Eco-friendly Synthesis of Novel Phosphorus Flame Retardants for Multiple Purposes

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Abstract

The synthesis methods of most parts of phosphorus (P)-based flame retardants apply harmful and toxic reagents, and the formation of byproducts is often inevitable. The synthesis of P-based flame retardants (FRs) according to the green chemistry approach has been investigated. Two FRs have been prepared via an addition reaction of phosphorus-pentoxide and alcohols. These molecules can be used as additive FRs after salt formation or as precursors for flame retardant surface treatments of natural fibers. The flame retardant efficacy of the synthesized additives was assessed in a bioepoxy resin system through UL-94 and limiting oxygen index tests, while their mode of action was determined by the investigation of gas-phase degradation products and thermogravimetric analysis (TGA). The prepared adduct was also used in the formulation of a reactive flame-retardant surface treatment for cellulosic fibers. In TGA tests, the treated fibers produced significant amounts of char residue.

Keywords

green chemistry, flame retardancy, bioepoxy resin, phosphorus-based flame retardants

1 Introduction

In the field of the flame retardancy of polymeric materials, besides coatings [1–4], two types of flame retardants (FRs) can be distinguished: additive- and reactive-type FRs [5]. The reactive ones are chemically bound to the matrix, while the additives are usually added to the polymer during processing. Flame retardants can act in the solid or the gas phase during polymer combustion by either physical or chemical processes. The degradation of hydrated molecules (e.g., polyalcohols) is endothermic, leading to the cooling of the degrading polymer matrix, while the forming H₂O serves as a diluent of the combustible gases. Flame retardants acting in the solid phase usually promote the formation of a protective layer on the surface of the polymer, which hinders the gas- and heat transport between the polymer and the combustion zone, thus inhibiting further degradation. Phosphorus-based flame retardants can usually act in the gas or solid phases, mainly depending on the oxidation state of the P-atom [6]. The P-species entering the gas phase are typically less harmful than the degradation products of the halogen-based FRs [7]. In the solid phase, a stable char layer is usually formed by the reaction between the phosphoric acid and the degraded polymer [8, 9].

Several types of phosphorus compounds can be used as flame retardants: phosphines, phosphine oxides, phosphonium salts, phosphonates, elemental red phosphorus, phosphites, and phosphoric acid derivatives can also be found in the market. In epoxy resins, the use of P-based flame retardants has many advantages: they decrease the mass reduction during combustion; the forming phosphoric-acid derivatives act as effective charring agents, decrease the degradation temperature, and facilitate the elimination of H₂O from the polymer structure [10, 11].

Among the nitrogen-based FR additives, melamine and its salts, such as melamine cyanurate, pyrophosphate, or polyphosphate, are the most abundantly applied materials [12]. Melamine has a significant blowing effect: ammonia is formed during its endothermic degradation, which also dilutes the fuel load in the combustion zone. Because of its aromatic structure, it enhances char formation on the surface of the degrading polymer [13]. Melamine salts of different phosphorous acids have been successfully used as flame retardants in epoxy resin [14–16].

According to previous findings [17], the balanced solid- and gas-phase effect of the applied flame retardants may
improve thermal stability and decrease the rate of polymer degradation to generate volatile fuel fragments. Three mass% P-containing samples were prepared with the application of RDP (resorcinol bis(diphenyl phosphate)) and APP (ammonium polyphosphate) and by combining them. When applied alone, both the RDP and APP-containing formulations failed the vertical UL-94 test, while when used in combination, self-extinguishing (V-0 rating) was reached. This was attributed to the balanced solid and gas-phase action.

Cellulose fibers can be used as reinforcing and char-ring agents in intumescent flame retardant systems. Flame retardant modification of cellulose can be achieved by the reaction of free –OH groups with P-containing molecules, e.g., different silanes [18,19], phosphoric acid derivatives [20], or even phytic acid [21].

Although progress in the environmentally-friendly synthesis of flame retardants has been made in recent years, in most cases, the industrially applied synthesis pathways for the phosphorus-based flame retardants, often using harmful/toxic reagents and producing such by-products, do not meet the requirements of green chemistry [22]. The applied reagents are mostly halogen-containing, unfavorable regarding environmental and health issues, so developing new, green alternatives to the existing syntheses is indispensable.

