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Research Article

# PHOTODEGRADATION OF POLY (VINYL CHLORIDE) FILMS WITH SOME COBALT $^{(111)}$ COMPLEXES AND SCHIFF BASES AS ADDITIVES

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**ABSTRACT**
In this paper, some compounds were used and their impact on the photodegradation of poly (vinyl chloride) (PVC) was study. The PVC films containing concentration of compounds 0.05 w/w by weight (80µm thickness) were produced by casting method from tetrahydrofuran (THF) solvent. The photodegradation and photo stablization activities of these compounds were determined by many methods, monitoring the carbonyl ($I_{CO}$), polyene($I_{PO}$) and hydroxyl($I_{OH}$) indices, calculating the photodegradation rate constant (kd),weight loss method and the changes in viscosity average molecular weight of PVC films with and without additives with irradiation time. The Photo degradation activities of these additives takes the following order:

L5 > L4 > L3 > PVC > L2 > L1

Where L5 = [ 4-((2-hydroxybenzylidene)amino)-N-(5-methylisoxazol-3-yl) benzene sulfonamide]
L4 = Co [$S_2$CN ($C_2H_5$) $_2$ ]$_3$ Tris (diethyl dithio carbamato) cobalt (111)
L3 =[N-(2-hydroxybenzylidene)-4-(2-hydroxybenzylidene)amino) benzene sulfonamide]
L2 = Co ( $C_5H_7O_2$)$_3$ Tris (acetyl acetonato )cobalt (111)
L1 = Co ($C_6H_4NO_2$)$_3$ Tris (picolinato) cobalt (111).

**Keywords:** poly(vinyl chloride), Photodegradation and UV-Visible, weight loss method.

## INTRODUCTION

Polyvinyl chloride (PVC), is one of the most versatile polymers and is the third largest produced polymer in the world [1, 2]. The low cost and 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 structures, and siding. However, ultimate user of PVC products for outdoor building applications depends on their ability to resist photodegradation over long periods of sunlight exposure. However, PVC suffers from poor thermal and light stability. It undergoes rapid autocatalytic dehydrochlorination upon exposure to heat and light during its molding and use [3].In recent years, the use of polymeric materials has rapidly increased, but it is well established that rapid photodegradation of these materials is possible when they are exposed to natural weathering[4,5] .To ensure the weather ability 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. It is well known that all commonly used plastics degrade under the influence of sunlight. Thus, all synthetic polymers require stabilization material to deter the adverse effects. It is necessary to find ways to prevent, or at least reduce the damage caused by the environmental parameters such as light, air and heat. The photostabilization of polymers involves the retardationor elimination of photochemical process in polymers and plastics that occurs during irradiation. The following stabilizing systems have been developed which depend on the actions of stabilizers: (a) light screeners, (b) UV absorbers, (c) excited state quenchers, (d) peroxide decomposers and (e) radical scavengers [6-8] .

## MATERIALS AND EXPERIMENTAL

All the starting material were purchased commercially and used without any further purification. A literature methods were used for the preparation of the compounds used additives. $[Co(C_6H_4NO_2)]$[9], $[CO(C_5H7O_2)_3]$[9], $[Co[S_2CN(C_2H_5)_2]_3]$[10], [N-(2-hydroxy benzylidene)-4-(2-hydroxbenzylidene) amino) benzene sulfonamide][11] and [4-((2-hydroxybenzylidene)amino)-N-(5-methyli soxazol-3-yl) benzene sulfonamide][11] .

### Experimental techniques

### I) Films preparation

A solution of Poly(vinyl chloride) solution or modified Poly(vinyl chloride)(5 g /100 ml) in tetrahydrofuran was used to prepare (80 µm) thickness of polymer films, (measured by a micrometer type 2610 A, Germany). 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[12].

