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Article

A Process for the Synthesis and Use of Highly Aromatic Organosilanes as Additives for Poly(Vinyl Chloride) Films

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Abstract: Three organosilanes were synthesized in good yields from the condensation of 4,4',4''-((phenylsilanetriyl)tris(oxy))tribenzaldehyde and 4-substituted anilines under acidic conditions. The structure of the organosilanes was confirmed using a variety of techniques. Organosilanes were mixed with poly(vinyl chloride) (PVC) and homogenous films were produced. The effect of long-term irradiation on the films containing organosilanes was tested using various methods. Monitoring the infrared spectra of PVC films before, during and after irradiation processes showed the formation of side products comprising polyene, carbonyl and hydroxyl groups. The intensities of absorption bands due to these functional groups were much lower in the presence of organosilanes as compared to the blank film. Also, the decrease in the weight and molecular weight of PVC films after irradiation was lower in the presence of organosilanes. Additionally, there was a minimal surface change of irradiated PVC in the presence of organosilanes. Clearly, organosilanes act as inhibitors, particularly the one containing the hydroxyl group, for the photodegradation of PVC. Different mechanisms were proposed to speculate the role played by organosilanes in stabilizing PVC against long-term ultraviolet light exposure.

Keywords: organosilanes; Schiff's bases; photostability; dehydrochlorination; ultraviolet irradiation absorbers; weight and molecular weight loss

1. Introduction

The incorporation of additives to polymers has become a hot research topic and has attracted attention from the researchers' community [1]. Such process improves the physical, electrical, mechanical and thermal properties of polymers along with their performance in outdoor applications [2]. Poly(vinyl chloride) (PVC) is a very common thermoplastic and contributed to ca. 1.6 million jobs in Europe along with a turnover of EU 360 billion in 2019 [3]. Globally, PVC contributes to over 12% of the total produced plastics [4]. PVC can be produced as rigid and flexible materials. Rigid PVC is used in building constructions, credit cards and bottles. In contrast, flexible PVC is used in the production

of cables, wires, tubes, floorings and films for packing [5]. The applications of PVC are limited due to its low thermal and photochemical stability resulting from its photooxidation and photodecomposition [6]. At a high temperature and in the presence of oxygen, the direct exposure of PVC to ultraviolet (UV) light leads to undesirable changes. These changes include the formation of cracks, cross-linking, loss of colour, transparency, mechanical performance and volatiles, along with decreases in weight and molecular weight [7]. These limitations can be overcome by the addition of additives to PVC [8]. PVC has been embedded with a variety of materials that can improve its resistance toward chemicals and harsh environments and enable its use in many applications [9,10]. The additives are mainly present as solids in the form of flakes, powders, spheres and beads. The form of the additive mainly depends on the synthetic procedure used. Few additives can be used in the liquid form, but such process cannot be employed at high temperature to ensure homogeneity of the mixture [2].

Plasticizers are common PVC additives that enhance the toughness and flexibility of polymers. Additionally, they tend to reduce the glass transition temperature, melt viscosity and density of PVC [11]. Plasticizers produce secondary bonds among polymeric chains and act as spacers to hinder the interaction between PVC chains [12]. The most common PVC plasticizers are phthalic acid esters (e.g., diisononyl and diethylhexyl phthalates). They are colourless and soluble in most solvents. However, the health risk associated with phthalates hinder their use, particularly in medical applications [13]. Another class of PVC additives are flame retardants, which tend to reduce the formation of volatiles upon the exposure of polymers to sources of oxygen and heat [2]. Small volatile residues are produced because of the scission of PVC chains. The most common flame retardants are tetrabromobisphenol A, hexabromocyclododecane, aryl phosphates and aluminum hydroxide [14–17]. The toxicity of flame retardants poses risks to humans, animals and environment [18]. Impact modifiers (e.g., acrylic modifiers) are used to absorb harmful energy and can be added to PVC either at the polymerization or processing stage [19]. They increase the toughness of PVC to make it suitable for use in window frames [20]. The autoxidation process of PVC due to the formation of free radicals can be inhibited by the addition of antioxidants [21]. The limitations associated with commercial additives have inspired researchers to find and develop effective and toxicity-free PVC photostabilizers. The thermal stability of PVC has been improved using various hydrogen chloride (HCl) scavengers such as hydrotalcites [22,23] and silicon-based nanomaterials [24].

Recently, several Schiff bases containing aromatic or heterocyclic moieties [25–30], highly aromatic metal complexes [31–35], aromatics [36–38], polyphosphates [39–41] and other compounds [42–44] have been used as PVC additives. Silicon-containing compounds have shown promising results in the chemistry of polymers [45]. For example, silane compounds have been used to produce cross-linked PVC materials to improve its strength and gel content [46–48]. Therefore, this study reports the synthesis, structures characterization and use of three organosilane Schiff bases as the additives for PVC to inhibit its photodegradation upon exposure to UV irradiation. The synthesized organosilanes are highly aromatic and contain seven aryl rings. Aromatic units are the active ingredients for effective PVC additives because they act as absorbers for harmful UV irradiation. Indeed, the results showed that organosilanes remarkably improved PVC photostability.

