

Phosphorus Flame Retardants

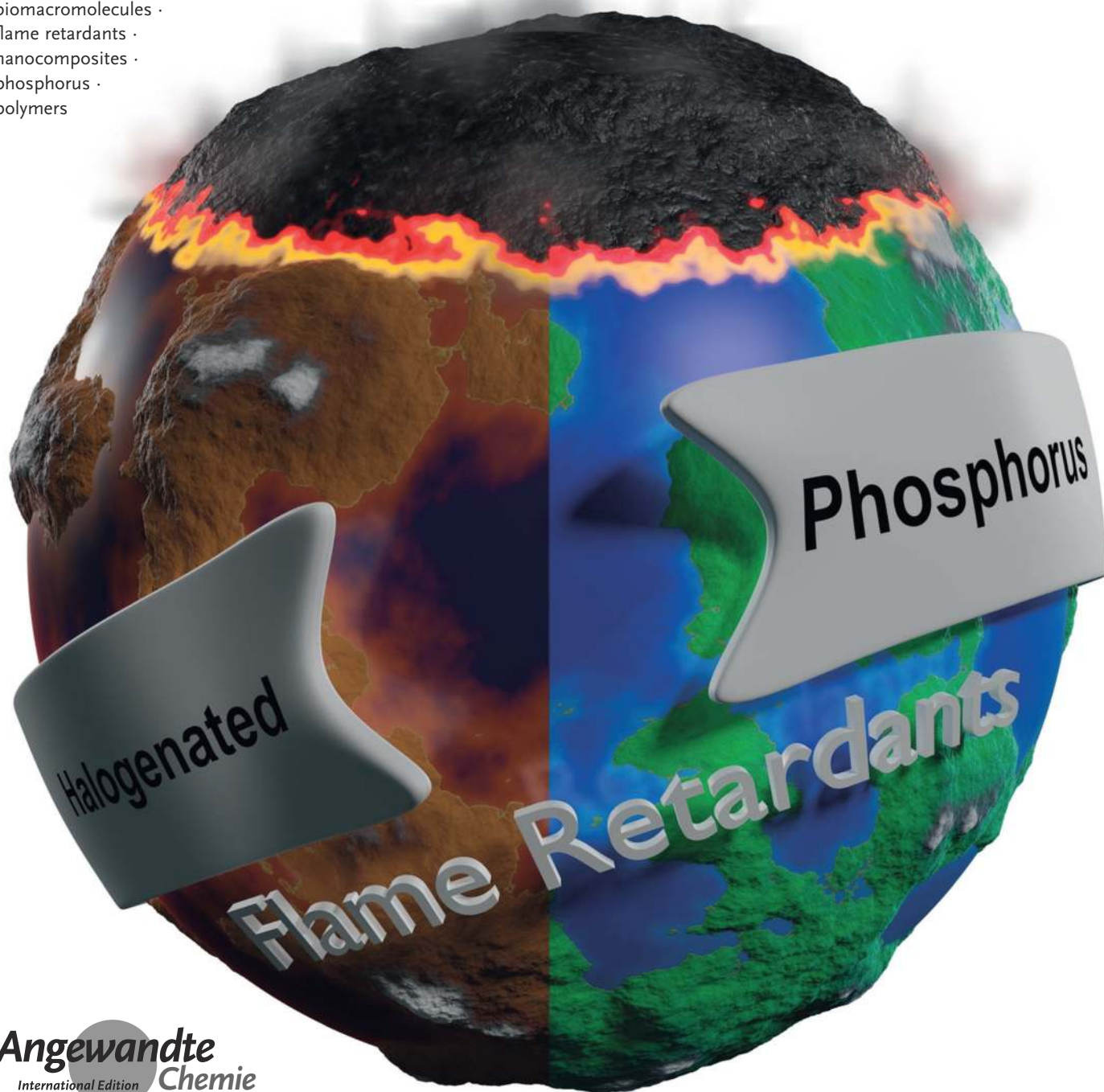
International Edition: DOI: 10.1002/anie.201711735
German Edition: DOI: 10.1002/ange.201711735

Molecular Firefighting—How Modern Phosphorus Chemistry Can Help Solve the Challenge of Flame Retardancy

Maria M. Velencoso⁺, Alexander Battig⁺, Jens C. Markwart⁺, Bernhard Schartel, and Frederik R. Wurm*

Keywords:

biomacromolecules ·
flame retardants ·
nanocomposites ·
phosphorus ·
polymers



The ubiquity of polymeric materials in daily life comes with an increased fire risk, and sustained research into efficient flame retardants is key to ensuring the safety of the populace and material goods from accidental fires. Phosphorus, a versatile and effective element for use in flame retardants, has the potential to supersede the halogenated variants that are still widely used today: current formulations employ a variety of modes of action and methods of implementation, as additives or as reactants, to solve the task of developing flame-retarding polymeric materials. Phosphorus-based flame retardants can act in both the gas and condensed phase during a fire. This Review investigates how current phosphorus chemistry helps in reducing the flammability of polymers, and addresses the future of sustainable, efficient, and safe phosphorus-based flame-retardants from renewable sources.

1. The Challenge of Flame Retardancy—Demands of a Good Flame Retardant

Polymeric materials are ubiquitous in nearly all aspects of modern life: from consumer electronics, packaged goods, and construction to transportation, aerospace, industrial machinery, and manufacturing processes. This development comes with an inherent risk of fire: hydrocarbon-based polymeric materials display a large fire load and high flammability. Sustained research on effective flame retardants (FRs) to reduce the risks is pivotal in safeguarding against accidental fires, costly damage to material goods, and in ensuring the health and safety of the populace.

Halogenated flame retardants, which were widely applied in the past, have come under increased scrutiny and prompted increased research into halogen-free and phosphorus-based flame retardants (P-FRs) in particular.^[1] This development is further attributed to legislation and decisive shifts in market demands, as increased attention has paid to producing more sustainable FRs. P-FRs have now become a prominent alternative to their halogenated counterparts.^[2] Phosphorus plays the key role in halogen-free flame retardancy as a result of its chemical versatility, multiple FR mechanisms, and high effectivity already at low loadings. As the demand for safe advanced materials grows, the question for material scientists is: what role can current chemistry play in solving the flame retardancy problem? To more closely understand the task at hand, it is necessary to first outline what constitutes a “good” FR:

- 1) Material properties must be conserved to the greatest possible extent, with price as the most determining factor.
- 2) The FR properties must match the polymer processing and pyrolysis characteristics.
- 3) Health regulations and market direction necessitates that formulations must become increasingly environmentally friendly, recyclable, and sustainable.

