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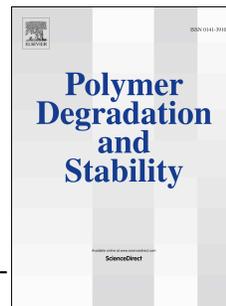
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Title: Sulfenamides in synergistic combination with halogen free flame retardants in polypropylene

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Keywords: Sulfenamide; radical generator; flame retardant; polypropylene; UL 94 V-0; cone calorimeter; thermal analysis

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29 **Abstract:**

30 Sulfenamide based radical generators that contain a nitrogen-sulfur (N-S) core, can alone provide
31 flame retardancy in polypropylene (PP), polyethylene and polystyrene, as we have earlier
32 demonstrated. Herein, sulfenamides potential as synergists with conventional halogen free flame
33 retardants has been explored. Thus, five different sulfenamides were individually combined with
34 selected eco-friendly, phosphorus based flame retardants or aluminium trihydroxide (ATH), and
35 their effect on polypropylene flammability was assessed by limiting oxygen index (LOI), vertical
36 flammability (UL 94 V) and cone calorimeter tests. Thermogravimetric analysis (TGA) and nuclear
37 magnetic resonance (NMR) studies were carried out to detect changes in thermal behaviour when
38 such two component FR systems were mixed together at different ratios. TGA-FTIR
39 (thermogravimetric analysis-Fourier transform infrared spectroscopy) was used to investigate the
40 differences in decomposition products of non-flame retarded versus flame retarded PP. Strong
41 synergistic effects were observed, and the UL 94 V-0 rating was reached for PP with a total FR
42 loading of 10 wt% using 8 wt% of phosphonate ester *AFLAMMIT*[®] *PCO 900* together with 2 wt% of
43 sulfenamide flame retardant. In a ternary mixture of an additional phosphazene additive (SPB-
44 100), the needed total concentration for V-0 rating was further reduced to 9 wt%. In addition, the
45 combination of 4 wt% of aluminum hypophosphite (AHP) with 0.5 wt% of sulfenamide offered a
46 unique halogen free solution for achieving UL 94 V-2 rating in PP. Cone calorimeter studies of an
47 ammonium polyphosphate-pentaerythritol based intumescent system in combination with 0.5
48 wt% of sulfenamide also showed encouraging results. The char stability was enhanced, the peak of
49 heat release rate (HRR), CO and CO₂ production and total smoke generation were all reduced
50 compared to the reference sample without sulfenamide.

51

52

53 1. Introduction

54

55 Polypropylene (PP) is widely used commodity plastic that can easily be processed and converted
56 into films, tapes, filament fibers, foams and moldings. As a flammable, non-charring polymer with
57 tendency to melt dripping, PP is not easily made self-extinguishing. Polypropylene formulations
58 passing the UL 94 vertical flammability test have become of particular interest, but especially the
59 UL94 V-0 rating, where flaming drops are not allowed, is difficult to achieve at low flame retardant
60 loadings. [1] At present, FR systems for PP include halogenated FR together with antimony trioxide
61 synergist (ATO), ammonium polyphosphate (APP) based systems, aluminum or magnesium
62 hydroxides (ATH, MDH) and some organophosphorus flame retardants.[2][3][4] A challenge is to
63 find alternative flame retardant formulations for polypropylene fibers and films, that require UL 94
64 V-0 rating and FR loading below 15 wt%, or preferably even below 10 wt%.[5]

65

66 In addition to sufficient flame retardant efficacy at acceptable cost, the impetus has now shifted
67 towards human health, safety and environmental issues (HS&E). Some health and safety issues are
68 perceived to exist for both halogenated flame retardants and antimony trioxide (ATO) and
69 therefore there is a great demand for halogen and ATO free solutions. GreenScreen[®] (GS) is a
70 method that has been developed by the Clean Production Action (CPA in US) to assess and
71 benchmark chemicals based on their environmental and health hazard. In 2016, the Danish
72 Environmental Protecting Agency published hazard profiles for 28 phosphorous flame retardants
73 available on the market, based on a modified GreenScreen[®] method (modGS).[6] The collected
74 data can be used to identify safer alternatives for the halogenated flame retardants in a European
75 regulatory context. Out of the ranked, non-halogenated flame retardants, ammonium
76 polyphosphate (APP) is listed as the safest alternative with the overall hazard score of 4 (score
77 range from 1 to 4; where 1 denotes highest and 4 lowest risk). However, the certified
78 GreenScreen[®] benchmark[™] for APP is still 3. [7]

79

80 APP releases ammonia gas upon exposure to heat or flames (> 250 °C), whereby polyphosphoric
81 acid is formed, which in turn can phosphorylate hydroxyl containing compounds upon
82 dehydration. In inherently non-char forming polymers like PP, APP is commonly combined with a
83 char forming polyol, such as pentaerythritol. In the presence of gas forming agents, spumifics, the
84 so formed carbonaceous layer swells and protects the host polymer through its heat insulating

85 effect. The extent of swelling and stability of the formed multicellular, solid protective layer is
86 affected by the viscosity of the molten material and the pyrolysis products. In cone calorimeter
87 test (CC), the ignition time and burning behaviour of the material are monitored under forced
88 flaming conditions. Intumescent FR systems are typically very effective in CC when the total FR
89 loading is > 25 wt%.[8] Since 1980's, the mechanism of action and the effect of different
90 combinations of IFR components in PP have been widely studied in the
91 literature.[9][10][11][12][13][14][15] The complexity of possible condensed phase reactions
92 between polymer, flame retardants and adjuvants is well illustrated in the work of ScharTEL et
93 al.[16] The interplay between radical species of the FR additives and of the polymer pyrolysis
94 products formed during the thermal treatment affects the formation of protective coating and
95 reduces the evolution of flammable gases. Le Bras et al. showed in electron spin resonance studies
96 that the enhanced FR behaviour is closely related to the increasing free radical content in the
97 carbonaceous material.[12] Therefore, it is well warranted to study combinations of APP and
98 radical generators to boost the flame retardant effect. N-alkoxy hindered amine stabilizer
99 (Flamestab[®] NOR 116) and novel macromolecules with free radical quenching ability have already
100 been favourably combined with different APP based intumescent systems for flame retardancy of
101 PP. [17][18][19] In one part of this paper, sulfenamide radical generator is combined with
102 traditional APP/PER system, and the effect of radical generator is studied in cone calorimeter
103 tests.

104

105 Aluminum hypophosphite (AHP) is also well perceived flame retardant from the HS&E point of
106 view (modGS score 3). [6] The AHP based, synergistic flame retardant combinations have been
107 developed for PP UL 94 V-2 applications (trade name Phoslite[®]). Improved flame retardancy in PP
108 has been reported when AHP is combined with proprietary non-halogenated or organohalogen
109 compounds and their combinations. [20] [21]

110 Aluminum trihydroxide (ATH, GS score 2 [22]) is a widely used flame retardant filler. It can be used
111 in PP if the polymer processing temperature does not exceed the decomposition temperature of
112 ATH, which is below 250 °C. However, to reach the UL 94 V-2 rating in PP, high loadings of even
113 60–70 wt% are needed. To decrease the total FR loading, or to enhance the flame retardant
114 properties, synergists can also be used, but only few non-halogenated alternatives are
115 available.[23][24]

116

117 All the phosphorus compounds mentioned above and ATH do not melt during blending, which in
118 combination with their high loading is detrimental for high extrusion speed and troublesome for
119 fiber and film production. Most flame retardants used in the fusible fiber forming polymers, like
120 PP, act by increasing melt dripping simultaneously when decreasing flammability of the drips.[25]
121 Organic spirophosphonate, *AFLAMMIT[®] PCO 900 series*, has melting temperature at around 230–
122 245 °C, which makes it a very viable FR candidate when seeking for UL 94 V-0 rating in films, fibers
123 and nonwovens at the low loadings of 5–10 wt-%. *AFLAMMIT[®] PCO 900* is on the Oeko-Tex list of
124 approved flame retardants.

125

126 An interesting compound combining phosphorus-nitrogen is phenoxyphosphazene SPB-100 from
127 Otsuka Chemical Co., Japan. It is hydrolytically and thermally very stable (5 % weight loss at over
128 350°C) and recommended e.g. for electronics and resin moldings.

129

130 We have recently introduced a group of sulfenamide flame retardants, which enable PP films and
131 fibers to self-extinguish even at a very low loading of 0.5–1 wt%.[26] A common nominator for all
132 of them is a nitrogen-sulfur bond of low basicity, which is stable at normal polymer processing
133 temperatures of polypropylene, but rapidly decomposes under fire conditions. The generated
134 aminyl and sulfenyl radicals are capable of interrupting the radical processes otherwise leading to
135 the fire propagation. Depending on the chemical structure of the compound and stability of the
136 incipient radicals, different interactions with the resin components and their degradation products
137 may occur both in the gas phase and in the condensed phase.

138

139 In this study, sulfenamide flame retardants were combined with environmentally benign, non-
140 halogenated and well-known PP flame retardant systems (Fig. 1). Thus, the FR effects of
141 bis(2,2,6,6-tetramethyl-1-(phenylthio) piperidin-4-yl) carbonate (SN-I), oligomeric sulfenamides
142 (SN-IV and SN-V) and of two new, well performing sulfenamide flame retardants (SN-II and SN-III)
143 were studied in combination with *AFLAMMIT[®] PCO 900*. SN-I was also tested in a mixture of PCO
144 900 and SPB-100 and together with AHP, ATH and an intumescent FR system based on APP/PER.
145 Limiting oxygen index (LOI), vertical flammability (UL 94 V) and cone calorimeter tests were used
146 to assess the flammability. Interactions between the flame retardant pairs were studied using
147 nuclear magnetic resonance (NMR), thermogravimetry (TGA) and thermogravimetry-Fourier
148 transform infrared (TGA-FTIR) techniques.

ACCEPTED MANUSCRIPT

150 2. Experimental section

151 2.1 Materials and sample preparation methods

152 Synthesis and characterization of compounds I, IV and V are described in our previous
153 publications.[26] [27] All chemicals used for the synthesis were of reagent grade and purchased
154 from Sigma-Aldrich, Finland, apart from the commercial samples Uvinul® 5050 H obtained from
155 BTC Europe (Denmark) and Sabo®stab UV 94 and Sabo®stab UV 70 obtained from Songwon
156 (Korea).

157 Phosphonate ester P-I, AFLAMMIT® PCO 900, was obtained from Thor GmbH., Germany (24% P,
158 melting 230-245°C). Aluminum trihydroxide (ATH) was Apyral 40CD grade from Nabaltec AG,
159 Germany. Aluminum hypophosphite [(H₂PO₂)₃ Al] (AHP, P-II) was received from Qingdao Fusilin
160 Chemical Technology Co., Ltd, China, ammonium polyphosphate P-IV (Exolit AP 422, fine grained
161 phase II, APP) from Clariant GmbH, Germany, phosphazene P-III (SPB-100, 13% P, melting 110 °C)
162 from Otsuka Chemical Co. , Ltd, Japan, decabromodiphenyl ethane (DBDE, FR-1410) and antimony
163 trioxide (ATO, 80% masterbatch in ethyl-methacrylate copolymer) were both received from ICL-IP
164 Europe, Netherlands.