### II) Irradiation experiments

UV- Light was used for irradiation polymer films, giving wavelength range between (250 to 380 nm) and the maximum wavelength light intensity is at (6.4 X $10^{-8}$ Ein $Dm^{-3}$ $S^{-1}$). The polymer film samples were fixed parallel to each other and the lamp of the UV. Incident radiation is vertically incident on the samples. The distance between the polymer films and the source was (10 cm). The polymer film samples were vertically fixed parallel to the lamps to make sure that the UV incident radiation is perpendicular to 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 [13].

### III) Photodegradation measuring methods

### A. Measuring the photodegradation rate of polymer films using infrared spectrophotometery

The degree of photodegradation and photostablization 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 at1770 $cm^{-1}$, polyene group at 1629 $cm^{-1}$ and the hydroxyl group at 3460 $cm^{-1}$. The progress of photodegradation during different irradiation times was followed by observing the changes in carbonyl, polyene and hydroxyl peaks. Then carbonyl (Ico), polyene (Ipo) and hydroxyl (IOH) indices were calculated by comparison of the FTIR absorption peak at 1770, 1629 and 3460 $cm^{-1}$ with reference peak at 1328 $cm^{-1}$ attributed to scissoring and bending of $CH_2$ group, respectively. This method is called band index method [14,15]

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

where As = Absorbance of peak under study, Ar = Absorbance of reference peak and Is = Index of group under study. Actual absorbance, the difference between the absorbance of top peak and base line (a Top Peak – a baseline) is calculated using the baseline method.

### B. Measuring the photodegradation rate of polymer films using Ultraviolet-visible spectrophotometer

Ultraviolet-visible spectrophotometry technique was used to measure the changes in the UV-Visible spectrum during different irradiation times for each polymer film at maximum absorption band (λmax = 200-400 nm). The photodegradation rate constant for the Photostabilizer (kd) was calculated using the first order kinetic equation.

$$\ln (a - x) = \ln a - k_d\, t \qquad \text{.......................} (2)$$

where: a =the additive concentration before irradiation

x = the additive concentration after irradiation time (t in sec).

If Ao represents the absorption intensity of the polymer film containing additive before irradiation, A∞ intensity at infinite irradiation time and At is the absorption intensity represents the absorption after irradiation time t, then :

$$a = A_o - A_\infty$$

$$x = A_o - A_t$$

$$a - x = A_o - A_\infty - A_o + A_t = A_t - A_\infty \qquad \text{...........} (3)$$

Substitution of (a) and (a-x) from equations (3) in (2) gives:

$$\ln(A_t - A_\infty) = \ln(A_o - A_\infty) - k_d t \qquad \text{.................} (4)$$

Thus the plot of ln (At – A∞) versus irradiation time (t) gives straight line with a slope equal to (kd). This indicates that photodecomposition of the additive in first order[16].

### C) Measuring the Photodegradation by Weight loss

The stabilizing efficiency was determined by measuring the % weight loss of photodegraded PVC films in absence and in presence of additives by applying the following equation:

$$\text{Weight loss \%} = [(W_1 - W_2) / W_1]\, 100 \quad \ldots\ldots.(5)$$

Where $W_1$ is the weight of the original sample (before irradiation), and $W_2$ is the weight of the sample (after irradiation)[17].

### D)Determination of average molecular weight ($\acute{M}v$) using viscometry method

The viscosity property was used to determine the average molecular weight of polymer at room temperature, using the Mark- Houwink relation [18].