In the following sections, these aspects are explored in detail. Then, state-of-the-art P-FRs and their modes of action are discussed and show how these features are embraced.

From the Contents

1. The Challenge of Flame Retardancy—Demands of a Good Flame Retardant	10451
2. Phosphate Rock—A Finite Natural Resource	10454
3. Recent Developments in Reactive Phosphorus Compounds	10456
4. Recent Developments in Additive Phosphorus Compounds	10458
5. Modern Trends and the Future of Phosphorus-Based Flame Retardants	10460
6. Conclusions	10464

Finally, we highlight modern trends of P-FRs and their potential future application. To that end, representative examples for each section were chosen, but this Review is not meant to be a comprehensive summary. For further reading, we recommend the reviews of Weil and Levchik,^[3] Malucelli et al.,^[4] and Bourbigot and Duquesne.^[5]

1.1. Retaining Material Properties: A Question of Price

The chemical composition of the polymer determines the material properties, production routes, application areas, and bulk price (Figure 1). Thermoplastic polyolefins (e.g. poly-

[*] Dr. M. M. Velencoso,^[†] M. Sc. J. C. Markwart,^[†]

Priv.-Doz. Dr. F. R. Wurm
Physical Chemistry of Polymers
Max Planck Institute for Polymer Research
Ackermannweg 10, 55128 Mainz (Germany)
E-mail: wurm@mpip-mainz.mpg.de

M. Sc. A. Battig,^[†] Priv.-Doz. Dr. B. Schartel
Technical Properties of Polymeric Materials
Bundesanstalt für Materialforschung und -prüfung (BAM)
Unter den Eichen 87, 12205 Berlin (Germany)

M. Sc. J. C. Markwart^[†]
Graduate School Materials Science in Mainz
Staudinger Weg 9, 55128 Mainz (Germany)

[†] These authors contributed equally to this work.

The ORCID identification number for one of the authors of this article can be found under:
<https://doi.org/10.1002/anie.201711735>.

© 2017 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited, and is not used for commercial purposes.

ethylene, polypropylene, polyvinyl chloride) are common commodities and mass produced at low costs; $\text{Al}(\text{OH})_3$, the most common FR, is both effective and inexpensive to produce, but requires high loadings, which affects the material properties (e.g. coloration, opacity, tensile strength).^[6] Commercially available P-FRs (e.g. ammonium polyphosphate, APP) require significantly lower loadings for similar effectiveness, and thereby retain the respective material properties.^[7] Moreover, adjuvants and synergists (e.g. metal oxides, charring agents, nanofillers, additional P-FRs) increase the efficacy and further lower the loadings required.^[8]

Engineering polymers (e.g. polyamides, polycarbonates, polyurethanes, polyethylene terephthalates) are applied in more advanced areas (e.g. electronics/electrical engineering, transport, manufacturing). These materials can be synthe-

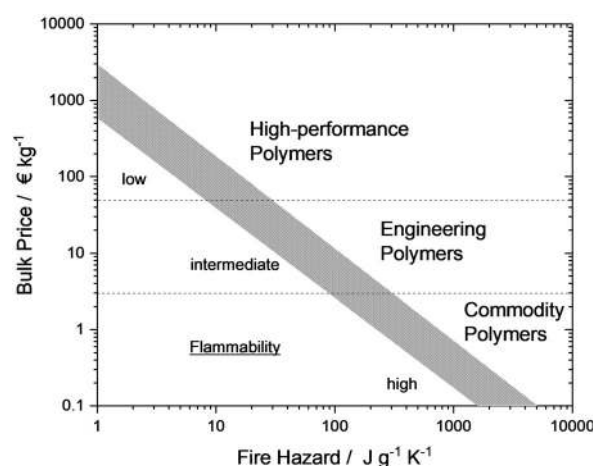


Figure 1. Fire hazard versus bulk price of various polymeric material classes.^[14]

sized as thermoplasts, elastomers, or thermosets in foams, fibers, or foils, and so a wider array of FRs exist. The use of these FRs depend on the polymer's price, quality grade, and precise application.^[9] Notable formulations contain aluminum diethyl phosphinate, melamine polyphosphate, and Zn borate, or melamine cyanurate-microencapsulated red phosphorus.^[10]

High-performance polymers (e.g. epoxy/polyester resins, polyetherimides, polysulfones, poly(aryl ether ketones)) are used in specialized fields (e.g. adhesives, coatings, composites)



Dr. Maria M. Velencoso received her M.Sc. in Chemical Engineering from the University of Castilla-La Mancha (Spain) in 2008 and completed her Ph.D. there in 2014 with Prof. Antonio de Lucas Martinez for work on the synthesis and application of phosphorylated polyols as reactive flame retardants. For her research, she maintained a long-term collaboration with HUNTSMAN. She is currently a Marie Skłodowska-Curie Post-doctoral fellow in the group of Prof. Katharina Landfester at the Max Planck Institute for Polymer Research (Germany), where she is working on the development of nanoparticles for flame retardant applications.



Alexander Battig studied Chemistry (B.Sc.) and Polymer Science (M.Sc.) at the Free University Berlin, Germany. After establishing and running his own company, he joined the group of Bernhard Schartel at the Bundesanstalt für Materialforschung und -prüfung (BAM) in Berlin, for his Ph.D. in 2016. He is an active member of the doctoral student network at BAM, a member of its organizing committee, and a representative of the doctoral students. His research, supported by the Deutsche Forschungsgemeinschaft (DFG), focuses on the molecular understanding of hyperbranched polyphosphoesters/-amidates as multifunctional flame retardants.



Jens C. Markwart completed his M.Sc. in Chemistry at the Johannes Gutenberg-University of Mainz, Germany, in 2016, including a stay at the Polymer Science and Engineering Department at the University of Massachusetts in Amherst, USA, in the group of Prof. Alejandro L. Briseno. He joined the group of Dr. Frederik R. Wurm as a Ph.D. student at the Max Planck Institute for Polymer Research, Mainz, Germany. His research focuses on hyperbranched polyphosphoesters as multifunctional flame retardants. His research is supported by a fellowship of the MAINZ Graduate School and by the Deutsche Forschungsgesellschaft (DFG).



