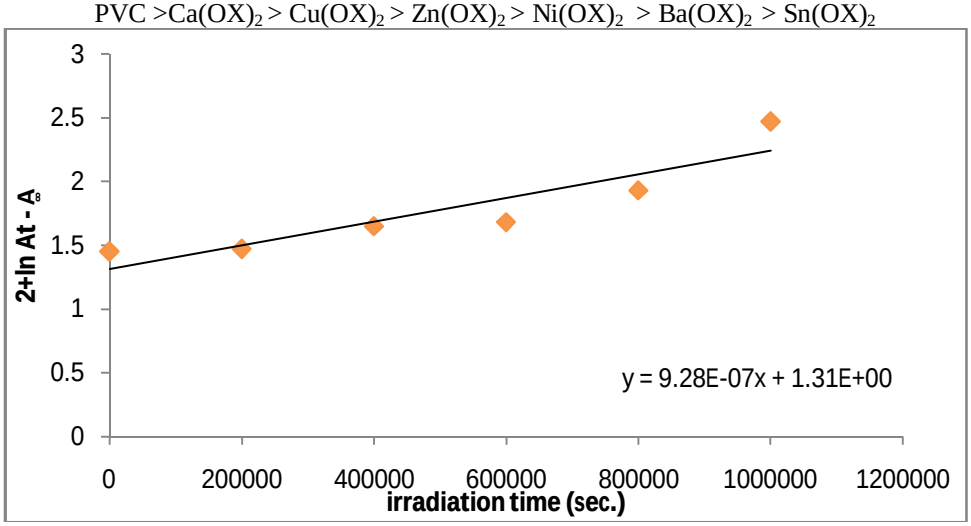


Figure 3: Variation of natural logarithm of (A_t - A_∞) with irradiation time of PVC (blank) film thickness (30µm).

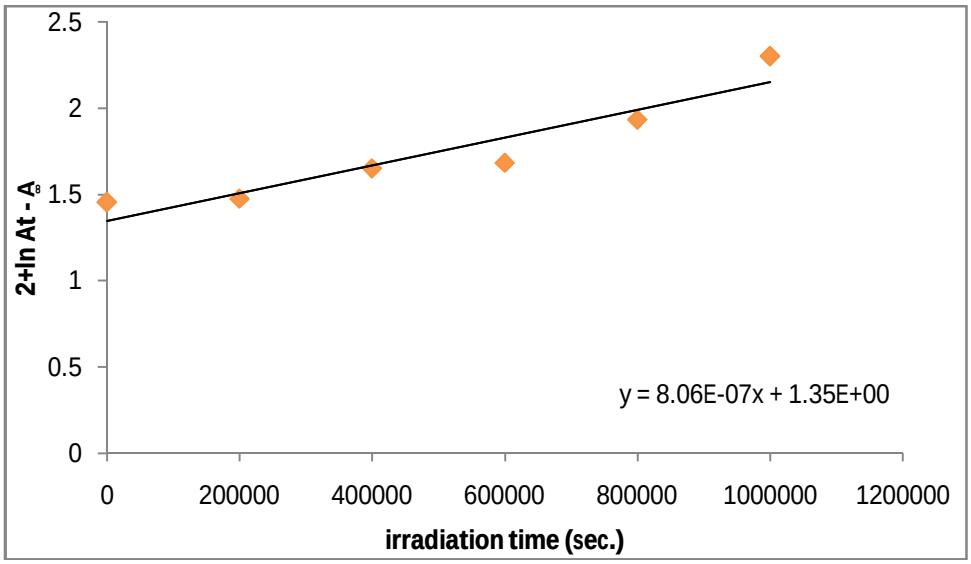


Figure 4: Variation of natural logarithm of (A_t - A_∞) with irradiation time of $Ca(OX)_2$ in PVC film thickness (30µm).

