



Morphological, Photochemical and Spectroscopic Studies of Ibuprofen-Tin Complexes

¹Ahmed Al-Ani*, ²Dina S. Ahmed, ¹Mohammed H. Al-Mashhadani, ¹Mustafa Abdallh, ¹Emad Yousif

¹Department of Chemistry, College of Science, Al-Nahrain University – Iraq

²Department of Medical Instrumentation Engineering, Al-Mansour University College – Iraq

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*Corresponding Author:

Ahmed Al-Ani

dr.ahmedalani75@gmail.com

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Abstract

Poly(vinyl chloride) (PVC) was prepared and the photo-stabilization of polymer films was studied using ultraviolet (UV) light. The efficiency of the synthesized polymer complex of ibuprofen-tin which is the photostabilizer in this study afterward of 300 hours of irradiation were evaluated by calculate the constant of PVC degradation rate. The outcome of this research has shown that the additives (ibuprofen-tin complexes) effect significantly on the decreased degradation constant compare to blank PVC, without additives the rate of degradation constant of PVC is greater than when the additives are added. The surface morphologies of the irradiated polymer film with additives were researches utilizing Field Emission Scanning Electron Microscope (FESEM). It can be seen that the polymer film with added additives is less roughness than the irradiated PVC (blank). The organotin complexes behave in this study as a photostabilizer to maintain the PVC from any decomposition by absorbing the incident light and convert it over the time as a heat to the polymeric chain.

1. Introduction

In the industrial area, the demand for polyvinyl chloride (PVC) exceeds 35 million tons per year [1]. Photodegradation caused by UV light absorption changes the polymer characteristics irreversibly. The incoming light has three spectra: ultraviolet (UV), visible (Vis), and infrared (IR), each with a different energy level. UV radiation accounts for just 8% of total incoming sunlight, although it is the primary cause of deterioration [2]. Dehydrochlorination at thermally labile sites defected the polymer chain, which started the breakdown process. When the levels of hydrochloric acid and polyenes reached a particular threshold, the polyenyl cation radicals that led to autocatalysis were formed [3, 4]. Coloration of the polymer caused breakage in the macromolecular chain, and because oxygen is present, oxidative processes occur, altering the physical characteristics of the polyvinyl chloride and weakening the substance. Organotin(IV) complexes have sparked a lot of interest due to their applicability in a variety of disciplines, including industrial, agricultural, and biocidal fields [5, 6]. The structure and coordination number (CN) of the Sn atom impact the bioactivity of organotin complexes in general [7]. The kd of PVC-prepared films containing three distinct ibuprofen tin complexes was studied in this work, and UV light was used to assess the stability of novel stabilizers.

2. Supplies and Procedures

2.1. Supplies

Petkim Petrokimya supplied the polyvinyl chloride (PVC) (Turkey). UV radiation (max = 365 nm; light intensity = $6.43 \times 10^9 \text{ ein dm}^3\text{s}^{-1}$) was used to irradiate the PVC sheets at 25°C using the weather-meter QUV tester (USA).

2.2. Ibuprofen-Tin Complexes I-III Preparation

The interaction of ibuprofen compound with tin(IV) chloride yielded three distinct organotin (IV) complexes [8]. The chemical structures of I-III were characterized using methods such as FTIR, ^1H -, and ^{119}Sn -NMR. In addition to FESEM, the surface morphology of the produced complexes was determined [8]. (Figure 1).

