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Photostabilization of Poly(vinyl chloride) Films Blended with Organotin Complexes of Mefenamic Acid for Outdoor Applications

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Abstract: This study develops a process for enhancing the photostabilization of PVC films blended with a low concentration of mefenamate–tin complex. One tri-substituted and three di-substituted organotin complexes containing mefenamate unit are synthesized, and their chemical structures are established. The reactions of mefenamic acid and a number of substituted tin chlorides gave the corresponding tin complexes in 70–77% yields. Tin complexes were blended with PVC and thin films. The effect of the addition of additives against long-term irradiation (290–400 nm, 300 h) is also tested. Changes in the infrared spectra, weight, and surface of the PVC blends due to irradiation are examined and analyzed. Any damage to the PVC surface and its chemical degradation level are noticeably low in the presence of additives. Minimal photodegradation levels and surface changes of the irradiated PVC films are observed when the triphenyltin complex is used. Such a complex is highly aromatic and can act as an ultraviolet irradiation absorber and a scavenger for hydrogen chloride and radicals produced due to the photooxidation and photoirradiation of PVC films.

Keywords: poly(vinyl chloride); mefenamate–organotin complexes; photostabilizers; radical scavengers; photodegradation; photooxidation; functional group indices; surface morphology

1. Introduction

Thermoplastics are common polymers with high molecular weight, which are moldable at elevated temperatures. The physical properties of plastics can dramatically worsen below their melting point and above glass transition temperatures. Along with polyethylene, polypropylene, and polystyrene, polyvinyl chloride (PVC) is a well-known plastic with unique properties that allows for its use in several applications. PVC is produced in large quantities in both rigid and flexible forms [1]. Rigid PVC is frequently used in the production of construction materials (e.g., pipes, doors, and windows), bottles, cards, and packaging. Hence, the addition of plasticizers can reduce PVC brittleness and make it as soft as rubber. Soft PVC is used in manufacturing cable insulation, plumbing, and flooring. Pure PVC is a brittle white solid that is soluble in tetrahydrofuran (THF). The

majority (80%) of PVC is produced through suspension polymerization along with 20% emulsion usage and bulk polymerizations. PVC has excellent properties and is inexpensive to produce; however, it suffers from photodegradation if exposed to sunlight for long durations and therefore, must be protected for outdoor applications [2].

In the presence of oxygen, PVC photodegradation occurs due to ultraviolet (UV) irradiation, which leads to weathering as a result of chain scission [3]. Consequently, this results in changes to its mechanical properties and turns the PVC into brittle material. The photodegradation process starts with the production of free radicals that react with oxygen. These chain reactions involving radicals lead to changes in mechanical and physical properties. Additionally, PVC photodegradation leads to the formation of volatile by-products, such as hydrogen chloride (HCl), deformation, discoloration, and cracking [4]. PVC photodegradation is mainly caused by defects and irregularities in the polymeric chains along with the formation of hydroperoxides, double bonds, and carbonyl groups [5]. Photostabilizers can efficiently absorb UV light; thus, their addition to PVC can inhibit photodegradation. PVC additives should be non-volatile and chemically stable, have low production costs, be compatible with the polymer, and be used at a low concentration to avoid color changes [6]. In terms of toxicity and volatility, many limitations are associated with using previously developed additives, such as polychlorinated biphenyls, phthalates, phosphites, and mixed metals [7,8]. Therefore, research has continued to synthesize and use new PVC additives to enhance photostability. Various additives have been used to overcome the problems associated with the creation of side products and small fragments from PVC when exposed to UV irradiation. Common PVC additives include aromatics [9–12], polyphosphates [13–15], Schiff bases [16–21], carbon nanotubes [22], and titanium dioxide [23–27], among many others [28–30].

Compounds containing tin have unique physical and chemical properties and are widely used in the pharmaceutical industry [31]. Organotin compounds containing carboxylate moiety showed potential for use as a cancer chemotherapy drug [32]. They can be used as antimicrobials [33], anti-inflammatory agents [34], antitubercular agents [35], biocides and wood preservatives [36], and catalysts [37]. The biological performance of organotin compounds is dependent on the nature of organic units and the number and types of substituents (alkyl or aryl) present [38]. We recently successfully synthesized various organotin complexes and investigated their uses as PVC photostabilizers [39–47]. Continuing our interest in the polymer photostabilization subject, we can now report the successful synthesis of different tin complexes containing the mefenamic unit and their effect in enhancing the PVC photostabilization.

