Experimental Relationships between Surface Roughness, Irradiation Time and Photodecomposition Rate Constant of PVC Films Doped by Polyphosphates

Emad Yousif [1]*, Dina S. Ahmed [1], Ahmed A. Ahmed [2], Ayad S. Hameed [3], Rahimi M. Yusop [4], Amamer Redwan [5], Salam A. Mohammed [6]

[1]Department of Chemistry, College of Science, Al-Nahrain University, Baghdad 64021, Iraq
[2]Polymer Research Unit, College of Science, Al- Mustansiriyah University, Baghdad, Iraq
[3]Department of Chemistry, College of Science, Tikrit University, Tikrit 34001, Iraq
[4]School of Chemical Science and Food Technology, Faculty of Science and Technology, University Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia
[5]Department of Chemistry, Faculty of Science, Bani Walid University, Bani Walid, Libya
[6]Department of Chemical and Petrochemical Engineering, College of Engineering and Architecture, University of Nizwa, Nizwa 616, Sultanate of Oman

Corresponding author: emadayousif@gmail.com

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ABSTRACT

The photodegradation rate constant and surface morphology of poly(vinyl chloride), upon irradiation with ultraviolet light was investigated in the presence of polyphosphates as photostabilizers. Poly(vinyl chloride) photodegradation rate constant was lower for the films containing polyphosphates compared to the blank film. In addition, the surface morphology of the irradiated poly(vinyl chloride) containing polyphosphates, examined by scanning electron microscopy, indicates that the surface was much smoother compared to the blank film.

Keywords: *Polyphosphates, PVC films,* K_d*, UV irradiation, Scanning electron microscope*

INTRODUCTION

Each year, a huge amount of waste plastics is discarded, which causes serious environmental problems. The recycling of such waste plastics may not be economically viable [1]. The main issues associated with mechanical recycling of soft PVC are related to degradation occurring during re-processing [2], which usually requires addition of thermal stabilizers [3], and photodegradation, which can occur by outdoor exposure of soft PVC components during their service life [4]. The durability of materials is a key factor for many applications which affects the performance of polymer-based materials. The sun is the major source of energy for the earth and emits a vast range of wavelength in which only ultraviolet (UV) light, visible and infrared light (IR) reach the earth [5]. Organic UV-absorbents have long been employed for stabilization of polymers. However, organic UV-absorbents themselves can be wasted within polymers. Furthermore, organic UV-absorbents may pose safety problems when used at high concentrations [6]. The aim of this work to investigate the photodegradation rate constant (*kd*) and surface morphology of PVC polymeric films that contain polyphosphates as photostabilizers upon UV irradiation for 300 hours.

EXPERIMENTAL

Synthesis of polyphosphate 1–3

Three polyphosphates **1–3** (Fig. 1) were investigated as previously reported [7,8] from reactions of tris(formylphenyl)phosphates, obtained from reaction of phosphoryl chloride and appropriate hydroxybenzaldehyde, with benzidine under reflux. The structures of **1–3** were confirmed by various spectral and analytical data.

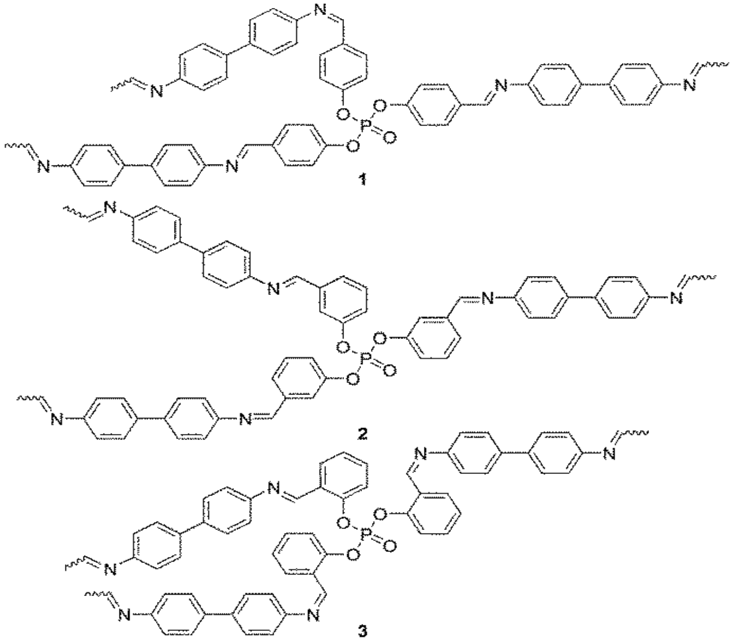

Fig. 1 Polyphosphates 1–3.