The development of alternative pathways for synthesizing phosphorus-containing flame retardants has been accomplished. A green chemistry approach was utilized by replacing the currently applied harmful and toxic reagents and increasing the atom economy of reactions. For this purpose, different alcohols were treated with phosphorus pentoxide [23, 24]. The resulting acidic phosphates were used as reagents for the preparation of P-silane compound, which can be used as reactive flame retardants for cellulose, or were neutralized with melamine. With the application of these additives, 3 mass% P-containing samples were prepared, and their flammability and thermal stability were investigated.

2 Materials and methods
2.1 Materials used in the syntheses and sample preparation

For the syntheses, absolute ethanol, water-free ethylene glycol, phosphorus pentoxide, and SeccoSolv tetrahydrofuran, as well as 3-(triethoxysilyl)propyl isocyanate purchased from Merck were used without further purification. Dibutyltin didecanoate under the trade name of OXAM was received from T-Silox Kft. Arbocel BC-200 type cellulose fibers from JRS were used.

As a bioepoxy matrix sorbitol polyglycidyl ether (SPE, trade name Erisys GE-60), received from Emerald Performance Materials, was cured with a cyloaliphatic amine-type hardener (3,3'-dimethyl-4,4'-diaminodicyclohexylmethane (MH3122)), supplied by Ipox Chemicals Ltd. The mixing ratio of the SPE – MH3122 system was 4:1 by mass. After homogenization at room temperature, the resin was poured into silicon molds of appropriate size and then was cured at room temperature for 24 h, followed by a post-curing at 80 °C for 2 h and 120 °C for 2 h.

2.2 Applied methods

$^{31}$P NMR spectra of the synthesized flame retardants were recorded with a Bruker AV-300 NMR spectrometer in D$_2$O. Mass spectrometric analysis was performed on a Perkin Elmer Sciex API 365 LC/MS/MS system. The sample was introduced into the mass spectrometer with a flow rate of 10 mL/min. The instrument was operated in ESI mode with positive ionization. Mass spectra were recorded in Q1 scanning mode between m/z ratios of 50–500. The FTIR spectra were recorded on a Bruker Tensor 37-type Fourier transform infrared (FTIR) spectrometer equipped with DTGS (deuterated triglycine sulfate) detector with a resolution of 4 cm$^{-1}$.

Thermal stability of the different samples was determined using a TA Q5000 device of TA Instruments in the range of 25–500 °C or 600 °C, with a heating rate of 10 °C/min, in a N$_2$ gas atmosphere with a flow rate of 30 mL/min. Platinum-HT sample pan was used, and the sample size was about 5 mg in each case.

The laser pyrolysis-FTIR method (LP-FTIR), developed in our research group recently [25], was used for investigating the gas-phase pyrolytic degradation products of the samples. The system comprises a laser pyrolysis unit with a CO$_2$ laser (10.6 nm, SYNRAD 48-I) and a Bruker Tensor 37-type FTIR spectrometer.

The fire behavior of the reference and flame retarded systems was characterized by limiting oxygen index (LOI) measurements, according to ISO 4589-2:2017 [26]. The sample size was 120 mm × 15 mm × 4 mm. Standard UL-94 flammability tests (according to ISO 9772:2012 [27] and ISO 9773:1998 [28], respectively) were also carried out with a sample size of 120 mm × 15 mm × 4 mm. UL-94 classification is used to determine ignitability, dripping, and flame spreading rates and burning times. Based on them, samples can be classified to categories from HB (horizontal burning) through V-2, V-1 to the best, V-0 rating.
2.3 Synthetic procedures for the preparation of flame retardant compounds

2.3.1 Synthesis of ethyl-phosphate (EtP)
11.7 mL absolute ethanol (0.2 mol) in a 50 mL round-bottomed flask was cooled with an ice bath to 0 °C. After cooling, 3.55 g (0.025 mol) P_2O_5 was added in 6 quasi-equal portions, in all cases, to a 0 °C cold reaction mixture. After adding the last portion of P_2O_5, the reaction was let to warm up to room temperature, where it was further stirred for 12 h. The excess ethanol was removed by rotary evaporation, resulting in a low-viscosity colorless liquid (7.01 g, yield: 95%).

