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Photo Stabilization of Poly (Vinyl Chloride) Films by Some Nickel Complexes

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Abstract

This study looked at the utilization of certain nickel complexes and their effects on the photodegradation of poly vinyl chloride. PVC films were cast using a 0.05 w/w by weight compound concentration Tetrahydrofuran (THF) solvent (80µm thickness). Numerous techniques, including measuring the carbonyl (I_{CO})index, calculating the photodegradation rate constant (k_d) and tracking changes in the average molecular weight of PVC films with and without additives while increasing irradiation time, were used to determine the photodegradation and photo stabilization activities of these compounds. The order of these additives' photo stabilization activity is as follows:

PVC + C1 > PVC + C2 > PVC pure

C1=1-(4-{(E)-[(2-hydroxyphenyl) methylidene] amino} phenyl) ethan1-one nickel (II)

C2 = 2-{[(4-methyl phenyl) imino] methyl} phenol nickel (II)

Key words: Photodegradation, photostabilization, polyvinyl chloride, nickel complexes

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التثبيت الضوئي لرقائق كلوريد متعدد الفاينيل باستخدام بعض معقدات النيكل كمضافات

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الخلاصة

شملت هذه الدراسة استخدام بعض معقدات النيكل وتأثيراتها على التفكك الضوئي لكلوريد متعدد الفاينيل. تم استخدام مذيب تتراهيدروفوران (THF) في عملية الصب لتكوين أغشية PVC بتركيز (0.05 w/w) وسمك (80µm). تم استخدام العديد من التقنيات لمتابعة التفكك، بما في ذلك قياس معامل الكربونيل (I_{CO})، وحساب ثابت معدل التفكك الضوئي (k_d)، وتتبع التغيرات في معدل الوزن الجزيئي لرقائق PVC مع وبدون إضافات مع زيادة وقت التشعيع، لتحديد نشاط التفكك الضوئي والتثبيت الضوئي من هذه المركبات. أظهرت هذه المركبات قدرتها على التثبيت الضوئي. وكان ترتيب فعاليتها بالشكل التالي:

PVC + C1 > PVC + C2 > PVC pure

الكلمات المفتاحية: التثبيت الضوئي، التفكك الضوئي، كلوريد متعدد الفاينيل، معقدات النيكل.

Introduction

Most materials significantly deteriorate when exposed to UV radiation. Pigment discoloration, weathering, plastic yellowing, gloss loss, mechanical property loss (cracking), skin cancer, and other UV-related issues are typically caused by UV effect. Manufacturers of cosmetics, contact lenses, paints, and plastics are highly helpful in offering goods that remain constant for a long time when exposed to light [1,2].

When compared to other polymers, PVC is fairly affordable and offering a wide range of production and end-use options. It may be made in a variety of colors with enough strength and simple to maintain [3]. Such materials that have been properly made, outside weathering is also quite good. PVC has similar uses in both medicinal and food applications. It combines well the stiffness with non-combustibility under, especially at thinner wall thicknesses. At room temperature, dimensional stability is also favorable. It has high water vapor barrier also resistant to a variety of chemicals, oils, and greases [4]. It offers effective electrical insulating qualities in its flexible form. It may be ornamented using a variety of methods and has a high strength-to-weight ratio [5]. The usage of polyvinyl chloride (PVC) products in construction has grown due to their low cost and high performance, particularly in exterior applications such as window profiles, frame cladding, and panels [6]. Additionally, it has a variety of uses, including electrical wiring, flooring, packing, and architecture [7]. PVC's thermal stability and photo-stability restrict its usage in building construction, albeit [8].

Experimental

All the chemicals used are from the Sigma-Aldrich company and were utilized without further purification. The prepared complexes were used in scientific papers as additives

C1=1-(4-{(E)-[(2-hydroxyphenyl)methylidene]amino}phenyl)ethan1-one nickel(II) [9]

C2 = 2-{[(4-methylphenyl)imino]methyl}phenol nickel(II) [10]

Films preparation

PVC (1gm) was dissolved in tetrahydrofuran (20 ml) to create the polymeric films. Then, in order to finish the molding process and ensure solvent evaporation, pour the solution into the glass molds and let them stand for 24 hours. The polymeric films are removed from the mold once the molding process is complete, their thickness is measured using a micrometer type (2610A), and a slot (23) cm is used to attach them to cardboard sheets [11].