$$[\eta] = K\, \acute{M}v^{\alpha}. \ldots.\ (6)$$

where as $[\eta]$ = the intrinsic viscosity $\alpha$ and K, 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 $t_0$ $\eta$respectively. Specific viscosity ($\eta$ sp) was calculated as follows:

$$\eta_{sp} = \eta_{re} - 1 \ \ldots..\ (7)$$

$\eta_{re}$ = Relative viscosity

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

$$[\eta] = (\sqrt{2}/C)(\eta_{sp} - \ln\eta_{re})^{1/2} \ \ldots.\ (8)$$

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

By applying equation 6, the molecular weight of degraded and the virgin 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:

$$[\eta] = 1.38\times10^{-4}\ (\bar{M}_V)^{0.77} \ldots\ldots(9)$$

## RESULTS AND DISCUSSION

The irradiation of PVC films led to a clear change in their FTIR spectra, appearance of bands in 1770 $cm^{-1}$ and 1724 $cm^{-1}$ was attributed to the formation of carbonyl groups .A third band was observed at 1629 $cm^{-1}$ was related to polyene group, a band at 3440 $cm^{-1}$ attributed to hydroxyl group. The absorption was calculated as carbonyl index (ICO),polyene index(IPO) and hydroxyl index (IOH) are calculated with irradiation time. The effectiveness of this complexes on the rate photodegradation of PVC films was monitored by following the($I_{CO}$) ($I_{PO}$)and ($I_{OH}$) with irradiation time. Results shown in figs (1-3) .Since the growth of($I_{CO}$) ($I_{PO}$)and ($I_{OH}$) with irradiation time is higher than PVC control, illustrate that some compounds are active in sensitization of the photodegradation processes (L 5, L 4, L 3) and another compounds are active as photosatbilizers (L 2, L1).The Photo degradation activities of these additives takes the following order:

L5 > L4 > L3 > PVC > L2 > L1.

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

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 [19] .Poly (vinyl chloride) suffers from poor thermal and light stability. The prepared metal compounds were used as photo degraded to Poly (vinyl chloride) films comparing with Poly (vinyl chloride) films (blank). The physical properties of additives and polymers play a very important role in determining the additive efficiency in photo stabilization or photo degradation of polymers [20] .The additives used in this study were chosen to be completely soluble in polymer solvent, THF. Thus the photodecomposition rate constant (kd) was calculated. The (Kd) values were computed using the UV spectra changes of PVC films thickness (80 μm) containing 0.05% of additives. The plot of irradiation time versus ln (At-A∞), gives straight line which indicates primarily the first order reaction. The slope equal to the decomposition rate constant kd. The values of the first order rate constant of all the additives decay in PVC films (Kd) calculated by the same way and shown in Table (1).

### Measuring of the Stabilizing Efficiency for Poly(vinyl chloride)Films by Weight Loss Method

The photodegradation of Poly(vinyl chloride) is commonly known to be accompanied by a dehydrochlorination process (the evolution of HCl gas); consequently, weight loss occurs, which increases with the increasing of irradiation time. Thus, the weight-loss percentage as a function of the irradiation time can be a good measure of the degree of degradation and consequently can measure the stabilizing potency of the stabilizer and how long thatstabilizer would protect the polymer. Weight loss measurements were carried out according to the equation 5. The results of the weight loss as a function of the irradiation time are shown in Fig.(4). This results clearly show the low extent of weight loss (i.e., the low extent of dehydrochlorination as evolved HCl is the main degradative product) of photodegraded Poly(vinyl chloride) degradation by the compounds in comparison with the weight loss of photodegraded of PVC [2] [1] . The degradation efficiency of the investigated photodegraded for some additives was found to follow this order:

**L5 > L4 > L3 > PVC**

But two additives investigated the photo stabilization to poly (vinyl chloride) was found to follow this order:

**L1 > L2 > PVC**

### Variation in PVC Molecular Weight during Photolysis

Figure 5 shows the plot of( $\acute{M}v$) versus irradiation time for PVC film with and without additive . The average chain scission number (average number cut per single chain) (s) was calculated using equation (10) .

