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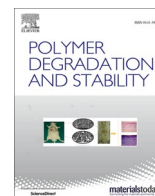
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Synthesis of silylamine and siloxyamine compounds: A novel approach to flame retardancy of polypropylene and Epoxy resins

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ABSTRACT

A series of innovative flame retardants containing N-Si and N-O-Si bonds have been synthesized. Their chemical structures were verified by nuclear magnetic resonance (NMR) spectroscopy and thermal stabilities determined by thermogravimetric analysis (TGA). The results indicate that their thermal and hydrolytic stabilities could be adjusted by fine tuning their silylamine (N-Si) and siloxyamine (N-O-Si) skeletons. Thus, the substituents bonded to the phthalimides, such as diphenylmethylsilyl, dimethylphenylsilyl, diphenyl-*tert*-butylsilyl, triisopropylsilyl or diphenylmethylsiloxy; whichever was attached to the imide played a significant role on its thermal and hydrolytic properties. Upon thermal dissociation, the N-Si and N-O-Si compounds were shown to yield aminyl, silyl and oxygen-centered radicals that provided fire proofing effect in polypropylene (PP) films alone and a synergistic effect in combination with conventional phosphorous flame retardant in PP, linear low-density polyethylene (LLDPE) and epoxy resins (EP). Their efficacy as flame retardants alone in thin PP films were evaluated according to the DIN4102-B2 test. Both N-Si and N-O-Si significantly slowed down the burning of PP films. Moreover, their potential as adjuvants with a conventional phosphorous based flame retardant, i.e., spirocyclic phosphonate (AFLAMMIT® PCO 900) in PP and EP resins was evaluated according to the UL-94 V fire standard. A synergistic effect was observed when the phosphorous flame retardant was combined with either N-Si or N-O-Si containing compounds, since none of the flame retardants by themselves could provide V-0 rating in the UL94-V test in PP, LLDPE or EP resins even at much higher loadings. The thermogravimetric analysis carried out under inert atmosphere revealed enhanced and earlier onset of decomposition and thermal activation of phosphorous based flame retardant in the presence of N-Si or N-O-Si in comparison to spirocyclic phosphonate, N-Si or N-O-Si used alone, respectively. The interaction of the phosphorus flame retardant with N-Si was verified by ^{31}P NMR.

1. Introduction

Today the concept of circular economy plays a vital role for industrial production of all goods [1]. Therefore, the plastics industry is also undergoing an overall transformation to better meet the criteria of recycling, sustainable production, and products [2]. The increasing amounts of plastic debris, and specifically micro(nano)plastic particles, highlights the need to address these threats to the ecosystems. Unfortunately, plastic waste is often mismanaged, and it ends up in the environment posing a high risk to our ecosystems. One additional topic that warrants further attention is the hazards associated with plastic additives within micro(nano)plastic as they can be persistent and can be biologically activated after entering the environment [3]. Most polymers need various types of plastic additives to fulfill pivotal end-product properties including long-term durability at service conditions and fire

safety [4]. Plastic additives are commonly admixed into the polymer matrix by blending. Therefore, they constitute potential vectors for the introduction of these chemicals into the environment as they gradually leach from plastic during use or disposal [5]. This process can be further accelerated through degradation and exposure to weathering.

In recent years, several plastic additives have been under scrutiny due to their potential ecotoxicity, bioaccumulation and tendency to act as endocrine disruptors. Concerns have been raised in the public domain on phthalate type of plasticizers in children's toys, on the toxicity of antimicrobial agents, nanoparticles and above all diverse flame retardants [6]. Toxicological and epidemiological [7] studies have shown that several man-made brominated as well as aryl-, halogenated and alkyl-substituted organophosphorus flame retardants found in human blood serum, breastmilk and food may induce cytotoxic effects [8]. Therefore, several brominated flame retardants have been or are being

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phased-out or have been added to the list of chemicals of high concern. The consumption of organophosphorus flame retardants may also decline due to toxicological uncertainties and since elemental phosphorus has been recently added on EU's list of critical raw materials in 2020.

It must be underlined that plastic additives are intentionally added into the polymer and therefore we need to rethink and thoroughly assess what type of plastic additives can be introduced without an ecological risk. Conscientious producers of flame retarded plastic products have made major efforts to find alternative flame retardant solutions. Their aim is better overall environmental profiles and additives that exhibit higher efficacies at already low loadings of < 5%. This has stimulated the development of next generation of flame retardants that can enhance the flame retardancy of polymers by scavenging free radicals mainly in the condensed phase by starving the flame zone of fuel and/or alternatively by enhancing the yield of polymer residue by crosslinking. In theory, radical generators may also exhibit gas-phase activity by scavenging the most active propagating free radicals (e.g., H[•], HO[•], etc.) which are responsible for the rapid reaction rates observed in flames [9].

Already in the 1960s, radical generators were observed to boost the activity of brominated flame retardants by catalysing the formation of bromine radicals which then reacted with the hydrocarbon polymer to form HBr [10]. The formed HBr molecule effectively interfered with the radical chain mechanism taking place in the gas phase whereby the flame is extinguished. Interest in organic radicals grew following Gomberg's groundbreaking discovery in 1900 of the triphenylmethyl radical, the first stable carbon-based radical [11]. Another clean way of generating carbon-centered radicals is by thermal decomposition of diazene compounds. The class of diazene and related compounds have proven to be effective as standalone flame retardants for polypropylene films at low loadings of 0.5–2 wt% [12]. Today, carbon-based radical generators such as dicumyl derivatives are typically used as synergists with brominated polymeric flame retardants for flame retarded expanded polystyrene (EPS) and/or XPS. Recently, several other radical generator families have been successfully applied as flame retardants either alone or in combination with conventional flame retardants in various polymer types. For instance, N-alkoxyamine (NOR) and sulfenamide type of radical generators have been commercialized as flame retardant synergists [13]. Alkoxyamines are known to thermally decompose to give aminyl/alkoxy and nitroxide/alkyl radicals pairs that exhibit fire proofing effect specially in thin section polypropylene films [14]. An aminyl radical is a neutral nitrogen-centered radical that has two bonded substituent groups, an unpaired electron, and a non-bonding pair of electrons. The substituents bonded to the nitrogen atom could be hydrogen, alkyl, phenyl, or heteroatoms; the type of substituent plays a significant role in its radical stability, its electronic structure, and properties. The challenge with aminyl radicals is that many of them are short-lived, highly reactive species; they readily undergo radical reaction pathways such as dimerization and hydrogen atom abstraction. Oxyimides is another group of precursors of nitroxide and carbonyl radicals that has been found to exhibit fire proofing properties in thin polypropylene sections alone or in combination with phosphorous flame retardants in thick sections [15].

Sulfenamides thermally dissociate to give simultaneously both aminyl- and sulfur-based radicals that display high flame retardant efficacy as standalone flame retardants in polystyrene (EPS), polyacrylate coatings and polypropylene films [16,17]. Compounds containing sulfur such as sulfide and disulfides in various forms have also been used as adjuvants to promote the activity of phosphorous based flame retardants [18,19]. The presence of sulfur alters the decomposition pathway of the phosphorous flame retardant, and the generated S-radicals promote higher pyrolytic residue [20]. More highly oxygenated sulfur containing additives such as sulfonate type of flame retardants liberate sulfur dioxide that dilutes the concentration of fuel fragments and/or react with the flame-propagating radicals in the gas phase [21].

In the past it has also been reported that silicon and silicon radicals can play a vital role as synergists in flame retardancy of various

polymers. Silicon radicals can be generated from e.g., siloxanes or cyclic aminylsilyles. Silicon as a part of flame retarding system has been more used either as a coating for plastics than within the polymer matrix [22] or then as a part of the matrix as a charring agent [23]. Several studies have shown the improvement in flame retardancy by combining phosphorus-nitrogen and silicon moieties in the flame retardant formulations [24–27]. Noteworthy, is that in these formulations the nitrogen and silyl atoms are not chemical bond to each other. Typically, the added silicon additives are in polymeric or oligomeric forms and required loadings are relatively high, i.e., ca. 10–20 wt.%. The silicon containing additives contribution to flame retardancy has been mainly attributed to silicon compound's ability to form a protective silica layer that shield the polymer from further thermal degradation and its ability to retard oxidation of the char. In general, for the phosphorus-nitrogen and silicon flame retardant formulations it has been shown that by using the three diverse elements together a high flame retardant effect can be achieved, whereas when using the compounds as single elements it has been very difficult to reach any good flame retardant properties. To the best of our knowledge, the only example of utilizing aminylsilyl and aminylsiloxy compounds as synergistic radical generators at low loading of 1–2 wt% together with traditional phosphorous flame retardants have been recently reported in two patent applications by us [28,29].