165
166 Flame retardants were melt mixed with polypropylene (PP MFR25, MOPLEN HP552R from
167 LyondellBasell, Netherlands, MFR 25 g/10 min (230 °C/2.16 kg)), (PP MFR12, MOPLEN HP500N
168 from LyondellBasell, Netherlands, MFR 12 g/10 min (230 °C/2.16 kg)), (PP MFR 55 g/10 min (230
169 °C/2.16 kg), HJ40XI from Polychim Industrie, France), (PP MFR 2 g/10 min (230 °C/2.16 kg),
170 Tipplen R 659 KAU, MOL Group, Hungary) in a Haake Rheocord melt blender (60 rpm).
171 Polypropylene was melted first for one minute at 200–210 °C, where after acid scavenger Ca-
172 stearate (0.05 wt%, Baerlocher GmbH, Germany) and Irganox® B 225 (0.3 wt%, BTC Europe GmbH,
173 Denmark) stabilizer were added. B 225 is a processing and long term thermal stabilizer, blend of
174 50% tris(2,4-ditert-butylphenyl) phosphite and 50% pentaerythritol tetrakis[3-[3,5-di-tert-butyl-4-
175 hydroxyphenyl] propionate]. After one minute, flame retardants were added and the mixing was
176 continued for four minutes.

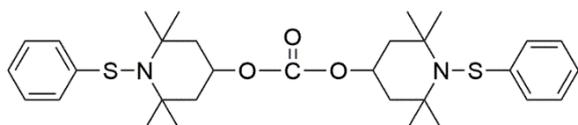
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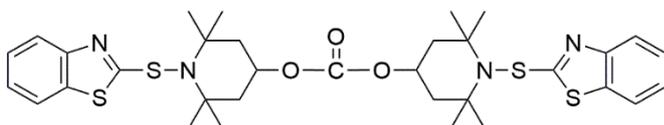
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Sulfenamides:

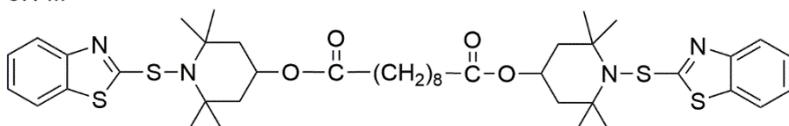
SN-I



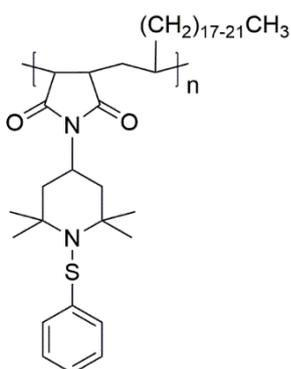
SN-II



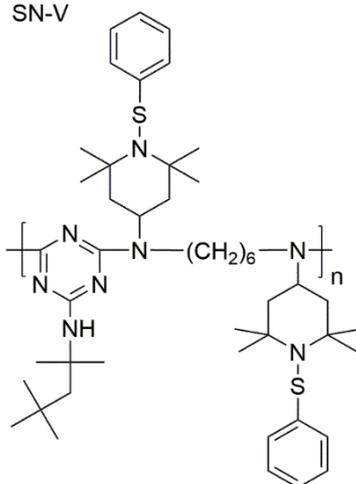
SN-III



SN-IV



SN-V



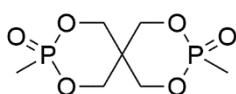
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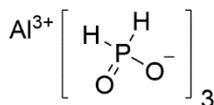
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Phosphorus compounds:

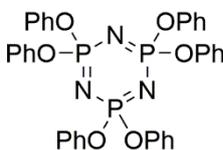
P-I (PCO 900)



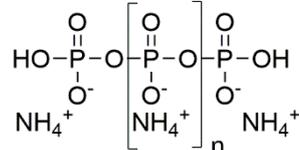
P-II (AHP)



P-III (SBP-100)



P-IV (APP)



183

184

Other FR compounds:

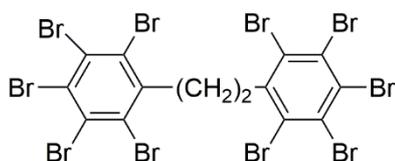
PER



ATH



DBDE



ATO



185

186

187

188

Figure 1. Flame retardants used in this work.

189 2.2 Characterization methods

190 **Nuclear magnetic resonance (NMR) spectra** (^1H , ^{31}P and ^{13}C) were recorded on a 500 MHz Bruker
191 AVANCE-III NMR-system. Thermal treatment of FR mixtures for NMR analysis was done in the
192 following manner: P-I, (18.4 mg), SN-I (4.6 mg) or their 4:1 mixture (23 mg) were weighed into
193 NMR-tubes and sealed under argon atmosphere. Samples were placed 6 cm deep into a sand bath
194 pre-heated to the desired temperature (RT, 230°C, 260°C or 290°C) and kept there for 5 minutes.
195 Depending on the sample, either dimethylsulfoxide-d₆ or chloroform-d was added to the tubes
196 before the NMR analysis.

197

198 **Thermogravimetric (TGA) and differential thermal analysis (DTA)** was performed using an SDT
199 Q600 apparatus from TA Instruments under N₂ atmosphere (flow rate 100 mL/min) and at the
200 heating rate of 10°C/min. Fourier transform infrared analysis (iS50 FTIR, Thermo Scientific) was
201 used in connection to the TGA analysis. Transfer line temperature was 280°C.

202

203 **Different scanning calorimetry (DSC)** was done under N₂ flow (50 mL/min) and heating/cooling
204 rate of 20°C/min with DSC250 device from TA Instruments. Temperature range of -90 °C – 150 °C
205 was used for the heat-cool-heat method.

206

207 **Burning behaviour**

208 UL 94 test for flammability of plastic materials for parts in devices and appliances (UL 94 standard,
209 Underwriters Laboratories Inc., US), and limiting oxygen index, LOI, defining minimum oxygen
210 concentration to support candle-like combustion of plastics (ASTM standard D2863), were used to
211 study flammability of samples. The equipment for UL 94 test was from Fire Testing Technology
212 (FTT, UK). The LOI test was carried out using Oxygen Index Module apparatus from Fire
213 Instrumentations and Research Equipment (FIRE, Belgium). Specimens of type IV were tested in
214 accordance with the test method A. In addition to LOI, nitrous oxide index, NOI, where oxygen is
215 replaced by N₂O, was measured similarly.

216 Cone calorimeter tests were conducted to characterize the burning behaviour under forced
217 flaming conditions according to the ISO 5660-1 standard. (Heat Release Rates from Building
218 Products, Cone calorimeter Method, The International Organization for Standardization, Geneva.
219 1993.) Cone calorimeter (FTT, UK) was operated at the heat flux of 35 kW/m².

220 Test bars for UL 94 test ($127 \times 12.7 \times 1.6 \text{ mm}^3$) and LOI test ($70 \times 6.5 \times 3 \text{ mm}^3$) as well as plates for
221 the cone calorimeter test ($100 \times 100 \times 5 \text{ mm}^3$) were compression moulded in a hot press at $190 \text{ }^\circ\text{C}$.
222 All samples were conditioned for 3 days at $23 \text{ }^\circ\text{C}$, 50 % RH prior to testing.

223

224 2.3 Synthesis of flame retardants SN-II and SN-III

225 **Preparation of benzothiazol-2-sulfenyl chloride:** To a suspension of di(benzothiazol-2-yl) disulfide
226 (120 g , 361 mmol) in 600 mL of dichloromethane (DCM), sulfonyl chloride (31 mL , 380 mmol) was
227 added in one portion. After 10 min of stirring at room temperature at reduced pressure (600
228 mbar), the mixture became dark orange. The mixture was slowly evaporated in vacuum to
229 dryness. The benzothiazol-2-sulfenyl chloride was dissolved in 200 mL of DCM and immediately
230 used for preparation of the sulfenamides.

231 **SN-II:** bis(2,2,6,6-tetramethylpiperidin-4-yl) carbonate (123 g , 361 mmol) and TEA (111 mL , 800
232 mmol) were dissolved in 500 mL of DCM. The mixture was cooled with ice water bath and the
233 solution of benzothiazol-2-sulfenyl chloride was added dropwise at a rate that kept the
234 temperature of the reaction mixture below 10°C ($\sim 1.5 \text{ h}$). After addition the reaction was left
235 stirring at room temperature overnight ($\sim 16 \text{ h}$). The reaction mixture was concentrated in vacuum
236 to the volume of 500 mL and then diluted with 1 L of ethanol (95%). The formed precipitate was
237 separated by filtration, washed with ethanol and then with hot toluene to give 175 g (260 mmol ,
238 yield 72%) of **SN-II** as white powder after drying.

239 ^1H NMR (500 MHz , CDCl_3) δ ppm 1.40 (s, 12 H , $4 \times \text{Me}$) 1.52 (s, 12 H , $4 \times \text{Me}$) 1.88 (dd, $J=12.4$, 11.9
240 Hz, 4 H , $4 \times \text{C-H}$ from Piperidine- CH_2) 2.24 (dd, $J=12.4$, 4.0 Hz , 4 H , $4 \times \text{C-H}$ from Piperidine- CH_2)
241 5.06 (tt, $J=11.9$, 4.0 Hz , 2 H , $2 \times \text{Piperidine-CH}$) 7.29 (ddd, $J=7.9$, 7.2 , 1.1 Hz , 2 H , $2 \times \text{C6}$ of
242 benzothiazole) 7.42 (ddd, $J=8.1$, 7.2 , 1.2 Hz , 2 H , $2 \times \text{C5}$ of benzothiazole) 7.79 (ddd, $J=7.9$, 1.2 , 0.6
243 Hz, 2 H , $2 \times \text{C7}$ of benzothiazole) 7.83 (ddd, $J=8.1$, 1.1 , 0.6 Hz , 2 H , $2 \times \text{C4}$ of benzothiazole).

244 ^{13}C NMR (126 MHz , CDCl_3) δ ppm 25.7 ($4 \times \text{Me}$) 32.6 ($4 \times \text{Me}$) 45.4 ($4 \times \text{C}$ from Piperidine- CH_2) 62.0
245 ($4 \times \text{quaternary C}$ from Piperidine) 70.4 ($2 \times \text{C}$ from Piperidine- CH) 120.8 ($2 \times \text{C4}$ of benzothiazole)
246 121.6 ($2 \times \text{C7}$ of benzothiazole) 123.7 ($2 \times \text{C6}$ of benzothiazole) 125.9 ($2 \times \text{C5}$ of benzothiazole)
247 134.5 ($2 \times \text{C7A}$ of benzothiazole) 154.2 (C=O) 154.5 ($2 \times \text{C3A}$ of benzothiazole) 180.5 ($2 \times \text{C2}$ of
248 benzothiazole).

