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Morphological and Photodecomposition Rate Constant Study of PVC Films Doped with Sulfadiazine Tin(IV) Complexes

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ABSTRACT

This article focus on the calculation of photodecomposition rate constant of PVC films that containing sulfadiazine tin(IV) complexes **1-3** as photostabilzers during UV radiation exposure. This constant calculated as a method for evaluating the efficiency of sulfadiazine tin(IV) complexes **1-3** when used as a PVC photostabilizers after 300 hours of irradiation. The experimental results showed that sulfadiazine tin(IV) complexes **1-3** have reduced the rate of photodecomposition constant value of PVC films significantly with comparison to PVC (blank).

Keywords: *Sulfadiazine; Tin Complexes; PVC films; Photodecomposition; Irradiation*

INTRODUCTION

Doping of polymers with new additives demonstrated improvement of physical and morphological properties of the polymeric materials. Doped polymers produce a wind range of novel materials with new characterizations which are better than un-doped polymers [1]. The polymer blends are preferred because they are easy to prepare and modify with requirement of little offered compare to synthesis a new polymers. Furthermore, it is easy to control their physical properties [2]. On the other hand, the homogeneity among the contents of the polymer films is responsible on the improving of the material properties on the molecular scale [3]. One of the most important plastic polymers is polyvinyl chloride (PVC) and usually it is used as a thermoplastic polymer because it has significant properties such as cheap, easy to synthesis and modifies with high resistance, excellent process-ability, and little combustibility. For all of that, PVC considers one of the main materials which are used in plastic industry; moreover, it could be utilized with fillers such as grating, alkali, and acid plastic resistance, plasticizer, and thermal stabilizer [4]. The ultraviolet (UV) light and the mechanical stress influence the plastic pipes [5], causing instability, cracking and vanishing [6].

When plastic pipes exposure to the sunlight, resulting a photo degradation of the polymer because the sunlight has a UV light between 100 to 400 nm. However the ozone layer absorbs the UV ray between 100-280 nm and only the UV light between 280-400 nm will reach the ground [7]. Photo-degradation considers as most significant problem threatening the plastic pipes because it leads to breaking of the polymer chains or making new crosslinking bonds. This will change the morphology and the physical properties of the polymer; furthermore it is change the mechanical properties of the plastic pipes. Photo-degradation can monitor by tensile strength technique [8]. The aim of this study is doping the PVC films with new type of photo-stabilizers (Sulfadiazine Tin Complexes) to decrease the photo degradation rate of the plastic.

EXPERIMENTAL

Chemicals and procedures

All regents and solvents were purchased from Merck (Germany) and used without further purifications. The alternation on the PVC films after irradiation was detected by utilizing UV spectrophotometer, Shimadzu (Japan).

Synthesis of Tin(IV) complexes

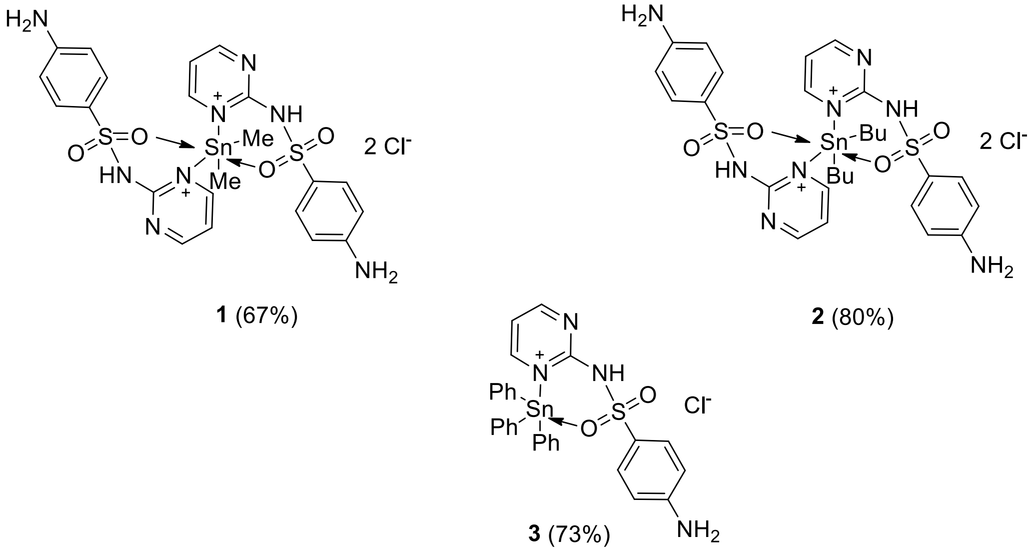
Compounds 1-3 (sulfadiazine tin(IV) complexes) were synthesized using the standard method by reacting excess of sulfadiazine with diorganotin(IV) and triorganotin(IV) chlorides in MeOH as reported in our previous work [9] (Figure 1).