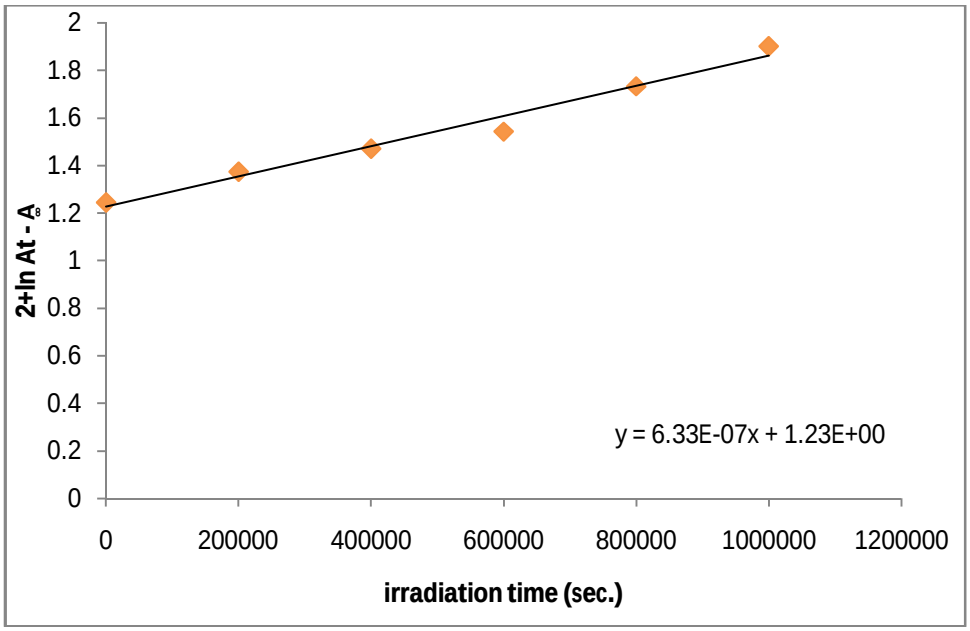


Figure 5: Variation of natural logarithm of (A_t - A_∞) with irradiation time of $Cu(OX)_2$ in PVC film thickness (30µm).

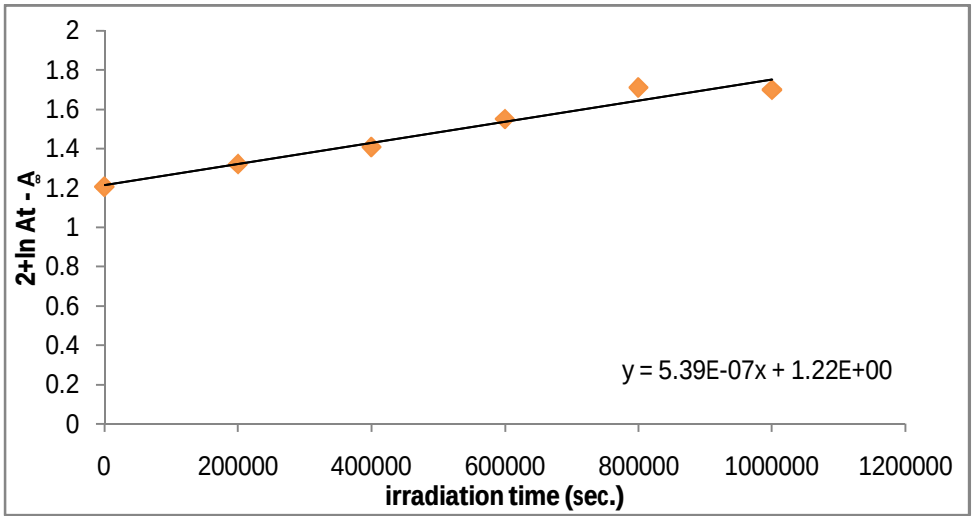


Figure 5: Variation of natural logarithm of (A_t - A_∞) with irradiation time of $Zn(OX)_2$ in PVC film thickness (30µm).

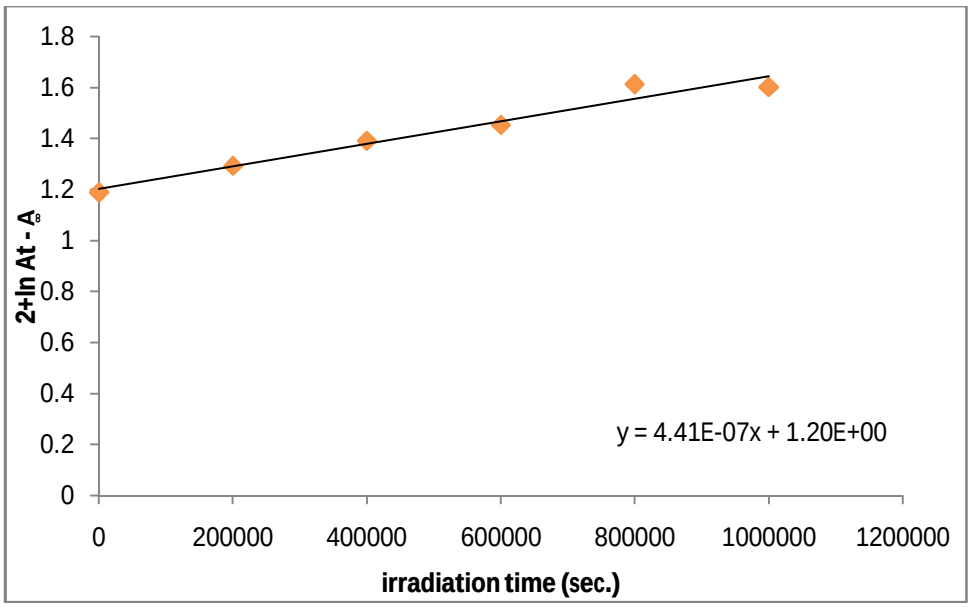


Figure 7: Variation of natural logarithm of (A_t - A_∞) with irradiation time of $Ni(OX)_2$ in PVC film thickness (30µm).