^31^P-NMR (D_2O, 300 MHz) δ_p (ppm): 0.205 (d; area: 0.6; monoethyl phosphate), −0.109 (d; area: 1.0; diethyl phosphate), −11.514 (m; area: 0.11; phosphoric acid derivatives). FTIR (KBr): 805 cm^{-1} (P–O–C); 1037 cm^{-1} (P–O); 1223 cm^{-1} (P=O); 1665 cm^{-1} (P=O)OH vibration of OH-group. MS: phosphoric acid (99 m/z); monoethyl phosphate (1223 cm^{-1} (P=O)); 1255 cm^{-1} (P=O); 1536 cm^{-1} (C=O) vibration of OH-group.}

According to the ^31^P results, the ratio of the mono- and diesters is approximately 2:3; accordingly, the P–OH equivalent is 100 g/mol, meaning that 100 g mixture contains 1 mol P–OH group. The EtP-melamine salt (EtP-Mel) was prepared by homogenizing the calculated amount of melamine with an excess of 5% (i.e., 1.05 mol melamine to 1 mol P–OH group) in a mortar. The product is a white powder.

2.3.2 Synthesis of ethylene glycol-phosphate (EGP)
3.31 g (0.053 mol) water-free ethylene glycol (EG) in a 50-mL round-bottomed flask was cooled with an ice bath to 0 °C. After cooling, 2.84 g (0.02 mol) P_2O_5 was added in five quasi-equal portions of 4-4 mL suspension in tetrahydrofuran (THF). After adding the last portion of P_2O_5, the reaction was let to warm up to room temperature, where it was further stirred for 12 h. The received two-phase system was separated; the residual THF traces were evaporated from the lower phase. The product is a colorless, viscous liquid (6.03 g, yield: 98%).

The EtP-Mel salt was prepared similarly to EtP-Mel.

2.3.3 Synthesis of P-silane
5.0 g EtP (containing 0.05 mol P-OH group) and 12.4 g (0.05 mol) TESPI in a 50-mL round-bottomed flask were stirred at room temperature without external heating or cooling for 3 h. Every 30 min, FTIR spectrum was taken from the reaction mixture. The reaction was completed within 2.5 h. The mixture was stirred further for 0.5 h to cool back to room temperature. The product is a yellow, slightly viscous liquid.

FTIR (NaCl): 795 cm^{-1} (P–O–C); 1037 cm^{-1} (P=O); 1252 cm^{-1} (P=O); 1536 cm^{-1} (C=O); 1721 cm^{-1} (C=O), 3000–2850 cm^{-1} (C–H); 3334 cm^{-1} (N–H).

2.3.4 Synthesis of P-cellulose
1.0 g cellulose was suspended in 200 mL toluene, and the appropriate amount of P-silane was added. 10 droplets (approx. 0.5 mL) of dibutyltin dineodecanoate were added as catalyst. The reaction mixture was refluxed for 5 h [29], then the cellulose was filtrated, washed twice with 20 mL cold toluene, and dried in an oven for 2 h at 100 °C. The product is a white powder.

3 Results and discussion
3.1 Synthesis of flame retardants
Due to the highly exothermic nature of the addition reaction, the ethanol was cooled to 0 °C with an ice bath. The calculated amount of phosphorus pentoxide was added to the cold ethanol in small portions. The applied molar ratio was 4:1 –OH group: P atom. After adding each portion of P_2O_5, the mixture's temperature reached 13–14 °C due to the reaction heat. Before the next portion, the mixture was cooled back to 0 °C. After adding the whole amount of P_2O_5, the reaction mixture was let to warm up to room temperature, and it was further stirred for 12 h. The residual ethanol was removed by rotary evaporation, resulting in a low-viscosity, colorless liquid. The pH of the formed product mixture is very low due to the free P–OH groups; thus, it was neutralized with a calculated amount of melamine (one molecule of melamine with 5% excess to one P–OH group). The resulting melamine salt
(EtP-Mel) is a white powder, with a P-content of 13.6% and a melamine-content of 55.3% (Scheme 1).