PVC thin films preparation

Drop casting method was used to prepare the blank and doped with photo-stabilizers, sulfadiazine tin(IV) complexes (**1**–**3**) PVC films utilizing tetrahydrofuran as a solvent to dissolve both the polymer and stabilizers. The PVC polymer was added to the THF solvent and the mixture was placed in an ultrasonic bath for 30 min, after that the photo-stabilizer was added by 0.5% concentration. Subsequently, the homogenous mixture was poured into glass plate with known diameter and left at room temperature overnight to be sure that the film is completely dry from any traces amount of the solvent [10]. The thickness of PVC films 40 μm was fixed using a Digital Vernier Caliper 2610A micrometer.

UV light exposure

Photo degradation was affected by using accelerated artificial UV-weathering which is irradiated in the whole region of the UV rang. Every investigated polymeric film was kept in the same distance from the irradiation source to avoid wrong measurements [11]. UV Light (λmax = 313 nm and light intensity = 6.2 × 10^{-9} ein.dm^{-3}.s^{-1}) was used to irradiate the PVC films.



1 (67%)

2 (80%)

3 (73%)

Figure 1: Chemical structures of compounds 1–3 (Sulfadiazine tin complexes).

UV-Vis Spectrophotometer

The photo degradation of the PVC films was detected by measuring the UV/Vis spectrum during the irradiation to detect the alternation in the intensity of the polymeric films. UV/Vis 160A-Ultraviolet Spectrophotometer (Shimadzu, Kyoto, Japan) was utilized for these measurements.

RESULTS AND DISCUSSION

The effect of sulfadiazine tin(IV) complexes **1**–**3** on PVC films photo-degradation was investigated. The plot of $ln(A_t - A_\infty)$ *versus* irradiation time (t) gives linear line in which the slope equal k_d. The photodecomposition of polymeric films shows a first order kinetics [12], as shown in Equation 1 below.

$$ln(A_t - A_\infty) = ln(A_0 - A_\infty) - k_d\, t \qquad (1)$$

Figure 2 until 5 shows the alternation in $ln(A_t - A_\infty)$ with the irradiation time (t) of PVC polymeric films with and without any additives.

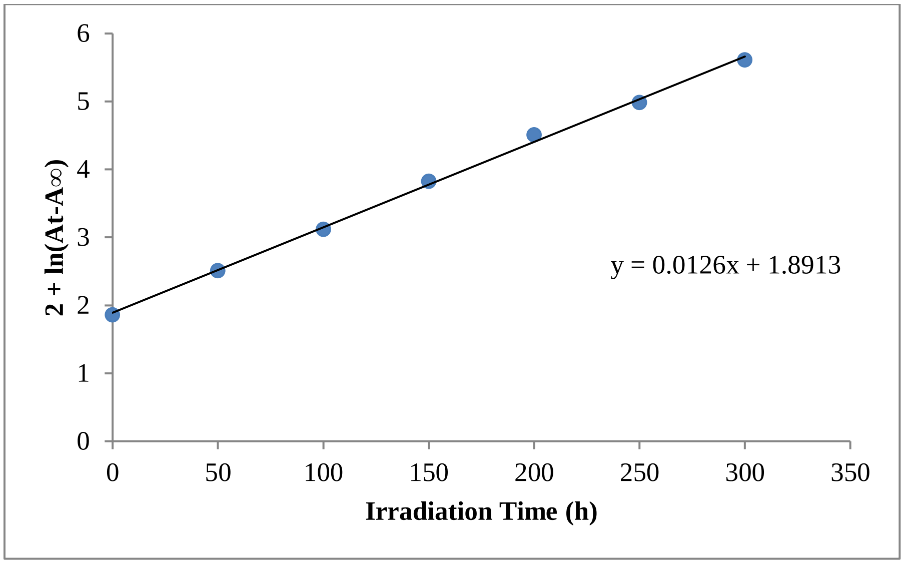


Figure 2: Alterations in $\ln(A_t - A_\infty)$ of blank PVC film versus irradiation time.