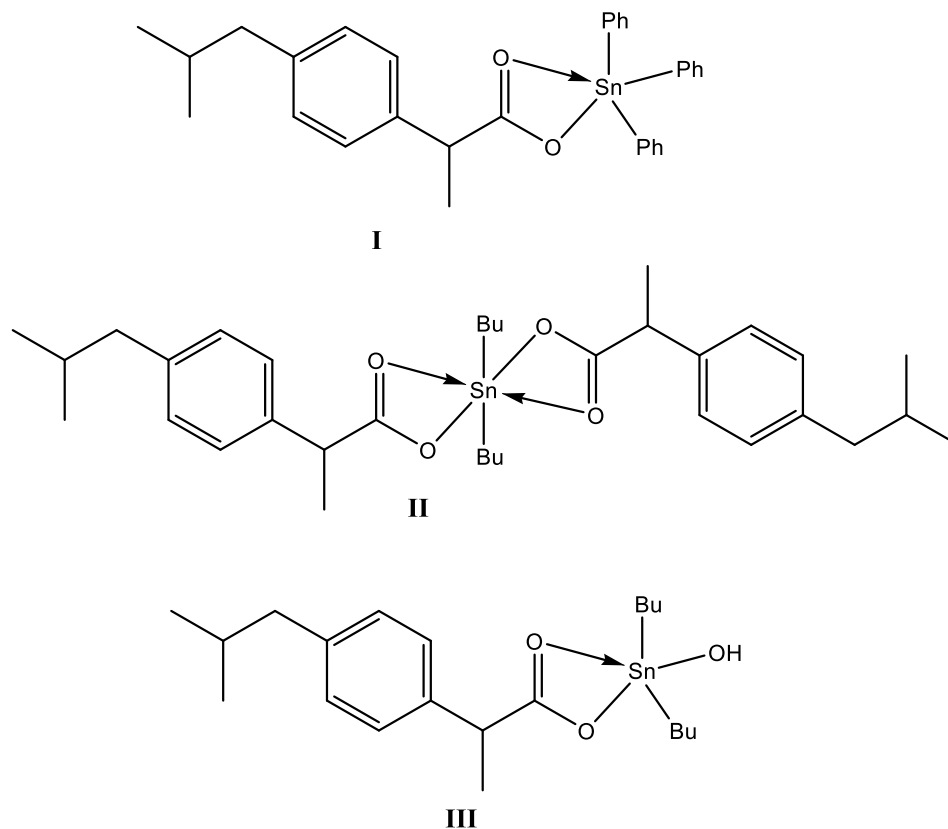


Figure (1). Synthesized complexes chemical structures I-III.

2.3 Polymeric Film Synthesis

At 25°C, PVC (5%) in tetrahydrofuran solution was made. The produced organotin complexes were then added to the preceding solution (0.5 percent by weight) and agitated for half an hour to obtain the reaction mixture. To generate a dry stabilized PVC film, the mixes were put into a glass mold and allowed for one day [9].

2.4. Ultraviolet Approach

The accelerated UV light was tested by prepared chamber connected to 40-W UV. All prepared PVC films after and before adding photostabilizer were exposed to UV light at the wave length of 313 nm and intensity of $7.75 \times 10^{-7} \text{ Ein.Dm}^{-3}\text{S}^{-1}$, the measurements took after 300 hrs. [10].

2.5. UV Spectrophotometer

Spectrophotometer 160A UV-Vis, (Shimadzu, Japan), was utilized to evaluate the differences of UV of the prepared PVC films. All films were irradiated by UV light at wavelength (λ_{max}) of 313 [11]. The photodecomposition constant (kd) was calculated using equation (1):

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

Where a and x refer to the conc. of PVC before exposed to UV light and at a certain time t, respectively. By substituting a by $[A_0 - A_\infty]$, and x by $[A_t - A_\infty]$, the equation will be:

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

Where A_0 denotes the absorption intensity of PVC at a certain time, t_0 , A_∞ denotes the absorption intensity of PVC at t , and A_t is the absorption intensity of PVC following UV irradiation at t . Thus, the photodecomposition constant (k_d) value was derived from the slope of the first order process, which yields a straight line when $\ln(A_t - A_\infty)$ and the irradiation time (t) are plotted [11]:

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

3. Results and Discussion

The synthesized ibuprofen complexes have been utilized as photo stabilizers of PVC polymers, and it can be seen its effect protecting the polymer film from degradation when irradiated by UV light, as shown in Figures 2-5 by the diagram drawn between $[\ln(A_t - A_\infty)]$ and t (irradiation time). The first order kinetics reaction gives straight line in the figure, and the slope give the photodecomposition constant (k_d) of the prepared films. The figure between $[\ln(A_t - A_\infty)]$ and irradiation time (t) of with no additives are shown in Figure (2).