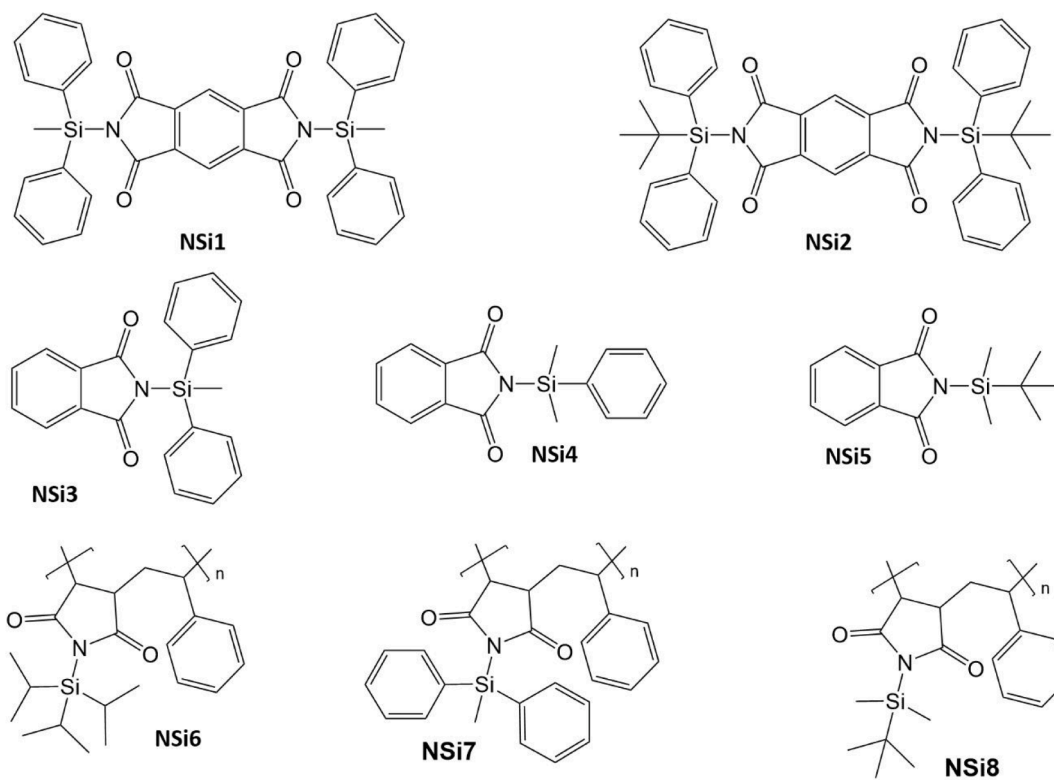
In the present paper we have shown for the first time that a new family of radical generators based on compounds containing N-Si and N-O-Si bonds can be used as flame retardants by themselves and that they exhibit a very high synergistic effect with traditional phosphorous compounds. Moreover, also polymeric aminylsilane and aminylsiloxy analogues have been successfully prepared. Their chemical structures are depicted together with the phosphorous flame retardant in Fig. 1. Their potential as standalone flame retardant in PP and as adjuvants with conventional phosphorous flame retardants for PP, LLDPE and epoxy resins was evaluated according to the UL-94 V standard.

2. Experimental part

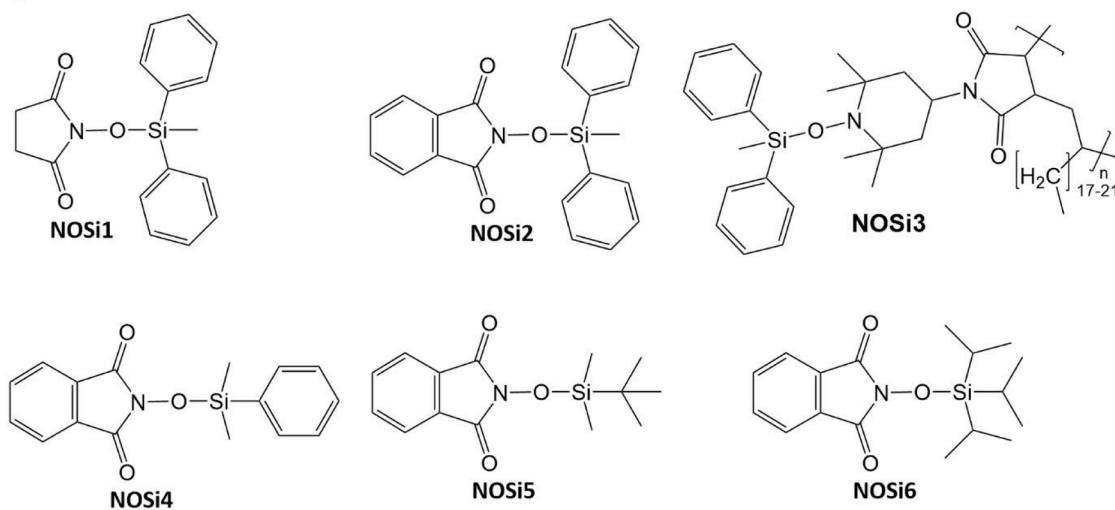
2.1. Materials and sample preparation methods

All chemicals used for the synthesis were of reagent grade. Solvents from Sigma-Aldrich, Finland were used directly from fresh bottles or dried over 3 Å molecular sieves for at least 48 h under argon atmosphere. Silanes were purchased from ABCR and used without further purification, whereas reagent grade phthalimide (>99%), pyromellitic diimide (97%), and triethyl amine (>99%) were purchased from Sigma-Aldrich and used without further purification. The phosphorous flame retardants AFLAMMIT® PCO 900 (24% P, melting 230–245 °C) (P1) and AFLAMMIT® PNN 978 (multi-component blend flame retardant based on ammonium polyphosphate) (P2) were obtained from Thor GmbH., Germany. Flame retardants were melt-blended with polypropylene (PP MFR25, MOPLEN HP552R from LyondellBasell, Netherlands, MFR 25 g/10 min (230 C/2.16 kg)). The polypropylene powder was mixed with an additional flame retardant synergist. This mixture was fed to a dosing balance of an extruder (model Coperion ZSK 18 K38). The silylamine or siloxyamine was fed to a side inlet of the extruder via a second dosing balance. Extrusion was carried out using the temperature profile detailed further below and at 300 rpm. The overall capacity of the extruder was 2 kg/h. The composition left the extruder via a slot die (dimensions 28 mm x 3 mm) and was cooled. The extruded strings were granulated to particles having a size in the range of approximately 0.1 to 0.5 mm. Temperature profiles in the extruder from polymer entry funnel to slot die in the case of polypropylene were: 180 °C / 190 °C / 195 °C / 200 °C / 195 °C / 190 °C / 185 °C. Test specimen of dimension 125 mm x 13 mm x 3.2 mm and 125 × 13 mm x 1.6 mm were prepared by injection molding, and subsequently stored at a relative humidity of 45 to 55% and a temperature of 20 to 25 °C for 24 h prior to testing of flame retardant efficacy according to UL-94 V standard. PP film samples for DIN 4102 tests were prepared by mixing the flame retardant to the

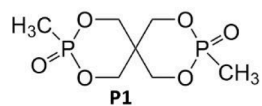
a) N-Si based flame retardants (1 to 8)



b) N-O-Si based flame retardants



c) Spirocyclic phosphonate



Uvinyl 5050

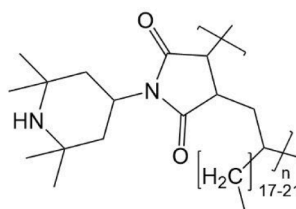


Fig. 1. Chemical structures of synthesized a) silylamines, b) siloxyamines and c) commercially available spirocyclic phosphonate (Aflammit PCO 900).

polymer with Haake Rheocord melt blender (Waltham, MA, USA) (60 rpm). Polypropylene, with processing aids Ca-stearate (Baerlocher, Unterschleißheim, Germany, 0.05 wt%) and Irganox® B 225 (0.3 wt%), was melted first for 1 min at 210 °C. Then flame retardant was added and the mixing was continued for five minutes. Crude polymer was crushed and then pressed with hydraulic press into a mold.