Irradiation experiments

UV light with a wavelength range of (250 to 380 nm) and the greatest wavelength light intensity is at (380 nm) was utilized to irradiate polymer films (4.4×10^{-5} Ein dm^{-3} S^{-1}). The samples of polymer films were attached parallel to one another and the UV lamp. in the samples, incident radiation is vertically. The separation between the source and the polymer sheets was (10 cm). To ensure that the UV incident radiation is perpendicular to the samples, the polymer film samples were vertically attached parallel to the lamps. To guarantee that all samples get the same amount of light, the irradiated samples were periodically rotated.

Measuring the photo-degradation rate of PVC films using FTIR.

The photo-degradation of the polymeric films was followed up using infrared spectroscopy (FTIR), as the absorption spectrum of the irradiated polymeric films was recorded within the range (400-4000cm^{-1}) using (FTIR 8300 shimaduz spectrophotometer). The absorption site of the active groups that appear in PVC was determined as the carbonyl group (C=O) at (1750cm^{-1}). The carbonyl and hydroxyl index were calculated and compared with the reference absorption peak of PVC (1427 cm^{-1}), which belongs to the (CH_2) group. This method is called the band index method.

$$\mathrm{I}_s = {}^{A_s}\!/_{A_{re}} \text{ ……… } (1)$$

Where I_s = the index of the group under study, A_s = absorbance of the group under study during irradiation A_r = the absorbance of the reference peak ($-CH_2$), which does not change during irradiation, The Beer-Lambert law is used to convert the percentage of transmittance to absorbance. Where the actual absorbance is the difference between the absorbance of the highest peak and the baseline.[12]

$$A = lo\,g(100/T\%)$$

$$A = log100 - logT\%$$

$$A = 2 - logT\% \text{ ……… } (2)$$

Measuring the photo-degradation rate of PVC films using Ultraviolet-visible spectrophotometer (uv-vis)

A UV-Vis Spectrophotometer (V-650-JASCO) was used to measure the changes in the UV-Vib spectrum as a result of exposure to periods of ultraviolet rays for each compound at the maximum wavelength (λmax). The absorption spectrum was measured in the range (200-400 nm) and (λ max) was recorded at each absorbance at different irradiation times. The infinite irradiation time was considered and the absorption to infinity ($A\infty$) was assumed to come after the infinite irradiation time. A first-order equation was used to calculate the rate of dissociation constant (k_d) for the modified (doped) polymers:

$\ln(a-x)=\ln a - k_d t$ .... (3)

Where a = indicates the concentration of the additive before irradiation, x= indicates the change in the concentration of the additive after irradiation (t) for a period of time, A_0 = absorbance of the polymer sheet containing the additive before irradiation, A_t= absorbance of the polymeric wafer after (t) of irradiation.

$a=A_o - A_\infty$

$x=A_0 - A_t$

$a - x = A_0 - A_\infty - A_0 + A_t$ .... (4)

When equaton (4) was substituted into equation (3), equation (5) formed

$\ln(A_t - A\infty) = \ln(A_0 - A_\infty) - K_d t$ .... (5)

From this equation, The plot was deduced between ln ($At - A\infty$) on the y-axis (Y) and time (t) on the x-axis (X) gives a divided line, and the slope is equal to the rate constant of dissociation (k_d) and this proves that the photo-degradation of the Additives It is a first-degree equation.[12]

Rate measurements of molecular weight by viscosity method

Another way to follow the photo-degradation that occurs as a result of exposure of polymeric films to radiation is the method of following the change in the rate of viscous molecular weight, and the Mark-Houwink equation is used to follow the relationship between viscosity and molecular weight. [13]

$[\eta] = K\bar{M}_V^{\alpha}$ .... (6)

$\bar{M}_V^{\alpha}$ = viscous molecular weight rate

[η] = intrinsic viscosity

Where K, α = constants that depend on the solvent system at a given temperature. The intrinsic viscosity of the polymeric solution is measured by means of a (Ostwald U tube) scale, where the polymer solution is prepared by dissolving the polymer in the appropriate solvent (gm/100ml). The descent time of the solvent (t_0) and the polymeric solution (t) are measured respectively and the relative viscosity and specific viscosity are deduced by the following two equations

$\eta_{re} = \frac{t}{t_0}$.. (7)

$\eta_{sp} = \eta_{re} - 1$ .... (8)

η_{re} = relative viscosity η_{re} = specific viscosity

The following relationship is used to find the intrinsic viscosity:

$[\eta] = \frac{\sqrt{2}}{c}(\eta_{sp} - \ln\eta_{re})^{1/2}$ .... (9)

C = concentration of polymer solution

$S = [\bar{M}v_0/\bar{M}v_t] - 1$ .... (10)

Where:

$\bar{M}v_0$, $\bar{M}v_t$ viscous molecular weight rate $befor\ and\ after\ irradiation$

S: average scission of polymeric chain

$\alpha = \bar{M}v_0 \,.\, S/\bar{M}v_t$ .... (11)

: degree of polymer degradationα

Result and discussion

PVC films showed a noticeable shift in their FTIR spectra after being exposed to radiation; the emergence of bands at 1770 cm-1 and 1724 cm-1 was attributed to the production of carbonyl groups. A band at 3440 cm-1 is linked to the hydroxyl group, and a band at 1629 cm-1 is related to the polyene group. The carbonyl index (I_{CO}) was used to compute the absorption along with the irradiation period. By comparing the (I_{CO}) with irradiation time, it was possible to determine how well these complexes affected the rate of photodegradation of PVC films. Since the growth of (I_{CO}) and (I_{PO}) with exposure duration is less than that of PVC control, this shows that complexes are active as photo-stabilizers (C1, C2). These additives' photo-stabilizers activities occur in the following order:

PVC + C1 > PVC + C2 > PVC pure

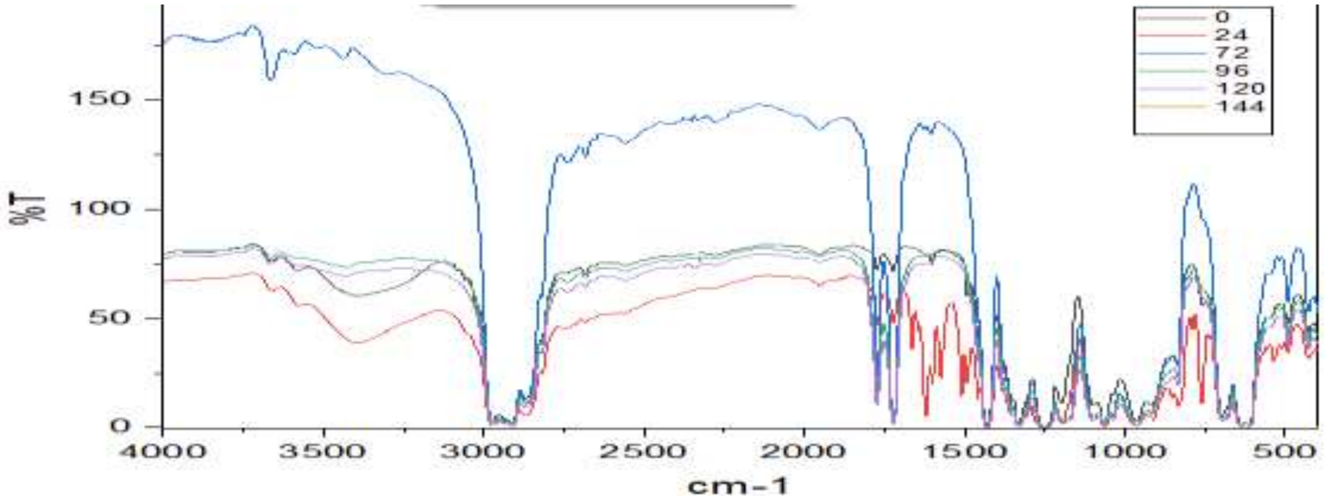

Figure 1: FTIR of PVC pure films before and after 144 hours of irradiation.