2. Materials and Methods

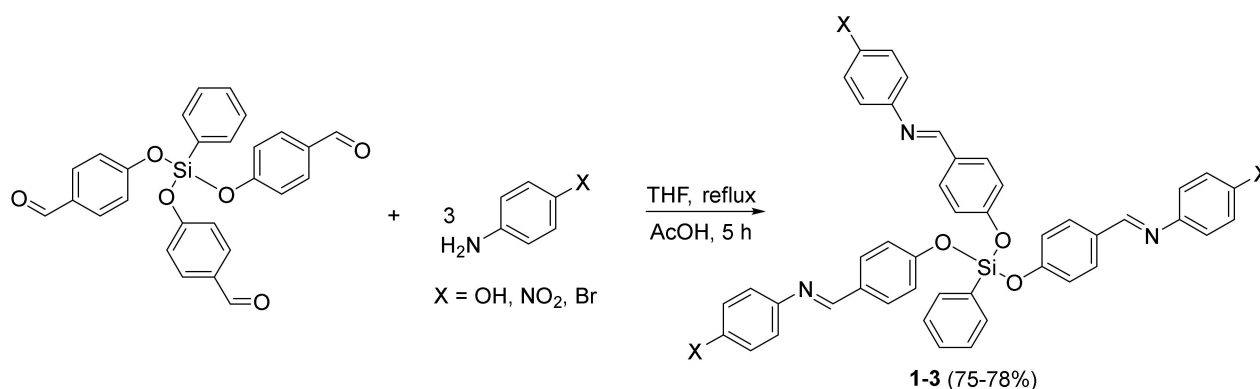
2.1. General

PVC was obtained from Petkim Petrokimya (Istanbul, Turkey). The PVC degree of polymerization was 800 with a K-value of 67. Chemicals were obtained from Sigma-Aldrich (Gillingham, UK). The melting points were recorded using a Gallenkamp apparatus (Galgary, Canada). Fourier-transform infrared (FTIR) spectra ($400\text{--}4000\text{ cm}^{-1}$; KBr disc) were recorded using a Shimadzu 8400 Spectrophotometer (Kyoto, Japan). ^1H (500 MHz) and ^{13}C Nuclear Magnetic Resonance (NMR) (125 MHz) spectra were recorded on a Bruker DRX-500 NMR spectrometer (Zürich, Switzerland) in dimethyl sulfoxide- d_6 (DMSO- d_6). The scan-

ning electron microscopy (SEM) images were recorded using a KYKY-EM3200 digital microscope (FEI Company; Prague, Czech Republic). A Bruker XFlash 6 10 (Bruker, Tokyo, Japan) was used to record the energy dispersive X-ray (EDX) spectra. The PVC films were coated by gold (Au; ca. 15 nm) before the EDX was performed. The PVC films were irradiated at 25 °C using a QUV-accelerated weathering tester obtained from Q-Panel Company (Homestead, FL, USA). The thickness of the PVC films was maintained and fixed at ca. 40 µm using a DIN 862 digital calliper micrometre (Vogel GmbH; Kevelaer, Germany).

2.2. Synthesis of Organosilanes 1–3

A stirred mixture of 4,4',4''-((phenylsilanetriyl)tris(oxy))tribenzaldehyde (4.68 g, 10 mmol) and aryl amine (33 mmol; 4-aminophenol, 4-nitroaniline or 4-bromoaniline) in tetrahydrofuran (THF; 25 mL) containing glacial acetic acid (AcOH; 0.5 mL) was refluxed for 5 h. The solid formed upon cooling the mixture was collected by filtration, washed with hexane and dried in a vacuum oven at 60 °C for 1 h to obtain the corresponding organosilane (Scheme 1) in 75–78% yield (Table 1). Tables 1–4 report the physical and spectroscopic data for organosilanes 1–3.



Scheme 1. Synthesis of organosilanes 1–3.

Table 1. Physical properties for 1–3 organosilanes.

Organosilane	X	Color	Yield (%)	Calculated (Found)		
				C	H	N
1	OH	Brown	75	72.85 (72.90)	4.76 (4.79)	5.66 (5.68)
2	NO ₂	Dark brown	78	65.21 (65.23)	3.89 (3.92)	10.14 (10.16)
3	Br	Light brown	77	58.08 (58.12)	3.47 (3.52)	4.52 (4.55)

Table 2. Some common Fourier-transform infrared (FTIR) data for organosilanes 1–3.

Organosilane	FTIR (cm ⁻¹)					
	C–O	Si–O	C=C	C=N	C–H	OH
1	1136	1161	1526	1624	3094	3460
2	1144	1178	1518	1595	3078	-
3	1136	1171	1502	1597	3061	-

Table 3. ^1H Nuclear Magnetic Resonance (NMR) spectral data for organosilanes 1–3.

Organosilane	$^1\text{HNMR}$ (500 MHz: δ , ppm, J in Hz)
1	9.93 (s, exch., 3H, 3 OH), 8.29 (s, 3H, 3 CH=N), 7.62 (d, $J = 8.0$ Hz, 6H, Ar), 7.51 (d, $J = 8.0$ Hz, 6H, Ar), 7.53–7.27 (m, 5H, Ph), 6.90 (d, $J = 8.0$ Hz, 6H, Ar), 6.41 (d, $J = 8.0$ Hz, 6H, Ar)
2	8.48 (s, 3H, 3 CH = N), 8.20 (d, $J = 8.0$ Hz, 6H, Ar), 7.75 (d, $J = 8.0$ Hz, 6H, Ar), 7.51–7.43 (m, 5H, Ph), 7.08 (d, $J = 8.0$ Hz, 6H, Ar), 6.82 (d, $J = 8.0$ Hz, 6H, Ar)
3	8.73 (s, 3H, 3 CH=N), 7.82 (d, $J = 7.9$ Hz, 6H, Ar), 7.79 (d, $J = 7.9$ Hz, 6H, Ar), 7.57–7.44 (m, 5H, Ph), 7.00 (d, $J = 7.9$ Hz, 6H, Ar), 6.88 (d, $J = 8.0$ Hz, 6H, Ar)

Table 4. ^{13}C NMR spectral data for organosilanes 1–3.