2.1.1. Epoxy thermosets were prepared as follows

Araldite GY 784, silylamine and the additional phosphorous flame retardant synergist were mixed for 30 s. Then Aradur 43 DB was added and carefully mixed by hand. Afterwards the system was mixed for 120 s. at 1,95 m/s with a dissolver (tooth plate, $d = 40$ mm, $n = 930$ rpm). After mixing the specimen was filled into a mold and stored for 24 h at a temperature of 23 °C and afterwards for 8 h at a temperature of 80 °C. Test specimen of dimension 125 mm x 13 mm x 3.2 mm and 125 x 13 mm x 1.6 mm were prepared by mill-cut and subsequently stored at a relative humidity of 45 to 55% and a temperature of 20 to 25 °C for 24 h.

2.2. Characterization methods

2.2.1. Characterization methods

NMR spectra (^1H , ^{31}P and ^{13}C) were recorded on a 500 MHz Bruker AVANCE-III NMR-system. Thermal treatment of FR mixtures for ^{31}P NMR analysis and radical mechanism verification study were done in the following manner: PCO-900 (18.4 mg) or 9,10-dihydroanthracene, N-Si denoted NSi2 (4.6 mg) or their 4:1 mixture (23 mg) were weighed into NMR-tubes and sealed under argon atmosphere. Samples were then placed in an oven and the temperature was set to 400 °C for 30 min. Depending on the sample, either dimethylsulfoxide- d_6 or chloroform- d was added to the tubes before the NMR analysis.

Thermogravimetric (TGA) and differential thermal analysis (DTA) was performed using an SDT Q600 apparatus from TA Instruments under N_2 atmosphere (flow rate 100 mL/min) and at the heating rate of 10 °C/min. Fourier transform infrared analysis (iS50 FTIR, Thermo Scientific) was used in connection to the TGA analysis. Transfer line temperature was 280 C. Different scanning calorimetry (DSC) was done under N_2 flow (50 mL/min) and heating/cooling rate of 20 °C/min with DSC250 device from TA Instruments. Temperature range of -90 °C to 150 °C was used for the heat-cool-heat method.

2.2.2. Test procedure of flame retardant properties

The flame retardant properties of test specimen were determined in a UL-94 fire chamber based on DIN EN 60,695–11–10. The test specimen was secured in the sample holders of the UL-94 15 fire chamber. The burner upper surface was positioned 1 cm below the lower surface of the test specimen, the flame was positioned in a 45° angle and a heating output of 50 W. The test specimen was exposed to the flame for 10 s, before removing the flame. If the test specimen extinguished by itself within 10 s, the process was repeated until the sample burned or until 5 cycles were performed. Test specimen which exhibited fire retardant properties below rating V 2 according to DIN EN 60,695–11–10 were marked as F. This rating was added to better distinguish the properties. It is not part of DIN EN 60,695–11–10. DIN 4101 tests were done in the same UL-94 test chamber, the specimen was attached to a frame so that the lower end of the film was 1 cm above the upper surface of the burner. Specimen were exposed to the flame for 15 s and the burning time and length were measured.

2.3. Synthesis of N-Si and N-O- Si type of flame retardants

2.3.1. Synthetic method

2.3.1.1. General procedure for the synthesis of silylphthalimides. To a solution of phthalimide (1 eq.) and Et_3N (1 eq.) in THF at 5 °C under argon atmosphere, was added dropwise the chlorosilane (1 eq.) in THF over 30

min. After complete addition, the mixture was allowed to warm up to room temperature and was stirred for 18 h. After filtration, organic solvent was evaporated under vacuum. The residue was treated with hot hexane and filtered while hot. The filtrate was cooled to -20 °C to yield, after filtration, crystals of silylphthalimide.

2.3.1.2. N-(diphenylmethylsilyl)phthalimide NSi3. Phthalimide (50.0 g, 0.27 mol), Et_3N (27.4 g, 0.27 mol), THF (180 mL), diphenylmethylchlorosilane (63.3 g, 0.27 mol), THF (80 mL) gave 84.3 g (90% yield) of N-(diphenylmethylsilyl)phthalimide.

^1H NMR (CDCl_3): 7.83 (dd, 2H), 7.72 (m, 6H), 7.49 (td, 2H), 7.43 (dd, 4H), 1.15 (s, 3H).

^{13}C NMR: 173.3, 135.1, 134.4, 134.0, 132.9, 130.4, 128.0, 123.3, -2.0 .

2.3.1.3. N-(dimethylphenylsilyl)phthalimide NSi4. Phthalimide (30.3 g, 0.20 mol), Et_3N (20.8 g, 0.20 mol), THF (400 mL), dimethylphenylchlorosilane (34.8 g, 0.20 mol), THF (200 mL) gave 37.6 g (65% yield) of N-(dimethylphenylsilyl)phthalimide.

2.3.1.4. N-(dimethyl-*t*-butylsilyl)phthalimide NSi5. Phthalimide (50.5 g, 0.34 mol), Et_3N (34.5 g, 0.34 mol), THF (500 mL), dimethyl-*t*-butylchlorosilane (51.5 g, 0.34 mol), THF (200 mL) gave 15.9 g (18% yield) of N-(dimethyl-*t*-butylsilyl)phthalimide.

^1H NMR (CDCl_3): 7.83 (dd, 2H), 7.71 (dd, 2H) 1.0 (s, 9H), 0.54 (s, 6H).

^{13}C NMR: 173.8, 134.0, 133.9, 123.0, 26.3, 19.0, -4.0 .

2.3.1.5.0. General procedure for the synthesis of pyromellitic diimides.

To a solution of pyromellitic diimide (1eq.) and chlorosilane (2eq.) in DCM at 0 °C under Argon, was added dropwise a solution of Et_3N (2eq.) in DCM. After complete addition, the mixture was refluxed for 20 h. The reaction was filtered, and the filtrate washed twice with 5% HCl solution, once with water, once with brine and dried over Na_2SO_4 . Solvent was evaporated under vacuum. The residue was washed with hexane to give the product as white solid.

2.3.1.6. N,N'-bis(diphenylmethylsilyl)pyromellitic diimide NSi1. pyromellitic diimide (0.9 g, 4.20 mmol), diphenylmethylchlorosilane (2.0 mL, 9.10 mmol) and Et_3N (1.4 mL, 9.01 mmol) in 30+10 mL DCM gave 0.40 g (15% yield) of the product.

^1H NMR (CDCl_3): 8.14 (s, 2H), 7.70 (dd, 8H), 7.50 (td, 4H), 7.44 (m, 8H), 1.15 (s, 6H). ^{13}C NMR: 172.2, 143.3, 138.6, 134.4, 134.0, 132.4, 122.7, 3.7.

2.3.1.7. N,N'-bis(diphenyl-*tert*-butylsilyl)pyromellitic diimide NSi2. Pyromellitic diimide (3.0 g, 13.9 mmol), diphenyl-*t*-butylchlorosilane (7.5 mL, 29.0 mmol) and Et_3N (3.9 mL, 29.0 mmol) in 50+15 mL DCM gave 2.7 g (28% yield) of the product.

^1H NMR (CDCl_3): 8.21 (s, 2H), 7.68 (dd, 8H), 7.48 (m, 4H), 7.41 (m, 8H), 1.30 (s, 18H).

^{13}C NMR: 170.9, 139.0, 135.5, 131.3, 130.4, 128.0, 118.7, 28.0, 20.0.