249 Elemental analysis calc. C, 59.07; H, 6.31; N, 8.35; O, 7.15; S, 19.11 found: C, 58.83; H, 6.24; N,
250 8.30; O, - ; S, 19.08 Mass-analysis $[\text{M}+\text{H}]^+ = 671.4$, $T_m = 278 \text{ }^\circ\text{C}$

251

252 **SN-III**: SaboStab UV-70 (174 g, 361mmol) and TEA (111 mL, 800 mmol) were dissolved in 500mL of
253 DCM. The mixture was cooled with ice water bath and the solution of benzothiazol sulfenyl
254 chloride was added dropwise at a rate that kept the temperature of the reaction mixture below
255 10°C (~1.5 h). After addition the reaction was left stirring at room temperature overnight (~16 h).
256 The reaction mixture was concentrated in vacuum and the solid residue was washed with 600 mL
257 of ethanol (95%) and filtered. After drying in vacuum, 246 g (303 mmol, yield 84%) of **SN-III** was
258 obtained as white powder.

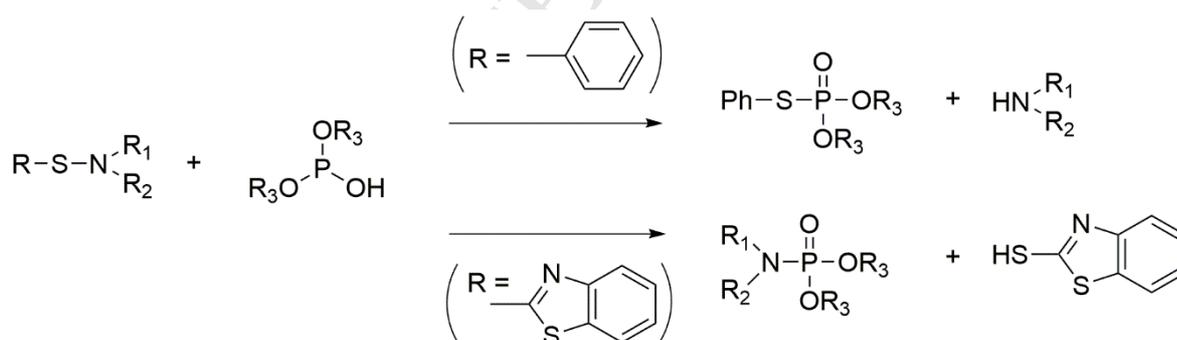
259 ¹H NMR (500 MHz, CDCl₃) δ ppm 1.28 - 1.37 (m, 8 H, 4 x CH₂ 4-7 of Sebacic acid) 1.37 (s, 12 H, 4 x
260 Me) 1.48 (s, 12 H, 4 x Me) 1.61 - 1.71 (m, 4 H, 2 x CH₂ 3, 8 of Sebacic acid) 1.79 (dd, J=12.1, 11.7 Hz,
261 4 H, 4 x C-H from Piperidine-CH₂) 2.11 (dd, J=12.1, 3.7 Hz, 4 H, 4 x C-H from Piperidine-CH₂) 2.33 (t,
262 J=7.5 Hz, 4 H, 2 x CH₂ 2, 9 of Sebacic acid) 5.20 (tt, J=11.7, 3.7 Hz, 2 H, 2 x Piperidine-CH) 7.27 (dd,
263 J=8.1, 7.6 Hz, 2 H, 2 x C5 of benzothiazole) 7.40 (dd, J=7.8, 7.6 Hz, 2 H, 2 x C6 of benzothiazole)
264 7.77 (d, J=7.8 Hz, 2 H, 2 x C7 of benzothiazole) 7.81 (d, J=8.1 Hz, 2 H, 2 x C4 of benzothiazole)

265 ¹³C NMR (126 MHz, CDCl₃) δ ppm 25.0 (C3 and C8 of Sebacic acid) 25.75 (4 x Me) 29.08 (C5 and C6
266 of Sebacic acid) 29.1 (C4 and C7 of Sebacic acid) 32.59 (4 x Me) 34.56 (C2 and C9 of Sebacic acid)
267 45.46 (4 x C from Piperidine-CH₂) 61.98 (4 x quaternary C from Piperidine) 66.02 (2 x C from
268 Piperidine-CH) 120.78 (2 x C4 of benzothiazole) 121.52 (2 x C7 of benzothiazole) 123.59 (2 x C6 of
269 benzothiazole) 125.90 (2 x C5 of benzothiazole) 134.54 (2 x C7A of benzothiazole) 154.48 (2 x C3A
270 of benzothiazole) 173.36 (2 x C=O) 180.84 (2 x C2 of benzothiazole).

271 Elemental analysis calc. C, 62.19; H, 7.21; N, 6.91; O, 7.89; S, 15.81 found: C, 62.10; H, 7.18; N,
272 6.75; O, - ; S, 15.62, mass-analysis [M+H]⁺ = 811.3, T_m = 163 °C

273 **3. Theory**

274 The sulfenamide flame retardants SN-I, SN-IV and SN-V presented in Figure 1 were chosen to this
 275 study based on our earlier observations that they are very powerful flame retardants in thin film
 276 applications.[26] Moreover, sulfenamides can easily be blended during processing of PP. Novel
 277 sulfenamides SN-II and SN-III bearing a benzothiazole thiyyl instead of phenyl thiyyl moiety were
 278 synthesized in order to further elucidate the structure-property relationship. In addition to the
 279 thermal stability of the S-N bond, other factors such as proton abstraction efficiency (basicity),
 280 radical stability and kinetics of the thiyyl addition/fragmentation reactions may play a critical role
 281 when sulfenamides are used as flame retardants in different polymers alone, or in combination
 282 with e.g. phosphorus-based flame retardants. It is known that aromatic disulfides and
 283 sulfenamides can react with phosphorus compounds, and specifically with P(III).[28][29][30]
 284 Phosphorus compound as a nucleophile attacks the electron deficient sulfur atom. Interestingly,
 285 Torii et al. showed that sulfenamides react differently with alkyl phosphites depending on the
 286 substituent on S.[31] As illustrated in Figure 2, the nucleophilic attack is directed to the N by the
 287 benzothiazoyl substituent, and to the S by the phenyl substituent due to the differences in S-N
 288 bond polarization. This inversion in the bond polarization is caused by the strong electron
 289 withdrawing effect of the benzothiazole moiety. Benzothiazole containing sulfenamides also have
 290 higher hydrogen abstraction efficiency in comparison to the corresponding phenyl sulfenamides,
 291 and are commonly used as rubber vulcanization accelerators.



292

293 **Figure 2.** Reactions of sulfenamides with alkyl phosphites. (Redrawn and simplified from reference
 294 [31])

295

296 The possible radical reactions that occur in the plain polypropylene-sulfenamide mixture at
 297 elevated temperatures are already numerous, and the situation becomes even more complicated
 298 when the number of components in the blend increases. However, the electronic structure and
 299 reactions of thiyyl[28] and aminyl [32][33] radicals under more controlled conditions have been well

300 studied in the literature. In the case of radical generators for flame retardant applications, the
301 radical formation is thermally triggered when the polymer is subjected to an excessive heat source
302 (e.g. flame). Kinetics of the subsequent radical reactions may depend on the environment
303 (polar/apolar) and structure of the molecule itself. In general, aromatic thiyl radicals are more
304 stable than the aliphatic ones due to charge dissipation, and electron donating groups (EDG) on
305 aryl make the radicals less reactive, i.e. have a stabilizing effect.[28] Theoretical quantum chemical
306 calculations made on phenylthiol radicals even suggest that both electron donating and
307 withdrawing groups on phenyl ring would increase the stability of the radicals and hinder the
308 formation of the corresponding disulfides.[34] The formed radicals are, however, capable of
309 hydrogen abstraction from weak bonds and addition reactions to the C-centered radicals, which
310 are both reversible reactions.[28] The diverse and facile chemistry of thiols and disulfides is
311 nowadays very well-known in the chemical synthesis, and most reactions, like the thiol-ene
312 coupling reactions are known to proceed via thiyl radical intermediates (Fig. 3). If oxygen is
313 available, also thiol olefin co-oxidation reactions can take place (Fig 3). Alkene isomerization
314 reactions via thiyl addition-fragmentation constitute a facile route to trans-unsaturated fatty acids
315 (Fig 3). This process is possible due to the reversibility of the sulfide formation reaction. Although
316 thermal generation of thiyl radicals without any additional initiator (radical or photolytic) is rather
317 poorly documented in the literature, it is known to occur in addition reactions of thiol compounds
318 to alkenes and their respective polymerizations. Thiyl formation in the absence of other initiators
319 is suggested to happen via molecule assisted homolysis (MAH) facilitated by an electron
320 donor/acceptor complex.[35]

321

334 benzothiazole. SN-III again had slightly lower melting temperature (T_m) than SN-I, but there was no
 335 significant difference in the weight loss temperature $T_{5\%}$. SN-III has the same benzothiazole moiety
 336 as SN-II, but the recorded lower T_m was attributed to the high flexibility of sebacate connecting
 337 the 2,2,6,6-tetramethylpiperidyl rings in SN-III in comparison to the stiff carbonate unit in SN-II.

338 **Table 1.** Thermal properties of SN-I, SN-II and SN-III. TGA-DTA heating rate 10 °C/min, under N₂.

Flame retardant	Thermogravimetric-differential thermal analysis (TGA-DTA)	
	Melting point T_m (°C)	Weight loss $T_{5\%}$ (°C)
SN-I	192	277
SN-II	278	290
SN-III	163	289

339

340 The TGA weight loss temperature $T_{5\%}$ for both oligomeric sulfenamides SN-IV and SN-V was around
 341 260°C. Oligomers did not show melting, but with differential scanning calorimeter (DSC) broad
 342 glass transition region was detected for SN-IV with the half height temperature (T_g) of -33 °C. No
 343 clear T_g was visible for SN-V.