Organosilane	$^{13}\text{CNMR}$ (125 MHz: δ , ppm)
1	170.4, 156.9, 154.2, 145.4, 144.3, 132.7, 132.1, 131.6, 129.9, 128.1, 124.3, 120.2, 115.4
2	170.4, 154.2, 151.8, 145.5, 131.9, 131.6, 131.0, 129.9, 129.0, 127.8, 126.1, 122.8, 120.2
3	170.3, 154.2, 150.6, 149.8, 131.4, 130.6, 129.4, 129.1, 128.9, 126.1, 122.8, 120.7, 120.2

2.3. Preparation of PVC Films

The casting solution technique was used to prepare the PVC films. A mixture of the appropriate organosilane (25 mg) and PVC (5 g) in THF (50 mL) was stirred for 2.5 h at 25 °C. The homogenous solution was poured into a glass plate containing holes with a thickness of ca. 40 μm . The films were allowed to dry at 25 °C for 16 h followed with drying in a vacuum oven at 40 °C for 4 h.

2.4. Irradiation of PVC Films

A UV light ($\lambda_{\text{max}} = 365$ nm) with a light intensity of 6.2×10^{-9} ein $\text{dm}^{-3} \text{s}^{-1} \text{nm}$) was used to irradiate the PVC films. During the irradiation process, the films were allowed to rotate regularly to ensure their exposure to a similar light intensity from all the sides.

3. Results and Discussion

3.1. Synthesis of Organosilanes 1–3

Reactions of 4,4',4''-(phenylsilanetriyl)tris(oxy)tribenzaldehyde and three mole equivalents of an aryl amine (4-aminophenol, 4-nitroaniline or 4-bromoaniline) in boiling THF containing AcOH for 5 h gave the corresponding organosilanes 1–3 in high yields (Scheme 1). Table 1 shows some of the physical properties of organosilanes 1–3.

The FTIR spectra of organosilanes 1–3 (Figures S1–S3) confirmed the absence of the carbonyl group of the starting material and the appearance of azomethine bond ($-\text{CH}=\text{N}-$) as a strong adsorption band within the 1595–1624 cm^{-1} region. Table 2 shows some of the most common FTIR absorption bands for organosilanes 1–3.

The structures of organosilanes 1–3 were further confirmed using the NMR spectroscopy. The ^1H NMR spectra of organosilanes 1–3 (Figures S4–S6) showed the presence of azomethine proton as a singlet at 8.73–8.29 ppm (Table 3). The appearance of such signal at a very low field confirms the formation of Schiff bases. For organosilane 1, the hydroxyl proton appeared at 9.93 ppm as an exchangeable singlet. Additionally, the spectra showed the presence of aryl protons at the predicated chemical shifts.

The ^{13}C NMR spectra (Figures S7–S9) showed the presence of 15 signals for each organosilane at the predicated chemical shifts (Table 4). The azomethine carbon appeared down-fielded at 170 ppm region, which is an evidence for the formation of organosilanes 1–3.

3.2. FTIR Spectroscopy Study of Photodegradation by UV Irradiation

The photodegradation of PVC starts at the surface and then penetrates deep within the polymer due to the absorption of the UV light. In the presence of oxygen, the photooxidation of PVC occurs, further causing cross-linking, chain scission, bond breaking

and the elimination of volatiles [49]. Low molecular weight fragments containing alkenes (C=C), ketones (C=O) and alcohols (OH) are the most common by-products of PVC photodegradation [50]. Therefore, the development within the FTIR spectra with respect to the intensity of the absorption bands corresponding to the C=C, C=O and –OH groups was used to measure the degree of photodegradation for the irradiated PVC films.

To test the role of organosilanes 1–3 as additives, they were mixed with PVC at a concentration of 0.5% by weight and thin films with a thickness of ca. 40 μm were produced. Such concentration of additives has been proven to be effective, as previously reported [51], without causing undesirable change in the colour of polymer [36]. The PVC films were irradiated with a UV light for a time ranging from 50 h to 300 h and the FTIR spectra of the irradiated films were recorded. Figure 1 shows the FTIR spectra of PVC (blank) before and after irradiation (300 h). It was clear that, after irradiation, the absorption bands at 1604 cm^{-1} (C=C), 1722 cm^{-1} (C=O) and 3500 cm^{-1} (OH) became more intense as compared with that for the C–H bond in PVC. The C–H bond was used as a reference because its intensity is not altered by irradiation.