2.3.1.8.0. General procedure for the synthesis of siloxyphthalimides.

To N-hydroxy phthalimide (1eq) in THF (50 mL) and Et_3N (2eq) under inert atmosphere chlorosilane (0,75eq) in THF (20 mL) is added dropwise. The mixture is maintained at 20 °C for 4 h. The mixture is then filtrated and the solution phase is concentrated under vacuum. Hexane is added and the solution is again filtrated and solvent evaporated to give the pure compound as a white powder.

2.3.1.9. N-(methyl-diphenylsilyl)oxy succinimide NOSi1. N-hydroxy succinimide (4 g, 34,76 mmol), diphenylmethylchlorosilane (7,9 ml, 36,5 mmol) and triethylamine (8,6 ml) in 150 ml THF. White powder, 18% yield. ^1H NMR (CDCl_3): 7,77 (4H, dd), 7,48 (2H, tt), 7,41 (4H, tt), 2,40 (4H, s), 1,00 (3H, s).

2.3.1.10. *N*-(methyl-diphenylsilyl)oxy phthalimide NOSi2. N-hydroxy phthalimide (5 g, 30.66 mmol), diphenylmethylchlorosilane (7.4 ml, 34 mmol) and triethylamine (8.6 ml) in 150 ml THF. Light yellow powder (3.86 g, 36%).

¹H NMR (CDCl₃): 7.81 (4H, dd), 7.73 (2H, dd), 7.68 (2H, dd), 7.46 (2H, m), 7.41 (4H, t), 0.97 (3H, s). ¹³C NMR: 164.3, 138.9, 134.5, 134.0, 129.2, 128.0, 127.8, 123.2, -0.7.

2.3.1.11. *N*-(dimethylphenylsilyl)oxy phthalimide NOSi4. White powder.

¹H NMR (CDCl₃): 7.76 (4H, m), 7.70 (2H, m), 7.40 (3H, m), 0.66 (6H, s).

2.3.1.12. *N*-(*t*-butyldimethylsilyl)oxy phthalimide NOSi5. White powder, 81% yield. ¹H NMR (CDCl₃): 7.80 (2H, m), 7.73 (2H, m), 1.07 (9H, s), 0.27 (6H, s).

2.3.1.13. *N*-(tri-isopropylsilyl)oxy phthalimide NOSi6. White powder, 64% yield. ¹H NMR (CDCl₃): 7.81 (2H, m), 7.74 (2H, m), 1.35 (3H, m), 1.20 (18H, s).

2.3.1.14. Polymeric *N*-(methyl-diphenylsilyl)oxyamine from Uvinyl 5050 H NOSi3. Uvinyl 5050 H was dissolved in THF under Argon atmosphere, the solution was cooled on ice bath and then the silane was added. Et₃N in THF was then added dropwise, precipitation started with the addition. The mixture was then stirred on ice bath for 4 h and then in RT overnight. Mixture was filtered and the filtrate evaporated under reduced pressure. MeCN was added and the mixture let stand overnight, the residue started to form more viscous structure. After another washing with MeCN, the residue was dried under vacuum at 50 °C, 59% yield, approx. 20% silylation rate. ¹H NMR (CDCl₃): 7.77 (4H, dd), 7.48 (2H, tt), 7.41 (4H, tt), 1.30 (72H, s), 0.92 (10H, t), 1.00 (3H, s).

2.3.1.15.0. General procedure for the synthesis of silylmaleimide monomer. To a solution of maleimide (1 eq.) and Et₃N (1.05 eq.) in DCM at 0 °C under inert atmosphere, was added dropwise a solution of the chlorosilane (1.05 eq.) in DCM. The mixture was refluxed for 22 h. After cooling to room temperature, the reaction was washed with 5% HCl solution, water and brine. Organic phase was dried over Na₂SO₄ and solvent was evaporated under vacuum. The residue was washed with hexane to yield a white powder.

2.3.1.16. *N*-(tri-isopropylsilyl)maleimide NSi6. Maleimide (4.0 g, 41.2 mmol), Et₃N (6.0 mL, 43.3 mmol) and tri-isopropylchlorosilane (9.2 mL, 43.3 mmol) in 100+30 mL DCM gave 3.6 g (34% yield) of the product.

¹H NMR (CDCl₃): 6.75 (s, 2H), 1.75 (m, 3H), 1.11 (d, 18H).

¹³C NMR: 177.0, 136.2, 18.1, 11.6.

2.3.1.17. *N*-(diphenylmethylsilyl)maleimide NSi7. Maleimide (5.5 g, 56.6 mmol), Et₃N (8.0 mL, 59.4 mmol) and diphenylmethylchlorosilane (12.5 mL, 59.4 mmol) in 150+60 mL DCM gave 12.7 g (76% yield) of the product.

¹H NMR (CDCl₃): 7.65 (dd, 4H), 7.48 (tt, 2H), 7.42 (td, 4H), 6.72 (s, 2H), 1.0 (s, 3H).

¹³C NMR: 175.7, 136.5, 134.8, 132.6, 130.4, 128.0, -2.4

2.3.1.18. *N*-(dimethyl-*tert*-butylsilyl)maleimide NSi8. Maleimide (4.0 g, 41.2 mmol), Et₃N (6.0 ml, 43.3 mmol), Dimethyl-*t*-butylchlorosilane (6.4 g, 43.3 mmol) in 100+30 mL DCM gave 4.2 g (48% yield) of the product.

¹H NMR (CDCl₃): 6.7 (s, 2H), 0.96 (s, 9H), 0.47 (s, 6H).

¹³C NMR: 176.5, 136.2, 26.2, 18.9, -4.6.

2.3.1.19.0. Polymerization. *N*-(diphenylmethylsilyl)maleimide (13.5 g, 46.2 mmol), styrene (5.3 mL, 46.2 mmol) and perbenzoic acid (30 mg) were dissolved in dioxane (50 mL). The solution was stirred at 70 °C for 12 h. Solvent was removed with rotary evaporator. The residue was dissolved in small volume of THF and precipitated by slow addition of methanol (400 mL) while stirring the solution rapidly. The procedure

was repeated twice. After filtration and drying under vacuum at 110 °C for 18 h, white solid material (15.03 g, yield: 82%) was obtained.

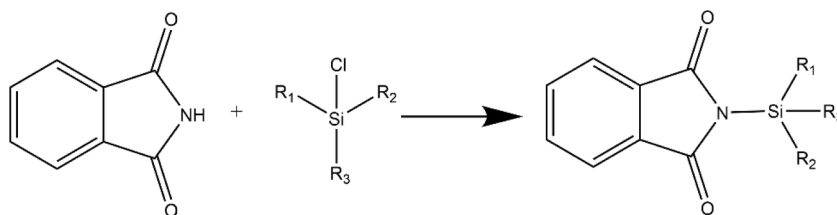
3. Results and discussion

The general synthetic route to silylamines (N-Si) comprised of reacting a monochlorosilane having the formula Cl-SiR₁R₂R₃ (R₁, R₂, R₃ = methyl, *tert*-butyl or phenyl) with a heterocyclic secondary amine such as phthalimide, pyromellitic diimide or maleimide in the presence of triethylamine to produce the desired N-Si compounds NSi1 to NSi5, as shown in Scheme 1. The synthetic yields varied between 15 and 100% in laboratory scale, during upscaling to pilot scale even higher yields could be obtained. Our attempts to prepare N-Si compounds using triphenylsilyl chloride with any of the secondary amines failed. Seemingly the triphenyl groups are sterically too crowded for the reaction to take place with the imide moiety. Whereas the polymeric silylamines (N-Si) 6, 7 and 8 were obtained by copolymerization of styrene with different N-(SiR₁R₂R₃) maleimides, respectively. While flame retardant candidates NOSi1, NOSi2 and NOSi3 were synthesized by reacting N-hydroxyphthalimide, Uvinol 5050H or 1-hydroxy-1-*H*-pyrrole-2,5-dione with diphenylmethylsilylchloride, respectively. Moreover, a series of sterically hindered N-O-Si compounds (NOSi4, NOSi5, NOSi6) were prepared by reacting N-hydroxyphthalimide with different sterically crowded silyl side groups, as shown in Table 1.