Films Preparation

Commercial PVC in tetrahydrofuran THF (5 g/100 mL) was re-precipitated with ethanol and dried for 24 hrs at 20 °C under reduced pressure. The polyphosphates **1–3** (0.5% by weight) were mixed with PVC at 20 °C and were fixed using aluminium plate stands (Q-Panel Company, Homestead, FL, USA) [9].

Light Exposure and Photodegradation Rate (k_d) of PVC Films

UV light (290–360 nm; λmax = 313 nm) was used to irradiate PVC films for 300 hrs and QUV tester (Philips, Saarbrücken, Germany) was used for the measurements [10,11]. A Shimadzu UV-Vis 160A-Ultraviolet Spectrophotometer (Shimadzu Cooperation, Kyoto, Japan) was used to measure the changes in the UV-visible spectra of PVC films during irradiation. Equation 3, derived from Equations 1 and 2, was used to calculate PVC photodecomposition rate constant (k_d).

$$ln(a - x) = lna - k_d\, t \qquad (1)$$

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

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

Where, $a = A_0 - A_\infty$; $x = A_0 - A_t$

a = concentration of PVC before irradiation; x = change in PVC concentration at time t during irradiation; A_0 = the absorption intensity of the PVC at t_0, A_∞ = the absorption intensity at t_∞ and A_t = the absorption intensity after irradiation time t.

The plot of $ln(A_t - A_\infty)$ *versus* irradiation time (t) gives straight line in which the slope equals to k_d. The photodecomposition of PVC follows a first order kinetics [12].

RESULTS AND DISCUSSION

Plastic materials can be stabilized against the action of solar radiation by dissolved organic substances capable of absorbing the solar radiation energy in the ultraviolet range. The energy taken up by these substances is transformed into other types of energy with no destructive effect on the polymers. The effect of polyphosphates **1-3** on the PVC films photodecomposition was studied. The PVC films containing polyphosphates **1-3** (0.5% by weight) were irradiated with a UV light (λ_{max} = 313 nm) for 300 hrs. A change in color takes place on irradiation which is an indication of PVC photodecomposition. The plot of $\ln(A_t - A_\infty)$ versus irradiation time (t) gave a straight line. The graphs showed first order kinetics in which the slope equalled the decomposition rate constant (k_d) for PVC films [13].

Figure 2 shows the change in $\ln(A_t - A_\infty)$ against irradiation time (t) for PVC films in the absence of any additives. Figures 3–5 show the changes in the $\ln(A_t - A_\infty)$ versus irradiation time for PVC films containing polyphosphates additives (0.5% by weight) as stabilizers for PVC films on irradiation with light.