2. Materials and Methods

2.1. General

Chemicals were purchased from Merck (Gillingham, UK). The PVC, with an average molecular weight of approximately 250,000, was supplied by Petkim Petrokimya (Istanbul, Turkey). The Mitamura Riken Kogyo MPD melting point apparatus (Tokushima, Japan) was used for the melting point determination. Elemental analyses were performed on a Thermo Scientific™ elemental analyzer (CE Instruments Ltd., Hindley Green, UK). An 8300 Shimadzu spectrophotometer (Shimadzu, Tokyo, Japan) was used to record the FTIR spectra (KBr disc). The ^1H NMR spectra (300 MHz) were recorded on a Bruker DRX300 NMR spectrometer (Bruker, Zurich, Switzerland). The PVC film preparation involved the use of a Kerry PUL 55 ultrasonic bath (Akribis Scientific Ltd., Cheshire, UK). The PVC surface morphology was inspected using a Meiji Techno microscope (Meiji Techno, Tokyo, Japan) and an Inspect S50 microscope (FEI Company, Czechia, Czech Republic; 15 kV). The PVC film irradiation was performed at 25 °C on an accelerated weather-meter QUV tester (Q-Panel Company, Homestead, FL, USA) using a UV light (290–400 nm) with a fixed light intensity (6.43×10^{-9} ein dm $^{-3}$ s $^{-1}$).

2.2. Synthesis of Triphenyltin Complex 1

A mefenamic acid solution (0.24 g, 1.0 mmol) in methanol (MeOH; 10 mL) was added slowly over 5 min to a stirred solution of triphenyltin chloride (0.42 g, 1.1 mmol) in MeOH (10 mL). The mixture was refluxed for 8 h and allowed to cool down. The solid obtained was then collected by filtration, washed with H₂O (10 mL) followed by MeOH (2 × 10 mL), and then dried. The dried solid was recrystallized using MeOH to give **1** (Scheme 1) as a white solid in 70% yield (Table 1).

Scheme 1. Synthesis of **1**.

Table 1. Physical properties of **1–4**.

Complex	R	Yield (%)	MP (°C)	Elemental Analysis (%)		
				Calculated (Found)		
				C	H	N
1	–	70	123–125	67.14 (67.22)	4.95 (5.05)	2.37 (2.46)
2	Ph	72	134–136	66.95 (66.98)	5.08 (5.15)	3.72 (3.77)
3	Bu	71	118–120	63.97 (64.02)	6.50 (6.23)	3.93 (3.95)
4	Me	77	213–215	61.07 (61.14)	5.45 (5.55)	4.45 (4.50)

2.3. Synthesis of Complexes 2–4

A mefenamic acid solution (0.48 g, 2.0 mmol) in MeOH (15 mL) was slowly added over 5 min to a stirred solution of the appropriate tin chloride (diphenyl, dibutyl, or dimethyltin chloride; 1.0 mmol). The mixture was refluxed for 8 h and allowed to cool down. The solid precipitate was collected, washed with H₂O (10 mL) followed by MeOH (2 × 10 mL), and dried. The crystallization of crude products using MeOH gave the corresponding complexes **2–4** (Scheme 2) as white solids in 71–77% yields (Table 1).

Scheme 2. Synthesis of di-substituted **2–4**.

2.4. Preparation of PVC Films Containing Tin Complexes

A mixture of **1–4** (25 mg) and PVC (5 g) in THF (100 mL) was stirred at 25 °C for 3 h in an ultrasonic bath. The mixture was transferred to a glass plate containing holes (15; 40 μ m) and left to dry at 25 °C for 24 h. The solvent traces trapped within the films were removed using a vacuum oven (45 °C; 8 h).