3.1. Thermal and hydrolytic stabilities

The TGA/DTA studies revealed that the sterically hindrance of the side-chain silyl group had a significant effect on the N-O-Si compounds thermal stabilities as shown in Table 1. Thus, the highest thermal stability of Td_{5%} (temperature of 5% mass loss) = 247 °C was recorded for diphenylmethylsilyloxyphthalimide (NOSi2) and the lowest for (*tert*-butyldimethylsilyloxy)phthalimide of 147 °C. Table 1 reveal that the thermal stabilities of the NOSi derivatives is dependent on the bulkiness of the silyloxy substituent, i.e. the thermal stability decreased in the following order: *N*-(methyl-diphenyl silyl)oxy phthalimide (NOSi2) > *N*-(tri-isopropylsilyl)oxy phthalimide (NOSi6) > *N*-(*t*-butyldimethylsilyl)oxy phthalimide (NOSi5). Moreover, NOSi compound having phthalimide group instead of succinimide exhibit a higher thermal stability (NOSi2 versus NOSi1). In general, it has been well established that N-O-Si type of molecules have rather high thermal stabilities, but they are easily hydrolysed in the presence of water or weak acids to silanol during storage and use. Therefore, we selected NOSi2 as the prime flame retardant candidate in the series of N-O-Si compounds, since it exhibited the highest thermal decomposition temperature, and it survived the polypropylene extrusion step conducted at 200 °C without decomposition. In addition, it exhibits a relatively high hydrolytic stability due to the sterically hindrance of the bulky phenyl substituents.

The determination of thermal stabilities of N-Si compounds turnout to be more challenging than for N-O-Si derivatives because many of the N-Si compounds evaporated prior to the onset of thermal decomposition. This tendency was verified by experiments were N-Si compounds such as NSi3 was heated above its boiling temperature and then recovered without significant decomposition according to subsequent NMR studies. The only monomeric N-Si compounds that thermally dissociated prior to evaporation were bis(diphenylmethylsilyl) pyromellitic diimide (NSi1) and bis(diphenyl-*tert*-butyl) pyromellitic diimide (NSi2) The recorded decomposition (10% wt. decomposition) temperatures were similar, i.e., 362 °C for NSi1 and 366 °C for NSi2. Furthermore, the polymeric flame retardant (NSi7) also decomposed at similar temperature of 353 °C. In connection to the foregoing, we investigated the thermolysis products of compound NSi3 to verify our hypothesis that silyl and aminyl radicals are generated by thermal splitting of the N-Si bond. Therefore, compound NSi3 was heated in a sealed NMR tube under a blanket of inert argon gas to 400 °C in the presence of 9,10-dihydroanthracene as hydrogen donor. After heating



Scheme 1. General synthesis route to silylamines (R1, R2, R3 = methyl, *tert*-butyl or phenyl).

Table 1
TGA data of different siloxyamine and silylamine derivatives.

Sample	Thermal stability Td 5% (°C)
Siloxamine	
NOSi1	196
NOSi2	247
NOSi3	232
NOSi4	205
NOSi5	147
NOSi6	190
Silylamine	
NSi1	362 (Td 10%)
NSi2	366 (Td 10%)
NSi3	249 (evap.)
NSi4	226 (evap.)
NSi5	220 (evap.)
NSi7	356

for 30 min, the tube was cooled, opened, and its contents extracted with *D*-chloroform. The results provide evidence that silyl radicals and aminyl radicals were formed as intermediates, since the 9,10-dihydroanthracene had been transformed to anthracene according to ^1H NMR spectra depicted in Fig. 2. In addition, traces of the phenyl containing silane could also be clearly detected as well as phthalimide in the ^1H NMR spectra. The decomposition mixture of NSi3 and 9,10-dihydroanthracene was also analysed with GC-MS, mass fragments with m/z 147.0, 178.1, 179.1 and 395.1 were found. These correspond to phthalimide, anthracene, 9,10-dihydroanthracene and 1,3-dimethyl-1,1,3,3-tetraphenyldisilane, respectively (see Fig. 3). The presence of phthalimide proves the breaking of N-Si -bond and conversion of 9,10-dihydroanthracene to anthracene via a radical decomposition

mechanism. NSi3 was also heated alone under argon, GC-MS shows phthalimide, 1,3-dimethyl-1,1,3,3-tetraphenyldisilane and then recombined NSi3, i.e., 3-((methyldiphenylsilyl)oxy)-1H-isoindole with one oxygen missing from phthalimide (m/z 329, see Fig. 4) (According to ^1H NMR the silane was no longer bonded to the phthalimide nitrogen atom). Whereas 3-((methyldiphenylsilyl)oxy)-1H-isoindole was not visible in the NMR spectra of decomposed NSi3 in presence of 9,10-dihydroanthracene.

Further analysis for investigating the synergism between silylamines and the phosphorous flame retardant was conducted by mixing P1 with NSi2 in a sealed NMR tube under inert atmosphere (Ar). The tube was then heated to 400 °C for 30 min and then the content was first extracted with *D*-chloroform and then with *d*₆-DMSO. The collected ^{31}P NMR (decoupled) data shows that the spirocyclic phosphonate (P1) has in fact reacted with NSi2. Thus, spirocyclic phosphonates ^{31}P NMR spectra reveals that P signal has been shifted and two new major products have been formed, one that is soluble in chloroform and another in DMSO (see Fig. 5). TGA analysis supports this chemical interaction, since the decomposition temperatures for both NSi2 and P1 when combined in 1:1 mass ratio is significantly lower than for the individual derivatives alone, as shown in Fig. 6. All three TGA curves exhibit a one-step degradation process with a single maximum weight loss. A significant difference in the amount of residues was observed, since P1, NSi3 and its mixture formed 2, 17 and 21% of residue at 600 °C, respectively. This is inline with earlier studies using flame retardants containing phosphorous- nitrogen- silicone were also a significant increase in char yield has been observed for the mixture in comparison to the individual flame retardants used alone [30–34].

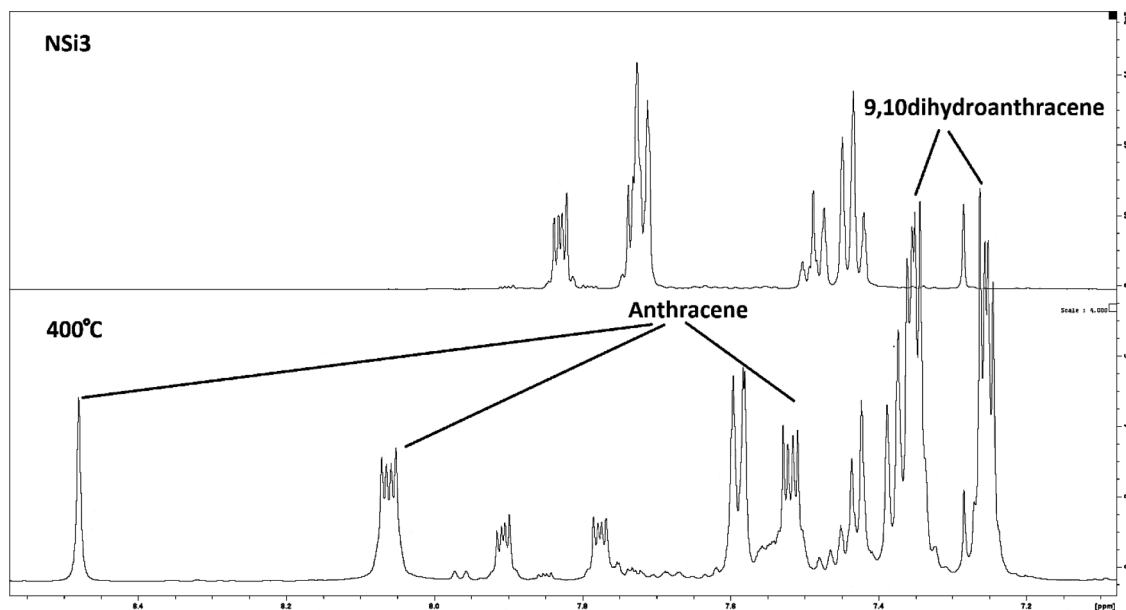


Fig. 2. A mixture of NSi3 and 9,10-dihydroanthracene in 1:4 ratio. The ^1H NMR before and after heating to 400 °C for 30 min.