Bernhard Schartel is head of the Technical Properties of the Polymeric Materials division at the Bundesanstalt für Materialforschung und -prüfung (BAM). He has been active in the area of flame retardancy of polymers for over 15 years, publishing more than 150 papers. He has served on the editorial boards of *Fire Mater.*, *J. Fire Sci.*, *Polym. Test.*, and *Fire Technol.*, and since 2012 has also edited *Polymer Degradation and Stability* for the topics Fire Retardants and Nanocomposites. His main interest is understanding fire behavior and flame-retardancy mechanisms as a basis for future development.



Frederik R. Wurm completed his Ph.D. in 2009 (JGU Mainz, Germany) with Prof. Holger Frey. After a two year stay at EPFL (Switzerland) as a Humboldt fellow, he joined the department "Physical Chemistry of Polymers" at MPIP and finished his habilitation in Macromolecular Chemistry in 2016. He currently heads the research group "Functional Polymers" at the Max Planck Institute for Polymer Research (MPIP). His group designs materials with molecular functions for the development of degradable polymers, nanocarriers with controlled blood interactions, adhesives, and phosphorus flame-retardants.

due to their chemical resistance, temperature stability, and high durability.^[11] Here, performance outweighs the production costs of the materials and the FRs. Correspondingly, FRs in this material category are the second most important in value terms behind polyolefins; therefore, complex-shaped, multicomponent, and multifunctional FRs are used.^[12] Notable formulations include 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) derivatives and variations of P species with synergistic moieties: nitrogen, silicon, sulfur, and boron.^[13]

1.2. Production Specifics: Finding a Match

The FR's mode of action is key when tailoring suitable formulations for polymer materials. Effective flame retardancy depends strongly on the interaction between the FR and the polymer matrix as well as the structure–property relationship between the two during thermal decomposition. The modes of action can generally be classified into condensed- and gas-phase mechanisms (Figure 2), and many successful P-FRs utilize both.^[15] In the condensed phase, many P-FRs mediate the formation of char by inducing cyclization, cross-linking, and aromatization/graphitization by dehydration of the polymeric structure. The formation of carbonaceous char reduces the release of volatiles, that is, fuel.^[16] Some P-FRs additionally act through intumescence: a multicellular residue acts as a protective layer, slowing down heat transfer to the underlying material.^[17] Many FRs alter the melt flow and dripping behavior by promoting either charring combined with a flow limit (non-dripping UL-94 classification) or flame inhibition combined with increased flow, for example, via radical generators (non-flaming dripping UL-94 classification).^[18] Some inorganic FRs (e.g. $\text{Al}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$, Zn borates, boehmite) decompose endothermically and vaporize water, absorbing heat in the condensed phase, and cooling the gas phase.^[19] Gas-phase modes of action, usually acting in parallel with condensed-phase mechanisms, crucially increase FR effects: releasing non-combustible gases during decomposition reduces the combustion efficiency (fuel dilution).^[20]

During the combustion of hydrocarbon fuels, H^\bullet and OH^\bullet radicals are formed, which propagate the fuel combustion cycle most notably through the strongly exothermic reaction $\text{OH}^\bullet + \text{CO} \rightarrow \text{H}^\bullet + \text{CO}_2$.^[21] Many P-FRs decompose to form P $^\bullet$ radicals which react with OH^\bullet radicals and lower their concentration (flame poisoning).^[22]

These mechanisms crucially depend on the decomposition temperatures of both the matrix and the FR. Therefore, FRs must be chosen to match explicit polymer processing and pyrolysis specifics. To ensure chemical interaction during pyrolysis but not during processing, premature FR decomposition must be avoided, whereas the overlap of the polymer and FR decomposition temperatures should be maximized.^[23] This is key for high-temperature thermoplastic processes (e.g. compounding, extrusion, injection/blow molding), as well as vulcanization for rubbers, or curing for thermosets.^[24] For foams, FRs with good foamability are important to maintain mechanical properties, while fiber and textile FRs must undergo spinning, weaving, and washing without loss of material or FR properties.^[25]

Today, no single FR can be used for the wide range of polymers available; a FR may work well for one matrix but not for another, as the structure–property relationship is specific to the polymer matrix.^[26] This makes the search for novel FRs with improved mechanisms essential for all fields of polymer applications.

1.3. Sustainability: A Regulatory and Market Goal

Health, environmental, and sustainability considerations play increasingly important roles in the development of novel FRs. Increased awareness has been paid to the “PBT” (i.e. persistency, bioaccumulation, toxicity) of FRs.^[27] Studies on human exposure pathways and ecosystems have highlighted risks of some FRs, thus emphasizing the need for increased control and regulation.^[28]

To curtail “PBT material” risks, regulatory bodies have enacted legislature to protect the environment and the general population: within the EU, REACH (Registration, Evaluation, Authorization, and Restriction of Chemicals), which acts upon the RoHS (Restriction of Hazardous Substances) and WEEE (Waste Electrical and Electronic Equipment) Directives, evaluates materials hazards and sets health and safety criteria for chemicals, including FRs.^[29] Notably, the use of penta-, octa-, and decabromodiphenyl ethers was restricted under the Stockholm Convention on Persistent Organic Pollutants because of health risks, thus highlighting the need for halogen-free alternatives.^[30]

The voluntary ecolabels introduced by ISO help prevent the circulation of PBT material and raise awareness of sustainable, environmentally aware production.^[31] The “EU Ecolabel” serves to reduce the environmental impact and