$S = (\acute{M}_{V,O} / \acute{M}_{V,T}) - 1$ …………(10)

Where $\acute{M}_{V,O}$ and $\acute{M}_{V,T}$ are viscosity average molecular weight at( zero and t) irradiation time, respectively. The plots of **S** versus time is shown in figure 6. For randomly distributed weak bond links ,which break rapidly in the initial stages of photodegradation ,the degree of deterioration as a function of irradiation is shown in figure 7. Figure (8) shows the (1/DP) versus irradiation time .Another way of degradation reaction characterization is the measurement of the quantum yield of the chain scission (φcs) ,the(φcs) values are tabulated in table 2 .

The (φcs) values for PVC films in the some presence additive (L5,L4,L3) are more than those of additive –free PVC (control).

**Table 1: Photodecomposition rate constant (kd) of PVC films (80 μm) thickness containing(0.05)w/w of additives**

| Additives | Kd |
|---|---|
| **0.004** | PVC(blank) |
| **0.001** | PVC+L1 |
| **0.002** | PVC+L2 |
| **0.019** | PVC+L3 |
| **0.011** | PVC+L4 |
| **0.007** | PVC+L5 |

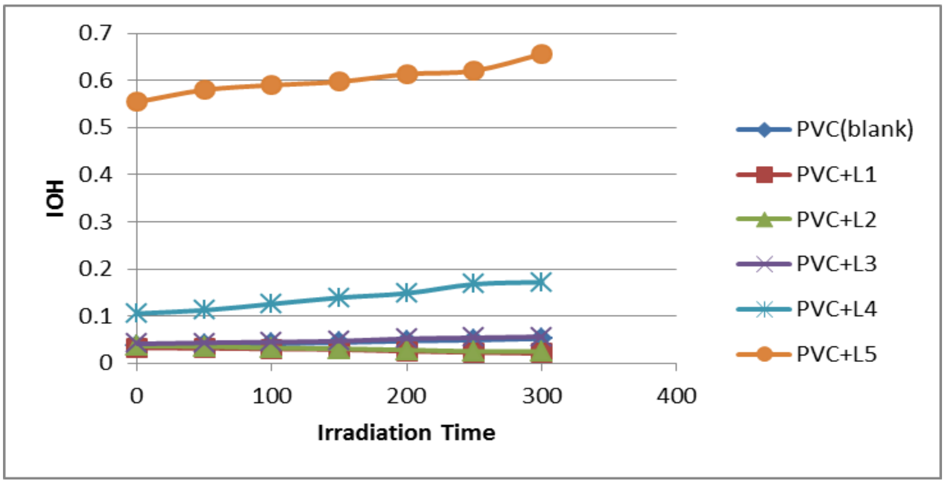

**Fig. 1: Change in hydroxyl index and irradiation time PVC films (80μm) thickness containing 0.05w/w additives**

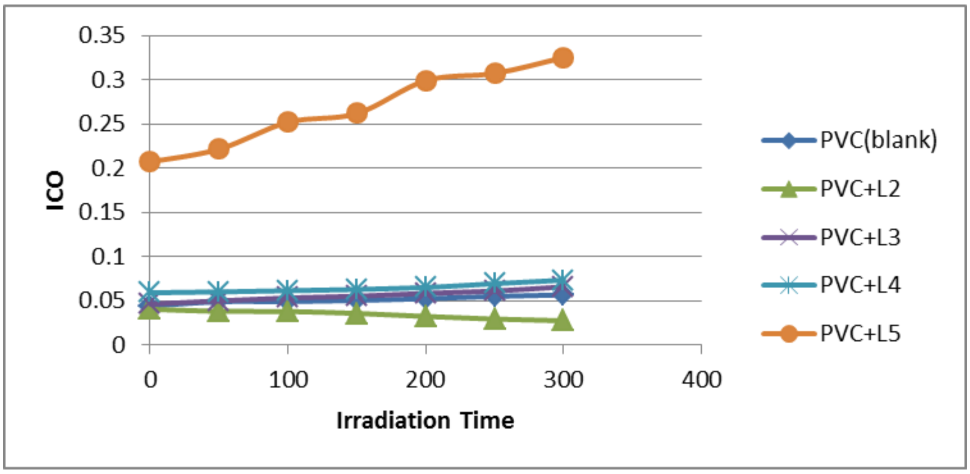

**Fig. 2: Change in carbonyl index and irradiation time PVC films (80μm) thickness containing 0.05w/w additives**

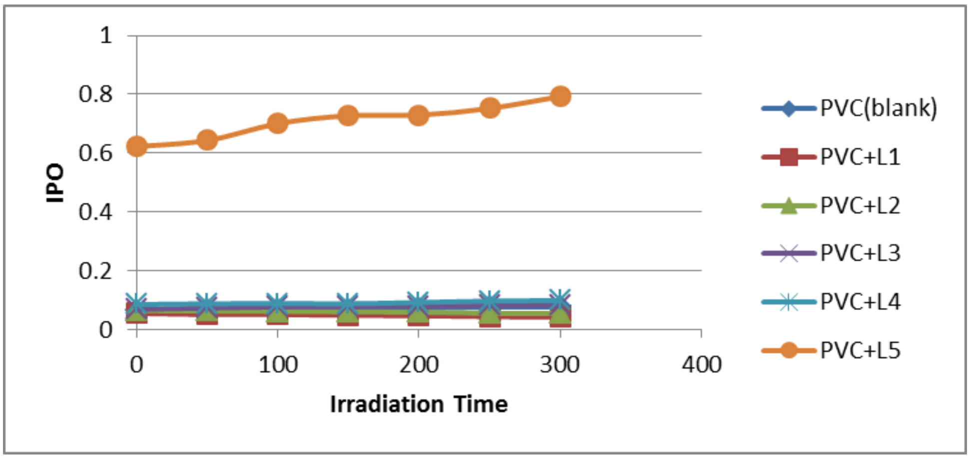

**Fig. 3: Change in polyen index and irradiation time PVC films (80μm) thickness containing 0.05w/w additives**

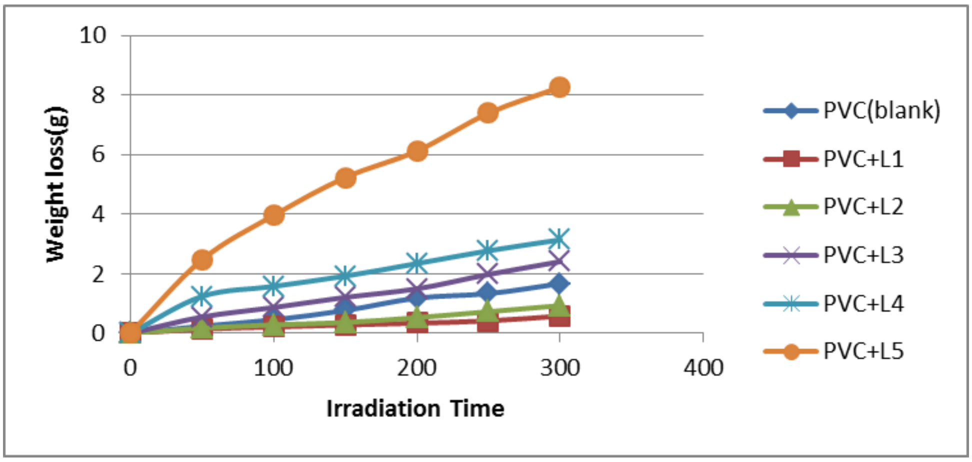

**Fig. 4: Variation of the weight loss of PVC films (80μm) thickness containing 0.05w/w additives with the irradiation time**

