Intumescent polypropylene in extreme fire conditions

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1 **Intumescent polypropylene in extreme fire conditions**

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6

7 **Highlights:**

8 • Intumescent polypropylene (PP) can resist to burnthrough test
9 • Long time of piercing using zinc borate as synergist
10 • Borophosphates forming a glass reinforcing the intumescent char

11
12 **Abstract:**

13 The paper deals with intumescent polypropylene (PP) undergoing extreme
14 fire (burn-through test with heat flux higher than 100 kW/m²). The purpose
15 of this unusual approach is to explore the possibility to design intumescent
16 plastic (here PP) resisting to burn-through test. A combination of
17 commercial intumescent flame retardants (ammonium polyphosphate-based
18 compounds containing a char former; AP766 (AP) and FlameOff (FO) of
19 the companies Clariant and FlameOff Inc) with zinc borate (supplied by US
20 Borax, ZB) or Kemgard (combination of ZB and molybdate supplied by
21 Huber, KZ) was incorporated in PP. Use of ZB and KZ as synergists in FO
22 formulations increases dramatically the time of piercing (formation of hole
23 through the plaque of polymer at 80 s without ZB or KZ vs. 280 s with KZ)
24 at the burn-through test (heat flux = 116 kW/m², propane burner) while the
25 combination with AP does not show any benefit. Analyses of the residues
26 obtained at different times of combustion by solid state nuclear magnetic
27 resonance (NMR) of ^{31}P, ^{11}B and ^{13}C shows the formation of
28 borophosphates creating a glass reinforcing the intumescent char: it acts as
29 a 'glue' providing flexibility and cohesion to the char.

30
31 **Keywords:** intumescence, fire chemistry, burn-through, polypropylene

32

33 **1. Introduction**

34 There is not a commonly accepted definition of the concept of 'extreme fire'.
35 According to its common use the expression 'extreme fire' is a complex

entity as it involves different realities and ways of looking. It contains at least three concepts [1]: (i) an idea of extension in the sense that 'extreme fire behavior' is very commonly associated to very large fires or fires that extend in large areas during extended periods of time; (ii) an idea of intensity in the sense that some properties of fire spread, namely its rate of spread or its rate of energy release acquire very large values; (iii) a third idea that is associated to 'extreme fire behavior' is related to rapid change in fire behavior conditions that is also linked to some degree of uncertainty in its prediction and danger. In this paper, we only kept the idea of high rate of energy.

It is common practice by fire scientists to quantify the intensity of a fire by the radiant heat flux rather than flame temperature [2]. There is an approximate relationship between fire type and heat flux but we should recognize it is a crude assumption because the incident heat fluxes depend on the spatial arrangement between the flame and the receiving target. The examples give a direct measurement of the heat flux from the source and they are: (i) small smoldering fire: 2-10 kW/m²; (ii) trash can fire: 10-50 kW/m²; (iii) room fire, open pool fire: 50-100 kW/m²; (iv) post-flashover room fire, confined pool fire: >100 kW/m², (v) jet fuel fire, open jetfire: 100-200 kW/m² and (vi) confined jetfire, BLEVE: >200 kW/m². In this research, heat flux corresponding to open jetfire or jet fuel fire was considered (it is high energy and hence it can be considered as extreme fire). Higher heat fluxes were not selected because the purpose was to investigate the response of an intumescent polypropylene (PP) in unconventional conditions for fire testing.

The intumescence process results from a combination of charring and foaming at the surface of the substrate [3]. The result of this process is the formation of a multicellular (alveolar) barrier, thick and non-flammable, which protects the substrate or residual material from heat or flame action. The charred layer acts as a physical barrier which slows down heat and mass transfer between gas and condensed phase. The formation of an intumescent char is a complicated process involving several critical aspects: rheology (expansion phase, viscoelasticity of char), chemistry (charring) and thermophysics (limitation of heat and mass transfer) [4]. This concept of intumescence enables to make flame retarded (FR) polymeric materials (including PP-based materials) exhibiting high performance in the case of reaction to fire (contribution of the material to fire growth) [5]. FR PPs are not used in the case of resistance of fire (ability of materials to resist the passage of fire and/or gaseous products of combustion), i.e. fire scenarios corresponding to burn-through, jetfire or structural response to fire, because they are not designed for this: they soften upon heating and fire can spread

77 out. Nevertheless, intumescent coatings applied on steel or composite act as
78 efficient fire barrier and we believe we should reach acceptable performance
79 using intumescent thermoplastics in the case of resistance of fire. It is an
80 unconventional testing for thermoplastics and no paper reports this type of
81 approach. At this time, there is no specific application for this type of
82 materials and the motivation of this paper is to explore the possibility to
83 design intumescent plastic (here PP) resisting to burn-through test.

84 The paper is organized in three parts. The first part is devoted to the design
85 of the intumescent formulation in PP considering potential synergists. Based
86 on the results of the first part, the second part deals with the determination
87 of mechanism of action using specific analyses by solid state nuclear
88 magnetic resonance (NMR). Finally, the effect of the fillers content
89 (loading) determined in the first part and incorporated in PP is examined in
90 the third part.

91

92 **2. Experimental**

93 **2.1. Materials**

94 Commercial grade of PP was used in this work: PP (ISPLEN PP 089 Y1E)
95 was supplied by Repsol (Madrid, Spain). PP 089 Y1E has a melt flow rate
96 (MFR) for a load of 2.16 g at 230°C of 31 g/10 min. Modified ammonium
97 polyphosphate (AP) is the commercial grade of Clariant (Knapsak,
98 Germany) with the brand name Exolit AP766. It is an intrinsic intumescent
99 system containing 24 wt% phosphorus and 15 wt% nitrogen acting in
100 synergy. Another modified ammonium polyphosphate as a powder was used
101 from the company FlameOff (Raleigh, NC – USA) and hereafter called FO
102 (the composition is proprietary). Zinc borate (ZB) was added in combination
103 with the intumescent additives as potential synergist. Its composition is
104 $2ZnO \cdot 3B_2O_3$ and it was supplied by the company US Borax (Boron, CA -
105 USA) under the brand name Firebrake. Kemgard 700Z is a complex mixture
106 of zinc molybdate/zinc borate (the composition is proprietary) from the
107 company Huber Engineered Materials (Atlanta, GA - USA): it was also used
108 in combination with the intumescent additives as potential synergist and it
109 is hereafter called KZ.