344 **4.1 UL94 V-0 formulations with sulfenamide flame retardants and phosphonate P-I**

345

346 Spirocyclic phosphonate P-I was blended with sulfenamides SN-I to SN-V in PP (PP MFR25). The
 347 compositions and the obtained UL 94 V flammability test results are presented in Table 2. P-I alone
 348 at 15 wt% loading (sample 1) gave UL 94 V-2 rating, whereas in combination with 1 wt% of either
 349 monomeric (SN-I, SN-II and SN-III) or polymeric sulfenamides (SN-IV and SN-V) the stringent V-0
 350 rating was reached with zero burning time (samples 2–6). Dripping of polymer melt was still
 351 observed, but the drops were non-burning and therefore the cotton placed underneath the
 352 specimens was not ignited. When the amount of P-I was reduced from 15 to 8 wt% the reference
 353 sample burned completely and therefore UL 94 rating was no longer reached (sample 7). In
 354 contrast, the total burning time for the combination of 8 wt% of P-I and 1 wt% of SN-I (sample 8)
 355 was again zero, and only one specimen out of five ignited the cotton. At the sulfenamide loading
 356 of 2 wt% (sample 9), the V-0 was again clearly reached. Phenyl and benzothiazoyl substituents
 357 seem to have equal FR efficiency in PP MFR25 (samples 9 and 10), although SN-II does not
 358 necessarily melt during the processing step. The benzothiazoyl derivative SN-III had slightly lower
 359 FR efficiency than SN-II (sample 10 and 11); this can at least partially be attributed to its lower

360 concentration of SN-units. A ternary mixture of P-I, P-III and SN-I also gave the desired V-0 rating
361 at the total FR concentration of 9 wt% (sample 12). As a reference, it is worth mentioning that 28
362 wt% of decabromo diphenyl ethane (DBDE) in combination with 14.4 wt% of antimony trioxide
363 (ATO) is needed to reach the UL 94 V-0 rating (sample 13). The observed enhancement in UL 94
364 rating when P-I and SN-compounds are combined is related to their synergistic action to inhibit
365 burning of PP, since none of them alone can provide V-0 rating in the test even at much higher
366 loadings. Inhibition of flame propagation in the bulk material as well as changes in drop viscosity
367 and temperature are likely the key parameters affecting the decreased flammability of PP.

368

369
370
371
372**Table 2.** Flame retardant compositions in polypropylene (MFR 25 g/min). Flame retardant amount in weight percent of total weight.

Sample no.	FR wt%	P-I	P-III	SN-I	SN-II	SN-III	SN-IV	SN-V	DBDE / ATO	UL94 test ¹⁾	
										Total burning time (s)	Rating
1	15									9.6	V-2
2	15			1						0	V-0
3	15				1					0	V-0
4	15					1				0	V-0
5	15						1			0	V-0
6	15							1		0	V-0
7	8									CB	NC
8	8			1						0	V-0/V-2
9	8			2						0	V-0
10	8				2					0	V-0
11	8					2				0	V-2
12	6	2		1						0	V-0
13									28/14.4	23.9	V-0

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- 1) UL 94 vertical test, total burning time after two successive, 10 s ignitions for all five specimens. Rating V-0 (no cotton ignition, single burning time <10 s), V2 (cotton ignition, single burning time < 30s), CB = complete burning, burns up to the clamp, NC = non-classified, does not fulfill any of the UL 94 V-criteria. Specimen thickness 1.6 mm.

379 4.1.1 Limiting oxygen (LOI) and nitrous oxide indices (NOI)

380

381 Limiting oxygen index gives the lowest oxygen concentration that sustains candle-like combustion
 382 of a test specimen in the flow of O₂/N₂ gas mixture at standardized test conditions. In the NOI test
 383 the oxidant is changed to N₂O. To sustain burning of virgin PP MFR25 resin, 17.4 % of O₂ or 41% of
 384 N₂O was needed, respectively. The LOI of PP MFR25 as a function of P-I concentration and in the
 385 presence or absence of SN-I was measured, and the results are shown in Figure 4. Only a relatively
 386 modest increase in LOI value from 19 to 21 was observed when the concentration of P-I increased
 387 from 4 to 15 wt%. However, in the presence of 1 wt% of SN-I, a substantial increase in LOI was
 388 recorded. Thus, the maximum rise of 4.8 percent units and the highest LOI of 24.6 was found at
 389 the P-I concentration of 8 wt%. Interestingly, a similar trend was found in the nitrous oxide index
 390 (NOI) (Figure 4 upper curves), except that the NOI did not increase within the P-I concentration of
 391 8–15 wt% even in the absence of SN-I. This indicates that P-I exhibits some gas phase activity.[36]

392

393 Quantification of synergism

394

395 Mathematical quantification of synergy based on LOI results has been discussed by Lewin[37] and
 396 others.[38][39] The term synergistic efficiency (SE) is used to describe the change in effectivity
 397 when flame retardant is combined with other additives versus if the same additives (A and B) are
 398 used alone at the same proportions (x and y), as exemplified in Equation 1a for PP matrix. Ratio of
 399 > 1 refers to synergistic effect, 1 refers to additive effect (superposition), and <1 means that there
 is antagonism when the components are used together.

400

$$401 \quad SE_{OI(xA,yB)} = \frac{(OI_{PP+xA+yB} - OI_{PP})}{(OI_{PP+xA} - OI_{PP}) + (OI_{PP+yB} - OI_{PP})} \quad \text{eq.1a}$$

402

$$403 \quad SE_{OI(8PI,1SNI)} = \frac{(OI_{PP+8PI+1SNI} - OI_{PP})}{(OI_{PP+8PI} - OI_{PP}) + (OI_{PP+1SNI} - OI_{PP})} = \frac{(24.6 - 17.4)}{(19.8 - 17.4) + (18.5 - 17.4)} = 2.1 \quad \text{eq.1b}$$

404

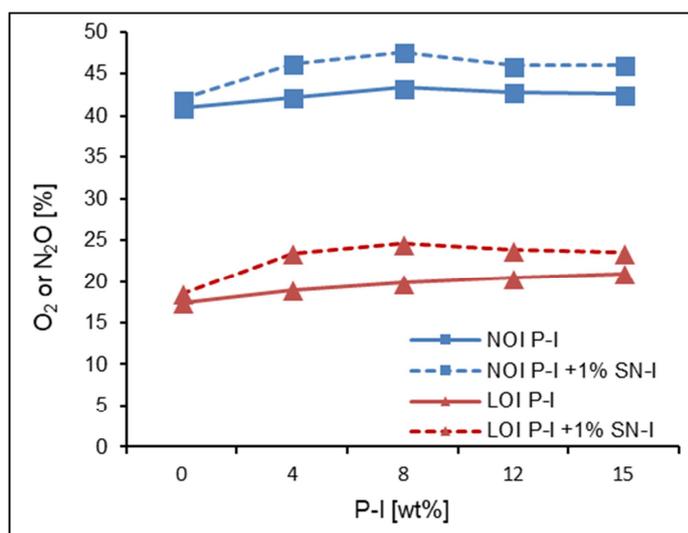
405 Equation 1. a) Synergistic efficiency (SE) of compounds A and B in polypropylene matrix (PP) in
 406 terms of oxygen index (OI). In the formula, x and y refer to the weight proportions of additives A
 407 and B, respectively. b) SE calculated for a FR system with 8 wt% of P-I and 1wt% of SN-I.

408

409 The SE can vary depending on the ratio of FR components. Studying the maximum of SE can help
 410 in finding an optimal ratio of components for a specific flame retardant-polymer system. However,
 411 it is realized that finding an optimal ratio in one fire test (like LOI) does not necessarily give the
 412 best result in other fire scenarios. As we knew that the sulfenamides are most efficient in PP at
 413 low loadings (0.5–2wt%), and that the effect then levels off, the synergy was studied at a fixed

414 concentration of 1 wt% of SN-I, and the concentration of the phosphorus compound P-I was
 415 varied. At the ratio of 8:1 SE_{OI} was 2.1 (eq 1b), which means that there is clear synergy between
 416 SN-I and P-I. At the ratio of 15:1, the SE_{OI} was 1.7, which also describes synergy, but based on the
 417 LOI value and the SE_{OI} the optimum loading would be at 8:1. However, the UL 94 results were
 418 better at the loading P-I + SN-I of 15 wt% + 1 wt% (V-0) than at the loading of 8 wt% + 1 wt% (V-2).

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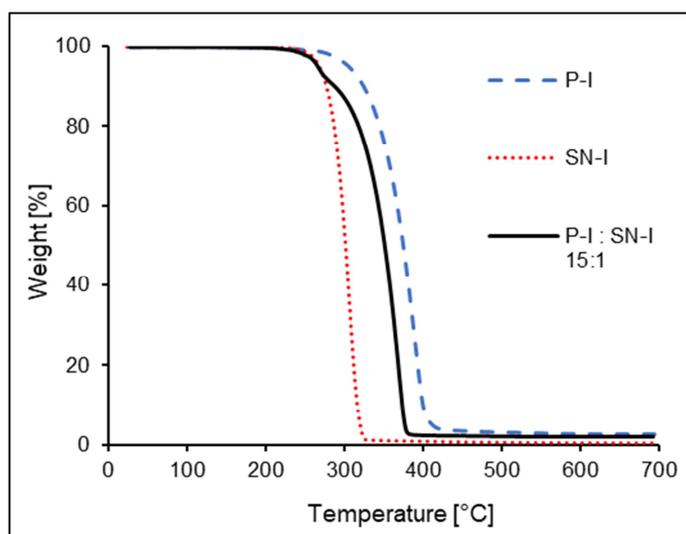
422 **Figure 4.** Limiting oxygen index (LOI) and nitrous oxide index (NOI) for PP MFR25 samples
 423 containing different concentrations of P-I alone (solid guide lines) or in combination with 1 wt% of
 424 SN-I (dashed guide lines).

425

426 4.1.2 Thermogravimetric analysis

427

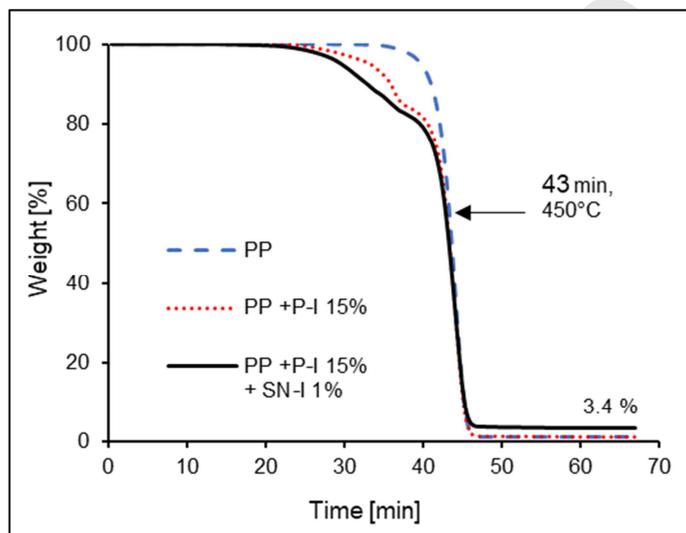
428 Weight loss curves for P-I, SN-I and their 15:1 combination are depicted in Figure 5. The weight
 429 loss starts slightly earlier for the combination than for the SN-I alone. The main difference is
 430 however at the end point temperature of the mass loss; in the presence of SN-I all P-I has been
 431 volatilized at around 380 °C, when the same for P-I alone takes place at around 420 °C.



432
433 **Figure 5.** TGA weight loss curves of P-I (dashed), SN-I (dotted) and their mixture at 15 to 1 ratio
434 (solid line).

435
436 TGA weight loss plotted for PP in combination with P-I and SN-I revealed that the final mass loss
437 rates of PP are similar with or without the additives (Figure 6). The amount of final residue is
438 roughly 2 wt% more for the PP sample containing P-I and SN-I than for the other samples.
439 However, this difference is not significant taking into account the normal variation in TGA
440 measurements.

