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Study of Photodecomposition Rate Constant and Surface Morphology of PVC Films Embedded with Tin(IV) Complexes

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ABSTRACT

Polymers became Irreplaceable components that enter all industries due to their exceptional properties and low costs. As there are many polymers, the production quantities differ from one type to another depending on the offered characteristics; among them, Poly (vinyl chloride) (PVC) was widely used in many applications. However, it undergoes many harmful changes when exposed to ultraviolet light. This paper concentrates on calculating the photodecomposition rate constant and surface morphology of PVC films before and after filling Tin (IV) complexes (1-3) as photo stabilizers. The photodecomposition rate constant was determined to indicate Tin (IV) complexes' impact on PVC films after 300 h exposure to UV irradiation. The surface morphology of PVC films was investigated by field emission scanning electron microscopy (FE-SEM) and Fourier-transform infrared spectroscopy (FTIR). However, the photodecomposition rate constant was calculated along with the irradiation time up to 300 hours for the plain and modified PVC films. According to the result, organotin compounds and Schiff bases were used as photo stabilizers. In this case, the photodegradation was significantly decreased. Prog. Color Colorants Coat. 15 (2022), 319-326© Institute for Color Science and Technology.

1. Introduction

Nowadays, ground, water, and air pollution have become environmental issues that should be addressed, where the plastic's effect is considered one of the main sources [1]. The incineration of plastic produces dioxins, which are very volatile and carcinogenic. This item can be found in most dust particles and municipal rubbish, causing a hazardous risk to the environment. The process that deteriorates polymer properties due to chemical, physical, or biological impacts (e.g., reactions) that lead to chemical transformation is recognized as polymer degradation. Degradation occurs in different environments and service conditions, limiting the polymer's lifetime [2]. Poly(vinyl chloride) (PVC) is a very interesting and acceptable material for a wide range of applications due to its low cost and outstanding performance [3]. In many modern applications, plastics are used to replace glass, metals, and wood due to their notable properties that can fulfill the desired requirements [4].

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In contrast with conventional materials, plastic can be engineered to offer superior properties and exceptional performance [5]. Plastic properties such as hardness, density, color, transparency, and rigidity are controlled during manufacturing [6]. Poly(vinyl chloride) is among the widely applied plastics; it ranks the second most synthesized resin in the world after polyethylene. Furthermore, PVC is the third most extensively used plastic in chemical engineering, architecture, packaging, transportation, and electronics after polypropylene and polyethylene [7]. One of the main properties of PVC is its high chlorine concentration (about 57 wt.%), which makes it non-combustible [4]. Polyvinyl chloride is a thermoplastic polymer with a polyethylene-like linear structure replacing one of the hydrogen atoms with a chlorine atom [8].

PVC is a solid white powder that can be heated up to 130 °C without disintegration [9]. It was firstly produced in Germany and the USA around 90 years ago in small quantities that contributed to different products. However, its intensive use began during the second world war, when highly flexible mixtures were produced and used as substitutes for rubber, mainly when natural rubber suppliers were hard to reach. In the early sixties of the last century, the development and use of rigid PVC has significantly increased. Now, Poly (vinyl chloride) has been commercially produced in massive amounts during the last 50 years [10].

It is known that the sun has a significant role in degrading all types of plastics. Several different stabilizers were successfully added and used to solve the problem of polymers' poor stabilization [11]. Thereby, the durability of PVC products for outdoor applications, such as building sheds, frames, and structures, is an essential factor in enduring photodegradation over long periods of sunshine exposure that will determine the polymers' acceptance and conformity to the set standards. The PVC resin must formulate homogeneously and process with the required additives to assure weather resistance. These complexes result in modified PVC behavior and properties that significantly differ from the plain PVC resin [12]. Recently, studies from our group dealt with investigating the effect of organotin compounds as photo stabilizers for Poly (vinyl chloride), where diorganotin (IV) complexes (Ph_2SnL_2, Bu_2SnL_2, and Me_2SnL_2) with naproxen ligand were studied as photostabilizers for the PVC [13]. Similarly, the effect of organotin (IV) complexes (Ph_3SnL, Bu_2SnOHL, Bu_2SnL_2, and Me_2SnL_2) with atenolol ligand was studied for the same purpose [14]. Furthermore, the photostabilizing efficiency of PVC was studied in the presence of organotin (IV) complexes, Ph_3SnL, Ph_2SnL_2, Me_2SnL_2, and Bu_3SnL with captopril ligand [15]. Many efforts were applied to solve problems affecting the environment in multiple approaches [16, 17]. Our research contributes to these attempts by lowering plastics production and extending the age of used ones.