3. Results and Discussion

3.1. Synthesis of Complexes **1–4**

The treatment of mefenamic acid and the appropriate substituted tin chloride gave the corresponding tin complexes **1–4** as white solids. The reaction of a 1:1 mixture of mefenamic acid and triphenyltin chloride in boiling MeOH for 8 h provided **1** (Scheme 1) in a 70% yield. Similarly, the reaction of two mole equivalents of mefenamic acid and di-substituted tin chloride gave compounds **2–4** (Scheme 2) in 71–77% yields. Table 1 presents the elemental analyses, melting points, and yields of complexes **1–4**.

The absorption peaks appeared at the 520–526 cm^{-1} and 447–449 cm^{-1} regions in the FTIR spectra of complexes (Table 2) and were attributed to the Sn–C and Sn–O vibrations, respectively [48,49]. The asymmetric (ν asym) and symmetric (ν sym) vibrations of the carbonyl group were observed at the 1641–1643 cm^{-1} and 1506–1508 cm^{-1} regions, respectively. The difference between the asymmetric and symmetric vibrations of the C=O group ($\nu_{\text{asym}} - \nu_{\text{sym}}$) ranged from 133 to 137 cm^{-1} . The $\Delta\nu$ value is evidence for the bidentate chelation mode between the tin atom and the O=C–O group of mefenamic acid [50–52]. The microanalytical results confirmed the structures and purity of **1–4**.

Table 2. FTIR data of **1–4**.

Complex	FTIR (ν , cm^{-1})						
	NH	C=O			C=C	Sn–C	Sn–O
		asym	sym	$\Delta\nu$ (asym – sym)			
1	3312	1643	1508	135	1452	525	449
2	3312	1641	1508	133	1450	520	448
3	3333	1643	1506	137	1456	526	447
4	3312	1643	1506	137	1454	524	447

The ^1H NMR spectra showed the presence of an exchangeable singlet at the 9.45–9.77 ppm region corresponding to the NH proton (Table 3). Multiplet signals were seen within the 7.90–6.67 ppm region due to aromatic protons. The methyl protons attached to the aryl ring appeared as singlet signals at approximately 2.5 and 2.1 ppm regions. Meanwhile, the methyl protons attached to the tin atom in complex **4** appeared as a singlet at a very high field (0.78 ppm) as a result of the shielding effect.

Table 3. ^1H NMR data ($\text{DMSO}-d_6$) of **1–4**.

Complex	^1H (δ , ppm, Hz)
1	9.46 (s, 1H, NH), 7.90–7.84 (m, 3H, Ar), 7.44–7.41 (m, 6H, Ar), 7.33–7.29 (m, 9H, Ar), 7.13–6.67 (m, 4H, Ar), 2.50 (s, 3H, Me), 2.09 (s, 3H, Me)
2	9.45 (s, 2H, 2NH), 7.89–7.80 (m, 6H, Ar), 7.36–7.10 (m, 10H, Ar), 7.03–6.67 (m, 6H, Ar), 2.50 (s, 6H, 2Me), 2.11 (s, 6H, 2Me)
3	9.77 (s, 2H, 2NH), 7.89–7.85 (m, 6H, Ar), 7.46–6.96 (m, 8H, Ar), 2.50 (s, 6H, 2Me), 2.04 (s, 6H, 2Me), 1.64–1.29 (m, 12H, 6CH ₂), 0.81 (t, J 7.6 Hz, 6H, 2Me)
4	9.45 (s, 2H, 2NH), 7.89–7.84 (m, 6H, Ar), 7.32–6.98 (m, 8H, Ar), 2.50 (s, 6H, 2Me), 2.08 (s, 6H, 2Me), 0.78 (s, 6H, 2Me)

