

TEM Study of Irradiated PVC Embedded with Tin Complexes of Heterocyclic and Aromatic Moieties

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Abstract

Poly(vinyl chloride) (PVC) could be considered as one of the highly manufactured plastics with a production capacity of multiple millions tons per year. Fillers are recently added to PVC in an attempt to increase its applications in various sectors, especially at tough exposing conditions. Therefore, the current work reports the morphological studies of PVC sheets that contain trimethoprim-tin complexes as additives. The PVC was blended with a low concentration of trimethoprim-tin complexes and thin films have been prepared from the homogenous mixtures. The ultraviolet irradiation impact on the morphology and physicochemical properties of the films was studied. It was found that the photodecomposition and photo-oxidation levels of PVC films were lower than the blank film's ones. The TEM images showed that the undesirable changes in the surface of irradiated PVC films, such as the appearance of dark spots, cracks, and roughness, were minimized once the tin complexes were filled compared with the blank PVC.

Keywords: trimethoprim-tin complexes, poly(vinyl chloride), roughness surface, photodegradation, photooxidation, transmission electron microscope

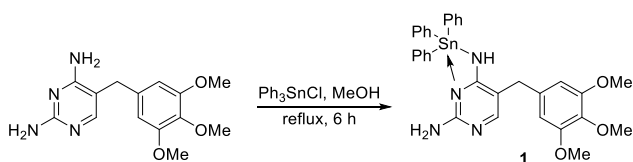
1. Introduction

Plastics are a sub family of polymers that synthesized from different raw materials and produced in different shapes. They gain their popularity because of their unique merits of being low-expensive, light-weighted, durable, and multidisciplinary potential for various applications. They became special alternatives for wood, glass, and metals [1–3]. For instance, in 2019, plastics industry offers 1.5 million career opportunity and produced 350 billion euros in Europe [4]. However, plastics are commonly synthesized from fossil residuals via synthesizing methods that were set earlier in the previous century. Nevertheless, their physical properties, such as, color, molecular weight, strength, rigidity, and density could be controlled during

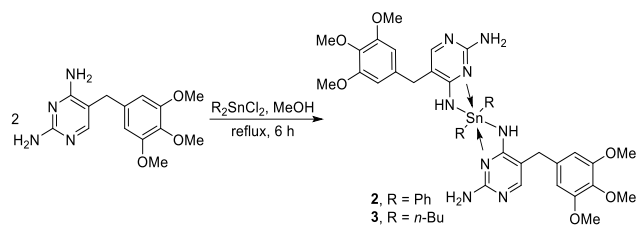
preparation. Among the mostly prepared plastics globally, polypropylene, polyethylene, polystyrene, polyethylene terephthalate, and PVC are the highly produced types [2,3]. Recently, a report was published and proposed China as the primary plastics producer with a contribution ratio of 51% to the globe production. Also, it showed the fields that plastics were mainly applied in, where packaging (39.6%) was the major industry, followed by construction materials (20.4%). Lower ratios were reported for other lines of industries, where 9.6% was in automotive, 6.2% was in electronics, 4.1% and 3.4% were for household and agriculture applications, respectively, and 16.7% was for other industries [4]. This huge intercalation of plastics in almost all fields led to through high quantities to the environment and led to generate a huge pollution

problem. Hence, governments and scientists put a lot of efforts to reduce this problem, such as the recycling attempts of Europe, where 4 million tons of plastics were reused in 2018. Yet, recycling methods are energy, time, labor, and money-consuming, since they include multiple steps, like collection, primary classification, ripping, washing, secondary classification, and extrusion [4].

PVC is a type of thermoplastics that has many advantages and applications. It is inexpensive, highly strengthened, highly chemically and electrically (good insulator) stable, corrosion resistant in severe conditions, and flame retardant as a result of high chlorine percentage (around 57 wt.%) [5]. Therefore, PVC is widely used in many sectors [6]. Plastics, in general, and PVC in particular experienced an increasing production rates over the years; the production line is anticipated to raise up more in the near future [7]. The flexibility/stiffness of PVC can be manipulated by filling plasticizers to allow its utilization in applications that require soft polymers [8]. The plasticizers generate free volume among the PVC chains via the introduction of new roles to the structure, which could be explained by softening the PVC by decreasing the glass transition temperature of the polymeric structure [9,10]. PVC, however, experiences photodegradation when temperatures higher than 100 °C and produces hydrogen chloride (HCl) that results in a weak structure. Eliminating the HCl yields to forming polyene compounds that associated with carbon-carbon double bonds. Dehydrochlorination of the PVC follows up a degradation in the thermal and physical properties, such as discoloration, which hinders its external applications [11,12]. PVC cannot absorb the high wave UV light ($\lambda > 220$ nm); therefore, polyene chains are initiated because of defects existed from PVC photodegradation [13,14]. Therefore, it became essential to utilize photostabilization additives to restrain the damages that take place due to photoirradiation [15]. Indeed, the design, synthesis, and use of new PVC additives are continuing and remarkable progresses have been made. This work presents the successful employment of trimethoprim-tin complexes as improvers and studies the surface morphology of thin PVC films by the transmission electron microscope (TEM) technique.