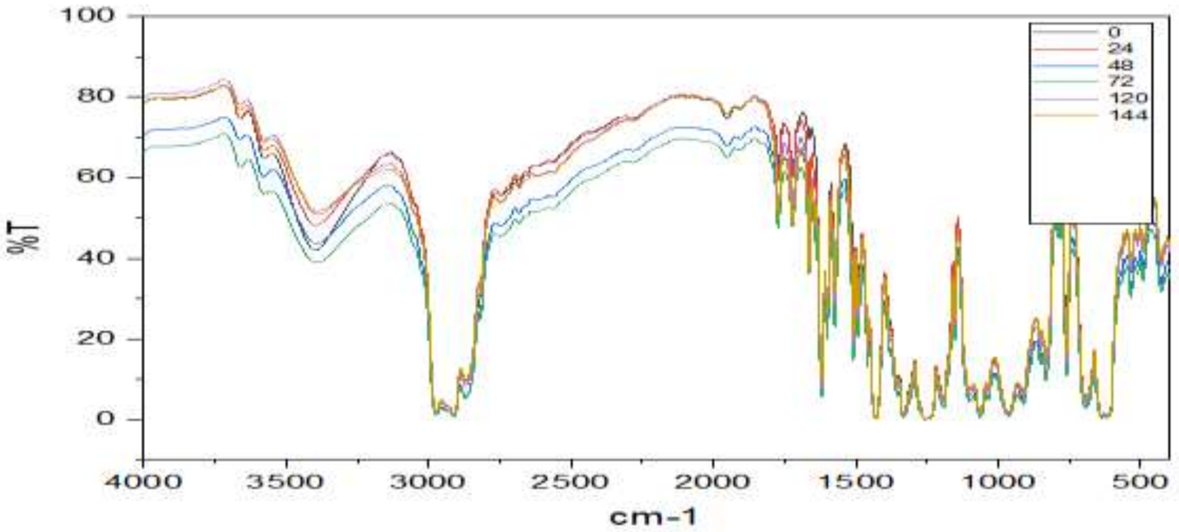

Figure 2: PVC + C1 films before and after 144 hours of irradiation.

Measuring the photo-degradation rate of PVC films using uv – visb spectroscopy.

The UV spectra variations of 80 µm thickness of PVC films containing 0.05 percent additives were used to calculate the Photodecomposition rate constant (K_d) values. The first order response is principally indicated by the straight line that results from the plot of ln ($At-A_\infty$) versus irradiation time. The slope is corresponding to the kd decomposition rate constant. The values of each additive's first order rate constant for decay in PVC films (K_d) were computed using the same formula and are displayed in Table (1).

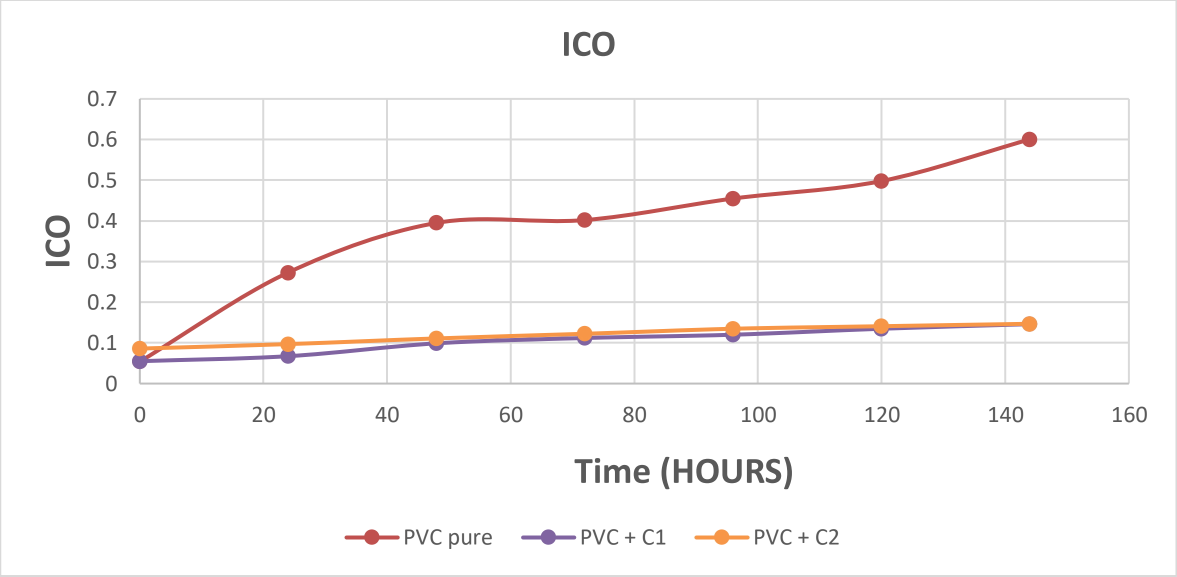

Figure 3: change of carbonyl index with different irradiation times

Table 1: k_d of poly vinyl chloride (PVC) films (80 µm) thickness containing (0.05) w/w of additives