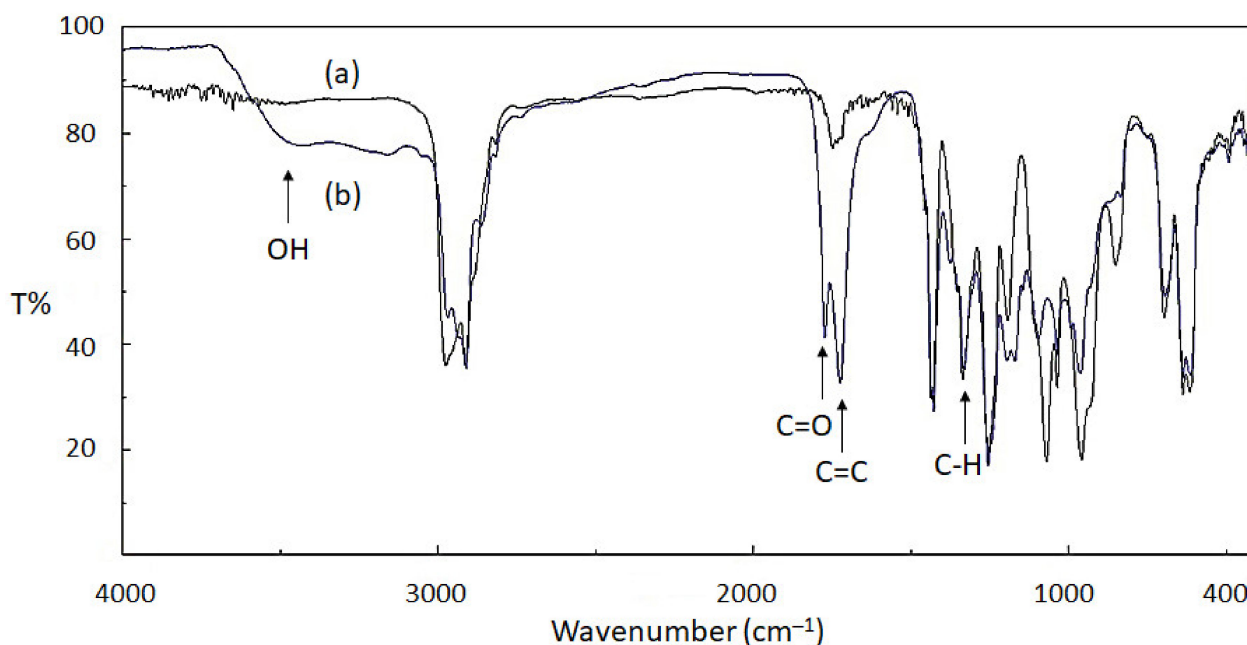


Figure 1. FTIR spectra of poly(vinyl chloride) (PVC) (blank): (a) Before irradiation and (b) after irradiation.

The growth in absorption bands for the C=C, C=O and –OH groups was monitored to test the effectiveness of organosilanes 1–3 as PVC additives. Equation (1) was used to calculate the functional index (I_g) using the absorbance of the functional group (A_g) and that for the C–H bond (A_r) [52,53].

$$I_g = A_g/A_r \quad (1)$$

Figure 2a shows the change in the $I_{C=C}$ versus the time of irradiation (hours). The change in the $I_{C=C}$ was very sharp in the first 50 h and then increased steadily with the progression of time. It was clear that the growth of the $I_{C=C}$ was much higher in the case of the blank film as compared with those containing organosilane 1–3. For example, the $I_{C=C}$ was 1.16 for the PVC (blank) after 300 h of irradiation. In contrast, the $I_{C=C}$ values for the PVC + 1, PVC + 2 and PVC + 3 films at the end of irradiation process were 0.72, 0.80 and 0.89, respectively. Clearly, these additives acted as inhibitors for PVC photodegradation. Organosilane 1 that contains a hydroxyl group showed the highest inhibitory effect for PVC photodegradation followed by 2 and 3.