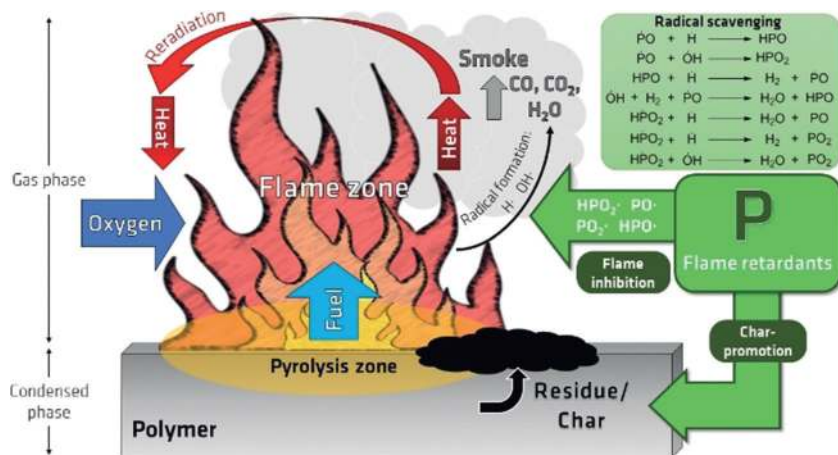


Figure 2. Flaming combustion of polymeric material and the role of phosphorus-based flame retardants.^[26]

health risk of goods, services, and the life cycle of products, much like preexisting labels in Germany and the Nordic countries.^[32] The Swedish TCO Certification specifically credits the sustainability of IT products, a key industry of non-halogenated FRs. Technology companies such as HP and chemical companies such as ICL-IP have implemented methods (GreenScreen, SAFR) to assess the chemical safety of their products.^[33]

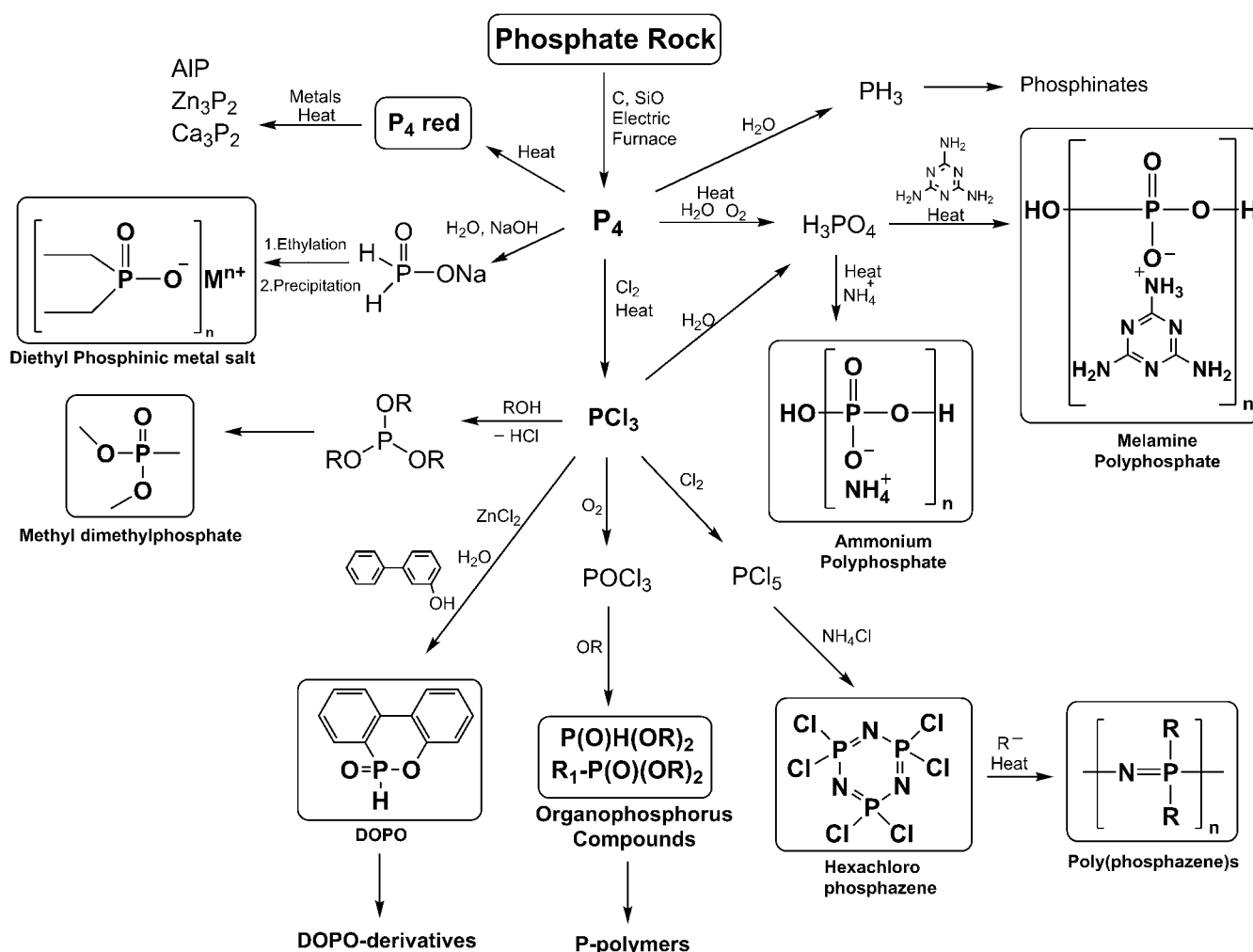
These trends are in line with consumer desires and the market shift toward more environmentally friendly (and ultimately sustainable) products, thus also prompting the use of bio-based materials and green chemistry in FR formulations.^[34] Currently, attention has been placed on recyclable FR materials, further decreasing the environmental impact.^[35]

Three key aspects—cost-effective conservation of material properties; matching the thermal stability and mode of action to processing and pyrolysis specifics; increased environmental friendliness with sustainability as a goal—constitute the characteristics of “good” flame retardants. In this respect, novel P-FRs will play a pivotal role in future products: their chemical versatility makes them ideally suited, as will be showcased more closely in the following.

2. Phosphate Rock—A Finite Natural Resource

Phosphorus chemistry is one of the oldest areas of chemistry, and involves the continuous development of new methods to improve the safety and sustainability of chemical processes. P-FRs are versatile: 1) the structure of P-FRs can vary from inorganic to organic; 2) the P content in these molecules can vary (e.g. from almost 100% for red P to 14.33% for DOPO); 3) the phosphorus can have different oxidation states, from 0 to +5, thereby resulting in different FR mechanisms (both in the gas and condensed phases). This architectural variation makes phosphorus unique for the design of FRs with tailored property profiles, such as density or glass transition temperatures (T_g), by changing the binding pattern (e.g. from alkyl to phenyl groups).

Most compounds that contain phosphorus are manufactured from phosphorite, commonly known as “phosphate rock”. The current industrial pathways for the synthesis of various P-FRs are shown in Scheme 1. Phosphate is reduced by an electrothermal process to elemental phosphorus (P_4),^[37] which serves as a precursor for the production of the main intermediate compounds in industry such as red phosphorus, phosphoric acid (H_3PO_4), phosphorus trichloride (PCl_3),



Scheme 1. Examples of industrial pathways to various P-based FRs from “phosphate rock”. (M is usually zinc or aluminum.)