ADDITIVES	K_D (H^{-1})
PVC pure	0.0037
PVC + C1	0.0004
PVC + C2	0.0007

PVC Molecular Weight Variation During Photolysis

Figure (4) shows the decrease in the molecular weight of the polymeric films with an increase in the irradiation time. When comparing the pure polyvinyl chloride film with the films containing the additives, a significant decrease in the viscous molecular weight rate indicates that these additives act as photo-stabilizers. The order of photo-stabilizers of films was as follows:

PVC + C1 > PVC + C2 > PVC pure

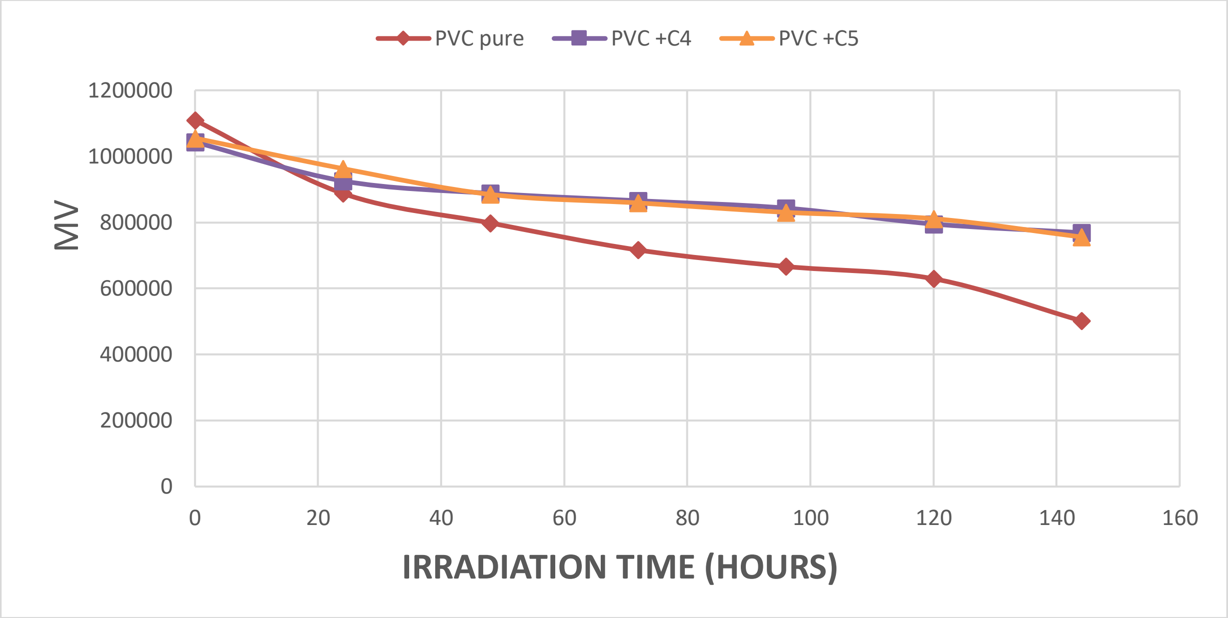

Figure 4: Change of Molecular Weight with different irradiation times

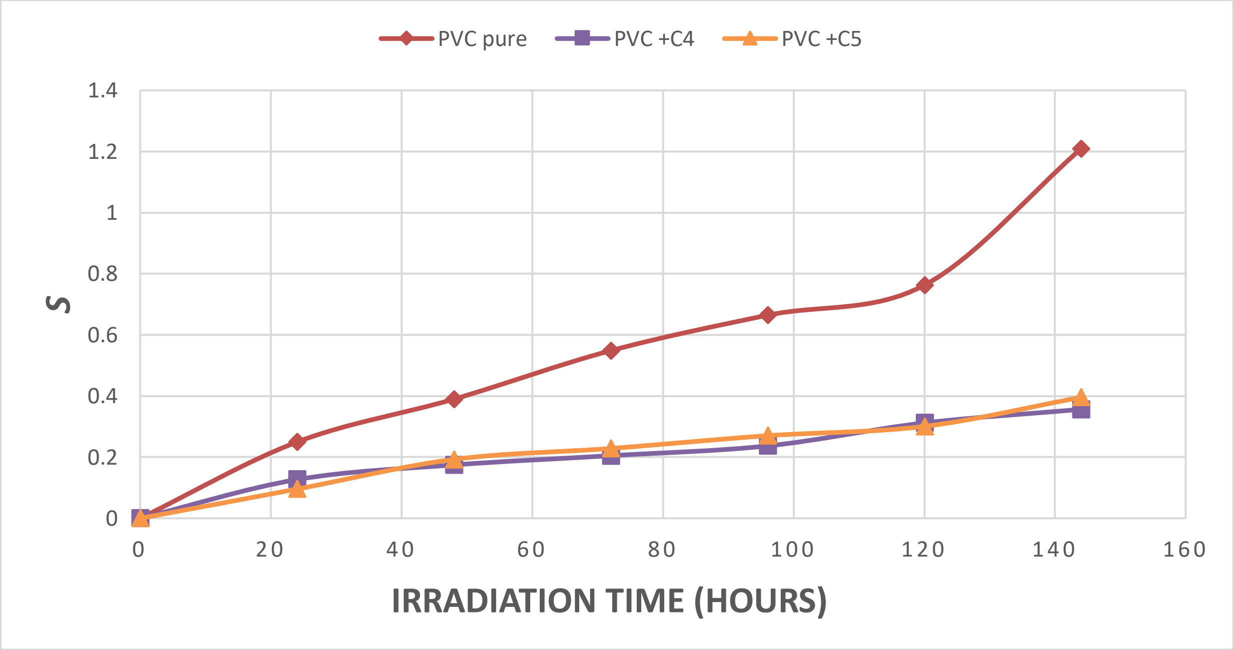

Figure 5: Change of S with different irradiation times