3.2. Investigation of PVC Photodegradation Using FTIR Spectroscopy

The PVC photooxidation caused cross-linking, bond breaking, and chain scission mainly caused by the HCl (dehydrochlorination) elimination. Subsequently, this process caused the loss of small fragments containing different functional groups, such as hydroxy (OH; alcohols and hydroperoxides), carbonyl (C=O; ketones and chloroketones), and alkene (C=C; polyenes) [53]. The changes in the absorption band vibrations of the OH (3510 cm^{-1}), C=O (1717 cm^{-1}), and C=C (1610 cm^{-1}) groups in the FTIR spectra could be used to assess the photostabilization effect induced by the additives [54]. The changes in the intensity of the peaks corresponding to these functional groups were compared herein with those of the CH₂ bonds (1328 cm^{-1}), which were not affected during irradiation [55]. Complexes 1–4 at 0.5% concentration were added to PVC, and thin films were produced. Such a concentration showed the most desirable stabilizing effect for PVC without causing changes in color [56]. The films were irradiated with UV light. The FTIR spectra were recorded every 50 h and up to 300 h. The functional group index (I_s) for OH, C=O, and C=C was calculated from its absorbance (A_s) and for the reference group (A_r ; CH₂) using Equation (1). The FTIR spectra of the pure PVC film before and after irradiation (300 h) is shown in Figure 1.

$$I_s = A_s / A_r \quad (1)$$

Figure 1. FTIR spectra of PVC film: (a) before and (b) after irradiation.

Figures 2–4 depict the IOH , $IC=O$, and $IC=C$ for the pure and blended PVC films with complexes at various irradiation times (50–300 h), respectively. The changes in the IOH were very significant after the beginning of irradiation (50 h) and sharper for the pure PVC film (Figure 2). At the end of irradiation (300 h), the IOH was 0.95 for the pure PVC

compared with 0.51 for the film containing complex 1. The PVC photodegradation that led to small polymeric fragments containing a hydroxyl group for pure film was approximately two-fold (187%) compared with that for the PVC + 1 blend. The complex containing the high aromatic content (three phenyl groups; complex 1) was the best PVC photostabilizer, followed by that containing two phenyl groups (complex 2) and those containing alkyl (butyl and methyl) substituents (complexes 3 and 4). Complex 1 behaved as a good UV absorber and a scavenger for radicals and HCl as a result of its high aromaticity.

Figure 2. The I_{OH} of the PVC films versus time.

Figure 3. The $I_{C=O}$ of the PVC films versus time.

Figure 4. The $IC=C$ of the PVC films versus time.

Figure 3 shows that increasing the irradiation time led to a significant increase in the $IC=O$; however, the changes were sharp up to 50 h. The $IC=O$ was 1.15 for pure PVC, 0.60 for PVC + 1, 0.69 for PVC + 2, 0.74 for PVC + 3, and 0.82 for PVC + 4 at the end of irradiation. Complexes 1–4, particularly those with highly aromatic qualities, provided significant protection to PVC against photodegradation.

Similar to both the IOH and $IC=O$, the changes in the $IC=C$ were larger for the pure PVC film (0.81 after 50 h and 1.15 after 300 h) than those with the polymeric blend containing 1 (0.45 and 0.58 after 50 and 300 h, respectively). Additive 1, again, showed the highest stabilizing effect, followed by 2, 3, and 4. Complexes 1–4 showed similar or better stabilizing performance compared with those reported for other additives [14–35].

3.3. Investigation of PVC Photodegradation Using Weight Loss

The PVC irradiation led to the elimination of volatiles, such as HCl gas, and a decrease in the polymer weight [57]. The polymeric material weight loss can be used as a tool for assessing the level of damage that the irradiation caused. Thus, the PVC films were weighed (W_1) and irradiated followed by a measurement of weight after every 50 h (W_2). The weight loss (%) was calculated using Equation (2). The results are presented in Figure 5. Complexes 1–4 led to a significant PVC photostabilization, in which 1 was the most effective additive. The weight loss (%) was highest (1.39%) for pure PVC and lowest (0.27%) for the blend containing 1 after 300 h irradiation. Complex 1 provided five-fold protection for PVC against photodegradation.

$$\text{Weight loss (\%)} = [(W_1 - W_2)/W_0] \times 100 \quad (2)$$

Figure 5. Weight loss (%) of PVC films versus time.