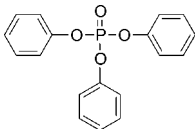
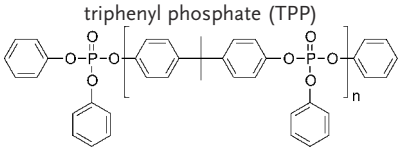
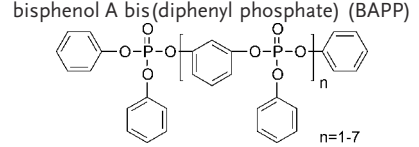
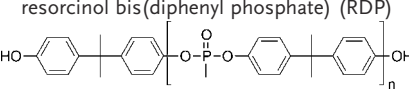
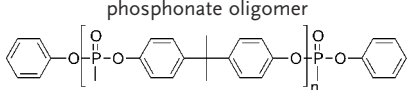
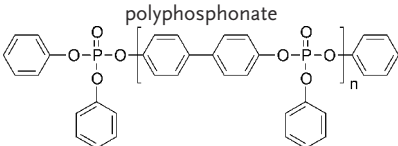
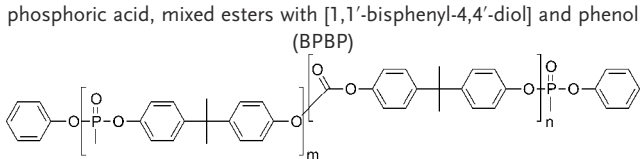
phosphorus pentachloride (PCl_5), phosphine (PH_3), and hypophosphite (H_2PO_2^-). The exploitation of all these pathways for the synthesis of many FRs, such as ammonium polyphosphate,^[38] melamine polyphosphate,^[39] phosphazenes,^[40] diethyl phosphonic metal salts, or DOPO,^[13b] validates the versatility of the phosphorus compounds used in FR applications.

Although a large fraction of the P_4 production is transformed into phosphoric acid, today PCl_3 is the main intermediate for the production of major industrial organophosphorus FRs such as triphenyl phosphate (TPP), resorcinol bis(diphenyl phosphate) (RDP), and bisphenol A bis(diphenyl phosphate) (BAPP), as well as for the production of oligomeric or polymeric FRs (Table 1). The common pathway for the synthesis of phosphorus-containing polymeric FRs is classical polycondensation (polytransesterification or via phosphoric acid chlorides),^[41] but more modern strategies such as olefin metathesis polycondensation^[42] or ring-opening polymerization^[43] (e.g. of cyclic phosphazene derivatives or cyclic phosphoric acid esters) were also studied more recently.

However, phosphorus-based chemicals make up less than 3 % of all the phosphorus extracted, with most of phosphate (82 %) being used as fertilizer or for other purposes, including animal feed additives (7 %), detergents, and cleaning products (8 %).^[44] Phosphate rock is a limited resource that is geographically concentrated in China, the United States, Morocco, Russia, and Jordan (according to the US Geological Survey released in January 2017).^[45] At current extraction rates, estimates point to phosphate rock reserves being depleted in the next 370 years, with the exception of the reserves in Morocco.^[45]

Currently, there is no alternative for this element; the phosphorus life cycle needs to be considered for agriculture in particular, but also for FRs. Consequently, the EU introduced phosphate rock to the list of critical raw materials in 2014 and elemental phosphorus followed in 2017.^[46] Therefore, to ensure that phosphate fertilizers and phosphorus chemicals are preserved for future generations, a sustainable phosphate management, novel methods to better employ feedstock, and recycling strategies are required globally. Possible technolo-

Table 1: Commercial P-FR alternatives to decabromodiphenyl ethers (d-PBDE) according to the United States (US) Environmental Protection Agency (released in January 2014).^{[a][36]}

Commercial P-FR alternatives to d-PBDE	Properties	Polymer applications
 triphenyl phosphate (TPP)	CAS: 115-86-6 M_w : 326.29	PPE-HIPS PC-ABS
 bisphenol A bis(diphenyl phosphate) (BAPP)	CAS: 181028-79-5 M_w : 693 ($n=1$); > 1000 ($n=2$)	PPE-HIPS PC PC-ABS
 resorcinol bis(diphenyl phosphate) (RDP)	CAS: 125997-21-9 M_w : 574.46 ($n=1$; CASRN 57583-54-7); M_w : 822.64 ($n=2$; CASRN 98165-92-5)	PPE-HIPS PC-ABS
 phosphonate oligomer	CAS: 68664-06-2 M_w : 1000-5000; 25 % $M_w < 1000$	thermosets
 polyphosphonate	CAS: 68664-06-2 M_w : 10000 to 50000; < 1 % $M_w < 1000$	elastomers engineering thermo-plastics
 phosphoric acid, mixed esters with [1,1'-bisphenyl-4,4'-diol] and phenol (BPBP)	CAS: 1003300-73-9 M_w : 650.6 ($n=1$); 974.8 ($n=2$); > 1000 ($n \geq 3$)	PPE-HIPS PC-ABS PC
 poly[phosphonate-co-carbonate]	CAS: 77226-90-5 M_w : > 1000; < 1 % < 1000	elastomers engineering thermo-plastics

[a] The mode of action in all cases involves chemical action in the condensed phase and char formation.