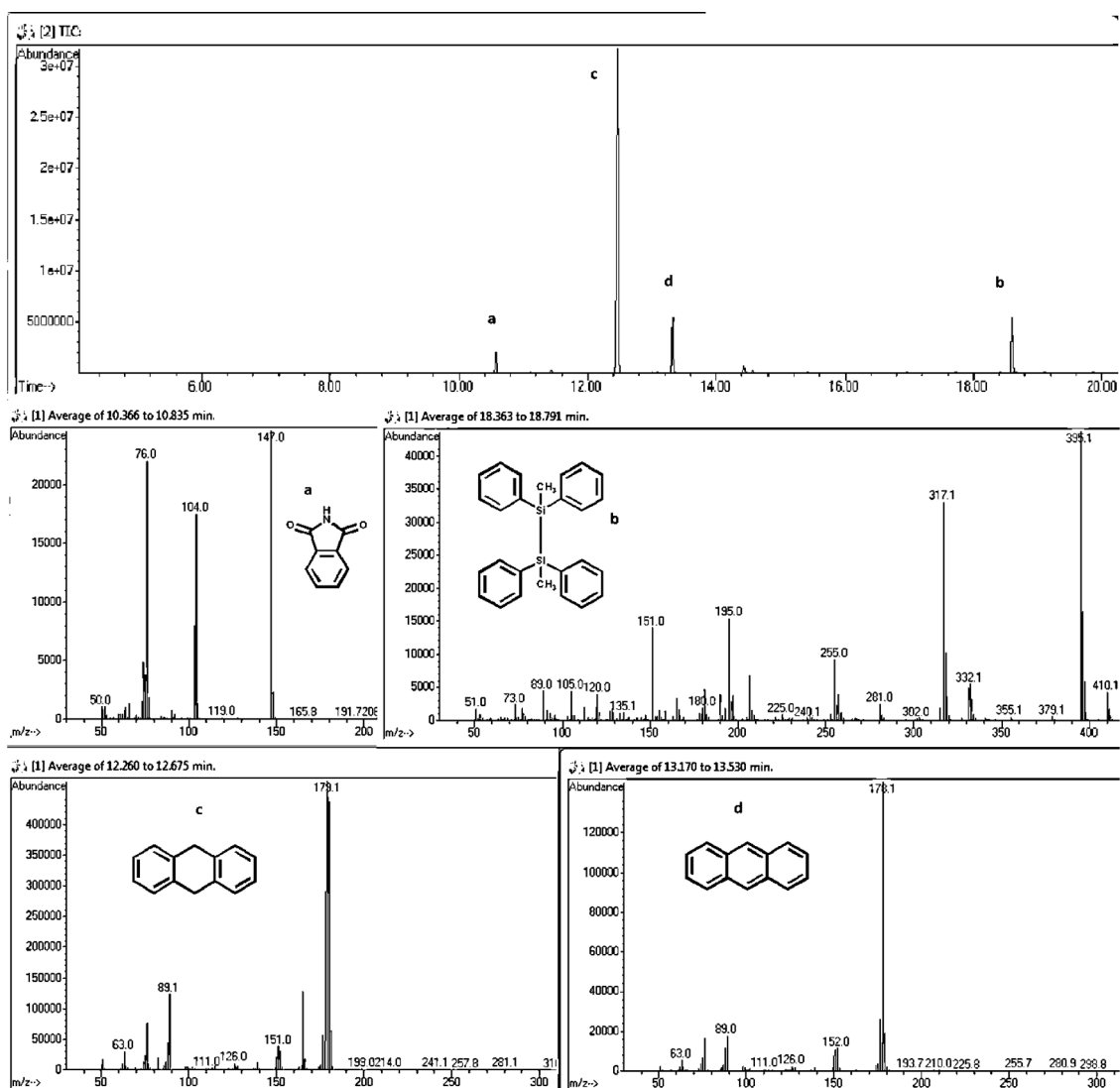


Fig. 3. GC chromatogram of NSi3 heated with 9,10-dihydroanthracene under Argon atmosphere and the MS spectra of the major fractions.

4. Flame retardant efficacy

First, we wanted to investigate whether the formed nitrogen-, silyl- and oxygen-centered radicals formed by thermolysis of N-Si bonds and N-O-Si bonds and the thereby triggered consecutive radical reactions could effectively suppress the burning of polypropylene films. As discussed earlier, for several radical generator-based flame retardants the proposed mechanism of action has been ascribed to their ability to interfere with the free radical chemical reactions during the combustion process and by their ability to promote the radically induced degradation of polypropylene whereby the formed non-volatile oligomers rapidly escape the flame zone by non-flaming dripping. The flame retardant efficacy was evaluated for polypropylene films based on DIN4102-B2 standard. The results reveal that both N-Si and N-O-Si compounds slowed down the burning process of polypropylene films at a loading of 2 wt%. The burning times clearly exceeded 20 s before it passed the 150 mm line. Noteworthy, is that several of the films burned slowly over the 150 mm mark. In general, the flame retardant efficacy of N-Si and N-O-Si compounds was considerable weaker than for sulfenamide or N-alkoxyamine based flame retardants as standalone flame retardants for PP films since PP films containing either sulfenamides or N-alkoxyamine at 2 wt% self-extinguish way before reaching the 150 mm mark [13].

Next, we wanted to explore the efficacy of the synthesized flame retardant candidates as adjuvants with the conventional spirocyclic phosphonate (P1) flame retardant for polypropylene and epoxy resins plaques. For the preparation of flame retarded epoxy samples, an epoxy resin formulation that was based on diglycidyl ether of bisphenol A (Araldite) that during mixing with a polyamine hardener (Aradur) underwent an exothermic addition reaction to give a fully cured and cross-linked 3D network were used.

The polypropylene specimens were subjected to UL94-V standard flame retardant test that classify the formulations according to their self-extinction times and presence of burning drops. In this study two different sample thicknesses were used, i.e., 1.6 mm and 3.2 mm plaques. Two thicknesses were used to better be able to evaluate the efficacy of different formulations.

The screening data in Table 2 clearly show that there is a strong synergistic effect between P1 and the synthesized aminylsilyl or aminylsiloxy based flame retardants. A similar strong synergistic effect on flame retardancy between NSi1 and P1 were observed also in the case of LLDPE and epoxy resins as shown in Tables 3 and 4. The siloxyamine compounds outperformed the silylamine compounds in the UL94V test, since two of the aminylsiloxy compounds NOSi1 and NOSi2 were the only formulations that gave UL94 V0 rating at a loading of 2 wt% in combination with 10 wt% of P1 for polypropylene samples of 1.6 mm