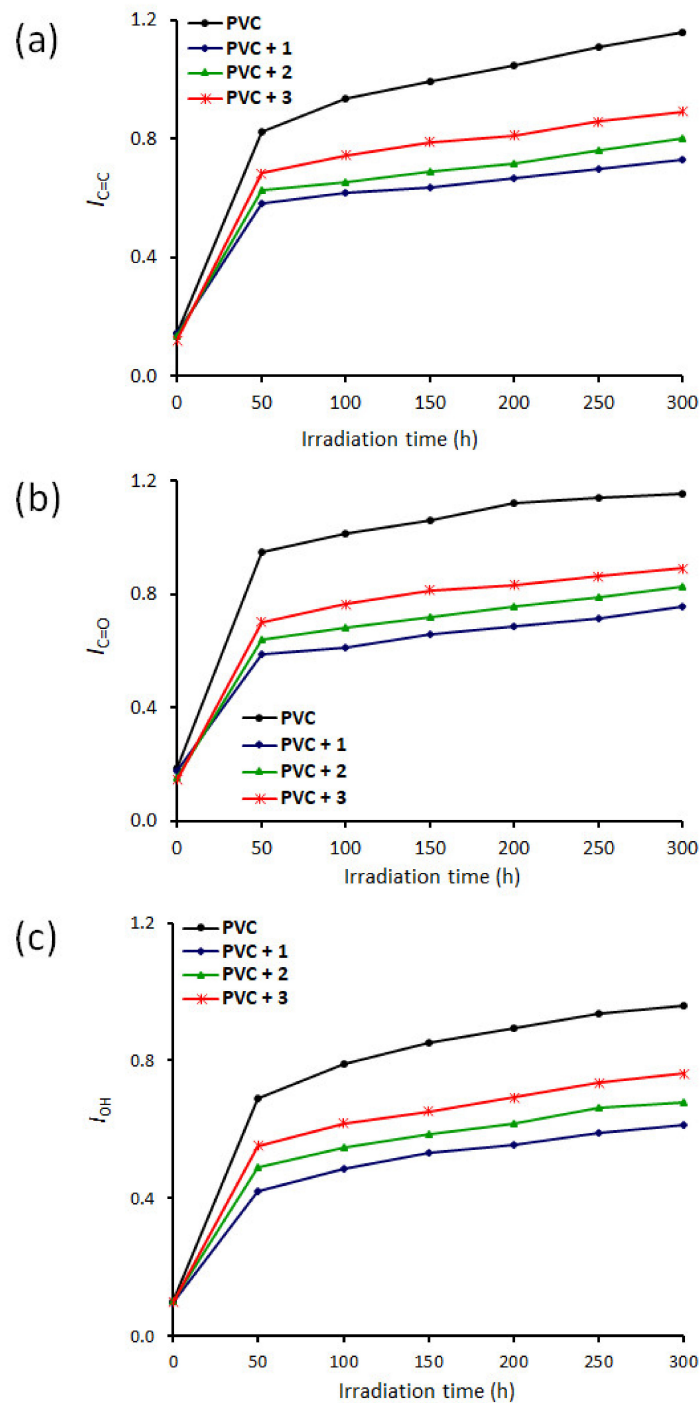


Figure 2. Effect of organosilanes 1–3 on the (a) $I_{C=C}$, (b) $I_{C=O}$ and (c) I_{OH} .

For the $I_{C=O}$, the change was lower for PVC films containing organosilanes 1–3 as compared with that for the blank film (Figure 2b). Again, organosilane 1 showed the most PVC-stabilizing effect. The $I_{C=O}$ values after 300 h of irradiation were 1.16, 0.76, 0.83 and 0.89 for the blank PVC film and those containing 1, 2 and 3, respectively.

Similarly, the change in the I_{OH} was higher for the blank PVC film as compared with the films containing organosilanes 1–3 (Figure 2c). After 300 h of irradiation, the I_{OH} values were 0.96, 0.62, 0.68 and 0.76 for the PVC, PVC + 1, PVC + 2 and PVC + 3 films, respectively. Clearly, monitoring and inspecting the FTIR spectra of irradiated PVC films indicated that organosilanes 1–3 acted as good PVC photostabilizers and inhibited the formation of by-product fragments that contained the C=C, C=O and OH groups.

3.3. Effects of UV Irradiation on Weight Loss and Average Molecular Weight

PVC photooxidation causes cross-linking and the elimination of HCl due to the formation of free radicals [54]. PVC dehydrochlorination process decreases the weight of polymer. The effectiveness of organosilanes 1–3 as PVC photostabilizers was tested through the measurement of weight loss resulting from photooxidation and photodegradation. Equation (2) was used to calculate the percentage of weight loss, where W_1 and W_2 are the PVC weight before and after irradiation, respectively.

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

The PVC weight loss was very sharp at the beginning of irradiation process (50 h) and was high in the absence of organosilanes 1–3 (Figure 3a). Clearly, the additives played an important role in stabilizing the PVC. The blank PVC film lost 0.70% and 1.39% of its weight after 50 h and 300 h of irradiation, respectively. For the PVC films containing organosilanes, the weight loss was 0.50%, 0.57% and 0.65% at the end of irradiation process. Again, organosilane 1 showed the most PVC stabilizing effect among the used additives. The weight loss from the blank film was 278% higher as compared with the one containing additive 1.