110

111 **2.2. Processing and formulations**

112 The strategy was to blend PP with FRs in a twin-screw extruder. The total
113 loading of FRs in PP was between 30 and 50 wt% varying the ratio between
114 the intumescent additives (AP or FO) and the synergists (ZB or KZ). The

115 formulations prepared in this work are gathered in Table 1. Note the loading
116 of ZB and KZ is low compared to AP and FO to get the highest
117 reinforcement of the intumescent char [6, 7].
118
119
120 Table 1. Formulations of the intumescent PPs

Formulation	PP (wt%)	AP (wt%)	FO (wt%)	ZB (wt%)	KZ (wt%)
PP	100	0	0	0	0
PP(70)-AP	70	30	0	0	0
PP(70)-AP/ZB(28:2)	70	28	0	2	0
PP(70)-FO	70	0	30	0	0
PP(70)-FO/ZB(29:1)	70	0	29	1	0
PP(70)-FO/ZB(28:2)	70	0	28	2	0
PP(70)-FO/ZB(27:3)	70	0	27	3	0
PP(70)-FO/ZB(25:5)	70	0	25	5	0
PP(70)-FO/KZ(29:1)	70	0	29	0	1
PP(70)-FO/KZ(28:2)	70	0	28	0	2
PP(70)-FO/KZ(27:3)	70	0	27	0	3
PP(70)-FO/KZ(25:5)	70	0	25	0	5
PP(50)-FO/ZB(29:1)	50	0	48.3	1.7	0
PP(50)-FO/ZB(28:2)	50	0	46.7	3.3	0
PP(50)-FO/ZB(27:3)	50	0	45	5	0
PP(50)-FO/ZB(25:5)	50	0	41.7	8.3	0
PP(50)-FO/KZ(29:1)	50	0	48.3	0	1.7
PP(50)-FO/KZ(28:2)	50	0	46.7	0	3.3
PP(50)-FO/KZ(27:3)	50	0	45	0	5
PP(50)-FO/KZ(25:5)	50	0	41.7	0	8.3

121

122 Compounding was performed using HAAKE Rheomix OS PTW 16 twin-
123 screw extruder. The extruder is a co-rotating intermeshing twin screw with
124 a barrel length of 400 mm and screw diameter of 16 mm (L/D = 25) with 10
125 zones. PP and FRs were incorporated using two gravimetric side feeders into
126 the extruder. Polymer flow rate is fixed to extrude about 500 g/h with a
127 screw speed of 300 rpm. The temperature profile of the extruder from feeder
128 to die was set at 200/ 200/ 200/ 200/ 200/ 170/ 185/ 180/ 200/ 200°C.

129

130 **2.3. Burn-through test**

131 In a previous work, a versatile fire test was developed with a complete set
132 of instrumentation to investigate the fire behavior of materials. The
133 description of this test is fully described in [8] and the reader could find all
134 information about the setup and the measurement. In this paper, only
135 required information to describe the operation of the test is given. This test
136 is a burn-through test which was designed to mimic the aeronautical fire test
137 defined in the standard ISO2685:1998. In this work, it was used as burn-
138 through test and to create an extreme fire for fire-retarded thermoplastics.
139 The equipment is described as follows and is shown in Fig. 1: (i) Propane
140 burner from Bullfinch, (ii) High purity propane supplied by Air Liquide
141 (N35, purity 99.95%), (iii) Propane flowmeter from Bronkhorst High-tech,
142 (iv) Water-cooled heat flux gauge from Sequoia, (v) Cooling thermostat
143 from Lauda Brinkmann (Lauda Proline RP845), (vi) Infrared (IR) camera
144 from FLIR SystemsTM (ThermovisionTM A40M Researcher) calibrated
145 from 0°C to 1000°C and (vii) Fireproof panels composed of silicate of
146 calcium from Final Advanced Materials (Calsil) of 10mm thick.

147 The burner can deliver a propane-air flame characterized by a heat flux up
148 to 200 kW/m². The burner was placed at 75 mm from the material and the
149 heat flux was calibrated at 116 kW/m² using a heat flux gauge in the same
150 conditions as the tested sample in a separate box (error less than 5%). The
151 temperature of the flame was measured with 5 aligned thermocouples (along
152 the flame) at 1100°C. The sample size was 10x10 cm² and was put between
153 the two panels in Calsil (see above). Temperature was measured in the center
154 of the sample using a thermocouple embedded in the polymer at the surface
155 of its backside. Infrared camera was also used to estimate the surface
156 temperature assuming the emissivity of the surface constant equaling 0.92
157 (black paint of known emissivity on the backside of the polymer plaque).
158 Reasonable agreement was observed between the two measurements and
159 only temperature measured by the thermocouple was shown in the
160 following. All experiments were repeated at least twice and all

161 measurements were within 10% error (in [8], we showed the error on
162 temperature measurement was less than 10%).