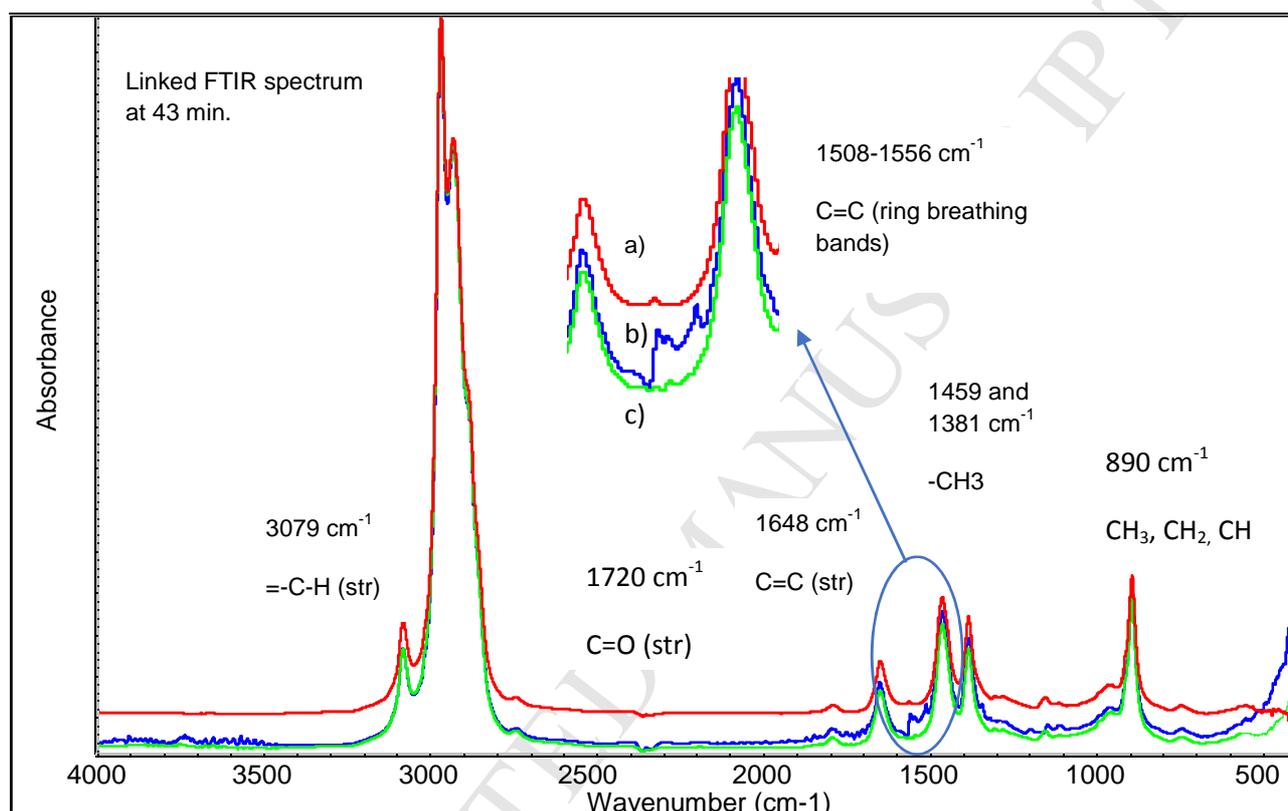
441



442
443 **Figure 6.** TGA weight loss curves for PP (dashed) in the presence of P-I (15 wt%) (dotted) and P-I
444 (15%) + SN-I (1 wt%) (solid line).

445
446 TGA-FTIR study revealed only some small differences in the decomposed PP fragments, when plain
447 PP and PP melt mixed with P-I and NS-I were compared. At around 450 °C, distinctive differences
448 were found in the FTIR spectra at the wave number region 1500–1600 cm^{-1} (Figure 7). This region
449 is typical for in plane stretching vibrations of heterocyclic fused rings (N-C=C, C=N, -S-C=C) as well

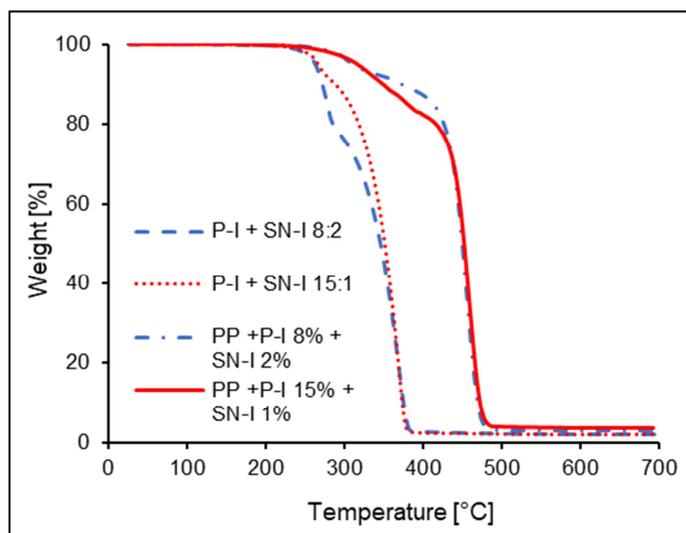
450 as for coordinated carbonates and carboxylates.[40] Together with the finding that the amount of
 451 residue in TGA is slightly higher for PP +P-I +NS-I than for the other samples (Fig. 6), increased
 452 formation of (heterocyclic) ring structures would best explain the occurrence of absorption bands at
 453 around 1550 cm^{-1} . Thereby enhanced carbonization, which in general is very low for PP, might
 454 occur in the presence of P-I and SN-I.
 455



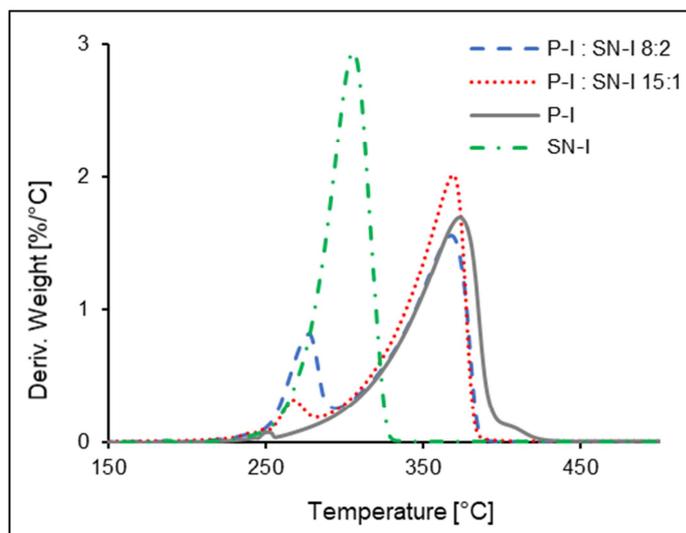
456 **Figure 7.** FTIR spectra of the TGA decomposition products at around $450\text{ }^{\circ}\text{C}$. a) PP b) PP + P-I + SN-I
 457 c) PP + P-I. Peak assignments based on lit.[40] [41] [42] [43]
 458

459 The influence of the ratio of P-I to SN-I was also investigated by TGA (Figure 8). At the ratios of
 460 15:1 and 8:2 (4:1), the onsets of decomposition and the end points of weight loss are almost equal
 461 for both powder mixtures. In addition to the obvious differences in the weight loss behavior due
 462 to the component mass ratio, differences can be seen in the mass loss rate (derivative weight in
 463 $\%/^{\circ}\text{C}$, Figure 9). The simultaneous weight loss of both P-I and SN-I starts right after melting of P-I
 464 (at $251\text{ }^{\circ}\text{C}$), and the rate is faster than the one for the superposition of individual components at
 465 the said ratios (calculated curves not shown). In the PP containing samples (Figure 8), the sample
 466 with 15 % of P-I has a greater loss before $425\text{ }^{\circ}\text{C}$ than the sample with 8 wt% of P-I due to a higher
 467 total loading of FR, but the PP decomposition step does not change markedly. Figure 10 illustrates

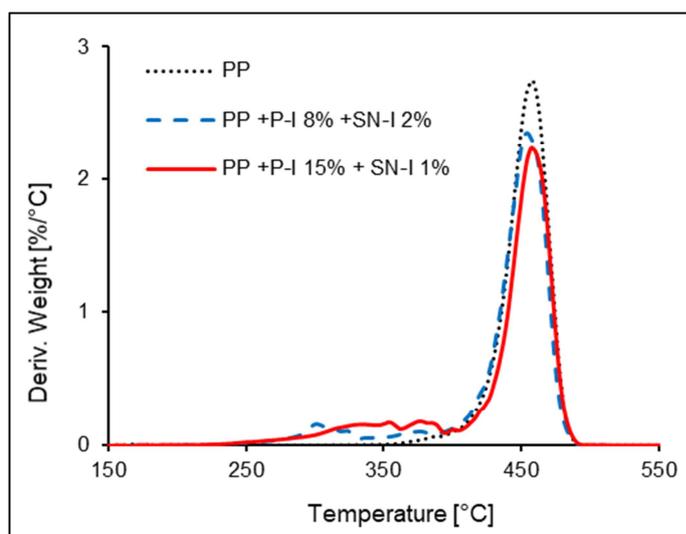
468 the rate of weight loss in PP blends. No big differences are observed in the rate of evolution of
 469 volatile fragments in PP.