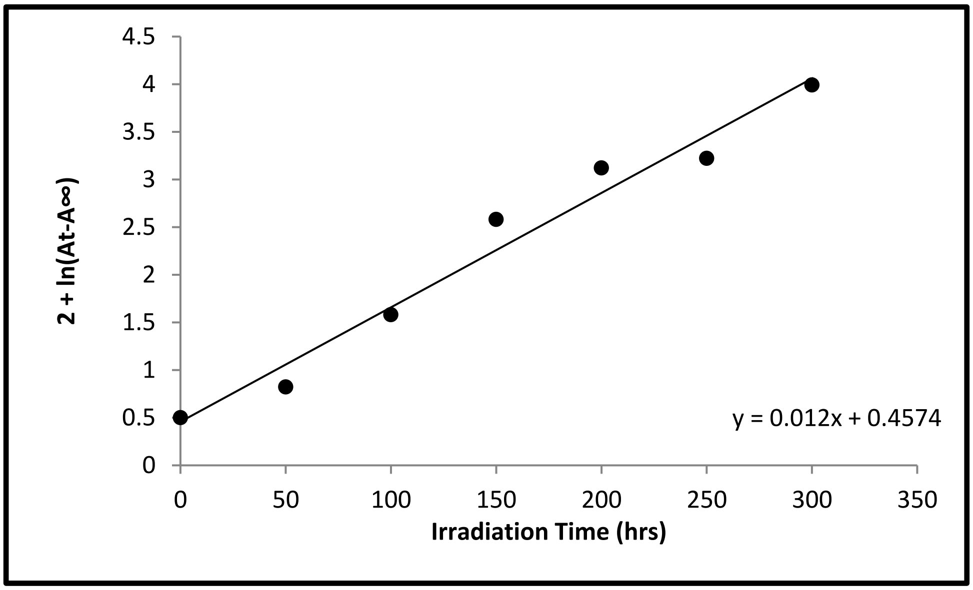

Fig. 2 Plot of $ln(A_t - A_\infty)$ for PVC film (Control) with irradiation time.

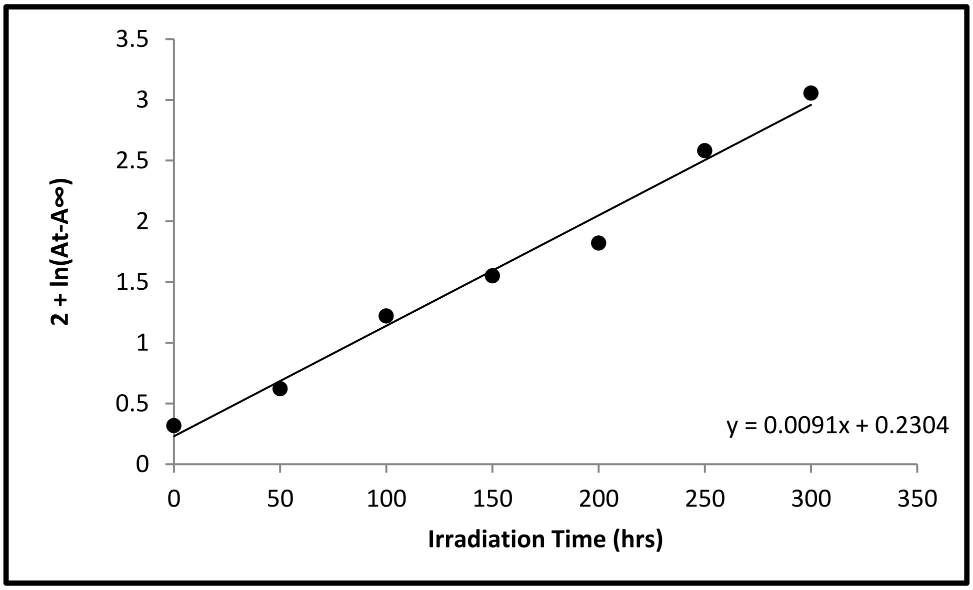

Fig. 3 Plot of $ln(A_t - A_\infty)$ for PVC film containing **1** with irradiation time.

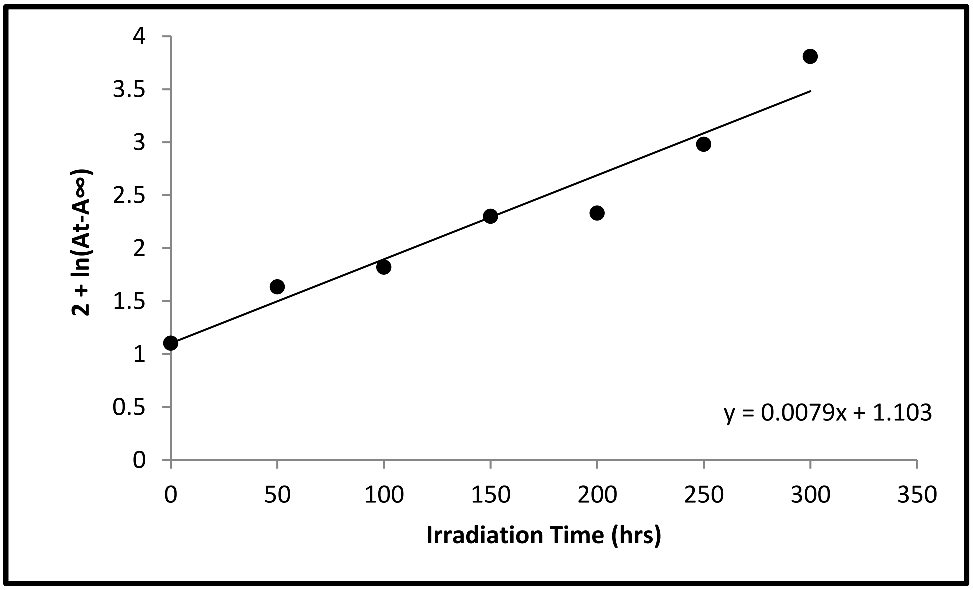

Fig. 4 Plot of $ln(A_t - A_\infty)$ for PVC film containing **2** with irradiation time.