Scheme 1. Preparation of trimethoprim-tin complex 1.



Scheme 2. Preparation of trimethoprim-tin complexes 2 and 3.

2. Materials and Method

2.1 Synthesis of Complexes

The trimethoprim-tin complexes were synthesized and characterized in our previous work [16]. A solution of triphenyltin chloride (Ph_3SnCl), diphenyltin dichloride (Ph_2SnCl_2), and di-*n*-butyltin dichloride ($n\text{-Bu}_2\text{SnCl}_2$) in methanol (MeOH) was added to a stirred trimethoprim-MeOH solution. This mixture was heated under reflux for 6 hours. The produced solid via cooling was filtrated, washed with MeOH, and named as complexes 1, 2, and 3 as they are made from Ph_3SnCl , Ph_2SnCl_2 , and $n\text{-Bu}_2\text{SnCl}_2$, respectively. However, Schemes 1 and 2 show the preparation reaction of the complexes. These complexes were then characterized by FTIR, NMR, and elemental analysis to check the purity [16].

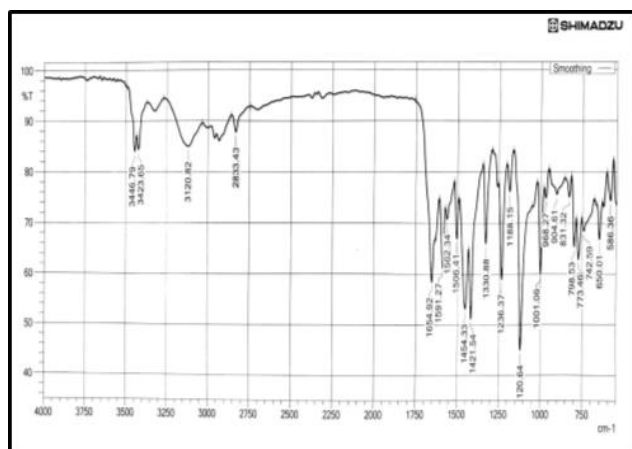


Figure 1. FTIR spectrum of complex 3.

2.2 Preparation of PVC Films

A small amount of trimethoprim-tin complexes (25 mg) was mixed with the polymeric solution that was made by dissolving 5.0 g PVC in 100 mL tetrahydrofuran (THF). The whole mixture was stirred for 2 hours under ambient conditions to reach full homogeneity. An aliquot of the obtained solution was collected and poured on a dry glass plate to form the required films. In fact, the used glass plate contains 15 rooms of dimensions 4 cm², 4 cm², and 40 μm for the length, width, and thickness, respectively. The solution on the plate was left at 25 °C to dry for 18 hours.

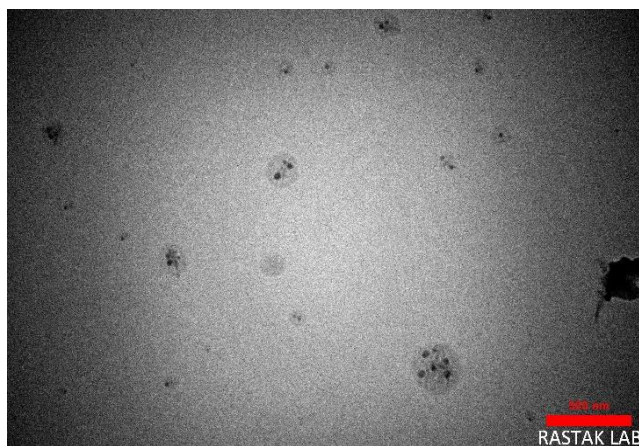


Figure 2. TEM image of blank PVC film.