163
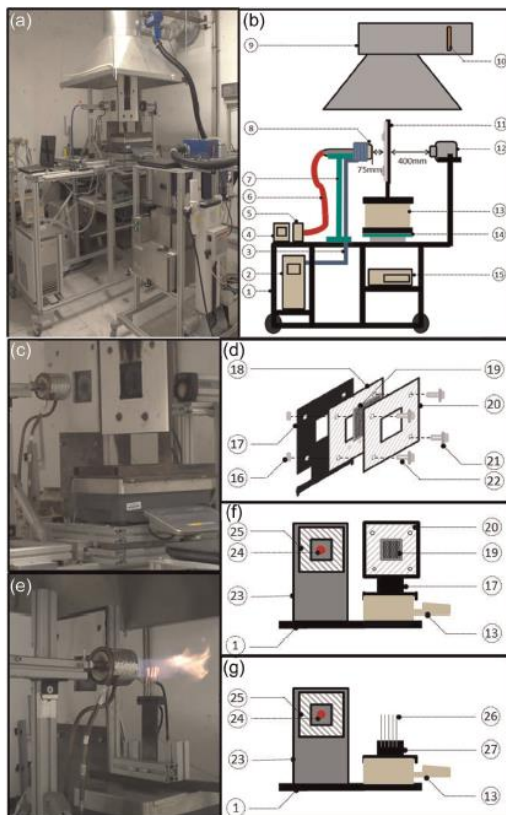
164
165 Fig. 1. Picture (a, c, e) and scheme (b, d, f, g) of the experimental apparatus - (1) Test
166 bench frame, (2) Cooling system, (3) Copper coil cooler, (4) Propane thermocontroller,
167 (5) Propane flowmeter, (6) Propane gas line, (7) Burner support, (8) Propane flame
168 burner, (9) Hood, (10) Ring sampler, (11) Sample holder, (12) Infrared (IR) camera, (13)
169 Precision scale, (14) Scale holder, (15) Data acquisition device, (16) Bolt, (17) Steel
170 support, (18) Fireproof boards, (19) Sample, (20) Fireproof boards, (21) Washer, (22)
171 Screw, (23) Water-cooled calorimeter holder, (24) Water-cooled calorimeter, (25)
172 Fireproof panel, (26) Aligned thermocouples, (27) Thermocouple holder (adapted from
173 [8])

174
175 **2.4. NMR analyses**

176 ^{11}B magic angle spinning – nuclear magnetic resonance (MAS-NMR) was
177 performed at 256.6MHz on a 18.8 T Bruker Avance III spectrometer with a
178 3.2mm probehead operating at a spinning frequency (ν_{rot}) of 20 kHz. The
179 spectra were recorded with a 1 ms pulse length (corresponding to a $\pi/12$ flip
180 angle determined on a liquid), a recycle delay (rd) of 10 s and 128 transients.
181 ^{13}C and ^{31}P MAS-NMR experiments were performed on a 9.4 T Bruker

182 Avance spectrometer at 100.6 and 162MHz, respectively. The $^{13}C(^1H)$
183 cross-polarization (CP) NMR experiment was conducted with a 4mm
184 probehead at ν_{rot} of 10 kHz with a 4 ms pulse length (corresponding to a $\pi/2$
185 flip angle), a rd of 10 s, a contact time of 1 ms and 1024 transients. The ^{31}P
186 NMR analysis was carried out with a 4 mm probehead under 1H decoupling
187 conditions. The spectrum was recorded with a ν_{rot} of 12.5 kHz, a 2 µs pulse
188 length (corresponding to a $\pi/4$ flip angle) a rd of 120 s and 16 transients. ^{11}B
189 and ^{31}P chemical shifts were referred to $NaBH_4$ and H_3PO_4 at - 42.06 ppm
190 and 0 ppm, respectively.
191
192 **3. Results and discussion**

193 **3.1. Design of the intumescent formulation**

194 Intumescent PPs are generally designed to exhibit high performance in terms
195 of reaction to fire but not in terms of resistance to fire. In this section, it is
196 our goal to examine the ability of intumescent PPs to resist to burn-through
197 test. This condition is unusual for commodity polymer such as PP but
198 intumescence is also used as protective coating for diverse substrates (e.g.
199 steel, wood or composites) to pass the burn-through test. Two types of
200 additives were incorporated in PP: (i) AP is a conventional intumescent
201 additive providing low flammability to PP for various fire scenarios such as
202 UL-94, glow wire or cone calorimeter and (ii) FO is a new intumescent
203 additive on the market and was made from intumescent ingredients of
204 intumescent paint. Based on previous works of this lab, zinc borate was
205 selected as potential synergist because it is known to reinforce intumescent
206 char [6]. ZB is a pure zinc borate and was already used in previous
207 formulations [7] but KZ has never been evaluated in combination with
208 intumescent ingredients. This last product was selected because its main
209 composition is zinc borate and to take advantage of the presence of
210 molybdate (known as synergist with metal hydroxides).

211 Intumescent PPs filled at 30 wt% loading were first evaluated (Fig. 2). The
212 temperature rise in all materials is similar up to 40 s. Virgin PP softens when
213 it reaches 140°C on its backside (melting temperature of PP is in the range
214 150-170°C) and it pierces just after (sharp increase of temperature at 150°C).
215 When AP and AP/ZB (ratio 28 to 2) are incorporated in PP, char formation
216 at the surface of the material can be observed but it cannot extend the time
217 to piercing. Visual observation suggests the expansion of the char is not fast
218 enough to provide a protection and it remains too soft to resist to the
219 impingement of the flame. In this case, there is no benefit to combine ZB
220 with the intumescent additive. On the contrary, the incorporation of FO
221 slows the temperature rise after 40 s thanks to the formation of an