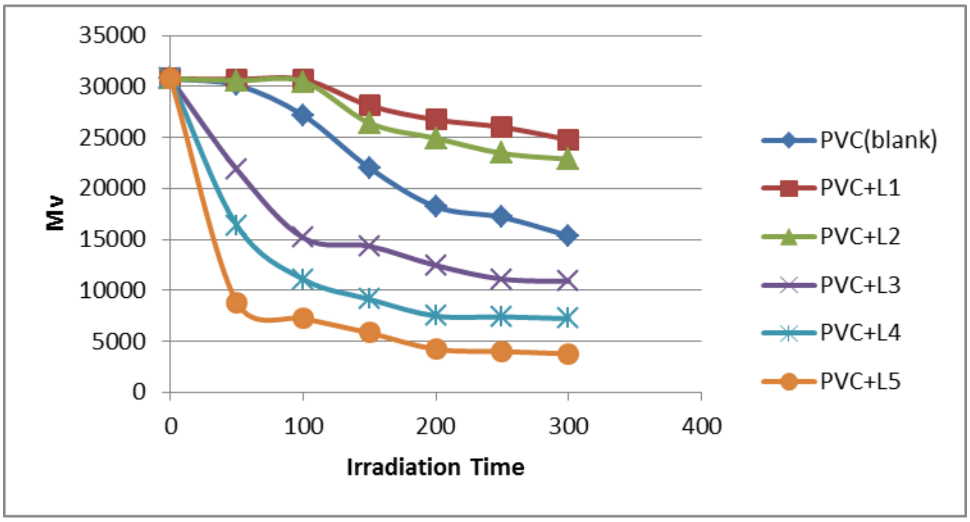

**Fig. 5: Change in viscosity average molecular weight (Mv) and irradiation time PVC films (80μm) thickness containing 0.05w/w additives**

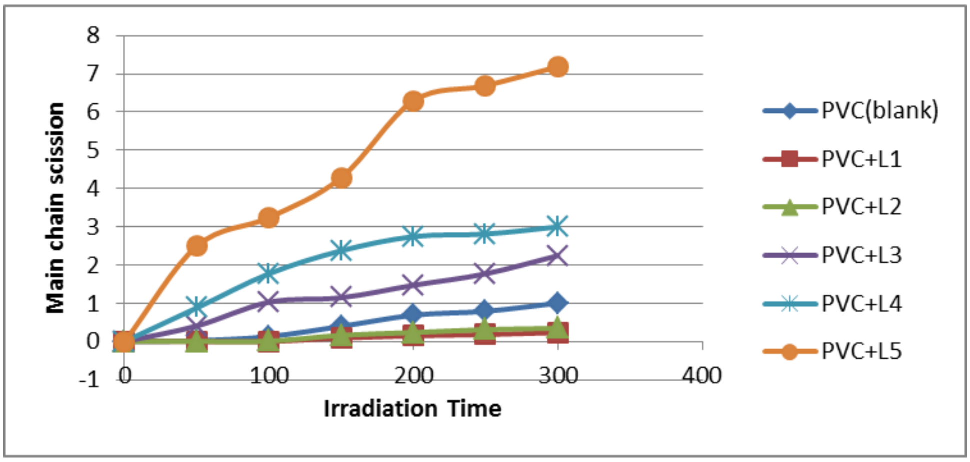

**Fig. 6: Change in main chain scission (s) and irradiation time PVC films (80μm) thickness containing 0.05w/w additives**