470
 471 **Figure 8.** Weight loss in TGA at different ratios of P-I to SN-I in powder mixtures (15:1 dotted, 8:2
 472 dashed) and in PP blends (PP + P-I 8% + SN-I 2% dash with dot, PP + P-I 15% + SN-I 1% solid line).
 473



474
 475 **Figure 9.** TGA weight loss rate for SN-I (dash with dot), P-I (solid line), 8:2 ratio of P-I to SN-I
 476 (dashed) and 15:1 ratio of P-I to SN-I (dotted).
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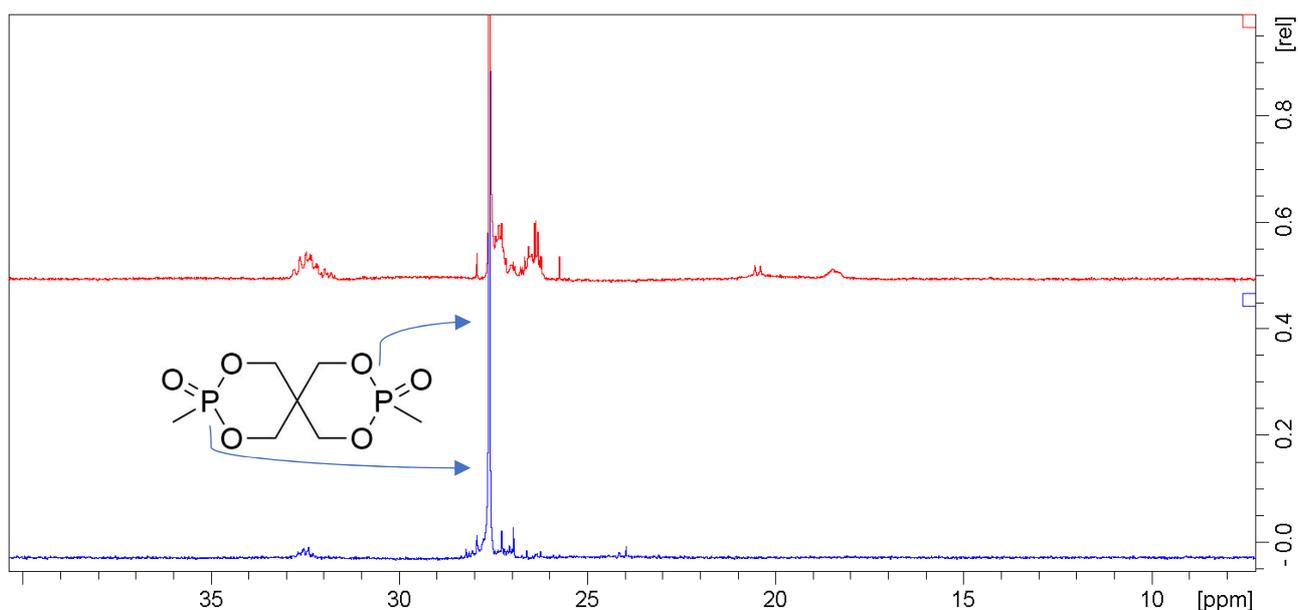
498

499

Figure 10. Derivative weight loss in TGA for PP (dotted), PP + P-I 15% + SN-I 1wt% (solid line) and PP + P-I 8% + SN-I 2wt% (dashed).

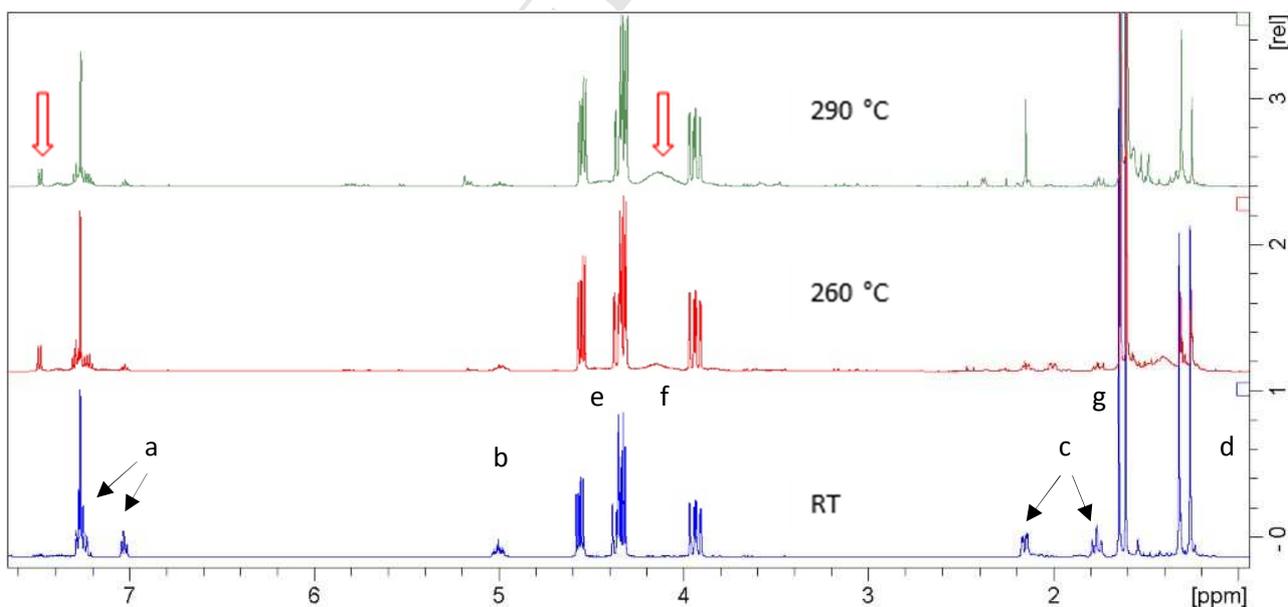
4.1.3 ^{31}P and ^1H NMR

The inspection of TGA curves presented in section 3.1.2 revealed that the weight loss starts earlier and is faster for the two-component FR systems than the P-I and SN-I alone (Figure 9). This means that P-I and SN-I interact at high temperatures, and therefore NMR studies were conducted to better understand the changes on a molecular level. Samples of P-I, SN-I and their 8:2 (4:1) combinations were heated for 5 minutes at 230°C, 260°C or 290°C, and the resulting products were compared with the samples that were kept at room temperature (RT) by running ^1H and ^{31}P NMR in a suitable solvent. SN-I was soluble in CDCl_3 and P-I in DMSO, so the changes in SN-I were mainly analyzed by ^1H measurements in CDCl_3 , whereas changes in P-I were analyzed by ^{31}P measurements in DMSO. In order to be able to analyze both samples, i.e. the DMSO soluble part and the CDCl_3 soluble part in the 8:2 mixtures, two sample tubes were heat treated at each of the above mentioned temperatures. The dissolved samples of the 8:2 combination were dark brown after the heat treatment at 260-290°C, whereas only slight discoloration was observed in the samples of P-I and SN-I alone.



500
501 **Figure 11.** ^{31}P (decoupled, DMSO) spectral comparison of P-I (below) and the mixture of P-I and
502 SN-I at the ratio of 4:1 (above) after heat treatment at 290°C.

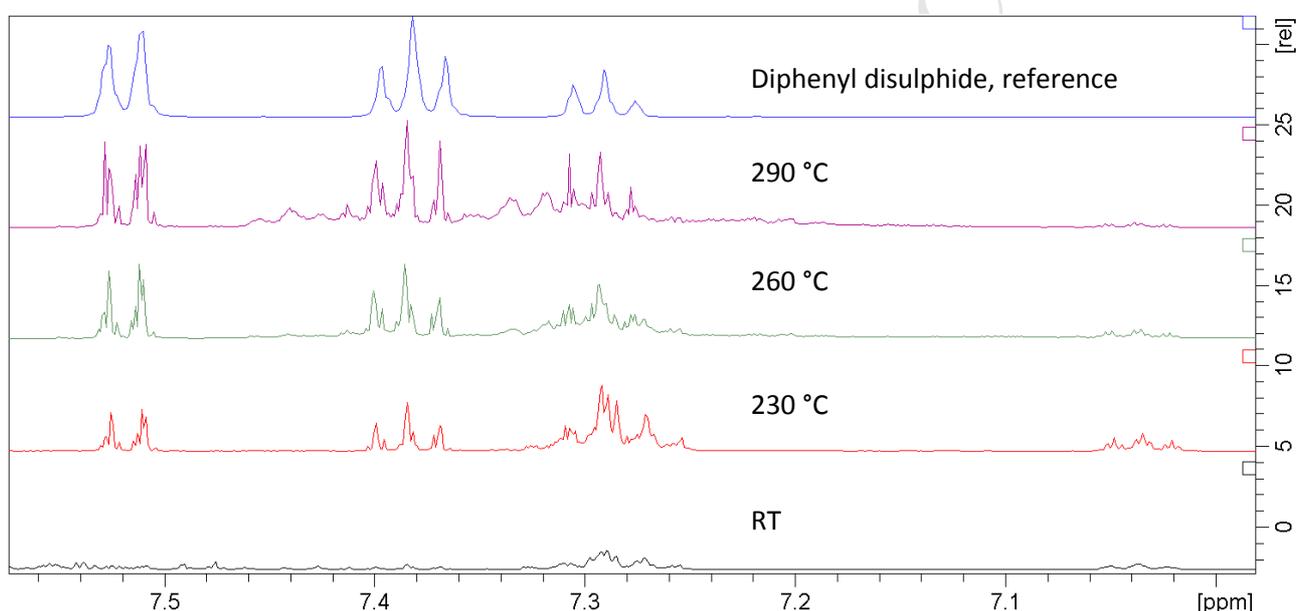
503 Figure 11 compares the P-H decoupled ^{31}P spectra of P-I and the spectra of P-I SN-I mixture after
504 the heat treatment at 290 °C. The pure compound P-I gives the main signal at δ 27.7 ppm. Larger
505 amount of diverse, unidentified phosphorus containing products can be seen in the mixture than
506 in the spectra of plain P-I.



507
508 **Figure 12.** ^1H NMR (CDCl_3) spectra for the mixture of P-I and SN-I at the ratio of 4:1 at RT, 260 °C
509 and 290 °C. a) SN-I, 10H, Ar b) SN-I, 2H, CH c) SN-I, 8H, CH_2 d) SN-I, 24H, CH_3 ; e, f) P-I, 8H, CH_2 g) P-
510 I, 6H, CH_3

511

512 In the proton spectra main changes are visible in the aromatic region (δ 7-7.5 ppm) and at around
 513 δ 4.0-4.2 ppm (Fig. 12). The former was assigned to the formation of diphenyl disulfide, and the
 514 latter to the simultaneous formation of free amines. Homolytic thermal decomposition of the S-N
 515 bond and subsequent recombination to the disulfide are most likely the cause to the observed
 516 changes. The formed disulfide is more soluble in DMSO than the parent molecule, and therefore it
 517 can be detected also in the ^1H NMR recorded in DMSO (Fig. 13). In addition to the disulfide,
 518 formation of an unidentified aromatic product at δ 7.41–7.46 and 7.31–7.35 ppm was detected at
 519 an increasing temperature, especially at 290 °C. The SN-I alone under the same circumstances
 520 does not produce detectable amounts of disulfide.



521

522 **Figure 13.** Comparison of ^1H NMR reference spectra of diphenyl disulfide (the topmost spectra)
 523 and DMSO soluble decomposition products of SN-I in the P-I:SN-I mixture at RT, 230 °C, 260 °C and
 524 at 290 °C, respectively.

525

526 4.2 Cone calorimeter study on APP/PER/SN-I intumescent system

527 The effect of sulfenamide SN-I addition into ammonium polyphosphate (APP) and pentaerythritol
 528 (PER) based intumescent system was studied by means of cone calorimeter. Based on previous
 529 studies, it was envisioned that radical generators may enhance flame retardant properties of
 530 intumescent systems by altering melt flow and enhancing charring reactions. [18]

531

532 4.2.1 Sample compositions, UL94 and LOI results

533 Prior to cone calorimeter measurements, two different compositions were tested in UL94 and LOI
 534 tests, as described in Table 3. IFR1 and IFR2 with APP-PER ratio of 3:1 and the total APP-PER

535 amount of 17 wt% and IFR3 and IFR4 with a ratio of 2:1 and the total amount of 24.5 wt%, were
 536 evaluated. The UL94 study showed, that one can reach the V-2 rating with a very short total
 537 burning time (5 s) at the lower loading, if 0.5 wt% of SN-I was added (IFR2), whereas the reference
 538 samples IFR1 without SN-I burn up to the clamp (no classification). In the case of higher total
 539 loading (IFR3 and IFR4), all samples self-extinguish but the total burning time was shorter (0 s
 540 versus 32 s) for the IFR4. Also, the LOI values increased by 2.6–3 %-units when 0.5 wt% of SN-I was
 541 added to the intumescent systems. The calculated SE value of 1.28 confirmed the synergist effect,
 542 (Eq. 1a, chapter 4.1.1).