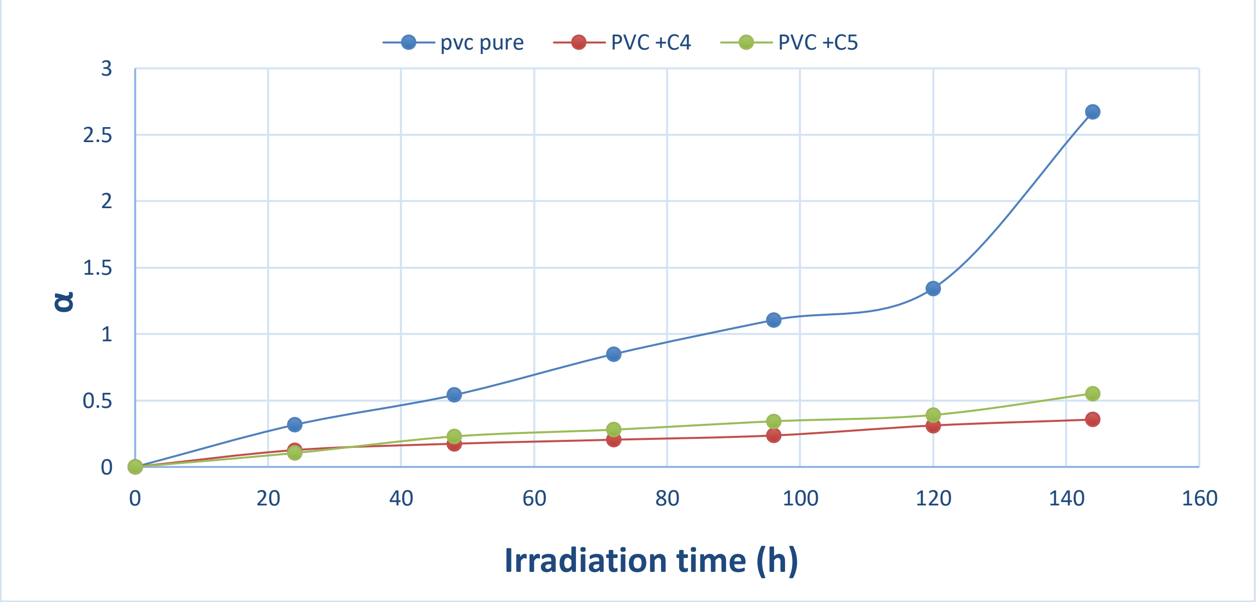

Figure 6: Change of α with different irradiation times

Conclusion

The addition of nickel complexes to PVC films of (0.05) W/W, (80 μm) thickness has proven effective as a photostabilizer. The carbonyl index, photodegradation rate constant (kd) of PVC films with and without additions, change in viscous molecular weight rate, and measurement of the carbonyl index were all used to track the photostabilization activities of these compounds (using THF solvent). The investigation's photostabilization was determined in order to have the following photostabilization efficiency in the following order:

PVC + C1 > PVC + C2 > PVC pure

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