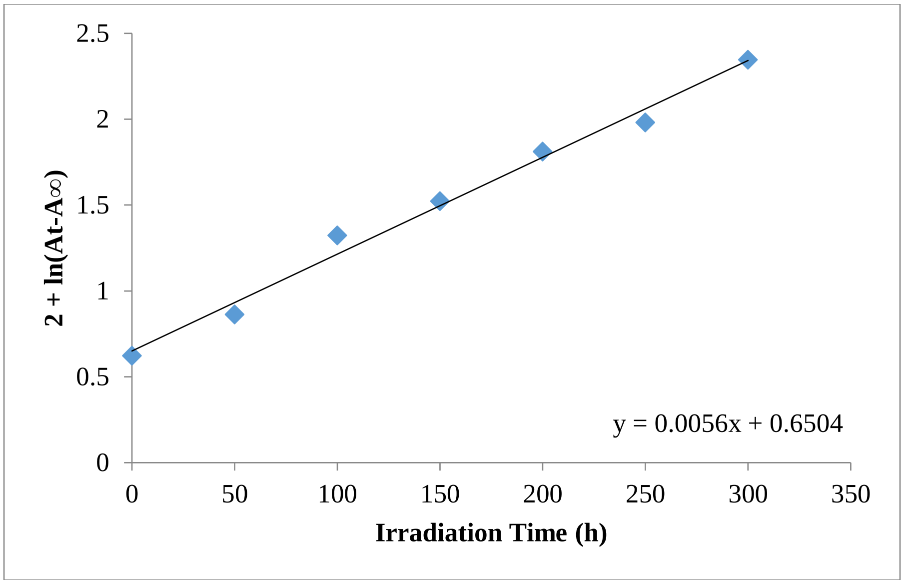


Figure 3: Alterations in $\ln(A_t - A_\infty)$ of PVC + 1 film versus irradiation time.

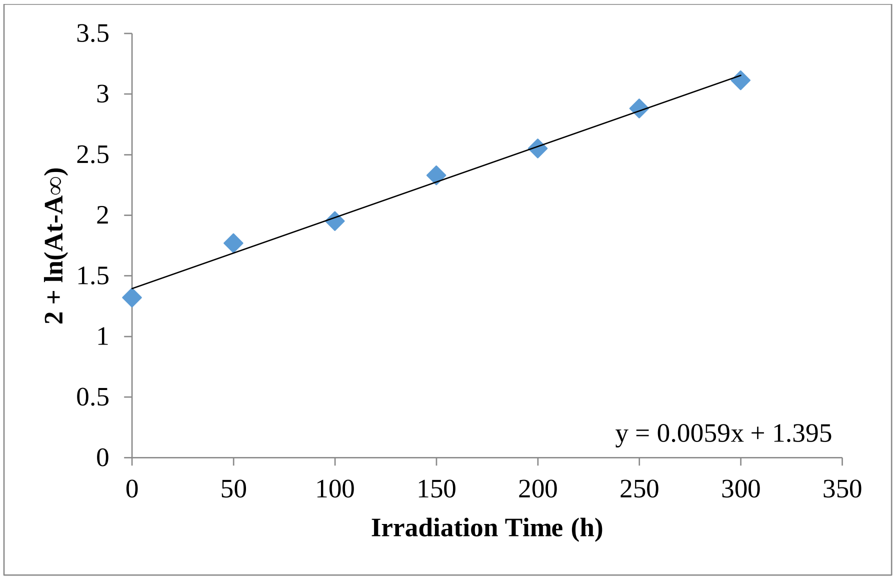


Figure 4: Alterations in $\ln(A_t - A_\infty)$ of PVC+ 2 film versus irradiation time.