In the case of ethylene glycol (EG), the reaction is too intense even at 0 °C, and instead of an addition reaction, water elimination occurs, leading to the charring of the EG. Therefore, the P₂O₅ was added to the cold EG as dry tetrahydrofuran suspension portions. (The molar ratio of the reactants was 2.65:1 –OH group: P-atom, according to previous experiences [29]). The temperature increased to 10–11 °C after adding each P₂O₅ portion. After adding the whole amount, the reaction mixture was stirred further for 12 h at room temperature. The products formed a viscous, colorless phase separated from the solvent. The residual solvent traces were evaporated, and the formed phosphorous acids were neutralized with melamine (Mel), as described above. The resulting EGP-Mel salt has a P-content of 11.5% and a melamine content of 54.8% (Scheme 1).

3.2 Flame retardant effect of the synthesized additives
The prepared flame retardant additives, the ethanol-based EtP-Mel, and the ethylene glycol-based EGP-Mel were added to a commercially available biobased epoxy system (SPE): 3 mass% P-containing samples were prepared with the application of the synthesized FRs.

The flame retardant efficacy of the phosphate ester melamine salts was determined by UL-94 and limiting oxygen index tests (Table 1).

The LOI values of the flame retardant-containing samples improved significantly compared to the reference system. The ethanol-based EtP-Mel increased the LOI by 8 V/V%, while the similarly aliphatic ethylene glycol-based EGP-Mel led to an increase of 13 V/V% at the same P-content. In the case of the UL-94 tests, although the best, V-0 rating could not be reached, neither flaming to the holding clamp nor the formation of flaming droplets was detected, leading to V-1 rating at 3 mass% P-content.

Comparing these results with those of the commercially available ammonium polyphosphate (APP) and resorcinol bis(diphenyl phosphate) (RDP) in the same matrix [17], it can be seen that the newly synthesized phosphate ester melamine salts overperform the commonly applied FRs in UL-94 tests, and reach the same levels in LOI.

3.3 Determination of the mode of action of the flame retardants
In order to investigate the possible gas-phase effect of the synthesized compounds, laser pyrolysis-FTIR coupled method was applied to detect the gas-phase degradation products of the samples. The recorded FTIR spectra are displayed in Fig. 1.

Comparing the relative intensity of the peaks, no difference in the amount of the forming CO₂ (2340–2360 cm⁻¹) and CO (2170–2120 cm⁻¹) can be detected. However, between these two gases, the peaks of the C≡N bond can be seen, which can be attributed to the formation of a small amount of cyanide (2260–2220 cm⁻¹) during the degradation of the melamine. The increment of the amine Table 1 LOI and UL-94 results of the synthesized flame retardants applied at 3% P-content in bioepoxy resin

<table>
<thead>
<tr>
<th>Sample</th>
<th>LOI (V/V%)</th>
<th>UL-94 rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>20</td>
<td>HB (20 mm/min)</td>
</tr>
<tr>
<td>EtP-Mel</td>
<td>28</td>
<td>V-1</td>
</tr>
<tr>
<td>EGP-Mel</td>
<td>33</td>
<td>V-1</td>
</tr>
<tr>
<td>APP [17]</td>
<td>31</td>
<td>HB (vert. 2nd ign.)</td>
</tr>
<tr>
<td>RDP [17]</td>
<td>28</td>
<td>HB (vert. 2nd ign.)</td>
</tr>
</tbody>
</table>

EtP-Mel (ethyl-phosphate melamine)
EGP-Mel (ethylene glycol-phosphate melamine)
APP (ammonium polyphosphate)
RDP (resorcinol bis(diphenyl phosphate))
HB (vert 2nd ignition): sample burned to the clamp at 2nd vertical ignition
vibrations in the gas phase (3400 cm$^{-1}$) can also be deducted from the direct degradation of melamine. A significant difference between the spectra of the reference and flame retarded samples is the appearance of aromatic C–H vibrations in the latter ones. The explanation of the C–H peaks is the intense char formation on the surface of the matrix, which then decomposes to some extent, resulting in aromatic gas-phase products. The peak related to the P=O bond (1220 cm$^{-1}$), and thus to the direct gas-phase effect of the flame retardant, can be only slightly seen in the spectrum of the EtP-Mel sample, which means that, contrarily to the aromatic ones [17], the aliphatic phosphates have only negligible gas-phase effect.