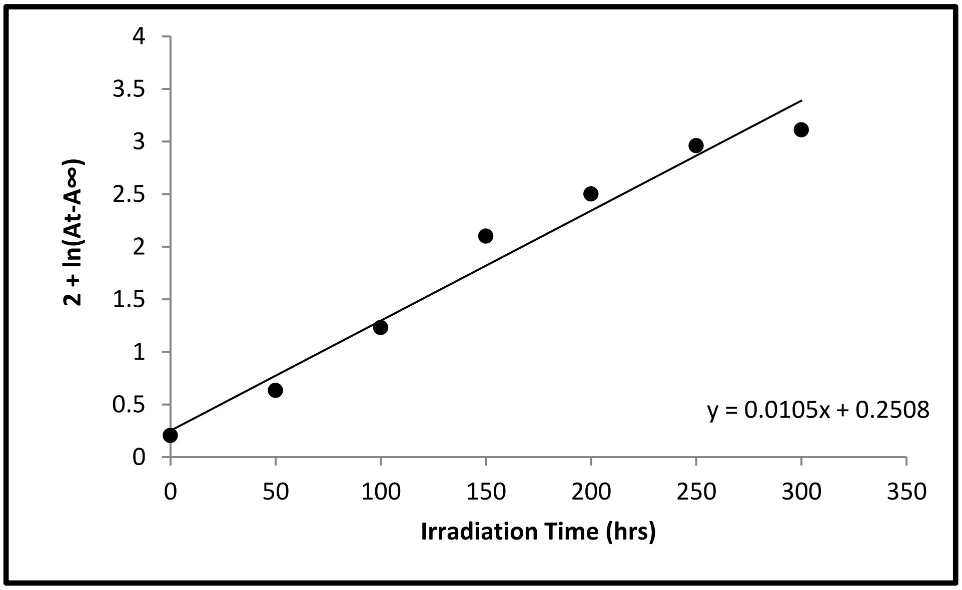

Fig. 5 Plot of $ln(A_t - A_\infty)$ for PVC film containing **3** with irradiation time.

The photodecomposition rate constant (k_d) values for PVC films containing polyphosphates along with that for PVC (blank) listed in Table 1.

Table 1. Photodecomposition rate constant (*kd*) for PVC films on UV irradiation (300 hrs).

Film	K_d **(Sec^{-1})**
PVC (control)	1.2×10^{-2}
PVC + **1**	9.1×10^{-4}
PVC + **2**	7.9×10^{-3}
PVC + **3**	10.5×10^{-3}

Table 1 and Figures 2–5 show that the rate constant (k_d) values are sensitive to presence of polyphosphates. The PVC photodecomposition rate constant for PVC films were high (1.2×10^{-2} sec^{-1}) in the absence of any additives. Such rate constant was reduced significantly when polyphosphates were used as additives. The photostabilization of PVC in the presence of polyphosphates follow the order of **1** > **2** > **3**.

Polyphosphate **1** was the most efficent than the other polyphosphates in photostabilization of PVC films presumably due to the reseonce of the extra phenyl group which acted as a better radical scavenger. Clearly, Polyphosphates have acted as photostabilizers for the photostabilization of PVC films. The most efficent photostabilizer always have low (k_d) value and that means these polyphosphates are stable towards UV light.

The morphology of the PVC surface before and after the irradiation process was examined at room temperature, using scanning electron microscope (SEM) at different magnifications. The morphological features of PVC (blank) film before irradiation is shown in fig. 6. The PVC surface was smooth, neat and has no cracks with little flaws. Clearly, no PVC porous structure was obtained before irradiation.