3.4. Investigation of PVC Photodegradation Using Surface Morphology

The surface morphology examination affords information regarding the roughness and defects of materials caused by photoirradiation. A long period of PVC photoirradiation leads to surface damage mainly as a result of chain scission and dehydrochlorination [58]. Non-irradiated PVC films have a more or less smooth surface with no noticeable irregularity compared with irradiated ones [21,39,40]. The surface of an irradiated PVC was inspected using an optical microscope. The microscopic images (Figure 6) showed that the PVC surface was damaged by the irradiation. They showed a degree of color change, roughness, cracks, spots, and grooves in the PVC surface. However, the damages were more apparent within the pure PVC surface compared to those containing additives, which reflected the role played by complexes 1–4 as photostabilizers in reducing the HCl elimination rate.

The surface of the irradiated films was also examined using a scanning electron microscope (SEM). The SEM images detect the shape and size of particles, compactivity of tin complexes with polymer, ionic conductivity, and stability of materials [59,60]. The SEM images recorded for the non-irradiated PVC films showed high levels of smoothness, regularity, and homogeneity [14,46]. The SEM images of the irradiated PVC films for 300 h (Figure 7) showed a damaged surface with noticeable spots, cavities, and cracks. The damages in the polymer surface were caused by the cross-linking in the polymer chains and the elimination of volatiles. The least noticeable damages in the PVC surface were seen in the films containing complexes 2 and 3. Interestingly, the SEM image of PVC + 1 showed a glass frit-like structure; such a pattern was similar to that obtained for the metallic oxide surface, Bi–Te–B–Si–P–O [61].

The SEM high-resolution images of the PVC + 1 surface at 100 and 20 μm magnifications showed a regular aggregation of particles with different shapes and sizes (Figure 8). Such phenomena could be caused by the HCl elimination at a constant rate over time. However, more work is needed to understand why complex 1 behaves differently and causes the formation of a shattered glass-like surface. Furthermore, the surface of the irradiated PVC containing nickel chloride and a Schiff base of dithiazole produced a homogenous honeycomb-like structure [62]. Additionally, the SEM images of the PVC containing a melamine Schiff base showed an ice rock-like structure.

Figure 6. Microscope images of PVC films.

Figure 7. SEM images of the PVC films.

Figure 8. SEM images of PVC + 1 at: (a) 100 and (b) 20 μm .

3.5. PVC Photostabilization Suggested Mechanisms

Complexes 1–4 contain aromatic moieties that can provide PVC photostabilization through UV light absorption (i.e., primary photostabilizers) and release the energy at a harmless level over a period of time [63]. Complexes with a higher aromaticity content (complexes 1 and 2) are better UV absorbers than those having a lower aromaticity content (complexes 3 and 4). The polarity of the carboxylate group and the $N\text{--Ar}$ bond within 1–4 and the C--Cl bond in PVC facilitate the coordination between the tin complexes and the polymer (Figure 9). Such coordination between the polarized atoms can assess and enhance the energy transfer from the excited PVC to the tin complexes, which can be dissipated over time [10,47].

Figure 9. Attraction between organotin 1 and PVC chains.

The PVC photooxidation produces peroxide radicals that can be scavenged by complexes 1–4. The aromatic moieties in the additive skeleton can interact with peroxide radicals (chromophores) leading to an excited state intermediate (Figure 10). Such an intermediate is highly stable via aromatic rings resonance [64].

Figure 10. Organotin 1 as a radical scavenger.

Complexes 1–4 contain the tin atom, which is highly acidic (Lewis acid) and therefore capable of scavenging HCl efficiently (i.e., secondary photostabilizers; Figure 11) [65].

Figure 11. Organotin 1 as a HCl scavenger.

4. Conclusions

New organotin compounds containing mefenamate moiety were synthesized in good yields and their structures were established. The complexes inhibited PVC photodegradation when irradiated with UV light. The formation of by-products, such as HCl and short-chain fragments, caused a decrease in weight, and undesirable changes within the PVC surface were noticeably lower in the presence of additives. The degree of aromaticity in complexes played an essential role in determining their efficiency as PVC photostabilizers. The organotin containing the highest number of phenyl groups were the most effective complex in reducing the PVC photodegradation. The additives acted as a PVC photostabilizer through coordination with polymeric chains and as UV light absorbers and scavengers for HCl and radicals.

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