2. Experimental

2.1. Instruments and chemicals

An accelerated weather meter QUV tester was employed to irradiate the PVC with UV light (λ_{max} = 313 nm) at room temperature was purchased from Q-Lab Company (Homestead, FL, USA). The scanning electron microscopy (SEM) MIRA3 LMU was from TESCAN (Kohoutovice, Czech Republic) that operated at 10 KV accelerating voltage. After irradiation, the ultraviolet (UV) test of PVC films was examined using a UV spectrophotometer, Shimadzu (Japan). All chemicals were supplied from Merck (Gillingham, UK) except PVC, which Petkim Petrokimya (Istanbul, Turkey) provided and owned a molecular weight cut of 171,000.

2.2. Synthesis of three novel tin complexes

Three mixtures were prepared in this work, first by mixing 0.260 g of 1.0 mmol 4-(benzylidene-amino)benzenesulfonamide with 0.3855 g of 1.0 mmol Ph_3SnCl. The second complex was prepared using the same amount of 4-(benzylidene-amino) benzenesulfo-namide but mixed with 0.3255 g of 1.0 mmol Bu_3SnCl. These two products were called complexes 1 and 3, respectively. The last mixture (complex 2) was obtained by adding 4-(benzylideneamino) benzenesulfonamide (0.520 g, 2.0 mmol) to Me_2SnCl_2 (0.219 g, 1.0 mmol); all mixtures were dissolved in 30 ml of methanol and refluxed for 6-8 hours at 65 °C. The resulting solution was filtered, washed, dried, and recrystallized to form the off-white powders. Figure 1 shows the chemical structure of the three complexes.

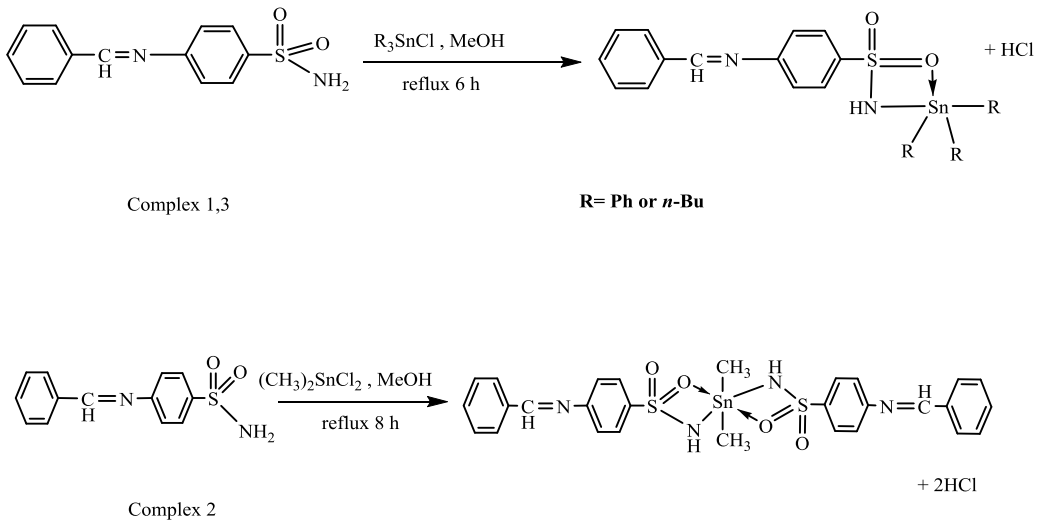

Figure 1: Synthesis of three tin complexes [3].

2.3. PVC films preparation

The modified PVC films were prepared by mixing 25 mg of Tin with 5 g PVC, dissolving it in 100 mL solvent of tetrahydrofuran (THF), and stirring it for 2 hours at 25 °C. The doped polymeric solution was then spread on a glass substrate and cast to 40 μm thick. Ultimately, the films were dried for 18 hours under a vacuum to remove the solvent's residues [18]. As the complexes named 1, 2, and 3 in the previous section, the doped PVC is called PVC-1. PVC-2, and PVC-3, respectively.