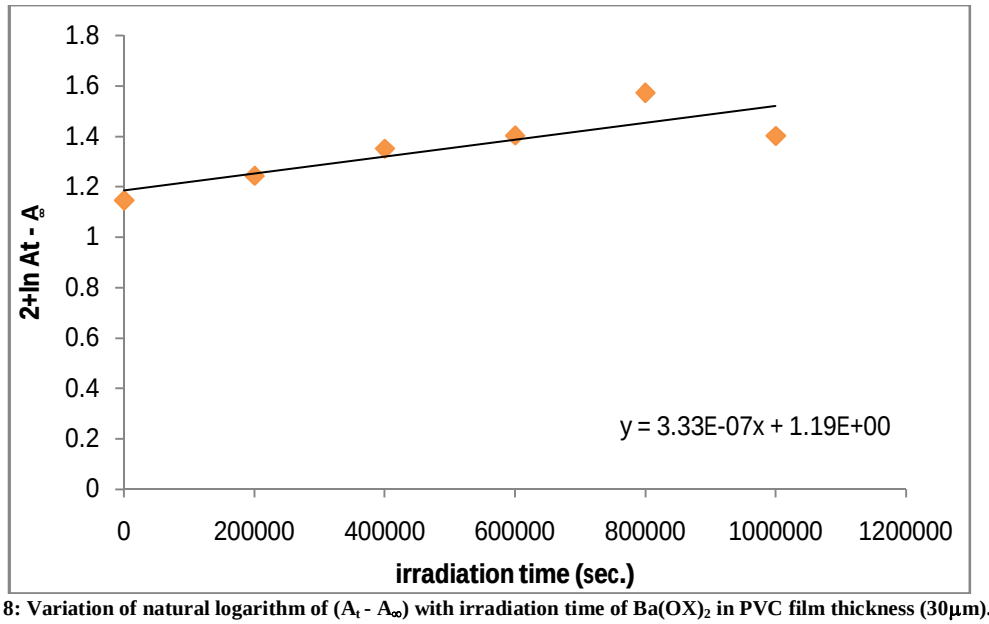


Figure 8: Variation of natural logarithm of (A_t - A_∞) with irradiation time of $Ba(OX)_2$ in PVC film thickness (30µm).

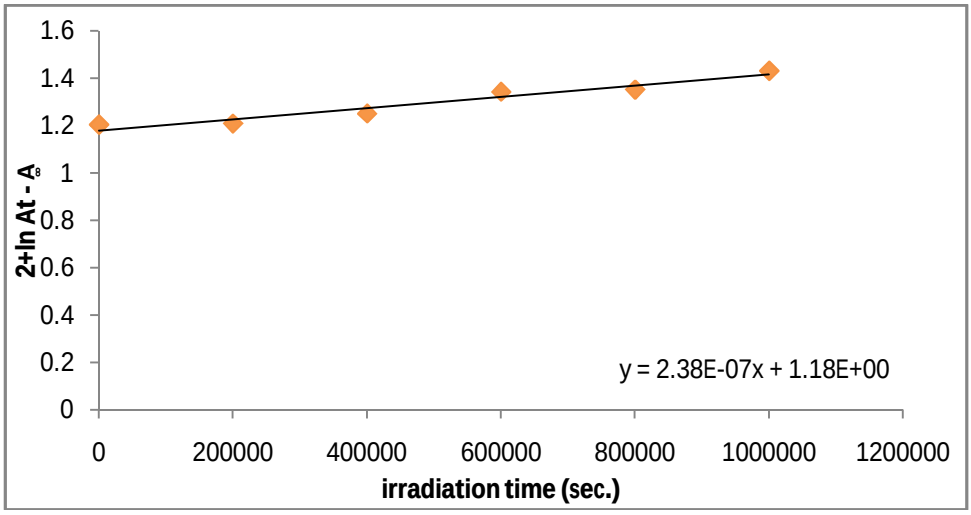


Figure 9: Variation of natural logarithm of (A_t - A_∞) with irradiation time of $Sn(OX)_2$ in PVC film thickness (30µm).

Table 1: Photodecomposition rate constant (K_d) of PVC films thickness (30µm) containing 0.5 % of additives

Sample	$K_d.10^{-7}$ (S^{-1})
$Sn(OX)_2$	2.38
$Ba(OX)_2$	3.33
$Ni(OX)_2$	4.41
$Zn(OX)_2$	5.39
$Cu(OX)_2$	6.33
$Ca(OX)_2$	8.06
PVC blank	9.28

CONCLUSION

The presented work and it's results authenticate the used or added complexes into PVC films were acted as photostabilizers. Different type of complex had different $K_d$value depends on the nature of that complex and accordingly PVC film decomposed resistant was improved in compare with blank PVC tested

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