intumescent char. The char resists to the impingement of the flame up to 90 s and it pierces after because of the too high softening of the material. The addition of ZB in the formulation dramatically improves the resistance to piercing of the system. The time to piercing is reached at 225 s thanks to the fast formation of an intumescent char which remains rigid (low softening) for longer times.
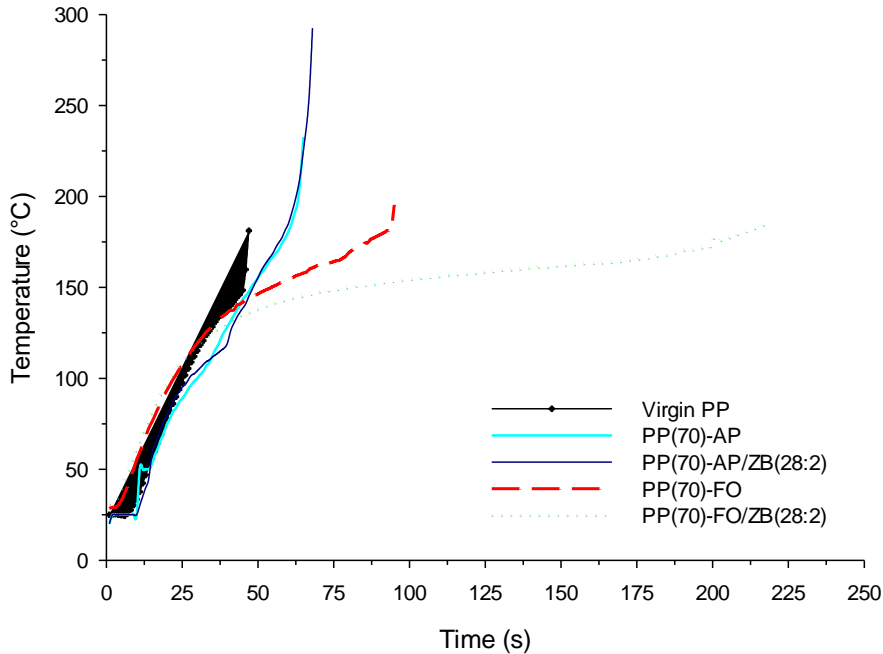
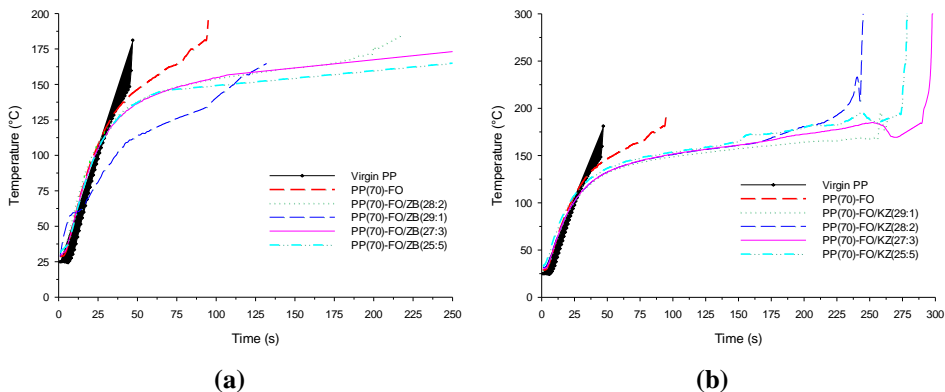Fig. 2. Temperature as a function of time on the backside of intumescent PPs containing AP and FO as main ingredient during a burn-through test at 116 kW/m².

From the results above, it is shown AP is not the right additive for PP to perform the burn-through test. In the following, we only focus our work on FO in combination with ZB and on determining the best ratio FO/ZB. We kept the loading of ZB low compared to FO (Table 1) because our previous work showed the ratio intumescent formulation over ZB should be high enough (typically 28:2) to get the highest efficiency of ZB [7]. Fig. 3 –(a) shows the temperature/time curves of the formulations varying the ratio FO/ZB compared to virgin PP and PP(70)-FO. The formulation having the ratio 29:1 pierces at 125 s and so, it does not show any enhancement compared to the ratio 28:2. Note the performance is highly sensitive to the content of ZB: only 1wt% variation of ZB permits to gain 100s before piercing. The two ratios 27:3 and 25:5 enhance the time to piercing at 250 s compared to 225 s for the ratio 28:2. According to visual observation, the addition of ZB permits keeping the rigidity of the intumescent char

247 undergoing the impingement of the flame and preventing too much
248 deformation at longer times (and hence the piercing of the sample). The
249 same experiment was done substituting ZB by KZ with the same ratio (Fig.
250 3 –(b)). The addition of KZ in the formulations PP(70)-FO/KZ permits for
251 all ratios to dramatically enhance the time to piercing compared to the use
252 of FO alone. The behavior looks similar and the longer time to piercing is
253 reached at about 300 s for PP(70)-FO/KZ(25:5). The same conclusion as
254 above can be made namely the addition of KZ permits to reinforce the char
255 strength keeping its rigidity.

256

(a)   (b)

257   Fig. 3. Temperature as a function of time on the backside during a burn-through test at
258   116 kW/m² of (a) intumescent PP(70)-FO/ZB and (b) intumescent PP(70)-FO/KZ.

259

260 **3.2. Role of zinc borate**

261 The previous section showed the role of ZB reinforcing the intumescent
262 char. Specific chemical reactions should be responsible for this
263 reinforcement and were characterized by solid state NMR. This technique is
264 very useful because it permits the selection of the nucleus (here ^{31}P, ^{11}B and
265 ^{13}C) and to observe its surrounding. So, it gives the chemical species formed.
266 Four materials were selected based on the results above (best ratio of
267 FO/ZB=27/3): PP(70)-AP, PP(70)-AP/ZB(27:3), PP(70)-FO and PP(70)-
268 FO/ZB(27:3). Note ZB was used instead of KZ because the main component
269 of KZ is ZB and we wanted to avoid other additional interactions. They were
270 submitted at the burn-through test and the combustion was stopped at
271 characteristic times namely, 50 s (all samples), 100 s (samples containing
272 FO) and 215 s (only PP(70)-FO/ZB(27:3)). The samples before testing were
273 used as reference.