3. Results and Discussion

3.1. PVC stabilization evaluation using UV spectroscopy

The photodegradation of PVC films was examined using 4-(benzylideneamino)benzene-sulfonamide tin (IV) complexes. Plotting $\ln(A_t-A_\infty)$ vs. irradiation time (h) shows almost a linear line, for which the slope represents the K_d value [19], as shown in Equation 1.

$$\ln(At-A_\infty) = \ln(A_0-A_\infty)- K_d\, t \qquad (1)$$

Here, A_0 = the initial PVC absorption intensity, A_∞ = the absorption intensity at t_∞, and A_t = PVC absorption intensity after a certain irradiation time. Figures 2-5 show the variation in ln(At- A_∞) along with the irradiation time (h) for pristine and modified PVC films.

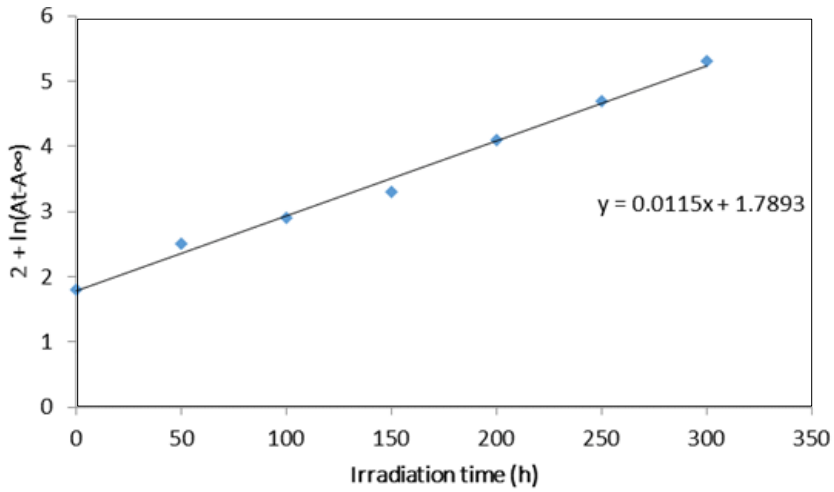

Figure 2: ln(At- A∞) relationship with irradiation time for pristine PVC film.

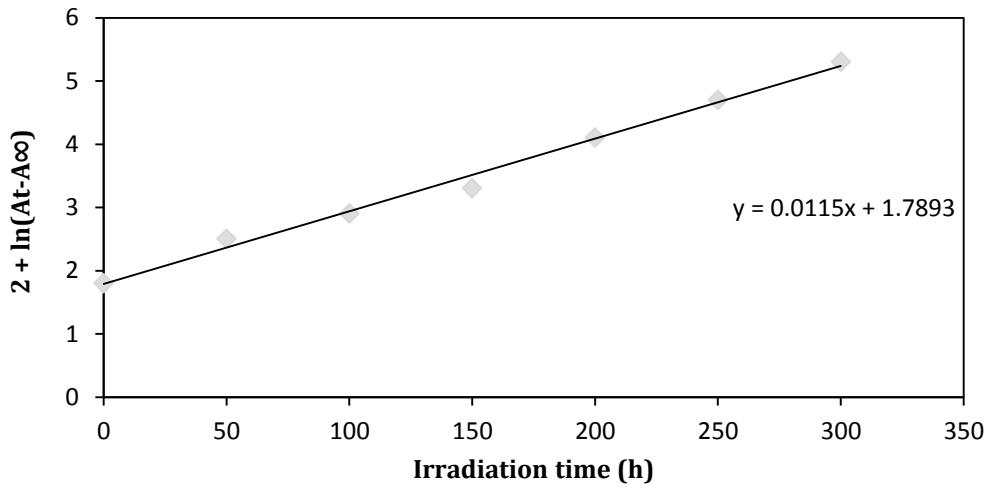

Figure 3: ln(At- A∞) relationship with irradiation time for PVC-1 film.