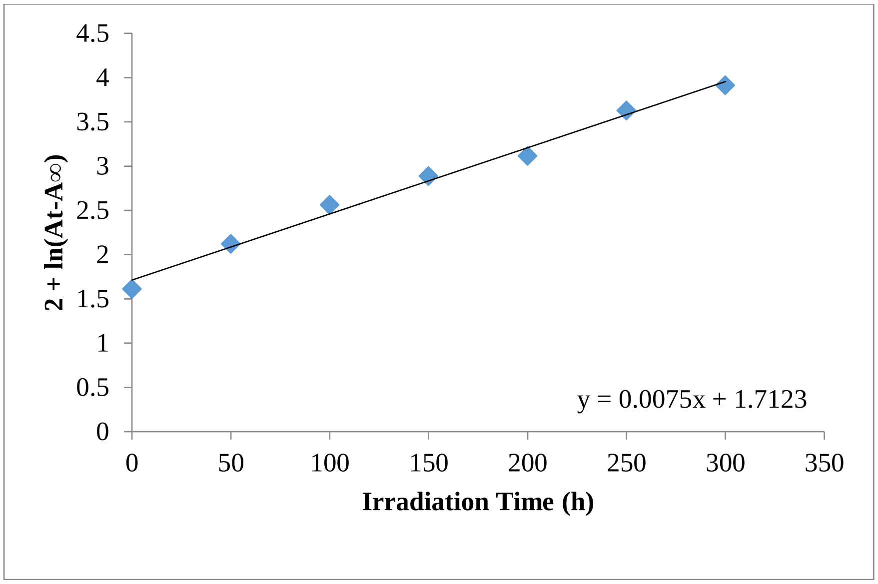


Figure 5: Alterations in $\ln(A_t - A_\infty)$ of PVC+ 3 film versus irradiation time.

From Table 1, it demonstrates clearly that the rate constant of photodecomposition influences by the existence of photo-stabilizers sulfadiazine tin (IV) complex [13,14]. The k_d of the blank PVC was 12.60 × 10^{-3} sec^{-1} without any additives which is the highest value as shwon in the Table 1. However it decreased signeficanly (7.50–5.60 × 10^{-3} sec^{-1}) in the presence of the photo stabilizers sulfadiazine tin (IV) complexes (1-3), and the lowest value was for compound 1 which is 5.60 × 10^{-3} sec^{-1}. Therefor using this kind of photo stabilizers is quint important to reduce the photo degradation of the PVC polymeric films.

Table 1: Summarized the kd (photodecomposition rate constant) of PVC polymeric films after irradiated with UV ray (300 h).

Film	**k_d (sec^{-1}) × 10^{-3}**
Blank PVC	12.60
PVC + **1**	5.60
PVC + **2**	5.90
PVC + **3**	7.50

Figure 6 is a graphical abstract shows how the photo-stabilizers can prevent the PVC films from photo-degradation *via* transfer the sunlight to the heat without damaging the polymer chemical structure. This is because the aromatic structure of the legand with metalic tin abosrbes on the UV region and that will decrease the photo-decomposition of the PVC films.

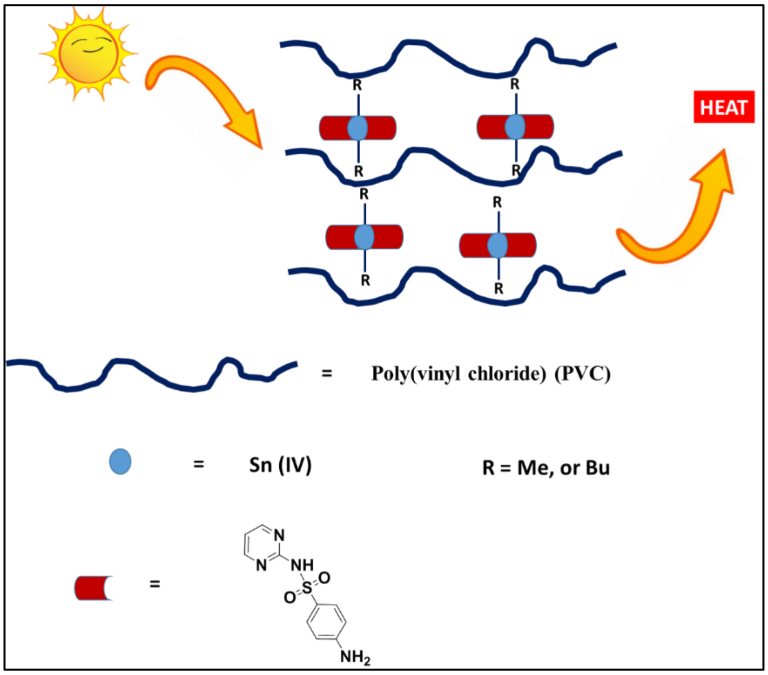


Figure 6: Schematic diagram of PVC thin film stabilized by sulfadiazine tin (IV) complexes.