2.3 Irradiation of PVC Films

A UV light source of light intensity = 6.2×10^{-9} ein $\text{dm}^{-3} \text{s}^{-1}$ and $\lambda_{\text{max}} = 365$ nm was utilized to irradiate the PVC sheets. Precautions and care were taken to guarantee an equal and full exposure of UV light for all sides by rotating the sample regularly. Ultimately, the prepared films were further dried in a vacuum oven for 18 hours at 25 °C.

3. Results and Discussion

3.1 Characterization of complexes by FTIR

The FTIR spectra of synthesized trimethoprim-tin complexes in Fig. 1 showed characteristic absorption bands at 1654–1656 cm^{-1} due to CH=N bonds vibrations. In addition, absorption bands corresponded to the vibrations of NH_2 , O-CH₃, C=N, and C=C groups in the aromatic systems were observed at the regions 3446–3470, 1120–1126, 1589–1595, and 1506–1506 cm^{-1} , respectively [16]. Moreover, the FTIR spectrum showed a broad absorption

band at 3319 cm^{-1} that is attributed to the OH group vibration [16].

3.2 Investigating the Photodegradation Effect on Surface Morphology

The damages occurred within the surface morphology of PVC films assigned to UV irradiation are investigated in this section. The TEM images for the surface of post-irradiated PVC films showed partial deformation when compared with the blank sheet. The number of cracks, grooves, and dark spots were highly recognized on the polymeric sheets after irradiation. The manifestation of dark areas is assigned to HCl release that comes from PVC decomposing [17]. In order to further investigate the surface of irradiated PVC, the TEM technique was employed to analysis of thin films microstructure [18]. Fig. 2 shows a TEM image of the blank PVC film before irradiation. This technique was used to determine the elimination rate of volatiles during the photodegradation process. It is an attempt to understand the changes that occur on the surface of the PVC before and after filling tin complexes as additives.

The TEM was utilized to exam the internal structure of materials at high resolution and magnification. This analysis method is employed to identify the crystal texture and defects of materials; hence it was applied to determine the main structure. The TEM images provided information about the damages that take place within the film due to radiation. Fig. 3 shows that the irradiated films contain cavities, loops, and segregation due to photoirradiation.

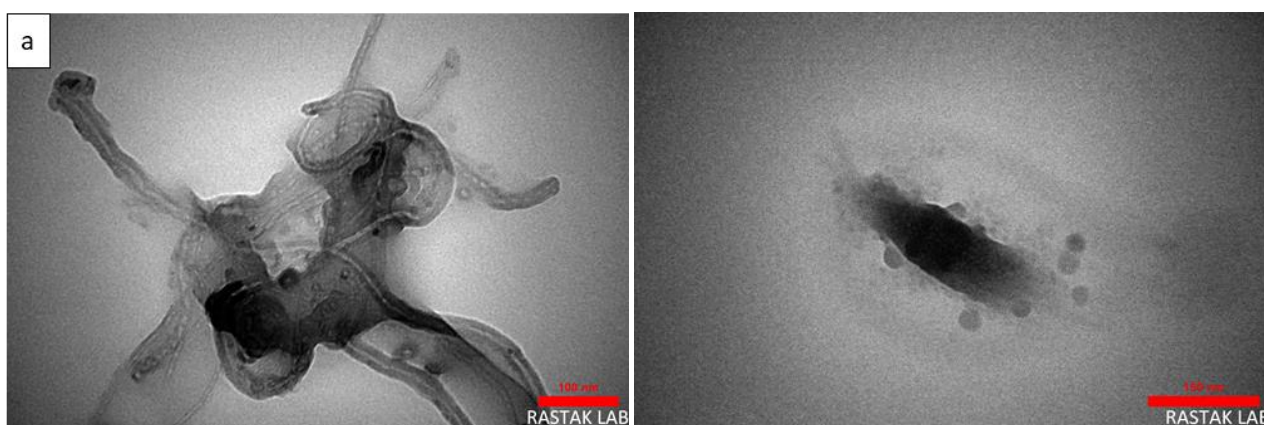


Figure 3. TEM images of PVC films doped with complex 1 (a), complex 2 (b), and complex 3 (c) (continued on the next page).