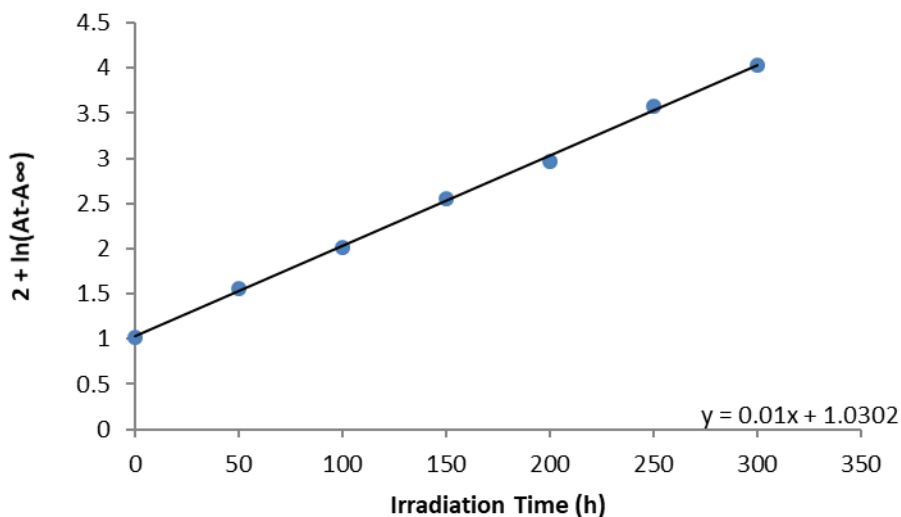


Figure (2). First-order rate plot of photo-decomposition constant for blank PVC.

Figures 3, 4 and 5 illustrate the relationship between the $\ln(A_t - A_\infty)$ and the irradiation time of PVC-produced films mixed with the novel ibuprofen compounds(I-III).

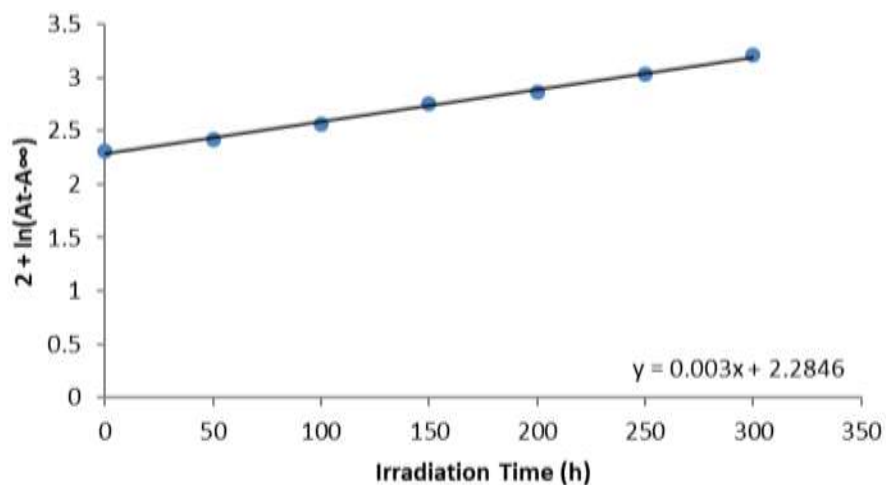


Figure (3). First-order rate plot of photo-decomposition constant for PVC + complex I.