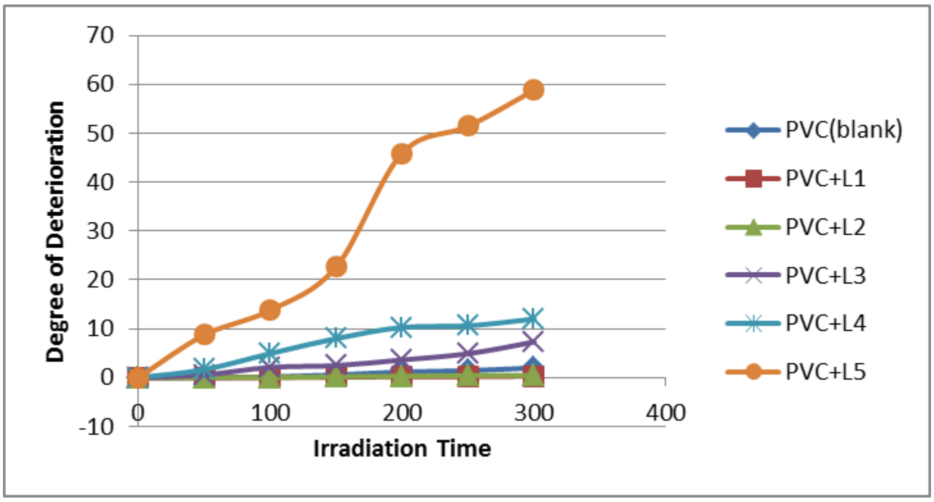

**Fig. 7: Change in Degree of Deterioration and irradiation time PVC films (80μm) thickness containing 0.05w/w additives**

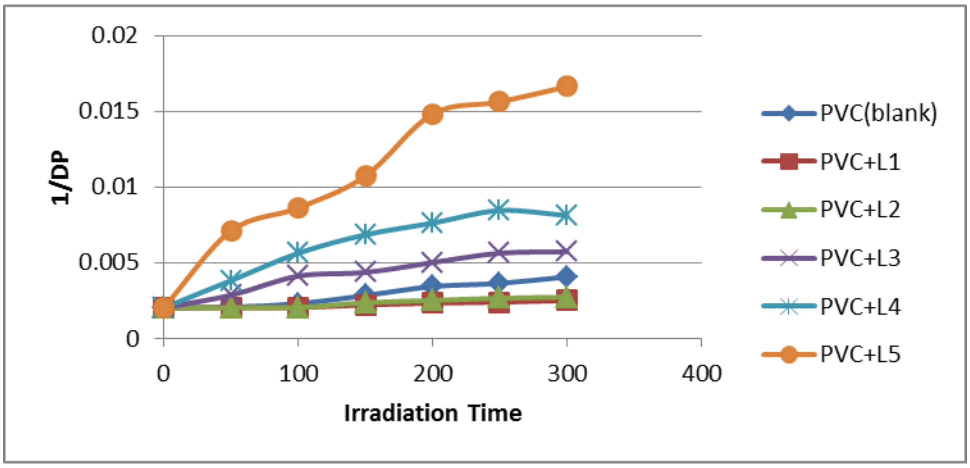

**Fig. 8: Change in 1/DP and irradiation time PVC films (80µm) thickness containing 0.05w/w additives**

**Table 2: Quantum yield (Φcs) for the chain scission for PVC film (80µm) thickness containing 0.05w/w additives**

| Quantum Yield($\Phi_{cs}$) | Additives |
|---|---|
| X $10^{19}$**1.89** | PVC(blank) |
| X $10^{18}$ 2.42 | PVC+L1 |
| X $10^{18}$**6.79** | PVC+L2 |
| X $10^{19}$**7.44** | PVC+L3 |
| X $10^{19}$**8.01** | PVC+L4 |
| X $10^{20}$**2.66** | PVC+L5 |

## CONCLUSION

Addition of the cobalt (111) complexes and shiffs base to PVC films (0.05W/W,80µm thickness),some compounds (L5,L4,L3) have successfully worked as induce photodegradation PVC films another compounds (L1,L2) increased photostabilization. The Photo degradation activities of these compounds were monitoring by many methods the carbonyl, hydroxyl and polyene indices, calculating the photo degradation rate constant (kd) for PVC films with and without additives ,the change in viscosity average molecular weight and measuring the weight loss of PVC films were also followed with irradiation time (using THF solvent). The degradation efficiency of the investigated photodegraded was found to follow this order: L5 > L4 > L3 > PVC > L2 > L1.

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