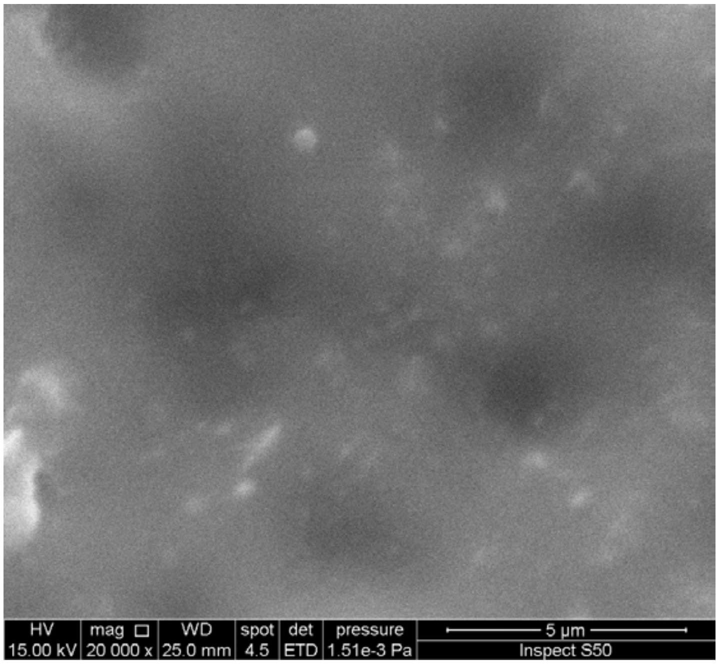

Fig. 6 SEM images of PVC (blank) before irradiation (300 hrs).

Long term irradiation of PVC films always lead to roughness, irregularity and defects within the surface [14,15]. The SEM images for PVC (blank) and those containing polyphosphates after irradiation are shown in Fig. 7.

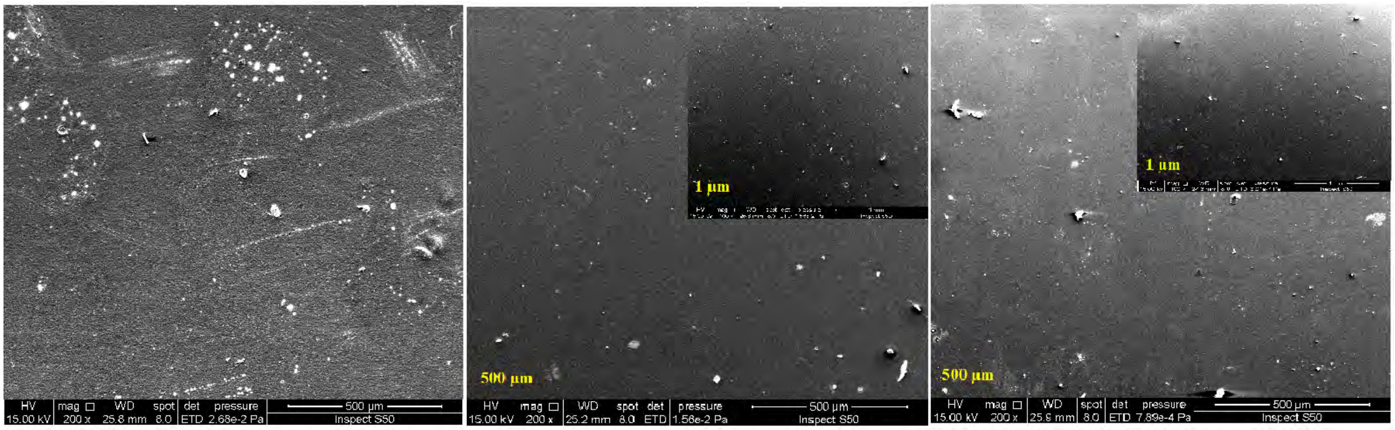

Fig. 7 The SEM images for PVC (blank) and those containing polyphosphates after irradiation.

The cracks, nodes and roughness within PVC surface were very noticeable in the case of the PVC (blank) compared to the films that contain the additives. Such dramatic changes in the PVC surface in the absence of additives could be due to the evaluation of HCl or crosslink and chain scission that led to formation of ripples [16-18].