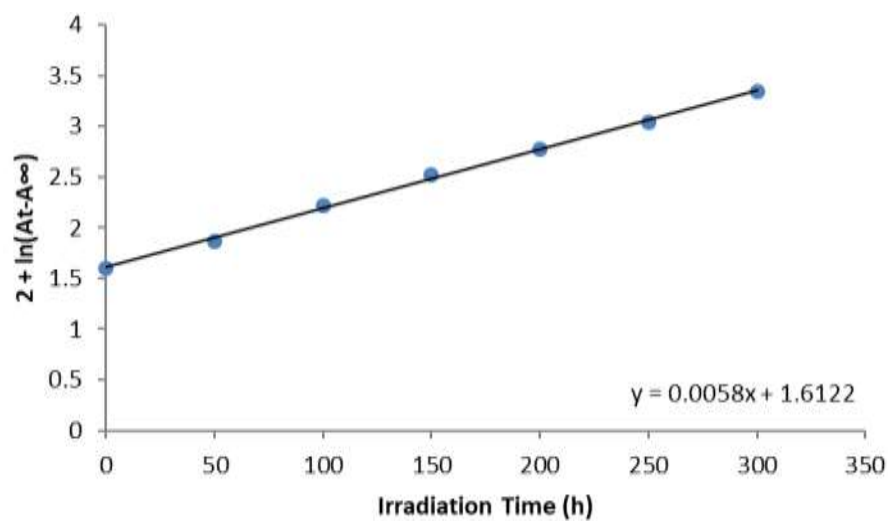


Figure (4). First-order rate plot of photo-decomposition constant for PVC + complex II.

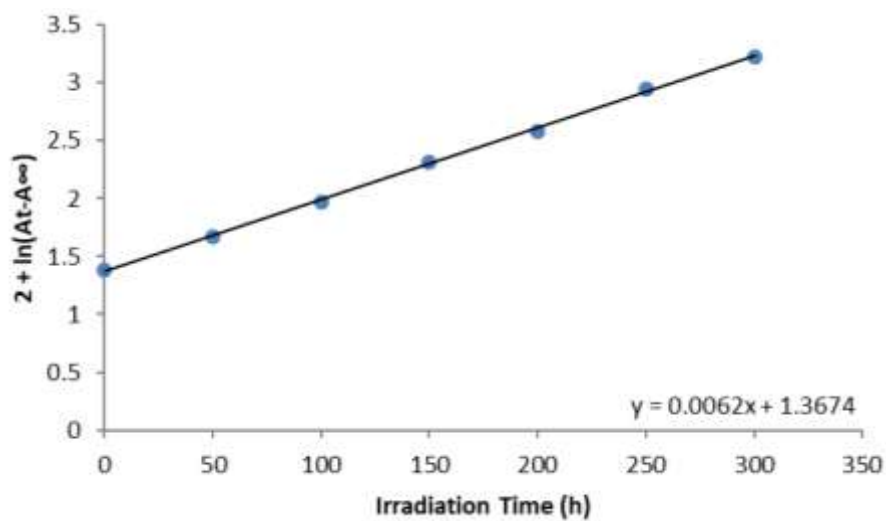


Figure (5). First-order rate plot of photo-decomposition constant for PVC + complex III.

Table (1) lists all photodecomposition constants for blank and blended PVC with complexes I-III.

Table (1). Photodecomposition constant (kd) of blank and blended PVC films after exposure to UV.

PVC Film +	K_d (s^{-1})
	9.8
complex I	2.7
complex II	6.0
complex III	6.5

Figures (3) to (5) and table (1) show the efficiency of the presence of ibuprofen-tin complexes as photostabilisers and their effect to reduce the kd values of the synthesised PVC films. The PVC as blank got the highest kd value, while all PVC films with additives got the lowest values. The rate constant dropped significantly from 10×10^{-3} to $6.20 \times 10^{-3} s^{-1}$ when ibuprofen-tin complex III was added. More studies need to be done to discuss the effect of different PVC stabilizers has different effect on the coloration of the prepared PVC films.

The surface morphology of the stabilized polymer film containing ibuprofen-tin complexes (I-I) was studied by FESEM [1, 2]. The images that we have got from FESEM show a significant difference between PVC (blank) and containing I-III complexes after exposure to the UV light.