274 Ammonium polyphosphate (APP) is contained in both AP and FO and is
275 one of the main ingredients of the intumescent flame retardants (Fig. 4 at
276 t=0 s). Upon heating, APP decomposes and yields acidic phosphates acting
277 as char promoter [3]. They play a significant role in the charring and in the
278 formation of an intumescent coating: the evolution of the phosphate species
279 should be revealed by ^{31}P NMR. The four samples were then characterized
280 by DD-MAS ^{31}P NMR as a function of burning time (Fig. 4). The number
281 of bridging oxygen atoms allows classifying the phosphate structure using
282 Q^n terminology where n represents the number of bridging oxygen atoms
283 per phosphorus tetrahedron. This terminology was used in the following [9].
284 The spectra of the neat materials (t = 0 s) exhibit a doublet located at -22
285 and -24 ppm assigned to Q^2 site. This doublet is characteristic of P in APP
286 as already reported in our previous work [10]. An additional band of low
287 intensity at 1 ppm can be distinguished on the two FO samples. It is assigned
288 to Q^0 site probably an orthophosphate linked to aliphatic species.

289 At t = 50 s, the two spectra of the samples without ZB exhibit three bands
290 but not located at the same chemical shift (Fig. 4 (a) and (b)). The bands at
291 0 and -12 ppm are common for the two materials and they are assigned to
292 Q^0 site (probably mainly phosphoric acid [11]) and to Q^1 site
293 (orthophosphates linked to aromatic species [12]) respectively. It is
294 noteworthy that the amount of species in Q^1 site is higher than that in Q^0 for
295 PP(70)-FO (ratio of the areas Q^1/Q^0 is higher). It suggests FO promotes the
296 formation of phosphate linked to char. The band at – 6 ppm (PP(70)-AP) is
297 attributed to Q^2 sites corresponding to pyrophosphates [12] and the broad
298 band centered at -27 ppm (PP(70)-FO) is attributed to the formation of
299 amorphous phosphate-type exhibiting Q^3 and Q^4 sites [13]. With the ZB in
300 the formulation, the two systems have similar spectra (Fig. 4 (c) and (d)).
301 The broad resonance (between 5 and -55 ppm) is the signature of a
302 distributed structure found in glasses or amorphous compounds while the
303 narrow resonances are characteristic of ordered phase. It can contain zinc
304 phosphate and borophosphate in addition to phosphate glass [9, 10]. The two
305 sharp bands at 0 and -6 ppm can be assigned as above. The band centered at
306 -30 ppm is assigned to borophosphate [14] and the broad band centered at -
307 12 ppm might be assigned as above in a disordered structure and/or to
308 borophosphate glass [9]. Finally, at higher testing times for PP(70)-
309 FO/ZB(27:3), the spectra are similar to those at 50s. Those results evidence
310 APP and its decomposition products react with zinc borate. It is not unusual
311 in intumescent systems and it was already reported in previous work [9].
312 The formation of borophosphate glass reinforces the char and acts as a 'glue'
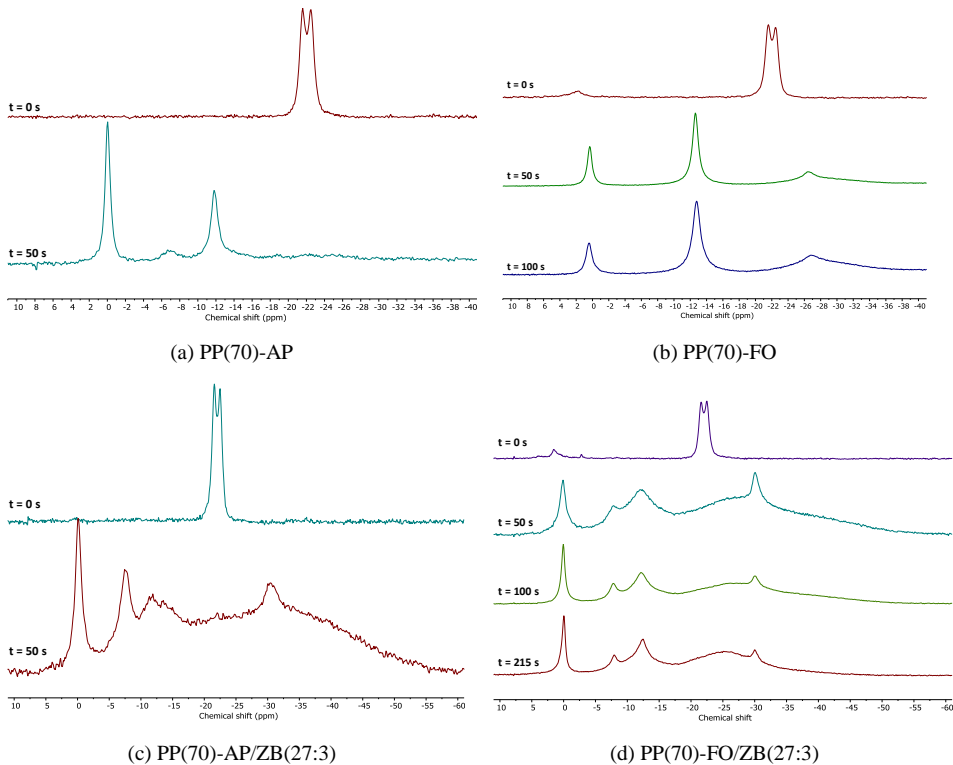313 providing flexibility and cohesion to the char.