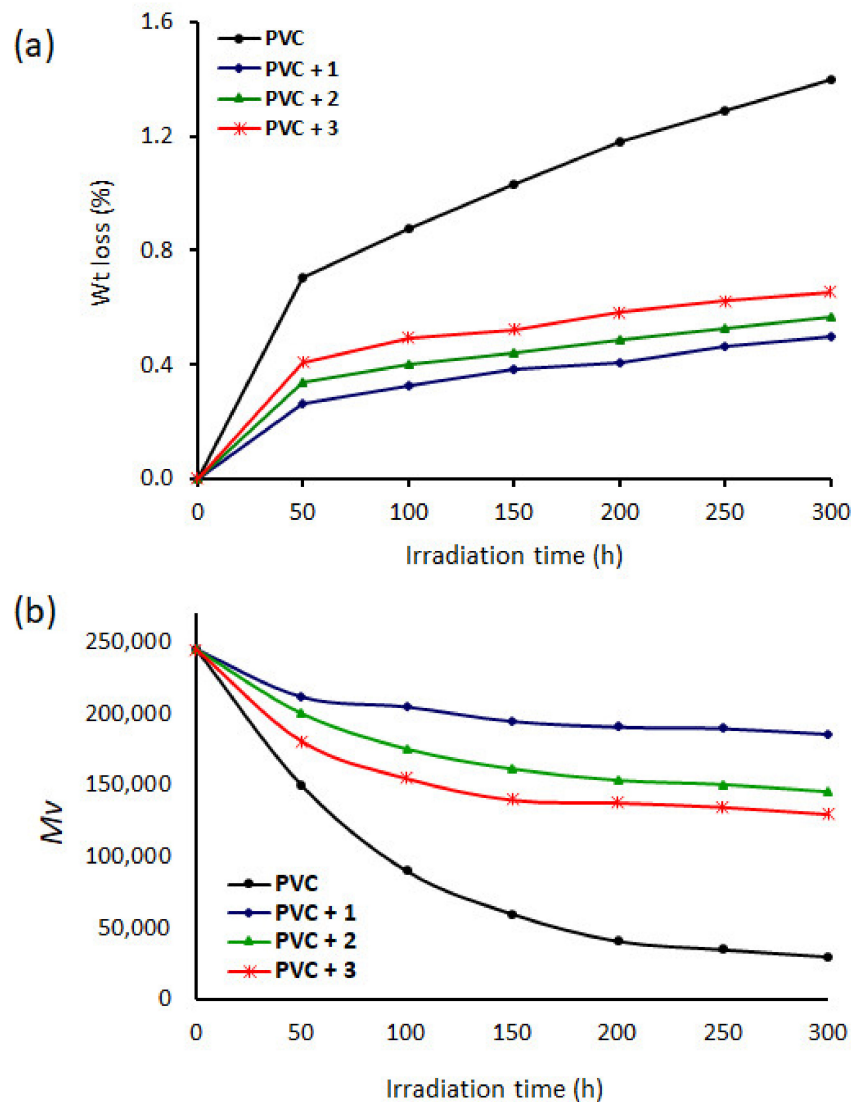


Figure 3. Effect of organosilanes 1–3 on the (a) weight loss (%) and (b) \bar{M}_V of PVC.

PVC photodegradation causes chain scission and the formation of small polymeric fragments and, therefore, a decrease in the average molecular weight (\overline{M}_V) [55]. Several PVC films were irradiated for different periods ranging from 50 h to 300 h. Following irradiation, THF was added to the films with stirring followed by filtration to remove the insoluble residues. The intrinsic viscosity $[\eta]$ was measured for the solutions using a viscometer and the \overline{M}_V was calculated using Equation (3) [56]. Figure 3b shows the decrease in the \overline{M}_V of the irradiated PVC films.

$$[\eta] = 1.38 \times 10^{-4} M_v^{0.77} \quad (3)$$

There was a massive decrease in the \overline{M}_V of PVC in the case where no additive was present as compared with the ones containing organosilanes. For the blank PVC, the \overline{M}_V decreased from 245,000 to 150,000 after 50 h of irradiation and decreased further to 30,000 at the end of irradiation process (300 h). The decrease in the \overline{M}_V was much less in the presence of the organosilanes, which clearly prove their role as photostabilizers for PVC. After 300 h of irradiation, the \overline{M}_V values were 186,000, 145,000 and 130,000 for the PVC + 1, PVC + 2 and PVC + 3 blends, respectively. The decrease in the \overline{M}_V was more than 87% for the blank film and only 24% for the PVC containing organosilane 1. Clearly, the results obtained from the FTIR spectroscopy show that weight loss and average molecular weight were in agreement and confirm that organosilanes and, in particular, complex 1, acted as PVC stabilizers against UV irradiation.

3.4. Effects of UV Irradiation on Surface Morphology and Chlorine Content by SEM/EDX

The effect of irradiation on the PVC surface in terms of smoothness, regularity and homogeneity was investigated using SEM [57,58]. The surface of nonirradiated PVC was free from defects, spots and cracks and showed a high degree of smoothness and regularity (Figure 4a). In contrast, the surface of the irradiated (300 h) PVC (blank) was irregular and comprised cracks and white spots (Figure 4b). The elimination of HCl from the PVC leads to a cross-linking and formation of cracks and spots, which vary in shape and size. The damage in the surface of PVC containing organosilanes 1–3 was less noticeable as compared to that which appeared within the surface of the PVC in the absence of organosilanes (Figure 4c–e). The minimum surface damages took place in the presence of organosilane 1 (Figure 4c).

The EDX spectra of PVC films (Figures S10–S14) showed strong absorption bands for the atomic chlorine and carbon. Additionally, the PVC containing organosilanes 1–3 showed new bands corresponding to silicon, nitrogen and oxygen atoms. The band corresponding to the atomic nitrogen was more abundant for the PVC + 2 blend as compared with the others. Furthermore, the EDX spectrum of PVC + 3 showed the presence of atomic bromine. The assignment of the EDX peaks is in agreement with those reported previously [59]. The atomic percentage of oxygen increased with the progression of irradiation. As a result, the increased rate of PVC photooxidation caused a decrease in the content of atomic chlorine due to the elimination of HCl. Moreover, there was a reduction in the atomic carbon as a result of cross-linking and formation of short-chain fragments. Following irradiation of the blank PVC, the EDX measurements showed that the percentages for both atomic carbon and chlorine were decreased. In contrast, the decrease in both atomic contents of carbon and chlorine for PVC/organosilane blends were less significant due to reduction of HCl fumes produced during the combustion processes [54]. Again, organosilanes were proven to act as PVC photostabilizers.