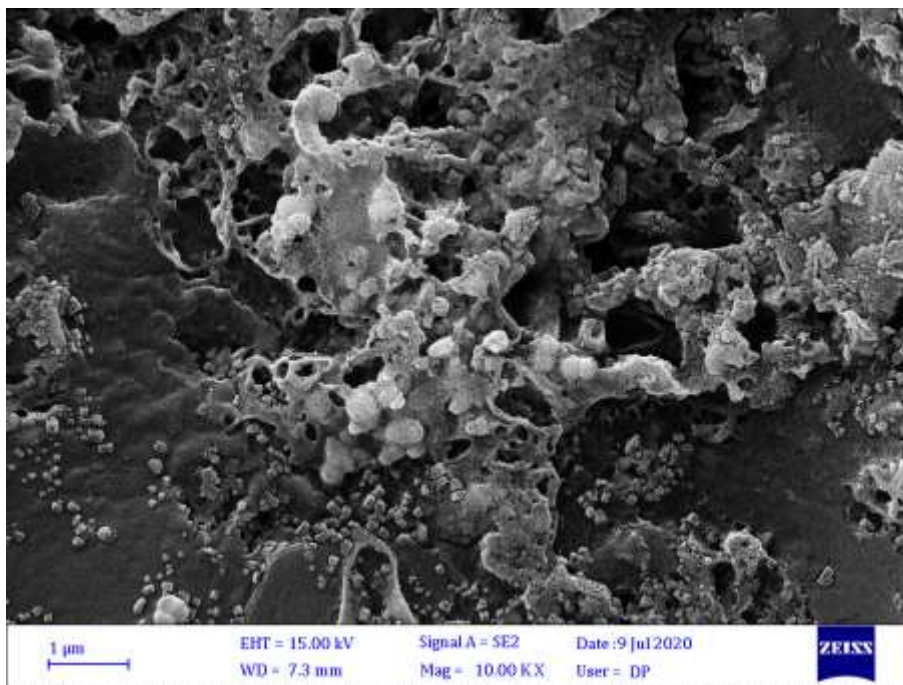


Figure (6). FESEM image of PVC (blank) after irradiation by UV light.

From figure 7, 8 and 9, The difference that we obtained between images of PVC (blank) and PVC with additives as a photostabilizer that the cavities, irregular shapes, cracks and diverse shapes and size.

The removal of HCl molecules and other fragments from the surfaces of the PVC films was attributed to the production of C=C or crosslinking through the polymeric chains [3]. The ibuprofen-tin complexes have a strong affinity for resisting dehydrochlorination and crosslinking, according to the surface analysis approach.

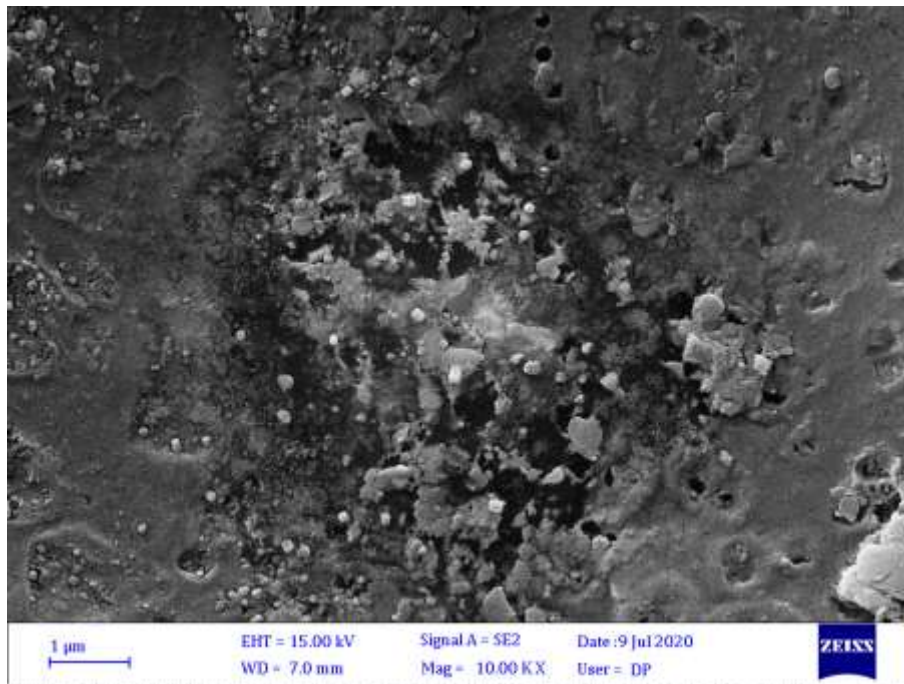


Figure (7). After exposure to UV FESEM image captured of PVC + complex I.