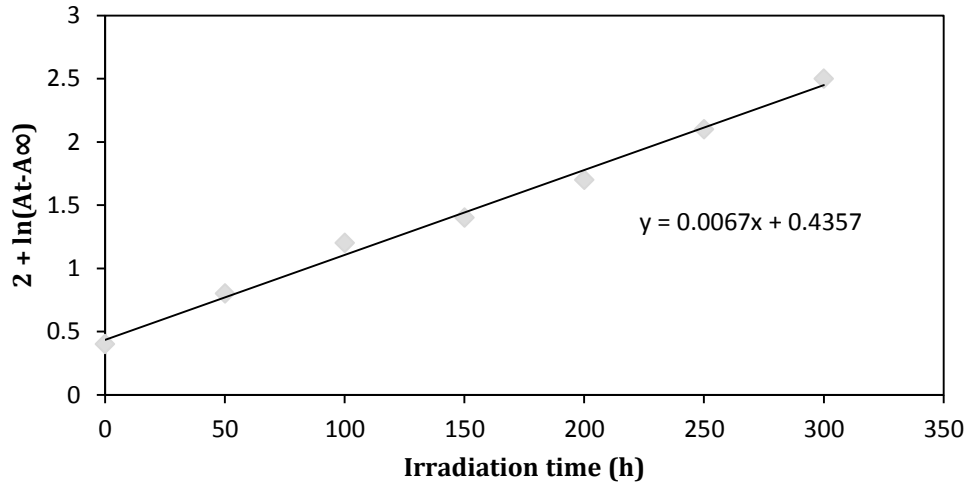

Figure 4: ln(At- A∞) relationship with irradiation time for PVC-2 film.

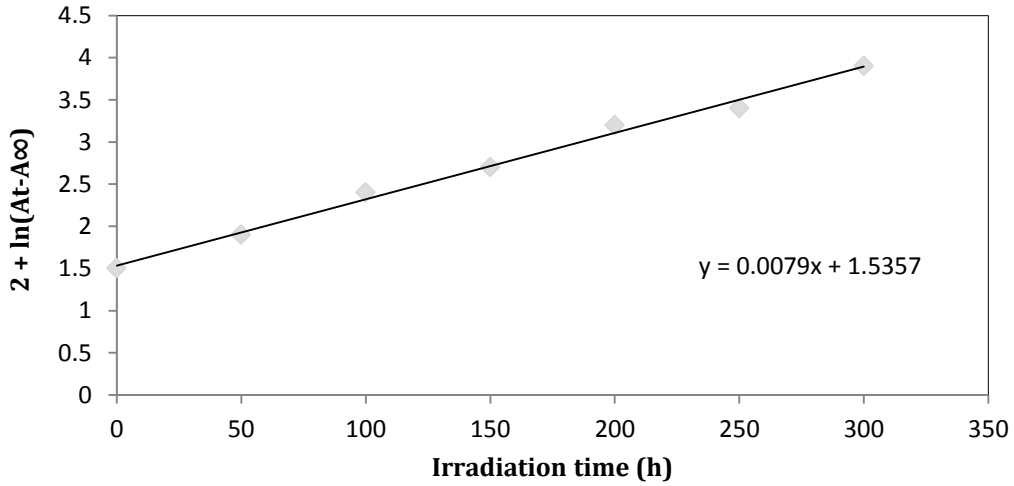

Figure 5: ln(At- A∞) relationship with irradiation time for PVC-3 film.

The rate constant of photo-stabilizers (organotin compounds) affects PVC films' photodegradation [20, 21]. The k_d value of blank PVC without additives was 11.5×10^{-3} sec^{-1}, representing the highest value compared with others, as illustrated in Table 1. However, when organotin (IV) 1-3 complexes photo stabilizers were presented, it decreased significantly ($6.7\text{-}8.4\times10^{-3}$ sec^{-1}), and complex 1's K_d was the lowest value, 6.7×10^{-3} sec^{-1}. As a result, utilizing photo stabilizers of this type is vital for reducing PVC films degradation.

Table 1: Photodecomposition rate constants (K_d) of blank and modified PVC films [2].