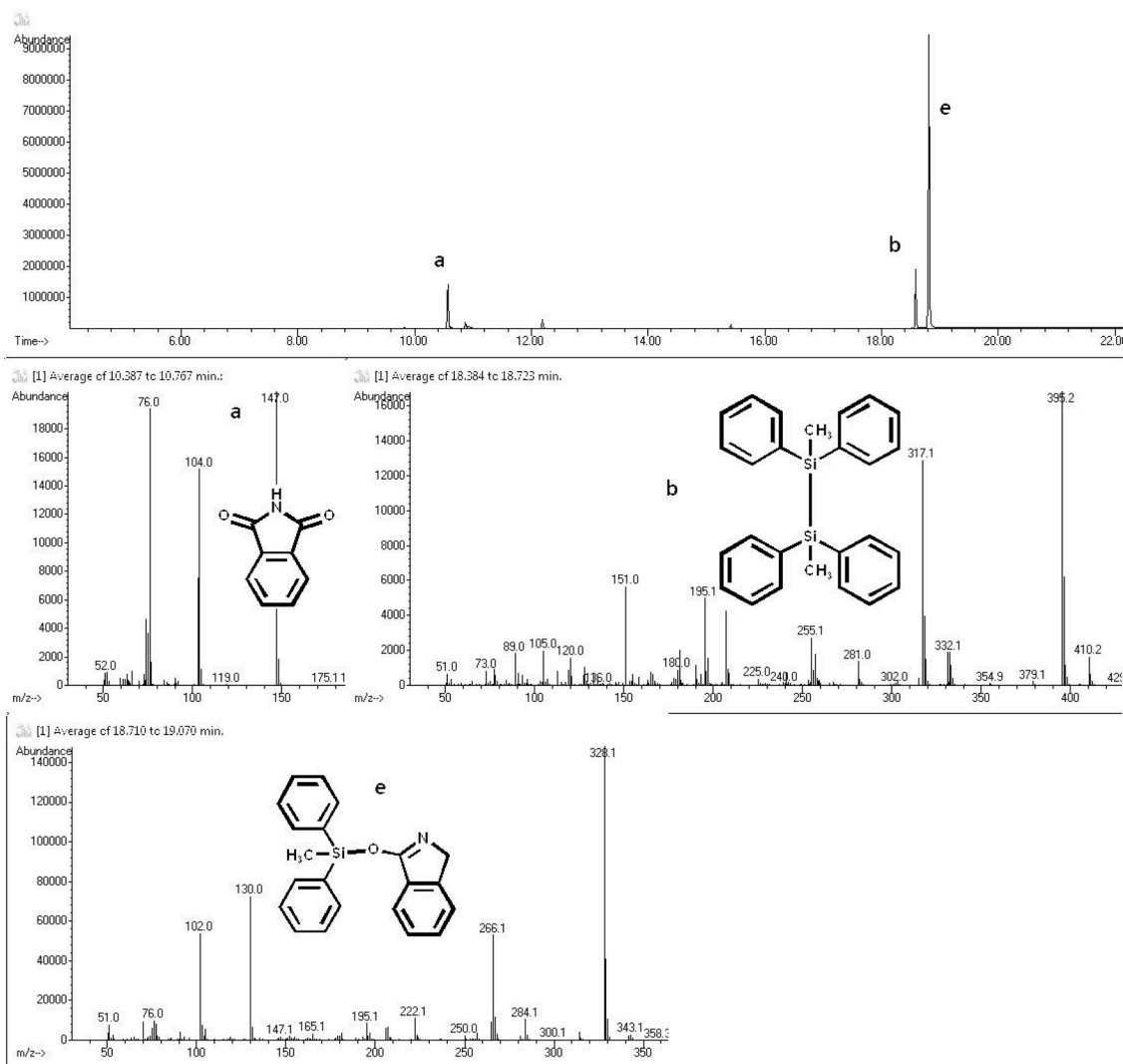


Fig. 4. GC chromatogram of NSi3 heated alone under Argon atmosphere and the MS spectra of the major fractions.

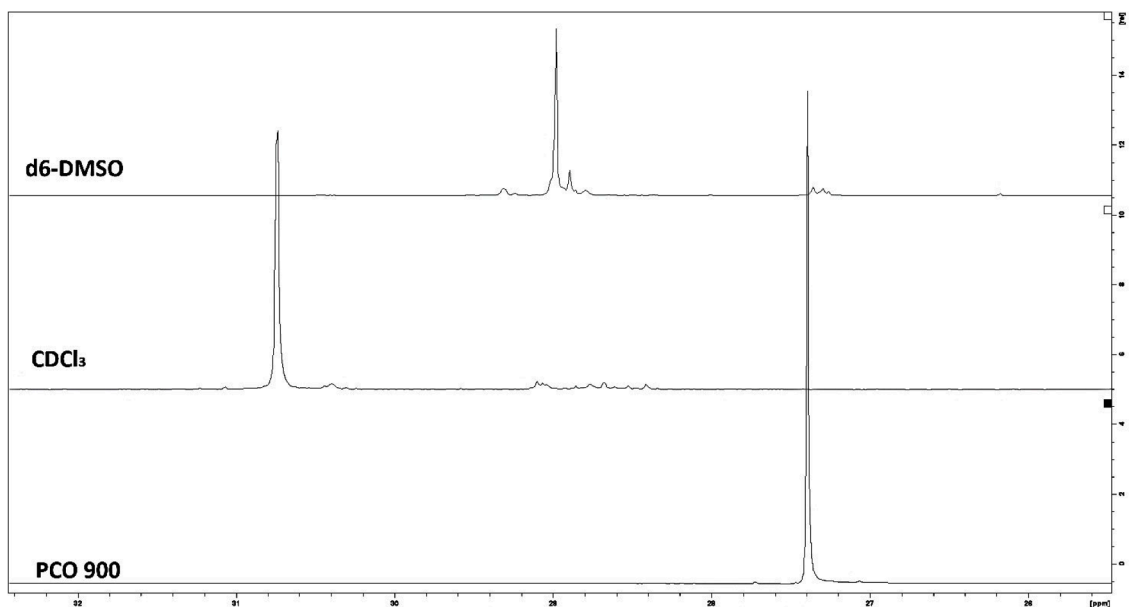


Fig. 5. ³¹P NMR spectra of P1 (PCO 900), when NSi2 is combined with P1, the ³¹P NMR shift changes and forms two products, one that is soluble in chloroform and another that is soluble in DMSO.

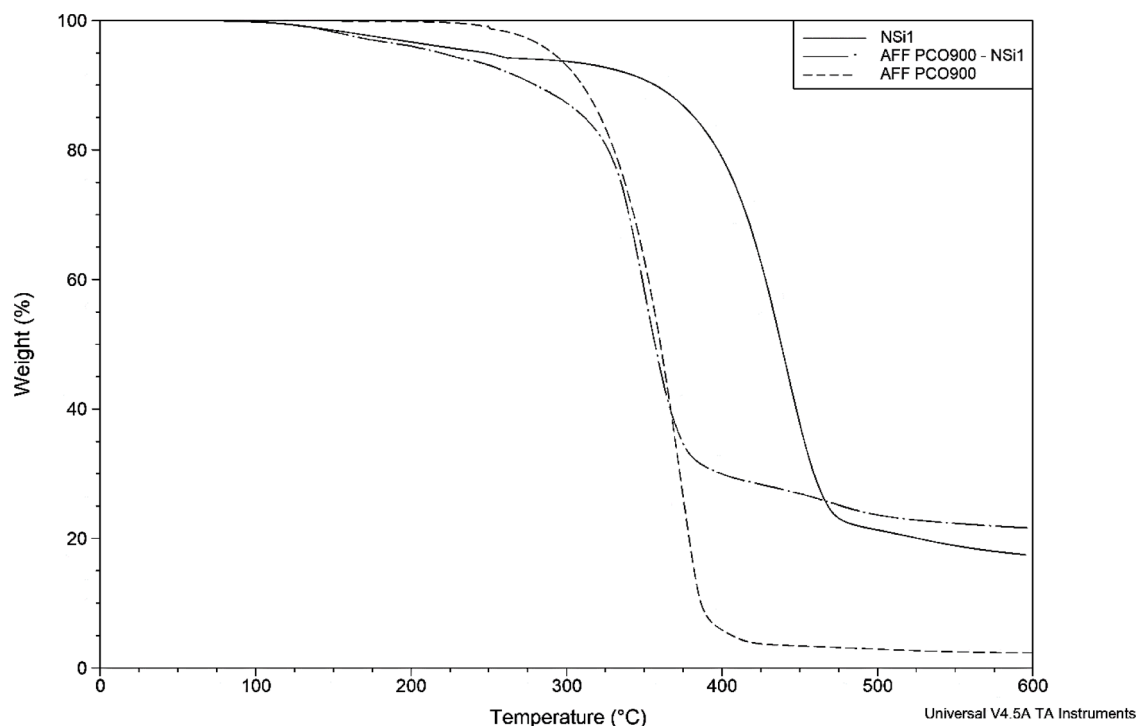


Fig. 6. TGA curves for a) NSi1, b) P1 and c) the mixture of NSi1 and P1 in 1:1 mass ratio.