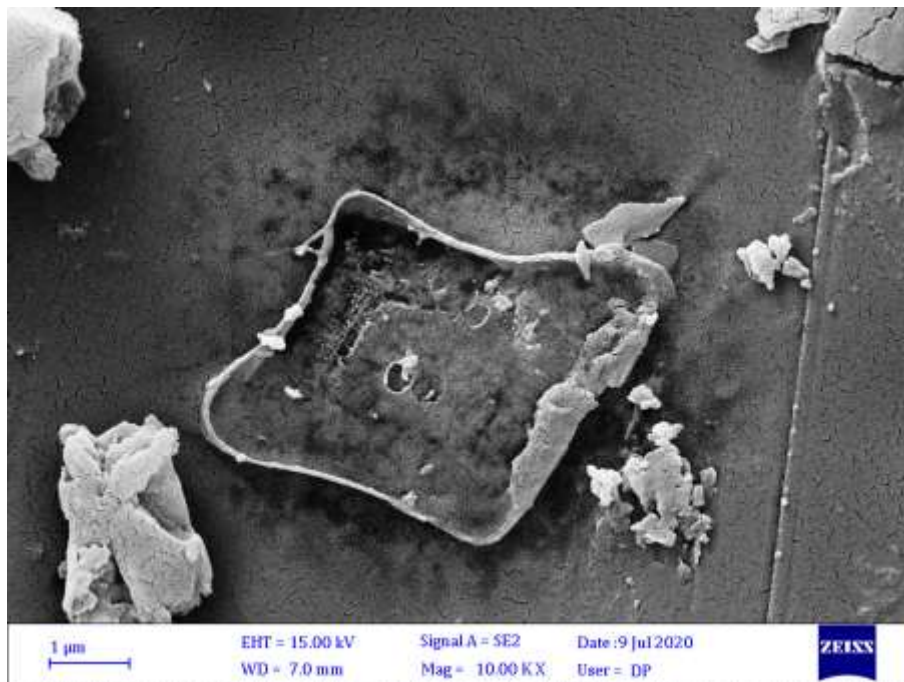


Figure (8). FESEM image for PVC + II after irradiation.

A compact surface made up of huge granular particles and flake-like particles defined the surface roughness (Figure 9).

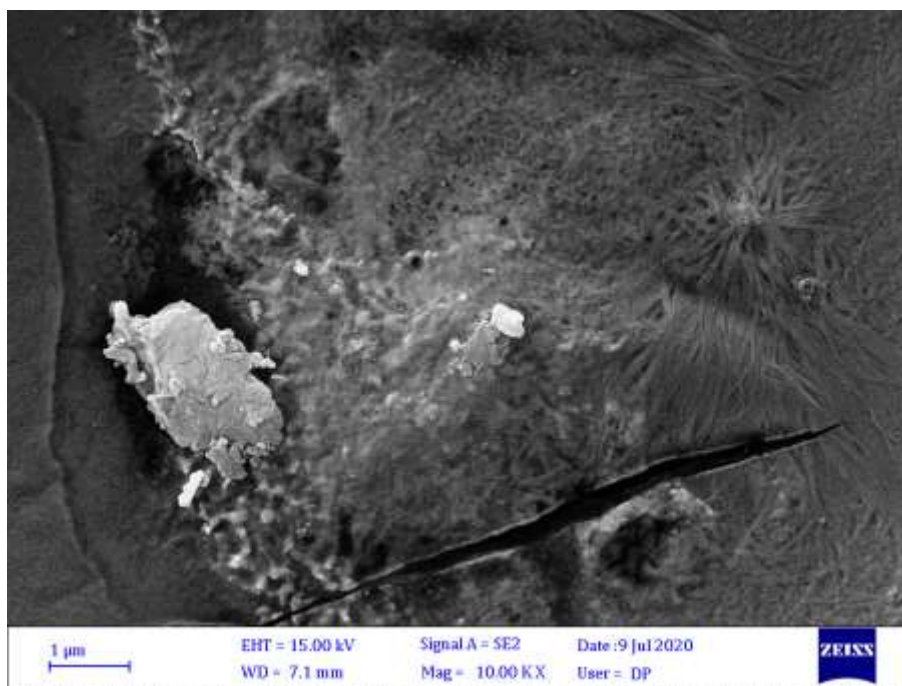


Figure (9). After exposure to UV FESEM image captured of PVC + complex II.