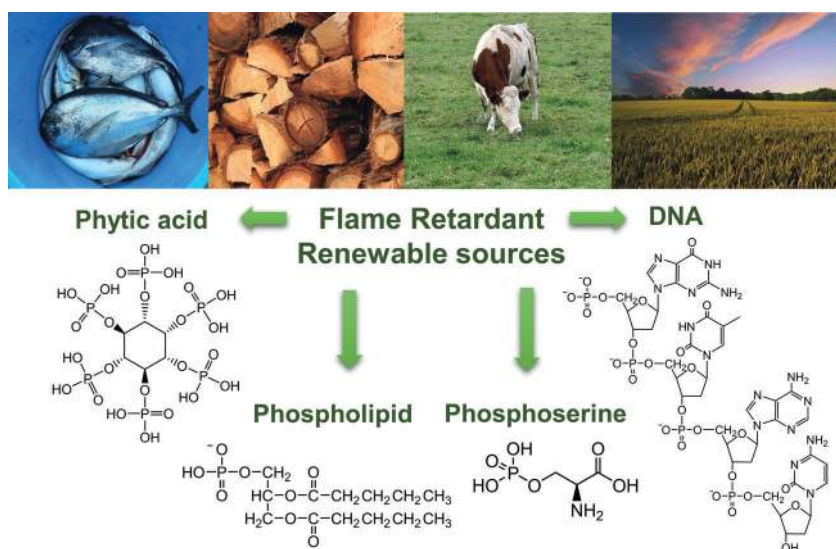


Figure 3. Renewable sources of P-FRs.

gies for phosphorus recovery include a wide range of strategies, such as phytoextraction (optimum annual P removal from Indian mustard seed equal to 114 kg P ha^{-1}), biochar (ca. 10 g P kg^{-1} biochar), or extraction from human urine and feces (recovery of over 80 % of total P from urine with approximately 0.5 and $1.3 \text{ g capita}^{-1} \text{ day}^{-1}$).^[47] In addition, it is estimated that the extraction of P from manure in the EU may be near to $1.8 \text{ million t a}^{-1}$, which would satisfy the annual demand of P required for EU fertilizers.^[48] On the other hand, as sugars are sometimes referred to as the “new oil” for tomorrow’s materials, the extraction of phytic acid or biomacromolecules (deoxyribonucleic acid and caseins) are also strategies to isolate P derivatives for the valorization of by-products from the agro- or food industry (see Section 5 and Figure 3) and P-FRs can be part of a sustainable phosphorus chemistry.

3. Recent Developments in Reactive Phosphorus Compounds

P-FRs can be implemented as either additive or reactive components. The latter allows for the FR to become part of the material’s constitution, thereby leading to “inherently” flame-retardant materials.

Reactive FRs are mainly used in thermosets, such as unsaturated polyesters, epoxy resins, or polyurethane foams. They are equipped with functional groups (alcohols, epoxy, amines, halogens, etc.), which allow incorporation into the polymer matrix during curing.^[1b,49] In epoxy resins, reactive FRs are preferred since they are covalently attached to the network and thus have a lower impact on the physical properties of the final product. In contrast, additive FRs result in decreased glass transition temperatures (T_g) and are prone to leaching (see Section 4). The decreased leaching of reactive FRs also reduces the potential pollution of wastewaters. However, additive FRs dominate the market, as they are easier to use and lower in price. In contrast, reactive FRs are

accompanied by the need for a significant reformulation of the curing process. This presents a disadvantage of reactive FRs, that is, each matrix needs a newly designed and formulated FR, while additives may be used for several polymer matrices.^[50]

3.1. Polyurethanes (PUs)

As a consequence of the wide use of polyurethanes (PUs) in foams, coatings, etc. and their inherent flammability, FRs are necessary. However, not only are the FR properties important, they also have an impact on the environment and physical properties. Biodegradable PUs are commonly synthesized with hydrolyzable soft segments.^[51] The use of P-FRs could achieve both, since these materials demonstrate good FR properties and can be both biocompatible and degradable.^[52] Chiu et al.^[51] synthesized PUs that achieve a V-0 rating in the UL-94 test (classification for the flammability of plastics) and presented efficient FR properties with limited oxygen indices (LOI, minimum oxygen concentration required to sustain combustion) higher than 27.7 %. The authors used 4,4-diphenylmethane diisocyanate (MDI) as the hard segment; 5-hydroxy-3-(2-hydroxyethyl)-3-methylpentyl-3-[2-carboxyethylphenylphosphine] propanoate (HMCPP, Figure 4) and polycaprolactonediol (PCL) as the soft segments; and 1,4-butanediol (BD) was used as a chain extender. By increasing the HMCPP content (7.5, 15.0, and 22.5 mol % with respect to MDI) in the PUs, the decomposition temperatures and the T_g values were reduced by several degrees.^[51]

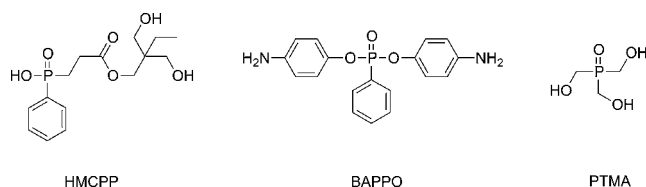


Figure 4. Examples of reactive P-FRs: HMCPP (5-hydroxy-3-(2-hydroxyethyl)-3-methylpentyl-3-[2-carboxyethylphenylphosphine]propanoate) used in PU; BAPPO (bis(4-aminophenyl)phenylphosphine oxide) used in PU; PTMA (phosphoryltrimethanol) used in PU.^[51,53]

As a water-based example, Çelebi et al.^[53a] followed a similar approach to synthesize aqueous dispersions of FR PUs, but instead of incorporating the P-FR as a soft segment, they incorporated it in the chain-extension step. Water-based PUs reduce the use of organic solvents and are, therefore, attractive from an environmental perspective. Bis(4-aminophenyl)phenylphosphine oxide (BAPPO, Figure 4) was used for the flame-retardant PU, and ethylenediamine for the non-flame-retardant PU. Poly(propylene-co-ethylene)polyol was used as a co-monomer. The physical properties of the two PUs are almost identical, except their gloss properties. This

was explained by the difference in the chain conformation of the two PUs. Furthermore, BAPPO increased the crystallinity of the hard segment, through its aromatic groups and longer chain length, which contribute to the higher packing capability of the hard segments.^[53a]

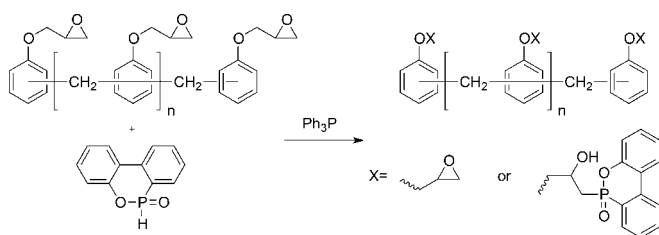
The majority of reactive FRs rely on halogens or phosphorus. Halogenated FRs are substituted nowadays because of toxicity and environmental concerns. It was reported that P-containing polyols are mainly the most appropriate reactive FRs for rigid PU foams, but they are rarely used in flexible PU foams (FPUF).^[54] Chen et al.^[53b] presented FPUFs, which contained phosphoryltrimethanol (PTMA, Figure 4) as a cross-linker. They proved that PTMA was mainly active in the condensed phase during a fire scenario. However, PTMA had a negative effect on the cell structure of the foam. With increasing PTMA content, the cell size increased and consequently the number of cell windows decreased. This behavior can be explained by the increased number of closed foam cells arising from the cross-linking nature of the PTMA further influencing the mechanical properties. The FPUF containing 3.2 wt % PTMA showed an increased tensile strength and elongation at break compared to the neat FPUF, because of the change in the foam structure.^[53b]