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 544
 545

Table 3. Composition and FR results for intumescent systems

Sample	Composition (wt%)				UL94 (thickness 1.6 mm) ¹⁾			LOI
	PP	APP	PER	SN-I	Total burning time (s)	Cotton ignition (Y/N) ²⁾	Rating	% O ₂
PP MFR25	100				CB	5 Y	NC	17.4
IFR1	83	12.75	4.25		CB	5 Y	NC	23.2
IFR2	82.5	12.75	4.25	0.5	5	2 Y/3 N	V-2	26.2
IFR3	75.5	16.3	8.2		32	3 Y/2 N	V-2	28.5
IFR4	75.0	16.3	8.2	0.5	0	3 Y/2 N	V-2	31.1

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1) UL 94 vertical test, total burning time after two successive, 10 s ignitions for all five specimens. Rating V-0 (no cotton ignition, single burning time <10 s), V2 (cotton ignition, single burning time < 30s), CB = complete burning, burns up to the clamp, NC = non-classified, does not fulfill any of the UL 94 V-criteria.

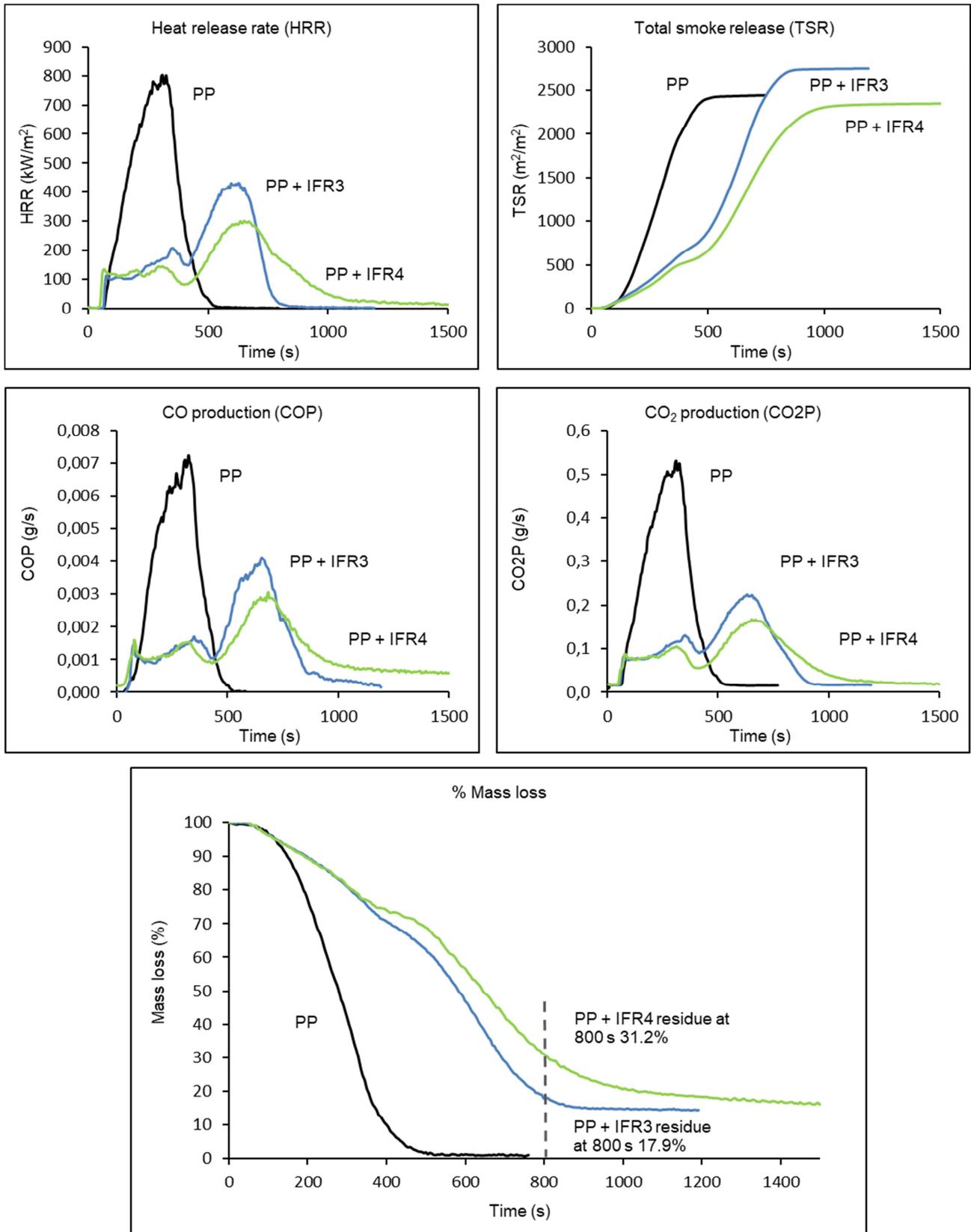
2) Amount of samples that ignite the cotton (Y) and do not ignite it (N).

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4.2.2 Cone calorimeter results

Samples IFR 3 and IFR 4 were chosen for the cone calorimeter test, and PP MFR25 was used as a reference. In the cone calorimeter test, the reaction of horizontally positioned samples to the irradiation at an incident heat flux of 35kW/m² were studied. Graphs of averaged (n=2) heat release rate (HRR), total smoke release (TSR), CO production (COP), CO₂ production (CO₂P) and mass loss percent (% mass loss) are presented in Figure 14. HRR curves show how the intumescent FR affects the heat release behavior of PP. Ignition time for the flame retarded PP is shorter due to the faster initial decomposition of the polymer, but once the protective layer has formed, the heat

562 release is strongly suppressed. After 400 s, the protective layer lost its integrity, and the peak of
563 heat release is found at around 600 s. The same phenomenon was seen both for IFR3 and IFR4,
564 but there seems to be difference in the stability of the protective layer to the benefit of IFR4; the
565 peak of heat release is lower and is delayed compared to the IFR3. The peak of heat release
566 decreases from roughly 800 kW/m^2 for the PP to 430 kW/m^2 for the IFR3, and further to 300
567 kW/m^2 for the IFR4. The increase in smoke release clearly follows the heat release curves as a
568 function of time, but the total smoke release was finally at the same level for all samples, or even
569 a slightly higher for the IFR3 than for the reference PP. CO and CO₂ production both follow the
570 heat release behavior. The mass loss curves (% from initial mass) of the intumescent systems start
571 to deviate at around 350 s, but the highest difference is at around 800 s. The residue at 800 s is
572 17.9 % for the IFR3, and 31.2 % for the IFR4, which can be attributed to the enhanced stability of
573 the intumescent layer.



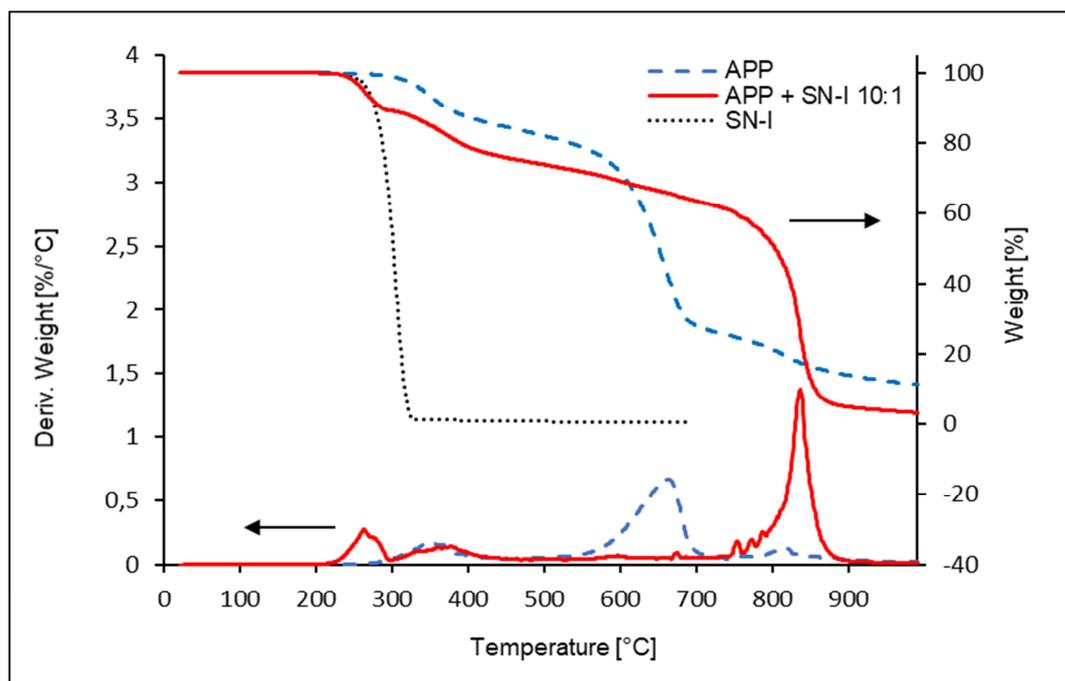
574

575 **Figure 14.** Average (n=2) cone calorimeter results for the heat release rate (HRR), total smoke
 576 release (TSR), CO₂ production (CO₂P) and mass loss (% mass loss) at the heat
 577 flux of 35 kW/m².

578

579

4.2.3 TGA results for the stabilization of APP



580

581 **Figure 15.** Overlay of the thermal decomposition curves for APP (dashed), SN-I (dotted) and their
 582 10:1 combination (solid lines). Lower curves give weight loss rate (left axis, derivative weight) and
 583 upper curves remaining weight in % (right axis).

584

585 TGA runs were done to detect possible interactions between APP and SN-I in the absence of PER
 586 and PP. APP to SN-I ratio of 10 : 1 was used in this study.

587 In the mixture, dissociation of the S-N bond and the first decomposition step of APP, ammonia
 588 evolution, take place at a similar temperature range as for their pure counterparts, but the last
 589 decomposition step between 500–900 °C is clearly delayed for the 10:1 combination (Figure 15). It
 590 was reasoned, that this somewhat unexpected thermal stabilization of the polyphosphate must be
 591 related to the chemical reactions between the decomposition products of SN-I and APP. The
 592 reactions leading to the enhanced stability would happen at an early stage, because volatile
 593 decomposition products of SN-I are formed before 330 °C. Lai et al. studied the mechanism of
 594 action in APP/PER/NOR116 system, and proposed that the nitroxyl radicals released from NOR116
 595 first react with APP, which leads to a more compact and thermostable intumescent char probably
 596 due to the delayed release of ammonia.[18] However, our TGA study done in the absence of PER
 597 did not indicate that the release of ammonia would be much delayed, and in this case the

598 enhanced stability of the formed protective layer would be due to some other radical interactions,
599 like the ones described in chapter 3, Theory.