Film	$K_d \times10^{-3}$ sec^{-1}
PVC (blank)	11.5
PVC/1	6.7
PVC/2	7.9
PVC/3	8.4

Photo stabilizers protect PVC films from photodegradation by converting solar energy to dissipate heat without harming the chemical structure of the polymer [22]. This improvement is attributed to complexes with an aromatic nature in the ligands. These additives can directly absorb UV light and gradually release the adsorbed energy at a low rate that maintains the PVC chains unbroken [23]. The aromatic ring activates free radicals with resonance and thus inhibits free radicals' action that increases photodegradation; therefore, the photodegradation of PVC films will be reduced [18].

3.2. PVC Stabilization Evaluation Using FTIR Spectroscopy

FTIR spectroscopy was employed to photo-activate organotin (IV) complexes, using as additives to photostabilize PVC films. Irradiating the PVC films to UV light for 300 hours causes changes in the reflected FTIR spectrum. The PVC spectrum after irradiation showed two absorption bands due to the generation of a polyene (C=C) at 1604 cm^{-1} and carbonyl (C=O) at 1722 cm^{-1} [24]. The rate of these peaks' growth concerns the reference peak 1328 cm^{-1} and could be used to estimate the PVC photodegradation [25]. Figure 6 shows FT-IR spectra of PVC films pre and post 300 hours of exposure to irradiation. From absorbed spectra of functional group (A_s) and standard peak (A_r), Equation 2 is applied to compute the functional group (C=C or C=O) index (I_s) [26].

$$I_s = A_s/A_r \quad (2)$$

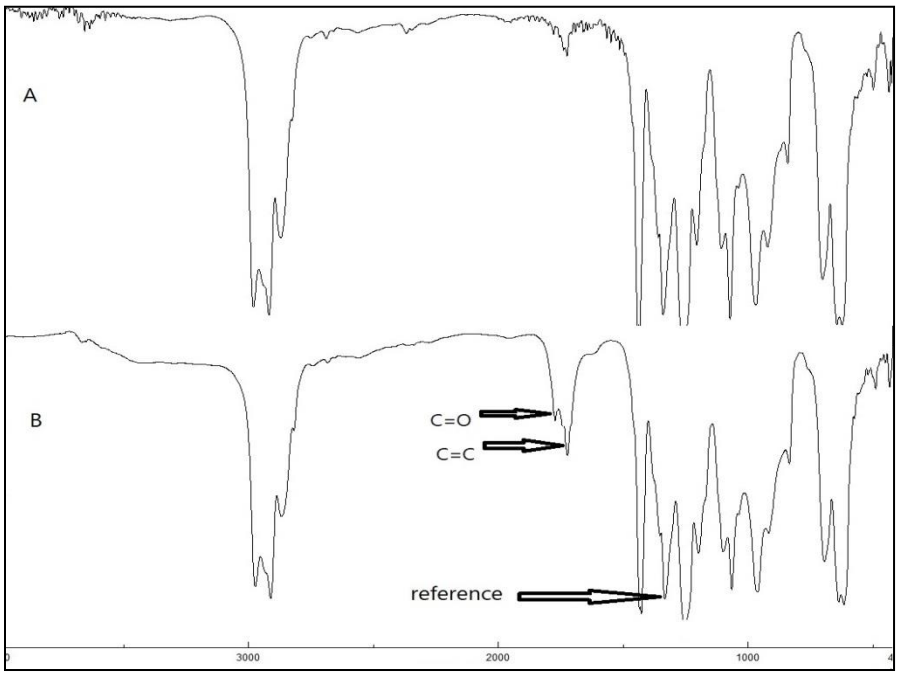

Figure 6: Changes in FT-IR spectrum of PVC film (A) before irradiation (B) after 300 h irradiation.

3.3. PVC stabilization evaluation using FE-SEM

SEM examination was utilized to analyze the morphology of PVC sheets. It was demonstrated that the plain PVC film was less lumpy and had a high level of homogeneity before radiation exposure [27]. After irradiation, bonds break within the polymer chains and HCl inducement, which leads to cracks and roughness forming on the PVC surface [28]. The PVC/Bu_3SnL blend had a smoother and cleaner surface after 300 hr irradiation than the plain irradiated PVC film, as shown in Figure 7.