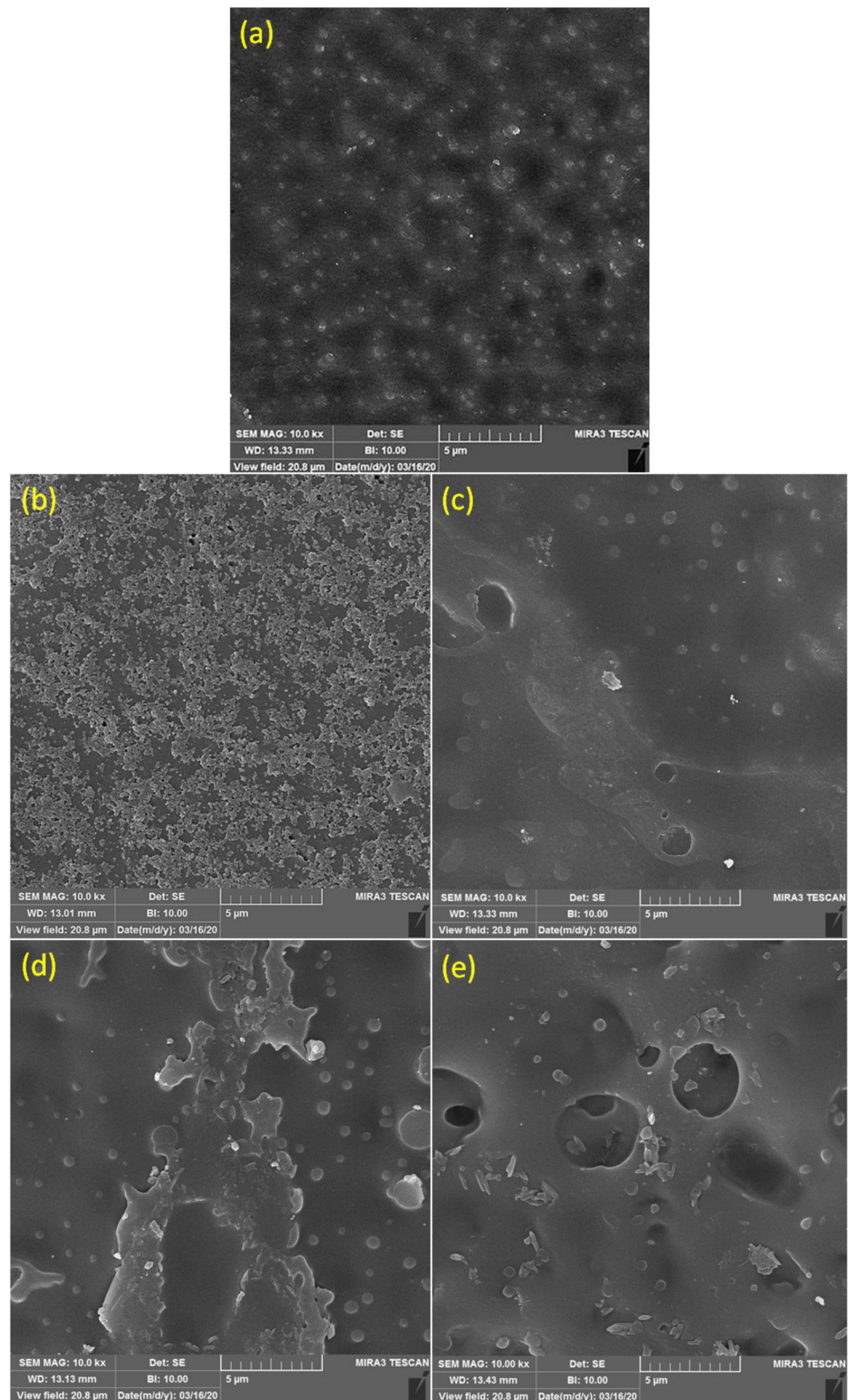


Figure 4. SEM images of the: (a) Blank PVC before irradiation and (b) blank PVC, (c) PVC + 1, (d) PVC + 2 and (e) PVC + 3, after irradiation.

3.5. Photostabilization Proposed Mechanisms

Photostabilizers provide protection for PVC against the UV light and hinder bond breaking within the polymeric chains. Organosilanes 1–3 can stabilize PVC against photodegradation through different mechanisms.

They can stabilize the PVC through their abilities of absorbing UV irradiation. The aromatic moieties (phenyl and aryl groups) that build up within the skeleton of organosilanes act as the absorbers for UV irradiation. These groups can release the absorbed energy as heat at a rate that does not cause harm to PVC [36]. The hydroxyl (strong electron-donating), nitro (strong electron-withdrawing) and bromine (inductive electron-withdrawing) groups attach to the aryl groups, leading to different performance outcomes of organosilanes. The hydroxy group leads to the most PVC stabilizing effect due to enhancing the resonance of the aryl groups. Additionally, the $-\text{CH}=\text{N}$ bond directly absorbs the UV light and forms an excited stable charge-separated species (Figure 5a). Such group can release the absorbed light energy as heat through rotation and vibration without harming PVC.

Organosilanes 1–3 can act as radical scavengers in the presence of a chromophore (POO) [60]. Organosilanes interact with chromophores (polymeric proxy radicals; POO^\cdot) [49] to produce stable complexes (Figure 5b). The effect of the absorbed energy can be neutralized and stabilized through the resonance of aryl groups and then transferred over a large number of atoms.

Organosilanes enhance the PVC photostability through coordination between the polarized atoms of the $-\text{CH}=\text{N}$ of the Schiff bases and the C–Cl bonds in the polymeric chains (Figure 5c). Additionally, the coordination between the polarized oxygen atoms within organosilanes with the carbon atoms of the C–Cl bonds can stabilize the polymer. The coordination bonds help in the transfer of the excited state energy from PVC to organosilanes without harming the polymer. However, the possibility of formation of strong coordination bonds within macromolecules is not high.