314

315

(a) PP(70)-AP

(b) PP(70)-FO

(c) PP(70)-AP/ZB(27:3)

(d) PP(70)-FO/ZB(27:3)

316   Fig. 4. DD-MAS ^{31}P NMR of intumescent PPs as a function of burning time

317

318   MAS ^{11}B NMR spectra exhibit two bands at t=0s (Fig. 5). The first band
319   lying from 10 to 20 ppm, shows the presence of trigonal (BO$_3$) borate units
320   while the second band (band centered around 1 ppm) is assigned to
321   tetragonal (BO$_4$) borate species [9]. Those two polyhedra can be
322   characterized according to their different chemical shifts but also through
323   their quadrupolar constant (C$_Q$). C$_Q$ of BO$_3$ is indeed much larger than that
324   of BO$_4$ because of the higher asymmetry of the planar BO$_3$ species (2.4-3.0
325   MHz and <1 MHz for the BO$_3$ and BO$_4$ units, respectively) [15]. This
326   explains why BO$_3$ signals are broader than BO$_4$ resonances. After burning
327   (t > 0s), the broad band assigned to BO$_3$ units disappears and the band
328   assigned to BO$_4$ units is shifted to -4 ppm (Fig. 5). The spectra are similar
329   for the two formulations and whenever the duration of testing. A main sharp
330   band can be distinguished at -4 ppm and a shoulder at -1.5 ppm which are
331   assigned to two types of borophosphates [16]. It is consistent with the
332   assignments of the DD-MAS ^{31}P NMR spectra. Borates react with

333 phosphates upon heating and they are all consumed by the reaction: they are
334 no longer 'free' borates in the intumescent coating.

335

(a) PP(70)-AP/ZB(27:3)   (b) PP(70)-FO/ZB(27:3)
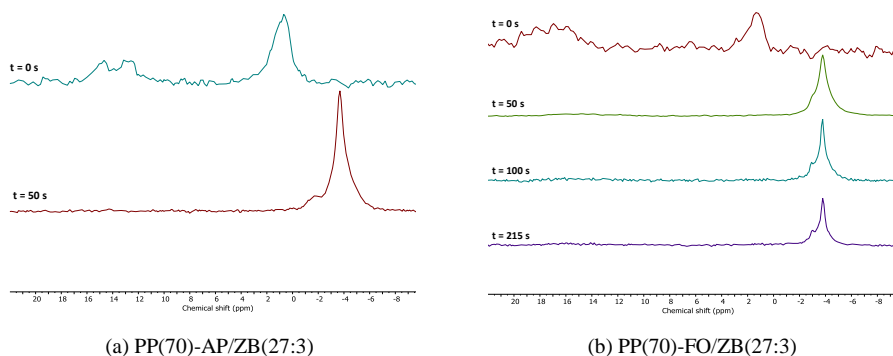
336   Fig. 5. MAS ^{11}B NMR of intumescent PPs containing ZB as a function of burning time

337 The basic principle of intumescence is to make a protective char. Visual
338 observation of the behavior of the materials evidences the charring of the 4
339 systems and hence, ^{13}C NMR should provide information on carbonaceous
340 species formed upon burning. All CP-DD-MAS ^{13}C NMR spectra exhibit
341 three resonance bands located at 21, 26 and 43 ppm (Fig. 6). They can be
342 assigned to polymeric chains of PP where the bands at 21, 26 and 43 ppm
343 are assigned to CH_3, CH and CH_2 groups respectively [17]. For the sake of
344 brevity, the spectra at t = 0 s were not shown because they only exhibit the
345 three mentioned bands and no additional insight was provided. It is
346 noteworthy the bands of PP are detected whenever the duration of testing. It
347 makes sense because the test is stopped when piercing occurs due to the
348 softening of PP. PP is therefore not completely decomposed and so, it can
349 be detected by NMR.

350 Intumescent char is constituted by condensed polyaromatic species
351 containing mainly carbon and sometimes heteroatoms like nitrogen and
352 oxygen [18, 19]. They are then detected by solid state NMR of carbon by a
353 broad band centered around 130 ppm corresponding to sp^2 hybridized
354 aromatic carbon atoms. Except for the samples containing FO, this band
355 cannot be detected with our experimental conditions (even when zooming
356 in) (Fig. 6). Two phenomena could explain this: (i) CP was used for the
357 acquisition of the spectra and because of the low number of protons on
358 aromatic rings, the magnetization transfer is low and hence, the intensity of
359 the band is low or undetectable and (ii) the formation of carbon free radicals
360 on aromatic ring creates a strong anisotropy of magnetic susceptibility and
361 then the loss of NMR signal [12]. Charring occurs for each sample and when
362 detectable, a broad band centered at 125 ppm can be distinguished. On the

spectra recorded on FO containing samples at 50 s (Fig. 6-b) and at 100 s
(Fig. 6-d), a tail to the higher ppm is observed. It suggests the formation of
oxidized carbons and of aromatic carbons bound to phosphates [20].
Additional bands can be distinguished on the spectrum of PP(70)-
FO/ZB(27:3) at t = 215 s (Fig. 6-d) located at 111, 121, 125 and 143 ppm.
They are relatively sharp on the broad band corresponding to the aromatic
carbons. The band at 111 ppm is assigned to protonated aromatic carbon,
those at 121 and 125 ppm are assigned to non-protonated aromatic carbons
and that at 143 ppm is assigned to aromatic carbons bound with phosphates
[20]. The shape of the 4 bands indicate carbon atoms are in an environment
of higher symmetry suggesting the formation of some crystalline species.
Overall, it is shown phosphates can be bound to the charred structure. The
presence of phosphate prevents the oxidation of 'carbons' [21] and provides
additional mechanical properties to the char (higher char strength and
flexibility) [22].