4. Conclusion

The photodecomposition constant (k_d) of all prepared PVC films as blank and after the addition of photostabilizers of ibuprofen-tin complexes (I-III) have been reduced which indicates that the photo stabilizers have a high efficiency to decrease the photodecomposition rate for PVC polymeric films.

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References

- [1] H. Hashim, G.A. El-Hiti, M.H. Alotaibi, D.S. Ahmed, E. Yousif, "Fabrication of ordered honeycomb porous poly(vinyl chloride) thin film doped with a Schiff base and nickel(II) chloride". *Heliyon*, vol. 4, p.743, 2018.
- [2] Fondriest Environmental. Solar Radiation and Photosynthetically Active Radiation 2014. Available online: <https://www.fondriest.com/environmental-measurements/parameters/weather/photosynthetically-active-radiation/> (accessed on 10 November 2020).
- [3] S. Nikafshar, O. Zabihi, M. Ahmadi, A. Mirmohseni, M. Taseidifar, M. Naebe. "The effects of UV light on the chemical and mechanical properties of a transparent epoxy-diamine system in the presence of an organic UV absorber. *Materials*", vol. 10, p. 180, 2017.
- [4] W. Shi, J. Zhang, X.M. Shi, G.D. Jiang, "Different photodegradation processes of PVC with different average degrees of polymerization". *J. Appl. Polym. Sci.*, vol.107, p. 528–540, 2008.
- [5] M. Mohammad, S. Khadija, M. Sohail, A. Saqib, B. Moazzam. "Synthesis, Spectral Characterization and Biological Applications of Triand Diorganotin(IV) Derivatives of 2-[N-(2,6-Dichloro-3-methylphenyl) amino] benzoic acid.", *Turk. J. Chem.*, vol. 28, p. 17- 26, 2004.
- [6] L. Tammy, M. Georges, "New applications of LC-MS and LC-MS2 toward understanding the environmental fate of organometallics", *Trends in Analytical Chemistry.*, vol. 24, p. 7-12, 2005.
- [7] T. Baul, C. Masharing, G. Ruisi, R. Jira ´sko, M. Holcapek, D. De-Vos, D. Wolstenholme and A. Linden, "Self-assembly of extended Schiff base amino acetate skeletons, 2-[[{(Z)-(3-hydroxy-1- methyl-2-butenylidene)] amino phenylpropionate and 2-[[{(E)-1-(2-hydroxyaryl) alkylidene] amino} phenylpropionate skeletons incorporating organotin(IV) moieties: Synthesis, spectroscopic characterization, crystal structures, and in vitro cytotoxic activity". *Journal of Organometallic Chemistry*, vol. 692, p. 4849-4862, 2007.

- [8] B. Wathq, E. Yousif, M.H. Al-Mashhadani, A. Mohammed, D.S. Ahmed, M. Kadhom, A.H. Jawad. A Surface Morphological Study, Poly(Vinyl Chloride) Photo-Stabilizers Utilizing Ibuprofen Tin Complexes against Ultraviolet Radiation. *Surfaces.*, vol. 3(4), p. 579-593, 2020.
- [9] A.G. Hadi, E. Yousif, G.A. El-Hiti, D.S. Ahmed, K. Jawad, M.H. Alotaibi, H. Hashim, "Long-term effect of ultraviolet irradiation on poly(vinyl chloride) films containing naproxen diorganotin(IV) complexes", *Molecules*, vol. 24, p. 2396, 2019.
- [10] E. Yousif, N. Asaad, D.S. Ahmed, S.A. Mohammed, A. Jawad, "A spectral, optical, microscopic study, synthesis and characterization of PVC films containing Schiff base complexes". *Baghdad Science Journal*, vol. 1, p. 16, 2019.
- [11] R. A. Hadad, R. Alsayed, D., S. Ahmed, M. Bufaroosha, N. Salih, S.A. Mohammed and E. Yousif, "Environmental performance of coordination complexes as PVC photostabilizers", *Materials Today*, vol. 42, p. 2849-2852, 2021.