3.2. Epoxy Resins

The copolymerization of FRs is not limited to PUs; epoxy resins, often used for their thermomechanical properties and processability, also exhibit high flammability and, therefore, require FRs. The FRs can be introduced to the epoxy- or nitrogen-containing compound.

Zhang et al.^[55] proved that it is possible to achieve high T_g values, high thermal stability, and an UL-94 V-0/V-1 rating by the addition reaction of DOPO and epoxy phenol-formaldehyde novolac resin (Scheme 2). DOPO was the first efficient halogen-free FR for epoxy resins based on novolac and gained much attention because of its high thermal stability, high reactivity of its P–H bond, and flame-retarding efficiency.^[56]

An alternative method to incorporate the FR into the polymer network is to use it in the hardener, a process commonly used for epoxy resins. An example of this approach is the work of Artner et al.,^[57] who compared two DOPO derivatives (Figure 5): one was modified with amine groups and was used as a FR hardener in epoxy resins, the other had



Scheme 2. FR-functionalized novolac resin for further use in epoxy resins.^[55]

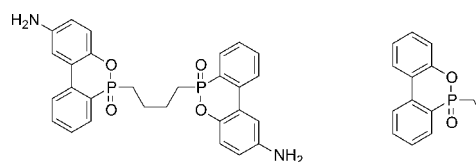


Figure 5. DOPO-based hardener (left), nonreactive analogue (right).^[57]

a similar structure, but was an additive FR. The authors revealed that the reactive FR has the potential to be superior over the additive FR.

By attaching the amine groups directly to DOPO, the solubility of the hardener was increased compared to previous studies. The resin with the DOPO-based diamine hardener presented comparable thermal- and fracture-mechanical properties as the reference epoxy material, namely the diglycidyl ether of bisphenol A with 4,4'-diaminodiphenylsulfone. In contrast to the reactive FR, the non-reactive additive showed a decrease in the T_g value by about 75 °C and a lower rubber modulus. However, the new hardener revealed a high reactivity, which led to an increase in viscosity during curing, thus posing a problem for application in composite materials because of the reduction in processing time.^[57]

In contrast, Ciesielski et al. illustrated that it is not necessary to use reactive FR components to maintain superior mechanical performance. By using the DOPO derivatives (DDM-(DOP)₂ and DDM-(DOP)₂-S) (Figure 6a,b), their epoxy resins achieved a V-0 rating at 1 % P in the resin without significantly lowering the T_g value. It was reported that phosphoramides can ring-open epoxides,^[58] so other P–N nucleophiles may also be incorporated into the polymer matrix, depending on the respective reaction kinetics.

Reactive phosphate-based FRs can also decrease the T_g value, which may be attributed to the flexibility of the P–O bond. However, Wang and Shi^[59] reported that reactive hyperbranched (*hb*) poly(phosphoester)s (PPEs; Fig-

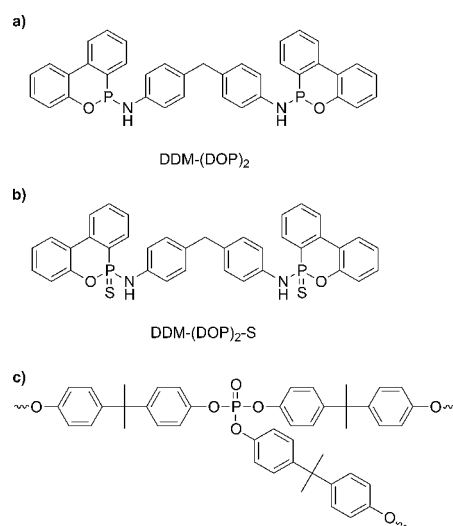


Figure 6. a,b) DOPO-based FRs achieving a V-0 rating at 1 % P in the epoxy resin; c) *hb*PPE FR for epoxy resins with a lower impact on the T_g value.^[58–59]

ure 6c)—because of their branched structure—reduce the T_g value to a smaller extent. This was attributed to the higher cross-linking density of the *hbPPE* having a greater influence than the P–O flexibility. The *hbPPE* was synthesized in an $A_2 + B_3$ approach by polycondensation of bisphenol A and phosphoryl chloride. This *hbPPE* was used to cure a bisphenol A based epoxy resin by PPh_3 catalysis, which led to a resin with a higher T_g value than the resin cured with only bisphenol A.^[59]

3.3. Phosphorus Oxidation State

The decrease in the T_g value by the presence of flexible P–O bonds was also reported by Jeng et al.^[60c] In addition, they stated that the introduction of sterically demanding groups such as P–O–C₆H₄–O–P can reduce the cross-linking density, thereby resulting in a further lowering of the T_g value. In contrast, the T_g value was reduced less when they used a FR with a more rigid P–Ph group. However, the FR mechanism was also influenced by exchanging a P–O bond by a P–C bond. Most reports indicate that phosphine oxides are rather poor char promoters, but are more active in the gas phase than other P-FRs with higher oxidation numbers such as phosphates.^[60] The higher gas-phase activity of phosphine oxides was also reported by Braun et al.^[62] who investigated the impact of the P oxidation state on its FR behavior in epoxy resin composites. They reported, in agreement with previous reports,^[60b] that the amount of stable residue increased and the release of volatiles containing phosphorus decreased as the oxidation state of P increased (Figure 7). However, in previous reports it was concluded that phosphates are the more efficient FRs, because of their higher efficiency as char promoters compared to phosphine oxides.^[60b] This conclusion differs from that of Braun et al., who ranked phosphine oxide as the best FR and phosphate as the worst through the observation of an increase in charring and decreased flame inhibition for the phosphates, which significantly accounted for the performance of FR in composites. These conflicting statements can be explained by the fact that Braun et al. investigated composites as a matrix, for which flame inhibition as a main mode of action plus minor charring was a very promising route for flame retardancy.^[12d,61] They showed that the key role of the oxidation state was in the type of interaction during the pyrolysis. The authors explained the

greater role of the gas-phase activity of composite materials with a high content of carbon fiber through a decrease in the relative impact of the charring.^[60b,62]

4. Recent Developments in Additive Phosphorus Compounds

Most FRs are added as additives during polymer processing steps instead of being built into the polymer backbone.