The thermal stability of the bioepoxy samples flame retarded with the synthesized compounds was investigated with TGA. This method also allows drawing some conclusions about the solid-phase effect of the flame retardants, as the char yield is one of the most important parameters representing the efficacy of the FR in promoting charring. The recorded TGA curves can be seen in Fig. 2.

It can be seen that the thermal degradation of the reference epoxy resin starts with a sudden drop, resulting in a high degradation rate. At the same time, those of the flame retarded samples show a more prolonged decrease. Comparing the curves of the flame retarded samples, no significant difference can be observed between them at the beginning of the degradation; however, at higher temperatures, the EGP-Mel shows slightly increased stability.

The degradation of all samples starts at the same temperature (263–264 °C), which also supports that the synthesized flame retardants have a negligible gas-phase effect. The temperature belonging to 50% mass decrease increased significantly in the case of the flame retarded samples, and the rate of degradation lowered by 50%. The temperature of the maximal degradation rate is increased by more than 30 °C in the case of the FR samples, all indicating that the decomposition of the system changed to an elongated, slow process.

The proof of the solid-phase mode of action of the synthesized additives can be seen from the amount of char residues at 500 °C: from the reference epoxy resin, only 6.6% remained in the platinum pan, while the flame retarded samples had more than four times higher residual mass (Table 2).

### 3.4 Synthesis of flame retardants for cellulose fibers

The synthesized P-esters having free P-OH groups are suitable starting materials for preparing P-containing silanes, which can be applied as reactive flame retardants for natural fibers like cellulose. Previously, a P-containing silane was prepared by our group with the reaction between a P-polyol and 3-(triethoxysilyl)-propyl isocyanate (TESPI) [29]. In the present study, to ensure a proper reaction, the synthesized EtP was used as P-containing species for the formation of a P-silane compound, as it can react with the isocyanate only with its P-OH group, leading to the formation of a new carbamate bond (Scheme 2.)

According to the $^{31}$P NMR results of the synthesis

### Table 2 TGA data of the reference and flame retarded samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{5%}$ (°C)</th>
<th>$T_{50%}$ (°C)</th>
<th>$\text{dTG}_{\text{max}}$ (%/°C)</th>
<th>$T_{\text{dTG}\max}$ (°C)</th>
<th>Residue (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>263.5</td>
<td>322.1</td>
<td>1.2</td>
<td>263.2</td>
<td>6.6</td>
</tr>
<tr>
<td>EtP-Mel</td>
<td>263.4</td>
<td>356.2</td>
<td>0.7</td>
<td>292.2</td>
<td>27.1</td>
</tr>
<tr>
<td>EGP-Mel</td>
<td>264.2</td>
<td>359.7</td>
<td>0.7</td>
<td>299.2</td>
<td>28.4</td>
</tr>
</tbody>
</table>

$T_{5\%}$: temperature belonging to 5% mass decrease; $T_{50\%}$: temperature belonging to 50% mass decrease; $\text{dTG}_{\text{max}}$: maximal rate of mass reduction; $T_{\text{dTG}\max}$: temperature belonging to $\text{dTG}_{\text{max}}$. 

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**Fig. 2** Effect of the synthesized additives on the thermal degradation of SPE bioepoxy resin
of EtP (see Section 2.3.1), the molar ratio of mono- and diethyl phosphates in the reaction mixture is 2:3; therefore, a stoichiometric amount of TESPI to the free P-OH groups was added into the round-bottomed flask. The mixture was stirred at room temperature for 3 h. As the reaction between the isocyanate and P-OH groups is highly exothermic, the temperature increased to 45–50 °C. As the reaction took place, the formation of heat decreased; finally, the mixture cooled back to room temperature, indicating the end of the process.

The completion of the synthesis was confirmed by FTIR spectrometry (Fig. 3).

The isocyanate (−N=C=O) peak of the TESPI (2283 cm$^{-1}$), as well as the P(O)OH peak (1665 cm$^{-1}$) of the EtP both disappeared from the spectrum of the product, indicating the completion of the reaction. The forming carbamate group of the product can also be identified from the spectrum: the N–H (3334 cm$^{-1}$), C=O (1721 cm$^{-1}$), and C–N vibrations (1536 cm$^{-1}$) show the successful formation of the product.