Table 2

UL-94 results of NSi and NOSi compounds in combination with PCO 900 (P1) and PNN 978 (P2, ammonium polyphosphate -based mixture).

Sample	Silylamine	Loading of silylamine /wt%	Phosphorous FR	Loading of Phosphorous FR /wt%	UL 94 classification	Plaque thickness /mm
1	-	-	-	-	Fail	1.6
2	-	-	-	-	Fail	3.2
3	-	-	P1	10	Fail	1.6
4	-	-	P1	10	Fail	3.2
5	NSi4	1	P1	10	V0	3.2
6	NSi3	2	P1	10	V2	1.6
7	NSi7	2	P1	10	V2	1.6
8	NSi8	2	P1	10	V2	1.6
9	NOSi1	2	P1	10	V0	1.6
10	NOSi2	2	P1	10	V0	1.6
11	NOSi3	2	P1	10	V1	3.2
12	-	-	P1	15	V2	1.6
13	-	-	P1	15	V2	3.2
14	NSi5	1	P1	15	V0	3.2
15	NSi3	1	P1	15	V1	3.2
16	NSi3	1	P2	15	V1	1.6

Table 3

UL-94 results for LLDPE in combination with NSi3.

Sample	Silylamine	Loading of silylamine /wt%	Phosphorous FR	Loading of Phosphorous FR /wt%	UL 94 classification	Plaque thickness /mm
1	-	-	-	-	Fail	3.2
2	-	-	P1	15	V2	3.2
3	NSi3	1	P1	15	V0	3.2

thickness (Table 1). The drawback of siloxamine compounds is their relatively low hydrolytic and thermal stabilities [35]. This became also clear during synthesis of aminylsiloxy compounds, for instance our attempts to isolate and store 1-siloxoy-2,2,6,6-tetramethylpiperidine type of derivatives failed due to their high propensity for hydrolysis and low thermal stabilities. This is in line with previous studies that have reported that only 1-fluorosiloxy substituted 2,2,6,6-tetramethylpiperidine

derivatives have sufficient hydrolytic stability for isolation and storage [36]. Jones et al. has reported that equilibrium constant, K , of the hydrolytic condensation of triethylsilyl chloride is ca. 500 lower than for $\text{ClCH}_2\text{Me}_2\text{SiCl}$. Thus, showing that strongly electronegative halogen groups increase their hydrolytic stabilities greatly. However, we were looking for halogen-free flame retardant alternatives and therefore the synthesis of fluorinated aminylsiloxy compounds were deemed not to be

Table 4
UL-94 results for Epoxy resin in combination with polymeric NSi6.

Sample	Silylamine	Loading of silylamine/wt%	Phosphorous FR	Loading of Phosphorous FR /wt%	UL 94 classification	Plaque thickness/mm
1	–	–	–	–	Fail	1.6
2	–	–	–	–	Fail	3.2
3	–	–	P1	2.5	Fail	1.6
4	NSi6	2	P1	2.5	V0	1.6
5	–	–	P1	2.5	V2	3.2
6	NSi6	2	P1	2.5	V0	3.2

of interest for this study.

Our studies show that N-Si and N-O-Si compounds having imide synthon such as imide phthalate or pyromellitic diimide give flame retardants that exhibit high thermal stabilities with improved hydrolytic stabilities compared to e.g., 2,2,6,6-tetramethylpiperidine based N-Si or N-O-Si derivatives.

Electron paramagnetic resonance (EPR) and theoretical studies for a-substituted silyl radicals ($X_3Si\cdot$) have been periodically conducted. In connection with the foregoing, trimethylsilyl and most trisubstituted silyl radicals have been found to have pyramidal configuration at the radical center. For instance, the calculated angle γ for $(Me)_3Si\cdot$ is 18.69° is less bent than for $(NH_2)_3Si\cdot$ that exhibits an angle of 21.53. Furthermore, calculations show that the single occupied molecular orbital (SOMO) the delocalization of the unpaired electrons onto the a-substituent is much greater for third than second row elements, whereas the population on Si-3 s increases linearly with the increasing electronegativity of the a-substituent. The radical stability is dependent on the bulkiness of the substituents and increased bulkiness such as *tert*-butyl and phenyl groups significantly stabilize the silyl radical by protecting the radical site from dimerization and other reactions. In the limited test series of N-Si compounds the lowest performance was recorded for NSi3 compound, since only UL94 V1 could be reached under the same conditions where the other N-Si compounds reached the UL94 V0 rating. This may partially be attributed to the higher volatility of NSi3 in comparison to the other tested NSi compounds. However, based on our preliminary test setting and the low loadings used N-Si compounds (1 to 2wt%), we could not see any other clear trend related to the impact of the a-substitution moiety on flame retardant efficacy together with P1.

Notably it has been reported that flame retardant combinations containing phosphorous-nitrogen-silicon have a strong synergistic effect in epoxy resins and polypropylene by forming a protective layer on top of the polymer. In these reports the individual effects of synergism has been ascribed to the following factors: the phosphorous moiety decomposes at low temperatures due to the weak bonds of phosphonate with respect to the polymer matrix with subsequent oxidation to form a protective char (or the phosphorous species may capture radicals in the gas phase), nitrogen containing compounds release incombustible gases that dilute the flame zone or promote the formation of a foamy carbon barrier, whereas elements of silicon contribute to the formation of a protective silica layers with enhanced thermal stabilities that effectively protect the polymer residues from further degradation and the silica layers also retard the oxidation of the char [30]. Noteworthy is that in all the prior reports and studies related to phosphorous-nitrogen-silicon synergistic flame retardant formulations the use of flame retardants molecules containing N-Si or N-O-Si bonds is unprecedented. Thus, instead the amine and silicon atoms are either in different molecules or they have been connected via e.g., alkyl chains in the same molecule. Moreover, the loading of silica and amine in the formulations are relatively high, i.e., typically between 10 and 20% and much higher than in the present study. In addition, these silica and amine containing synergists by themselves do not provide self-extinguishing properties in the absence of a phosphorus flame retardant. Therefore, a proper comparison of N-Si and N-O-Si compounds flame retardancy efficacy and mechanism of action together

with a phosphorous flame retardant with results from literature is quite difficult to conduct.

In the present formulation, we postulate that the key feature for the enhancement of flame retardancy is related to the thermal dissociation of the N-Si and N-O-Si bonds into aminyl, silyl and oxygen centered free radicals that effectively slowdown polymer combustion by themselves and especially boost the activity of phosphorous flame retardants by altering its decomposition pathway and decreasing its onset and maximum decomposition temperature.

5. Conclusions

In this work, several novel flame retardants having N-Si and N-O-Si bonds have been successfully synthesized and characterized. Upon thermal dissociation, the N-Si and N-O-Si compounds were shown to yield aminyl, silyl and oxygen-centered radicals that provided fire proofing effect in polypropylene (PP) films by themselves. Especially a strong synergistic effect was observed in combination with a conventional spirocyclic phosphinate flame retardant for PP, LLDPE and epoxy resins, since the stringent UL94-V0 rating could be reached at relative low loadings. This work offers a new family of radical generator-based flame retardants containing N-Si and N-O-Si bonds that can improve fire safety of polymeric materials.

Declaration of authors contributions

Timo Ääritalo: He conducted all the synthetic work and characterization of the flame retardants properties. He also participating in flame retardancy testing and in the writing of the manuscript. Carl-Eric Wilen: He participated in the original idea generation; formulation and evolution of overarching research goals and aims. He had the oversight and leadership responsibility for the research activity planning and execution, including mentorship external to the core team. He also participated in writing of the manuscript. Teija Tirri: She participated in the idea generation and in overseeing the experimental part. Melanie Aubert: She participated in the idea generation and in the design of synthesis routes and characterization work.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Carl-Eric Wilen reports financial support was provided by BYK-Chemie GmbH. Carl-Eric Wilen reports a relationship with BYK-Chemie GmbH that includes: funding grants. Carl-Eric Wilen has patent #Ääritalo, Silyl functional compound for improving flame retardant properties, WO2020212377A1 pending to BYK Chemie. There is no further conflict of interest.

Data availability

The data that has been used is confidential.

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