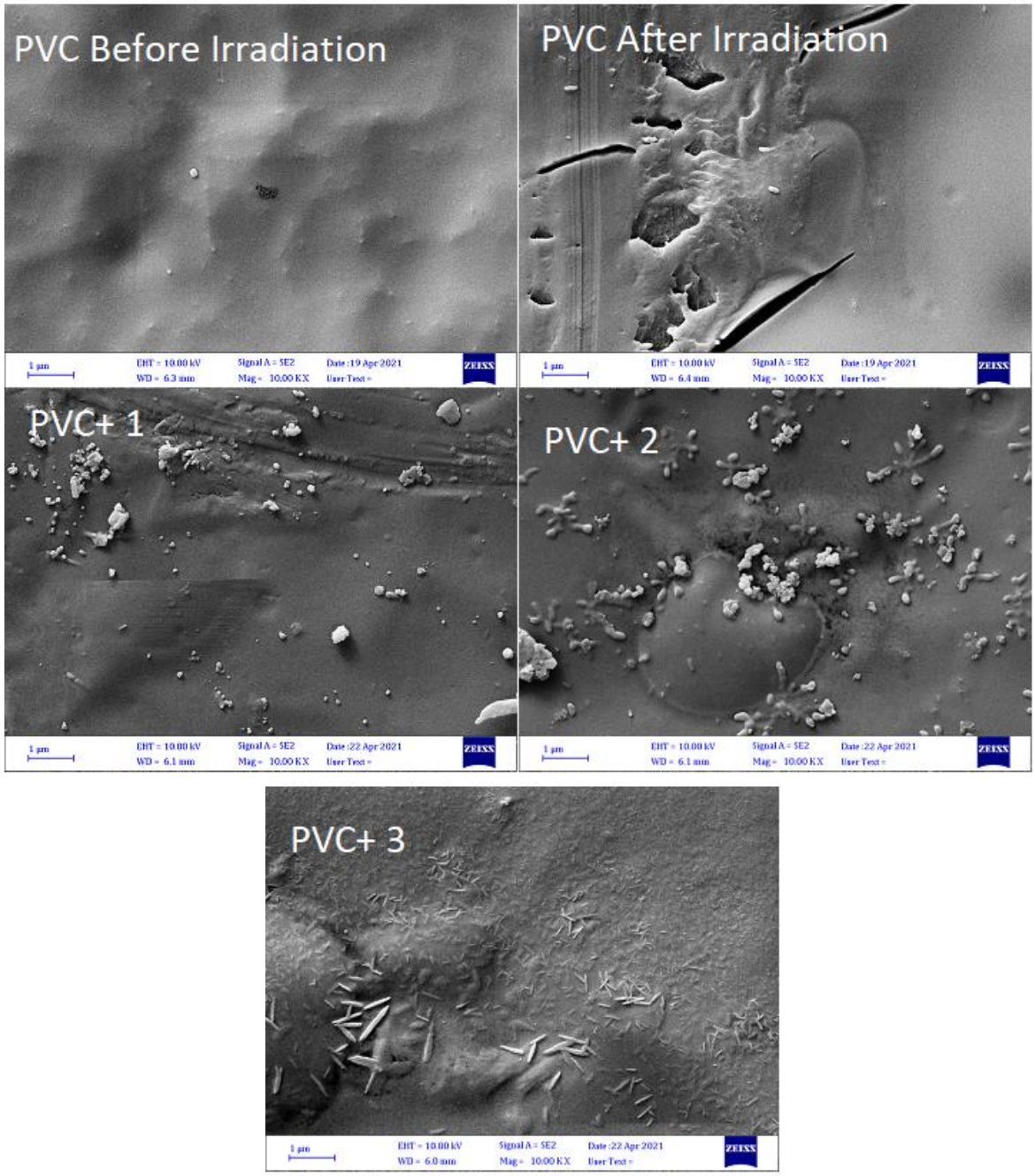

Figure 7: FE-SEM images of PVC films.

4. Conclusions

In this study, organotin (IV) complexes' efficacy as photo-stabilizers was proven. When compared to pristine PVC, it can lower the photodecomposition rate constant. The value of the photolysis rate constant was high for the pristine polymer films compared to the films filled with additives. Complex 1 exhibited noticeable stability of the PVC depending on the value of its low photodecomposition rate constant. FE-SEM images showed that the PVC films containing complexes are much smoother than the pristine PVC after UV irradiation. Similar findings were obtained when the FTIR test was applied.

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