### 3.5 Chemical modification of cellulose with P-silane

Cellulose is a macromolecule composed of β-D-glucose monomers with 3 free hydroxyl groups. Theoretically, one glucose unit in the cellulose can react with one silane molecule; however, the steric hindrance and the different reactivity of the free −OH groups must be considered. In order to determine the optimal ratio of P-silane and cellulose, several compositions were prepared, i.e., the mass ratio of cellulose: P-silane varied between 1:0.5 and 1:1.25 with 0.25 steps. According to previous experiences, the reaction was carried out in a relatively dilute suspension of the cellulose macromolecule, i.e., 1 g cellulose was suspended in 200 mL anhydrous toluene, and the desired amount of P-silane was added. In order to promote the hydrolysis of the ethoxysilyl group, a few droplets of dibutyltin dineodecanoate were added to form the reactive silanol species.

The grafting of P-silane to the cellulose was confirmed with FTIR spectroscopy. On the spectra displayed in Fig. 4., it can be seen that additional peaks appear compared to the neat cellulose, which proves the successful grafting of the P-silane: the C=O at 1700 cm$^{-1}$, C–H and N–H vibrations of the carbamate group at 1542 cm$^{-1}$, P=O vibration at 1250 cm$^{-1}$, P–O–C and Si–C vibrations at 778 cm$^{-1}$ all serve as evidence.

The effect of the different ratios of the P-silane to the cellulose on thermal stability was investigated by TGA measurements. In order to find an optimum between the flame retardancy and the thermal stability and thus the processability of the fibers, the beginning of the degradation (defined as the onset of the main degradation step) and the residual masses measured at 600 °C were compared.

Regarding the TGA curves (Fig. 5), it can be seen that cellulose fibers tend to absorb water from the air, which shows up as a 3–5% mass decrease at low temperatures. Considering the data presented in Table 3, it can be stated that with increasing the amount of P-silane in the reaction mixture increases its amount grafted to the cellulose.
Consequently, the thermal degradation of the modified cellulose is shifted to lower temperatures (the formation of acidic species facilitates the hydrolysis of cellulose). At the same time, the degradation rate of the samples decreases with increasing P-silane content; however, the maximal degradation rate is reached at somewhat lower temperatures than in the case of the unmodified cellulose. It can also be seen that over the 1:1 ratio, the parameters of the modified cellulose worsen, indicating that this composition is over the ideal. The residual mass significantly increases with the increment of the P-content: while the reference cellulose is almost completely degraded, the P-silane-treated samples show 28–38% char residue at 600 °C.

The best results were reached in the case of Cell: P-silane 1:1 sample: the onset point of the degradation and the amount of residue show an optimum compared to the other compositions, while the degradation rate is the slowest, and it has the highest amount of residue as well. The thermal stability of the phosphorylated cellulose is high enough in this case for processing at around 200 °C (the processing temperatures of, e.g., polypropylene and poly(lactic acid)). As cellulose might serve as a carbon source as part of an intumescent FR system, a good flame retardant effect is also foreseen due to the significantly improved char yield of the P-silane-treated cellulose.

4 Conclusions
The goal of this work was the atom economic preparation of simple phosphorus compounds, which can act as flame retardants in several polymer systems. A mixture of different P-esters was formed in the addition-type reaction of ethanol, ethylene glycol, and phosphorus pentoxide. These mixtures are suitable for flame retardant applications without purification. After salt formation with melamine, the synthesized compounds were tested in a sorbitol-based bioepoxy resin as additive flame retardants. Both additives increased the LOI of the epoxy resin significantly, and the UL-94 ratings were V-1. According to the laser pyrolysis-FTIR measurements, the gas-phase effect of the new additives is negligible; their flame retardant effect is primarily the promotion of char formation in the solid phase.

The chemical structure of the products makes them ideal precursors for synthesizing P-containing silanes, which can be reactively bound to the cellulose –OH groups of natural fibers. In this study, we optimized the ratio of the cellulose to the P-silane compound: the best results were reached when the mass ratio was 1:1. In this case, the thermal stability remained high enough for the processing temperatures of commodity thermoplastics, while the char formation improved significantly.

The elucidated mode of action of the synthesized FRs makes them promising candidates for application in non-charring polymers (e.g., polypropylene) as well; the EGP-Mel contains in one additive the carbon source (ethylene glycol), the P-acid, and the blowing agent (melamine).

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