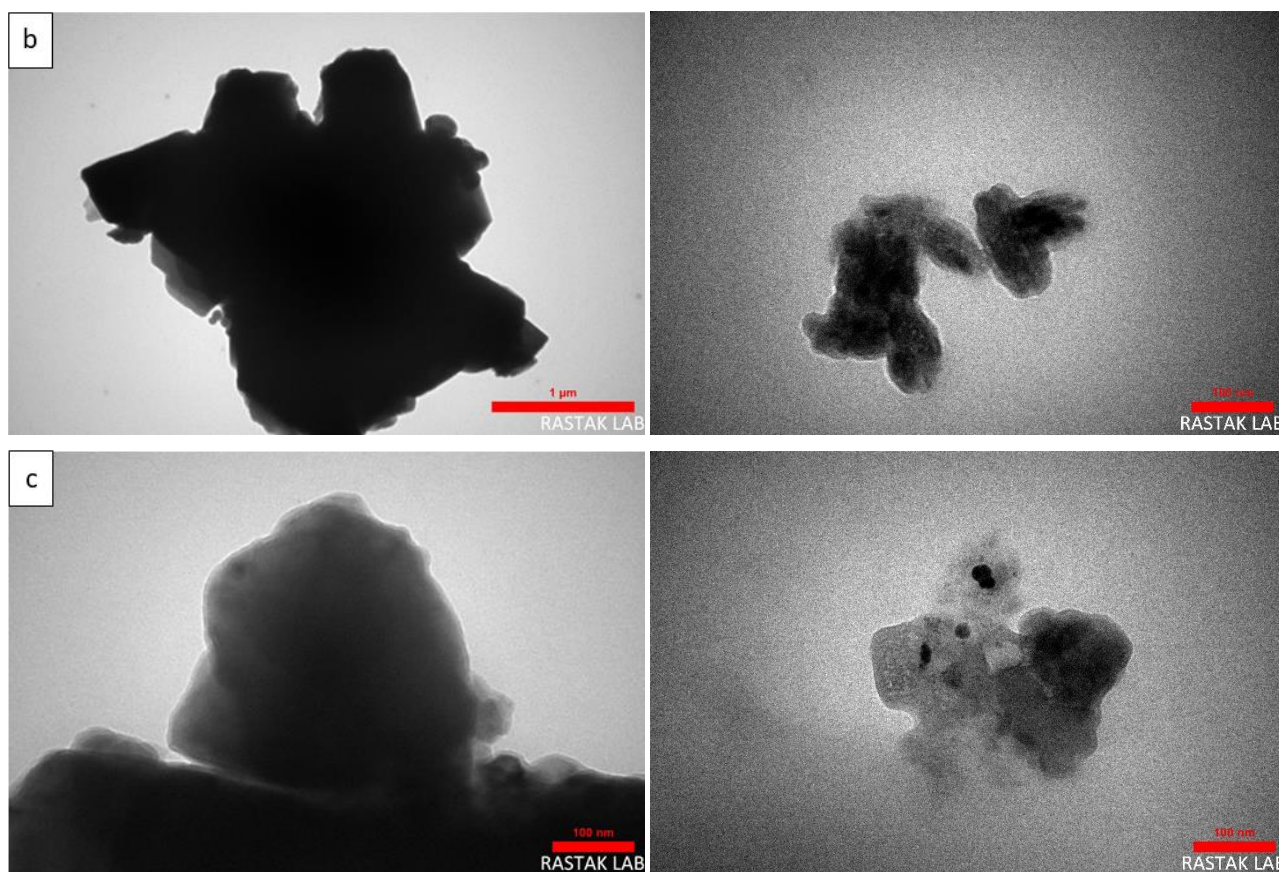


Figure 3. TEM images of PVC films doped with complex 1 (a), complex 2 (b), and complex 3 (c) (continued from previous page).

4. Conclusion

A simple preparation method for trimethoprim-tin complexes in a good productivity was introduced earlier and the effect on photodegradation properties was investigated here. These complexes were added to the PVC films and acted as photostabilizers, which led to a remarkable decrease in polymeric degradation occurred within the structural chains caused by photooxidation and photodegradation and investigated by TEM technique. Changes on the surface of PVC films can give an indication of degradation during irradiation. After damage occurrence, TEM images of PVC films' morphology recorded irregularities for post-irradiated films when compared with the pre-irradiated blank PVC. Furthermore, the heteroatoms (oxygen and nitrogen) that construct the trimethoprim-tins ease their interaction and coordination within the polymeric chains.

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