CONCLUSION

Polyphosphates acted successfully as photostabilizers against UV irradiation to protect PVC. The photodegradation rate constant (k_d) for PVC (blank) was high compared to the ones containing polyphosphates additives. SEM images demonstrated that the cracks and roughness were minimal in the presence of polyphosphates compared to the PVC (blank) after irradiation. Polyphosphate 1 was found to be the most efficient PVC photostabilizers compared to the others.

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REFERENCES

[1] Koushal V., Sharma R., Sharma M., Sharma R., Sharma V. Plastics: Issues Challenge and Remediation. Int J Waste Resources, 4:1 (2014).

[2] Grigore M.E. Methods of Recycling, Properties and Applications of Recycled Thermoplastic Polymers. Recycling, 2:24 (2017).

[3] Xiang X., Chen S., Zhang J., Chai R. Photodegradation of plasticized poly(vinyl chloride) stabilized by different types of thermal stabilizers. Polym Eng Sci, 51:624-631 (2011).

[4] Yousif E., Hasan A. Photostabilization of poly(vinyl chloride) – Still on the run. Journal of Taibah University for Science 9:421–448 (2015).

[5] McKeen L.W. The Effect of UV light and weather on plastics and elastomers;William Andrew: Norwich, NY, USA (2013).

[6] Serpone N., Dondi D., Albini A. Inorganic and organic UV filters: their role and efficacy in sunscreens and suncare products. *Inorg Chim Acta*, 360:794–802 (2007).

[7] Ahmed D.S., El-Hiti G.A., Yousif E., Hameed A.S. Polyphosphates as inhibitors for poly(vinylChloride) photodegradation. *Molecules*, 22:1849 (2017).

[8] Ahmed D.S., El-Hiti G.A., Yousif E., Hameed A.S., Abdalla M. New eco-friendly phosphorus organic polymers as gas storage media. *Polymers*, 9:336 (2017).

[9] Yousif E., Hameed A., Rasheed R., Mansoor H., Farina Y., Graisa A., Salih N., Salimon J. Synthesis and photostability study of some modified poly(vinylchloride) containing pendant benzothiazole and benzimidozole ring. Int. J. Chem, 2: 65–80 (2010).

[10] Yousif E., Hasan A., El-Hiti G.A. Spectroscopic, physical and topography of photochemical process of PVC films in the presence of Schiff base metal complexes. *Polymers*, 8:204 (2016).

[11] Yousif E., El-Hiti G., Hussain Z., Altaie A. Viscoelastic, spectroscopic and microscopic study of the photo irradiation effect on the stability of PVC in the presence of sulfamethoxazole schiff's bases. *Polymers*, 7:2190–2204 (2015).

[12] Khan S.R., Tawakkul M., Sayeed V.A., Faustino P., Khan M.A. Stability characterization, kinetics and mechanism of degradation of dantrolene in aqueous solution: effect of pH and temperature. *Pharmacol. Pharm*., 3:281–290 (2012).

[13] Mohammed R.F., Yousif E. A. Photochemical study of PVC filmes in presence of 2-[4-2)-methyl propyl) phenyl] propanoate complexes. *Arab J. Phys. Chem*., 2:67 (2015).

[14] Nikafshar S., Zabihi O., Ahmadi M., Mirmohseni A., Taseidifar M., Naebe M. 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*, 10, 180 (2017).

[15] Yonehara M., Matsui T., Kihara K., Isono H., Kijima A., Sugibayashi T. Experimental relationships between surface roughness, glossiness and color of chromatic colored metals *Mater. Trans.*, 2004, 45, 1027–1032.

[16] Gesenhues U. Influence of titanium dioxide pigments on the photodegradation of poly(vinyl chloride). *Polym. Degrad. Stab.*, 68:185– 196 (2000).

[17] Ghazi D., El-Hiti G.A., Yousif E., Ahmed D.S., Alotaibi M.H. The effect of ultraviolet irradiation on the physicochemical properties of poly(vinyl Chloride) films containing organotin(IV) complexes as photostabilizers. *Molecules*, *23*:254 (2018).

[18] Ahmed D.S., El-Hiti G.A., Hashim H., Noaman R., Hameed A.S., Yousif E. Physical and morphological properties of poly(vinyl chloride) films upon irradiation in the presence of tetra schiff bases as photostabilizers. *Arab J. Phys. Chem.*, 5 (2018).