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FTIR spectroscopy can be used as a complementary technique to monitor the formation of such functional groups from the photo-oxidation of PVC chains when subjected to UV irradiation [10]. The rates of PVC photo-oxidation were determined from the functional group indices after 300 h of irradiation (Figure 7).

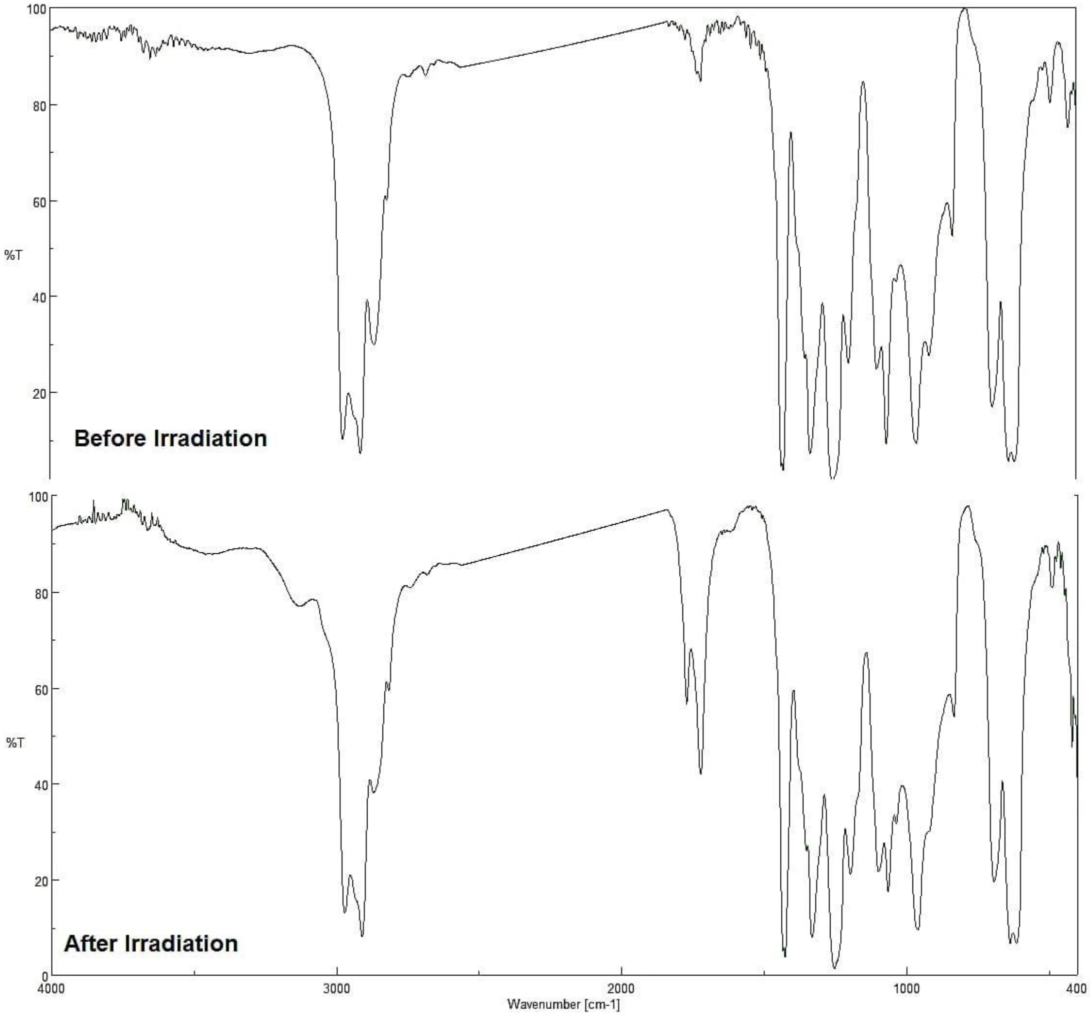

Figure 7: The FTIR spectra for PVC film before and after 300 h of irradiation.

The SEM images of the irradiated PVC films in the absence and presence of organotin(IV) Complexes 1–3 (0.5 wt%) are shown in Figure 8. The SEM image of the blank PVC sample showed a degree of photo-degradation had taken place that led to a rough surface and large number of aggregates as a result of cross-linking of the polymer chains. While, the surfaces of PVC films containing additives 1–3 were relatively smoother, regular, and homogeneous, with a few cracks of different shapes.