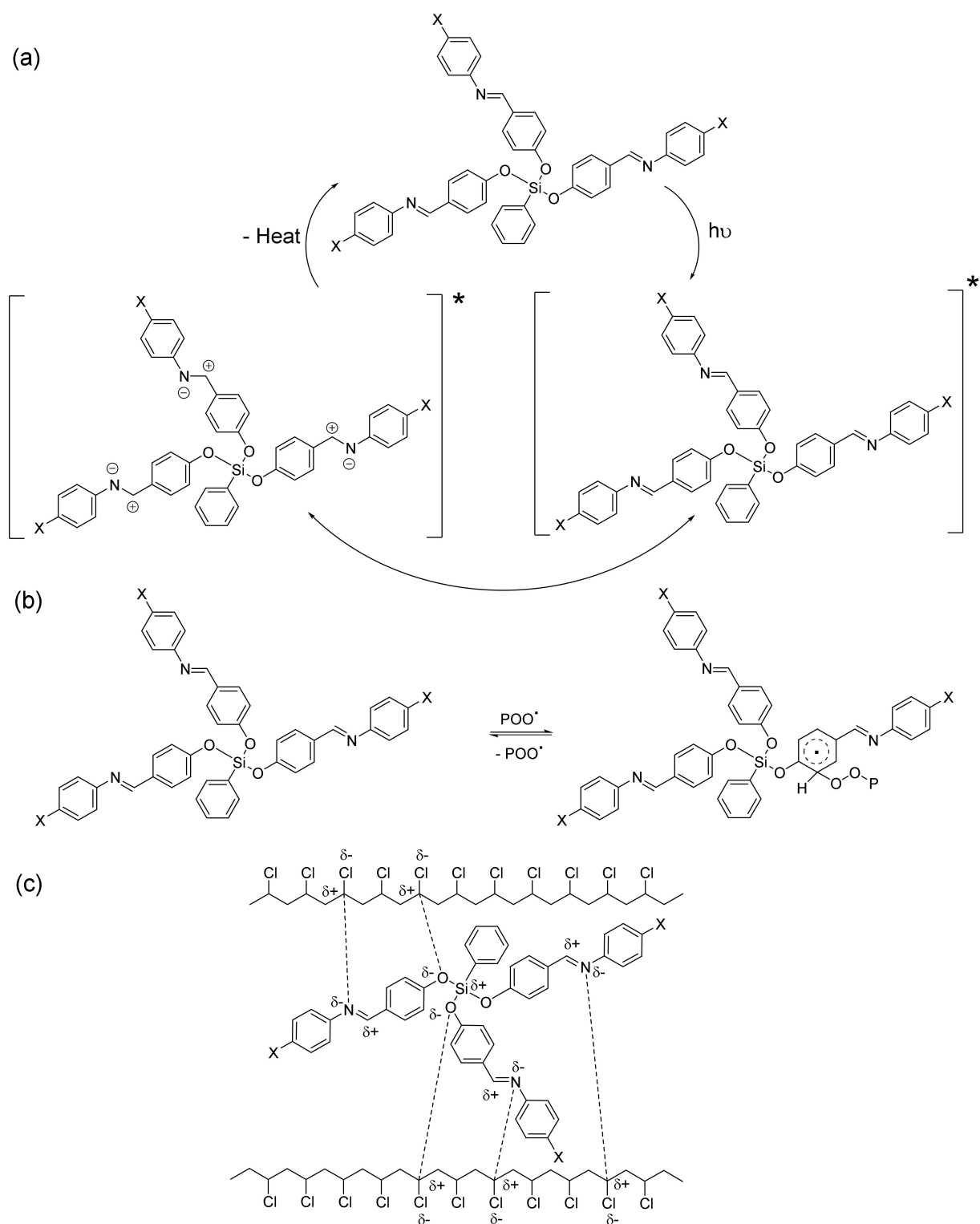


Figure 5. Organosilanes 1–3 act as: (a) UV irradiation absorbers, (b) radical scavengers and (c) stabilizers through the formation of coordination bonds with the polar C–Cl bonds within the PVC chains.

4. Conclusions

An efficient and simple synthetic procedure was used to produce three highly aromatic organosilanes that contained different substituents. The structure of the synthesized organosilanes was confirmed using a number of analytical and spectroscopic techniques.

The organosilanes acted as inhibitors for PVC photodegradation upon exposure to long-term UV irradiation. Organosilanes tended to reduce the formation of degradation by-products, decrease in weight loss and average molecular weight, and damage in the surface of polymer. The high aromatic content and azomethane moieties within the skeleton of organosilanes rendered them effective in reducing the rate of dehydrochlorination process and formation of small photodegradation by-products. Organosilanes acted as radical scavengers and absorbers for ultraviolet radiation.

Supplementary Materials: The following are available online at <https://www.mdpi.com/2227-9717/9/1/91/s1>, Figure S1: FTIR spectrum of **1**, Figure S2: FTIR spectrum of **2**, Figure S3: FTIR spectrum of **3**, Figure S4: ^1H NMR spectrum of **1**, Figure S5: ^1H NMR spectrum of **2**, Figure S6: ^1H NMR spectrum of **3**, Figure S7: ^{13}C NMR spectrum of **1**, Figure S8: ^{13}C NMR spectrum of **2**, Figure S9: ^{13}C NMR spectrum of **3**, Figure S10: EDX spectrum of PVC (blank) film before irradiation, Figure S11: EDX spectrum of PVC (blank) film after irradiation (300 h), Figure S12: EDX spectrum of PVC + **1** film after irradiation (300 h), Figure S13: EDX spectrum of PVC + **2** film after irradiation (300 h), Figure S14: EDX spectrum of PVC + **3** film after irradiation (300 h).

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