600

601 **4.3 V-2 formulations with ATH and AHP**

602 The impact of SN-I on the flame retardant efficiency of aluminum trihydroxide (ATH) and
603 aluminum hypophosphite (AHP) was also investigated (Table 4 and Table 5). The UL94 vertical test
604 results show that SN-I boosts the FR effect of both compounds when admixed into PP.

605

606 **4.3.1 ATH containing samples**

607

608 Two different PP qualities with melt flow rates 25 and 12 g/10 min (230 °C/2.16 kg) were tested.
609 At the loading of 30 wt% of ATH, the UL 94 V-2 level was obtained, when 1 wt% SN-I was added.
610 Unfortunately, due to very minor dripping V-0 could not be reached, although the total burning
611 time was only 3.1 s and 11.6 s in case of MFR 25 and MFR 12, respectively. Based on the UL 94
612 results, an addition of 1 wt% of SN-I was more beneficial than an addition of 2 wt%, which is in line
613 with our previous findings, that the sulfenamide radical generators are most effective at low
614 concentrations. Although in the LOI results the difference between 1 and 2 wt% was almost
615 negligible, the trend was the same. The increase in LOI between the reference samples (30 wt%
616 ATH) and the samples with SN-I was rather minor, and based on difference in LOI values alone,
617 only a weak synergistic effect was recorded. Thus, at the usage level of 1 wt% SN-I, the synergistic
618 efficiency, SE, reached 1.07, which is close to the additive effect (SE=1). Nevertheless, in UL 94
619 tests the benefit of combining these two compounds was clear.

620

621
622 **Table 4.** Composition of ATH samples and results in UL 94 and LOI tests.

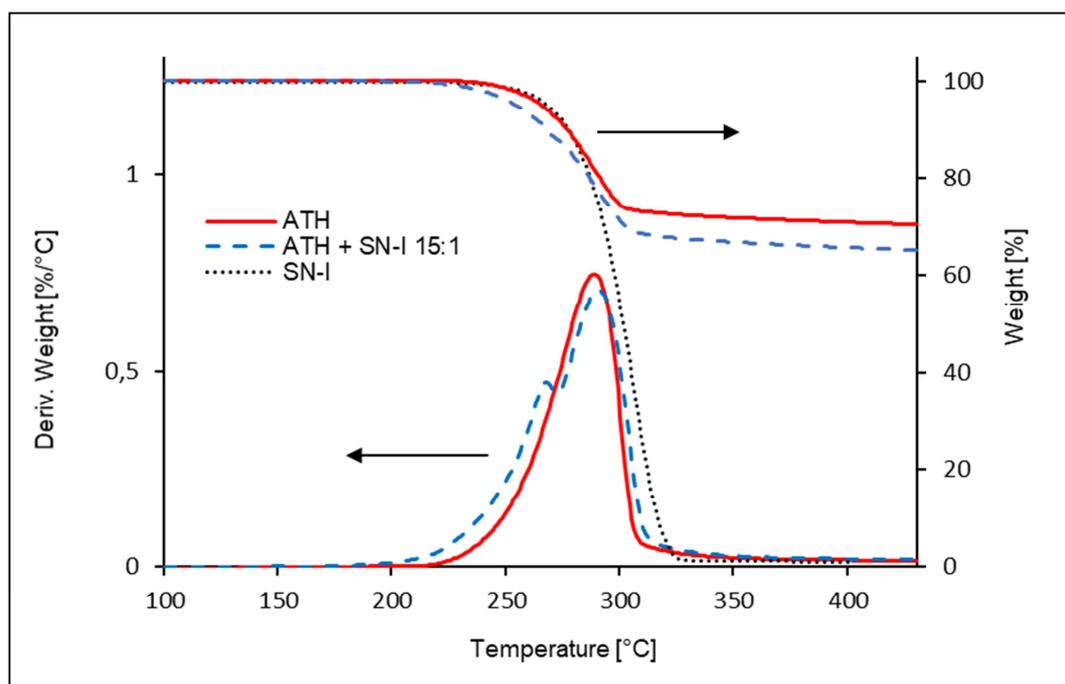
PP Melt flow rate	Sample composition (wt-%)			UL94 ¹⁾ , 1.6 mm		LOI (% O ₂)
	PP	ATH	SN-I	Total burning time (s)	Rating	
25	70	30		CB	NC	22.5
25	69	30	1	3	V2	23.7
25	68	30	2	22	V2	23.5
12	70	30		CB	NC	23.5
12	69	30	1	12	V2	23.9
12	68	30	2	38	V2	23.8

- 623
624 1) UL 94 vertical test, total burning time after two successive, 10 s ignitions for all five
625 specimens. Rating V-0 (no cotton ignition, single burning time <10 s, total burning time <
626 50 s), V2 (cotton ignition, single burning time < 30s, total burning time < 250 s), CB =
627 complete burning, burns up to the clamp, NC = non-classified, does not fulfill any of the UL
628 94 V-criteria.

629
630 **TGA**

631 The decomposition of ATH and SN-I commenced at approximately the same temperature of 250
632 °C, when tested separately in TGA (Figure 16). Whereas, the mixture of ATH and SN-I (15:1) started
633 to decompose already at around 230 °C, which can at least partially be ascribed to the formation
634 of aluminum-sulfenamide complex during the melting of SN-I. Aluminum at least has the potential
635 to accept lone electron pairs from the aromatic sulfenamide donor.

636



637
638

639 **Figure 16.** Overlay of the thermal decomposition curves for ATH (solid lines), SN-I (dotted) and
640 their 15:1 combination (dashed). Lower curves give weight loss rate (left axis, derivative weight)
641 and upper curves remaining weight in % (right axis).
642

642

643 4.3.2 AHP containing samples

644

645 Aluminum hypophosphite was tested with two different PP having melt flow rates of 2 and 55,
646 respectively (Table 5). It seemed to be more efficient in low MFR (2) than in high MFR (55) PP. V-2
647 classification was reached when 0.5 wt% of SN-I was added to 4 resp. 5 wt% of AHP. Without the
648 addition of SN-I, the burning behavior was non-regular between the parallel samples, leading to
649 very varying UL 94 burning times. Thus, some samples burned totally and some self-extinguished.
650 In the presence of SN-I, the burning behavior was more regular.
651

651

652

653 **Table 5.** Composition of aluminum hypophosphite (AHP) containing samples and UL 94 results.

PP Melt flow rate	Sample composition (wt-%)			UL94 ¹⁾ , 1.6 mm	
	PP	AHP	SN-I	Total burning time (s)	Rating
55	95	5		CB	NC
55	94.5	5	0.5	49	V-2
2	96	4		CB	NC
2	95.5	4	0.5	44	V-2

654 1) UL 94 vertical test, total burning time after two successive, 10 s ignitions for all five
655 specimens. Rating V-0 (no cotton ignition, single burning time <10 s, total burning time <
656 50 s), V2 (cotton ignition, single burning time < 30s, total burning time < 250 s), CB =
657 complete burning, burns up to the clamp, NC = non-classified, does not fulfill any of the UL
658 94 V-criteria.

659

660

5. Conclusions

661 In this work, the synergistic effects of sulfenamide based radical generators have been
662 investigated in polypropylene formulations together with commercially available FRs such as ATH,
663 AHP, APP-PER, phosphazene (P-III) and organic spiroposphonate AFLAMMIT[®] PCO 900 (P-I).

664 The synergistic efficiency is especially strong when the sulfenamides are combined with P-I, and
665 the UL 94 V-0 classification was reached at a total FR loading of only 10 wt%, i.e. 8 wt% of P-I and 2
666 wt% of SN-I. The total FR loading can still be reduced to 9 wt% by shifting to a ternary FR system
667 consisting of P-I (6 wt%), phosphazene P-III (2 wt%) and SN-I (1 wt%). The UL 94 V-2 standard,
668 which allows burning drips, was met by applying 4 wt% of AHP in combination with 0.5 wt% of SN-
669 I. In the presence of 30 wt% of ATH, the UL 94 V-2 classification with close to zero after flame
670 burning times was reached when adding 1 wt % of SN-I. In addition to PP V-0 applications,
671 sulfenamides thereby provide an interesting new option also in those applications, where V-2 is an
672 acceptable level of flammability or there is a need to significantly reduce the total loading of flame
673 retardants.

674 Cone calorimeter studies with APP-PER intumescent system revealed that an addition of 0.5 wt%
675 of SN-I significantly enhanced the thermal stability of the formed intumescent layer. The enhanced
676 integrity of the char was attributed to the increased number of radical reactions taking place

677 between the decomposition products of SN-I, polyphosphate and the polymer matrix, i.e. between
678 thiyl radicals, aminyl radicals, double bonds and diverse phosphorus containing moieties.

679 The reaction pathways between sulfenamide SN-I and the flame retardant P-I were investigated by
680 NMR and FTIR. The spectral analysis confirmed that sulfenamides at least partially undergo
681 chemical transformations in the presence of phosphorous based flame retardants such as P-I.
682 However, the NMR and FTIR studies did not yet allow to make comprehensive mechanistic
683 conclusions since the formed synergistic complexes were neither isolated nor fully characterized.
684 Moreover, TGA investigations were performed on neat sulfenamides, combinations of SN-I with
685 the commercial FRs as well as their blends in polypropylene matrix. The thermogravimetric
686 analysis revealed that the onset of thermal decomposition was reduced due to the interaction
687 between the flame retardants.

688 The future of radical generators as flame retardants looks promising. Their use either as
689 standalone flame retardants or as synergists with conventional flame retardants will grow when
690 chemistries are further refined, and their interactions with various polymers and other families of
691 flame retardants are better understood.

692

693

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812

Highlights

- The synergistic effects of five different sulfenamide based radical generators have been systematically studied in combination with commercially available eco-friendly halogen-free flame retardants in polypropylene.
- Strong synergistic effects were observed, and the UL 94 V-0 rating was reached for PP with a total FR loading of 10 wt% using 8 wt% of phosphonate ester *AFLAMMIT® PCO 900* together with 2 wt% of sulfenamide flame retardant. In a ternary mixture of an additional phosphazene additive (SPB-100), the needed total concentration for V-0 rating was further reduced to 9 wt%.
- The combination of 4 wt% of aluminum hypophosphite (AHP) with 0.5 wt% of sulfenamide offered a unique halogen free solution for achieving UL 94 V-2 rating in PP.
- Cone calorimeter studies of an ammonium polyphosphate-pentaerythritol based intumescent system in combination with 0.5 wt% of sulfenamide also showed encouraging results. The char stability was enhanced, the peak of heat release rate (HRR), CO and CO₂ production and total smoke generation were all reduced compared to the reference sample without sulfenamide

The future of radical generators as standalone flame retardants or as synergists looks promising.