(a) PP(70)-AP

(b) PP(70)-FO

(c) PP(70)-AP/ZB(27:3)

(d) PP(70)-FO/ZB(27:3)
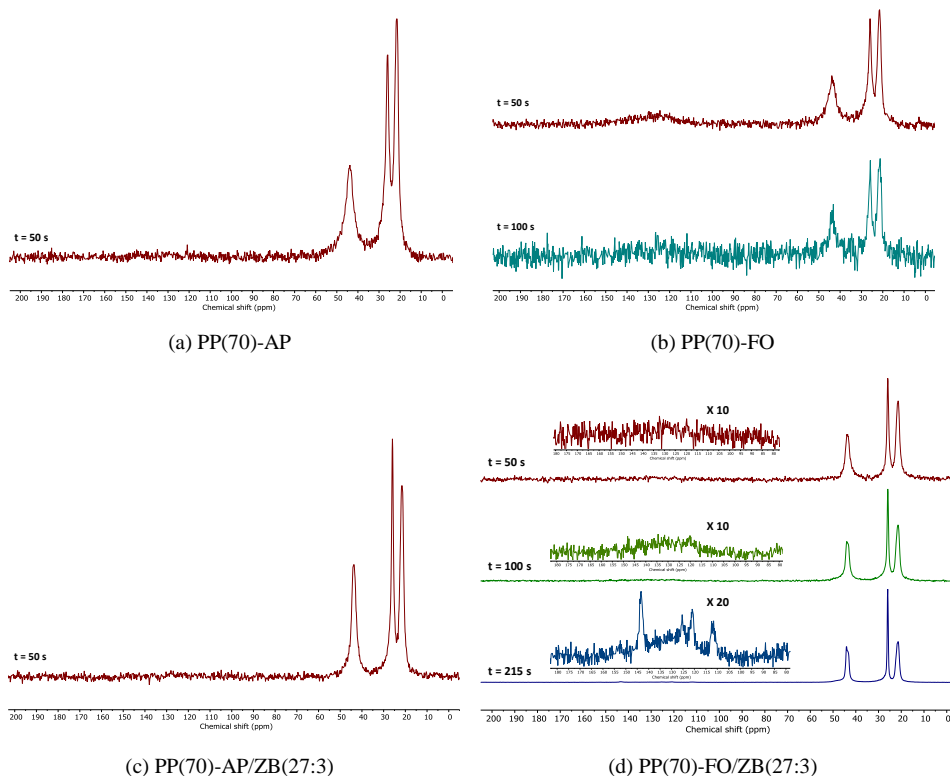
Fig. 6: CP-DD-MAS ^{13}C NMR of intumescent PPs as a function of burning time

3.3. Effect of loading

The first section showed that ZB and KZ in combination with FO provide superior performance at the burn-through test. The purpose is to increase the total loading of fillers (at 50 wt%) in PP to investigate its effect in terms of time to piercing. The time/temperature curves of all formulations are shown on Fig. 7. Surprisingly, the curves of the formulations containing ZB does not show any improvement compared to those at 30 wt% loading (Fig. 3 *vs.* Fig. 7). It is also true for the formulations containing KZ (times to piercing are even shorter) except for the ratio FO/KZ at 25 to 5 (Fig. 7-b). In this last case, the time to piercing reaches 330 s compared to the others exhibiting a time to piercing at 175 s. At high loading, it is observed higher charring but at the same time, the material looks softer. So, it implies that the impingement of the flame creates the piercing at shorter times because of its lower viscosity even if its efficiency as heat barrier might be higher.

(a)   **(b)**
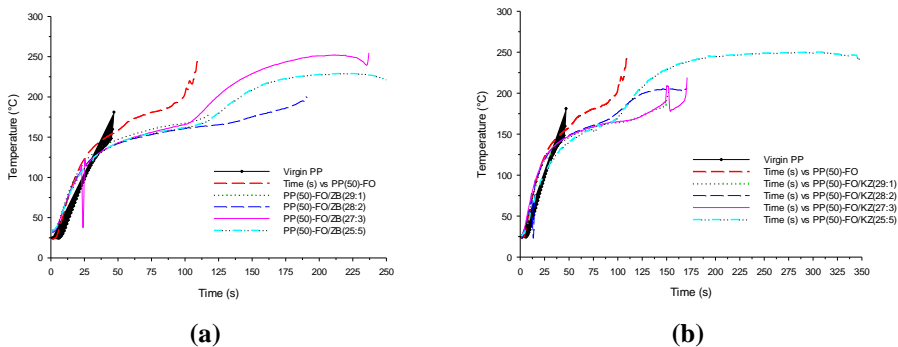
Fig. 7. Temperature as a function time on the backside during a burn-through test at 116 kW/m² of (a) intumescent PP(50)-FO/ZB and (b) intumescent PP(50)-FO/KZ.

4. Conclusion

This paper showed that intumescent PP could be designed to resist to burnthrough test. The selection of the intumescent system (or in another words the chemistry of the system) is essential to get long time to piercing (e.g. 100 s vs. 40 s when using FO instead of AP) and a synergist can dramatically extend the time to piercing (e.g. 215 s vs. 100 s when using FO/ZB instead of FO alone). Analyzing the residues obtained at different times of combustion by solid state NMR of ^{31}P, ^{11}B and ^{13}C, it is shown that phosphates were bound to the charred structure (in the case of FO containing systems) and that the formation of borophosphates created a glass reinforcing the intumescent char. This combination provides flexibility and cohesion to the char. The unusual fire resistance of FR plastics paves the way to other applications where burnthrough scenario can be involved. Such

scenario might happen in plants if leak of flammable products occurs
creating a torch impinging surrounded plastics. The fire resistance of our
formulations might bring therefore additional fire safety.