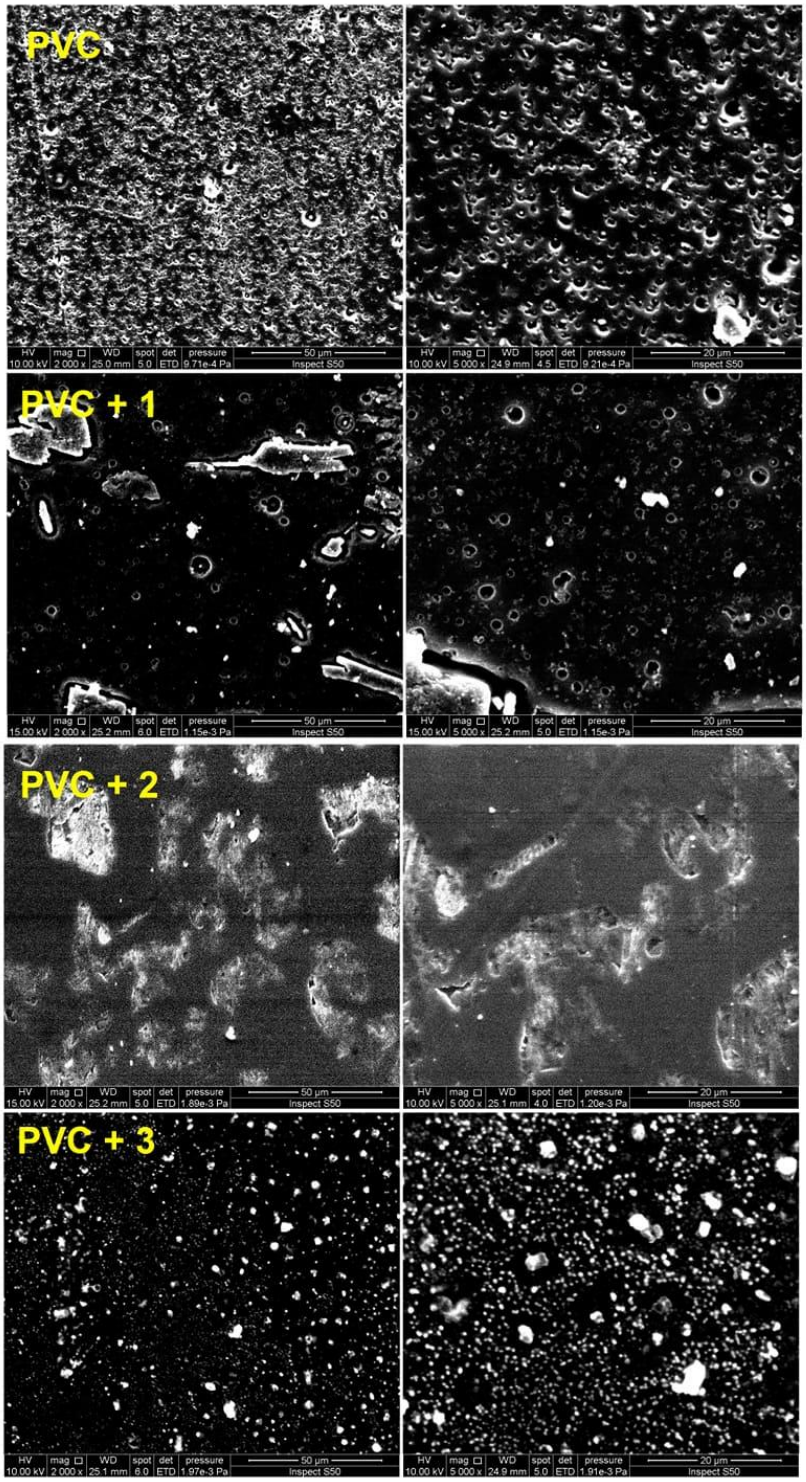

Figure 8: SEM images of PVC films after irradiation.

CONCLUSIONS

From the above results, several conclusions can be made. The efficiency of sulfadiazine tin (IV) complexes as photostabilizers was noticed by reducing the rate of photodecomposition constant compared to blank PVC. The photodecomposition rate constant showed the highest value in the absence of any additive. PVC films containing sulfadiazine tin(IV) complex (1) showed the lowest value of photodecomposition rate constant. The rates of PVC photooxidation were determined from the functional group indices after 300 h of irradiation. The surface morphology of irradiated PVC samples was investigated using scanning electron microscopies.

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