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6. References

[1] Viegas DX. Extreme fire behaviour. In. Extreme fire behaviour. Nova Science
Publishers, Inc., 2012, pp. 1-56.
[2] La Delfa G, Luinge JW, Gibson AG, Integrity of composite aircraft fuselage materials
under crash fire conditions, Plastics, Rubber and Composites, 2009;38: 111-17.
[3] Alongi J, Han Z, Bourbigot S, Intumescence: Tradition versus novelty. A
comprehensive review, Progress in Polymer Science, 2015;51: 28-73.
[4] Jimenez M, Duquesne S, Bourbigot S, Multiscale Experimental Approach for
Developing High-Performance Intumescent Coatings, Industrial & Engineering Chemistry
Research, 2006;45: 4500-08.
[5] Bourbigot S, Sarazin J, Bensabath T, Samyn F, Jimenez M, Intumescent
polypropylene: Reaction to fire and mechanistic aspects, Fire Safety Journal, 2019;105:
261-69.
[6] Casetta M, Delaval D, Traisnel M, Bourbigot S, Influence of the recycling process on
the fire-retardant properties of PP/EPR blends, Macromolecular Materials and
Engineering, 2011;296: 494-505.
[7] Fontaine G, Bourbigot S, Duquesne S, Neutralized flame retardant phosphorus agent:
Facile synthesis, reaction to fire in PP and synergy with zinc borate, Polymer Degradation
and Stability, 2008;93: 68-76.
[8] Tranchard P, Samyn F, Duquesne S, Thomas M, Estèbe B, Montès JL, Bourbigot S,
Fire behaviour of carbon fibre epoxy composite for aircraft: Novel test bench and
experimental study, Journal of Fire Sciences, 2015;33: 247-66.
[9] Hansupo N, Tricot G, Bellayer S, Roussel P, Samyn F, Duquesne S, Jimenez M,
Hollman M, Catala P, Bourbigot S, Getting a better insight into the chemistry of
decomposition of complex flame retarded formulation: New insights using solid state
NMR, Polymer Degradation and Stability, 2018;153: 145-54.
[10] Samyn F, Bourbigot S, Duquesne S, Delobel R, Effect of zinc borate on the thermal
degradation of ammonium polyphosphate, Thermochimica Acta, 2007;456: 134-44.
[11] Sut A, Greiser S, Jäger C, Schartel B, Synergy in flame-retarded epoxy resin:
Identification of chemical interactions by solid-state NMR, Journal of Thermal Analysis
and Calorimetry, 2017;128: 141-53.
[12] Bourbigot S, Le Bras M, Delobel R, Decressain R, Amoureux JP, Synergistic effect
of zeolite in an intumescence process: Study of the carbonaceous structures using solid-
state NMR, Journal of the Chemical Society - Faraday Transactions, 1996;92: 149-58.
[13] Mercier C, Montagne L, Sfihi H, Palavit G, Boivin JC, Legrand AP, Local structure
of zinc ultraphosphate glasses containing large amount of hydroxyl groups: 31P and 1H

457 solid state nuclear magnetic resonance investigation, Journal of Non-Crystalline Solids,
458 1998;224: 163-72.
459 [14] Jimenez M, Duquesne S, Bourbigot S, Intumescent fire protective coating: Toward a
460 better understanding of their mechanism of action, Thermochimica Acta, 2006;449: 16-
461 26.
462 [15] Hansen MR, Madsen GKH, Jakobsen HJ, Skibsted J, Refinement of borate structures
463 from11B MAS NMR spectroscopy and density functional theory calculations of11B
464 electric field gradients, Journal of Physical Chemistry A, 2005;109: 1989-97.
465 [16] Tricot G, Raguenet B, Silly G, Ribes M, Pradel A, Eckert H, P-O-B3 linkages in
466 borophosphate glasses evidenced by high field 11B/31P correlation NMR, Chemical
467 Communications, 2015;51: 9284-86.
468 [17] Laupretre F, Bebelman S, Daoust D, Devaux J, Legras R, Costa JL, NMR,
469 differential scanning calorimetry, and fourier transform infrared characterization of the
470 crystalline degree and crystallite dimensions of ethylene runs in isotactic
471 polypropylene/ethylene-propylene copolymer blends (iPP/EP), Journal of Applied
472 Polymer Science, 1999;74: 3165-72.
473 [18] Bourbigot S, Le Bras M, Delobel R, Breant P, Tremillon J-M, Carbonization
474 mechanisms resulting from intumescence - part II. Association with an ethylene
475 terpolymer and the ammonium polyphosphate-pentaerythritol fire retardant system,
476 Carbon, 1995;33: 283-94.
477 [19] Bourbigot S, Le Bras M, Delobel R, Gengembre L, XPS study of an intumescent
478 coating II. Application to the ammonium polyphosphate/pentaerythritol/ethylenic
479 terpolymer fire retardant system with and without synergistic agent, Applied Surface
480 Science, 1997;120: 15-29.
481 [20] Karrasch A, Wawrzyn E, Schartel B, Jäger C, Solid-state NMR on thermal and fire
482 residues of bisphenol A polycarbonate/silicone acrylate rubber/bisphenol A bis(diphenyl-
483 phosphate)/(PC/ SiR/BDP) and PC/SiR/BDP/zinc borate (PC/SiR/BDP/ZnB) - Part I: PC
484 charring and the impact of BDP and ZnB, Polymer Degradation and Stability, 2010;95:
485 2525-33.
486 [21] McKee DW, Spiro CL, Lamby EJ, The inhibition of graphite oxidation by
487 phosphorus additives, Carbon, 1984;22: 285-90.
488 [22] Bourbigot S, Le Bras M, Delobel R, Trémillon JM, Synergistic effect of zeolite in an
489 intumescence process: Study of the interactions between the polymer and the additives,
490 Journal of the Chemical Society - Faraday Transactions, 1996;92: 3435-44.
491