The major advantage of additive FRs is their cost-effectivity (i.e. performance value of the material) and ease of application in various matrices, thus they are widely used in industry.^[2b,63] Despite these advantages, additive FRs also exhibit several drawbacks, most notably their impact on physical properties such as the T_g value or mechanical stability. Leaching of the FRs over time is a major issue, especially for compounds with a low molecular weight. This may be partly prevented by using polymeric substances; however, phase separation needs to be prevented.^[64] The biggest challenge for additive FRs is, therefore, to find the optimal balance between the FR and the mechanical properties.^[50a,b]

4.1. Inorganic Phosphorus Flame Retardants

The “classic” example of an inorganic P-FR is red phosphorus, but in practice it is only used as an encapsulated substance to process FR thermoplasts, for example, glass-fiber (GF) reinforced PA 6,6, or in many types of multi-component FR systems.^[9a,65] The main advantages are an unparalleled high P content and efficiency already at small amounts: in GF-reinforced PA 6,6, in combination with metal oxides as synergists, only < 7 wt % was necessary to achieve excellent FR performance. While the use of red P alone is declining, it is proposed in combined formulations that include < 8 wt % red P, for example, in P + inorganic filler or in P–P mixtures combined with intumescent ammonium polyphosphate (APP) based systems.^[10b,66]

Tan et al. reported a hardener for epoxy resins based on inorganic APP which was modified with piperazine by cation exchange to later act as a hardener. This approach yielded efficient flame retardancy and showed improved mechanical properties compared to the dispersion of APP in the epoxy resin as a result of homogeneous incorporation without aggregation.^[67] Duan et al. used APP combined with a *hb*-phosphorus/nitrogen-containing polymer in polypropylene (Scheme 3).^[68]

Formulations using equal parts (10 wt %) of polymer and APP showed high LOI values of up to 30 %, compared to LOI values of approximately 20 % for 20 wt % of the individual compounds. These results suggested synergism between the *hb* polymer and the APP. Raman spectroscopy revealed that more graphitic char had been formed by the combination of these two compounds. The protective layer effect of the charred layers was also observed in thermogravimetric analysis (TGA) measurements through a higher temperature at maximum weight loss (T_{max}).^[68]

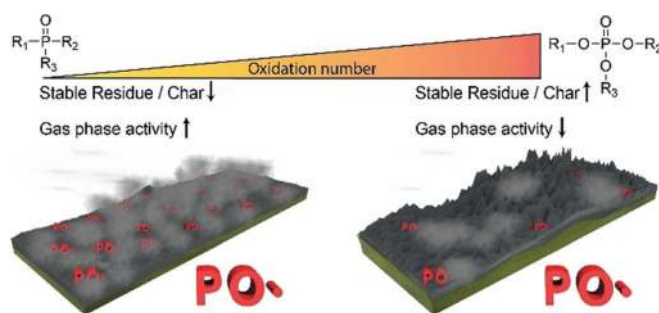
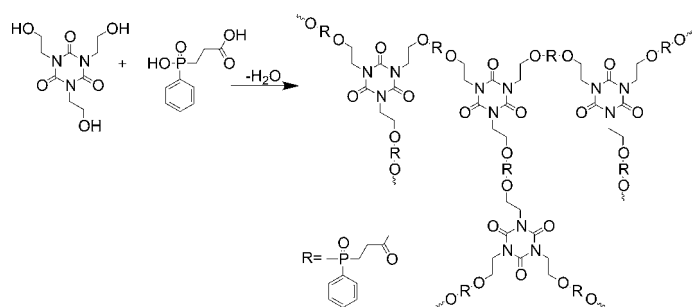


Figure 7. The char residue increases and the gas-phase activity decreases as the oxidation state increases.



Scheme 3. Synthesis of the *hb* FR polymers containing phosphorus/nitrogen.^[68]

Braun et al. showed that the reactivity of the P additive with the polymer matrix (here: GF-reinforced PA 6,6) has a great influence on its interaction with other additives as well as the main activity in the condensed or gas phase. This study illustrated that the main mechanism of melamine polyphosphate (MPP) is dilution of the fuel and the creation of a P-based protective layer. Aluminum phosphinate (AlPi), another FR currently widely applied, on the other hand, acts mainly in the gas phase. The combination of the two additives changes the dominant FR mechanism through the formation of a strong protective layer consisting of aluminum phosphate. The addition of zinc borate led to formation of a boron-aluminum phosphate layer, which showed a better protective layer performance than aluminum phosphate and resulted in the best cone calorimeter (most important instrument in fire testing, measuring heat release rate by the amount of oxygen consumed during combustion) performance of the samples, with hardly any ignition evident.^[10a,69]

The use of various salts of dialkylphosphinates, (e.g. aluminum, calcium, and zinc) as effective FRs for GF-reinforced thermoplasts were investigated by Clariant SE. The aluminum salts AlPi are commercially available under several trade names, such as Exolit OP 930, Exolit OP 935, and Exolit OP 1230. The Exolit OP line of products vary in the AlPi modification (e.g. encapsulation, particle size, etc.).^[13a]

The synergism between AlPi and nanometric iron oxide or antimony oxide was investigated by Gallo et al., who found different FR behaviors operated: in a redox cycle, Fe₂O₃ oxidized P to inorganic phosphates and was reduced to magnetite, thereby increasing the amount of P in the condensed phase. However, a catalytic effect on the cross-linking was postulated for Sb₂O₃, a nonreducible oxide, as no hint of the same mechanism was detected. The authors proposed that the surfaces of the metal oxides stabilize the oxygen-containing intermediate structures and thereby promote cross-linking reactions between the polymer chains and also the interaction with P-based intermediates.^[70]

Naik et al., and in a recent study Müller et al., compared the influence of the metals in melamine poly(aluminum phosphate), melamine poly(zinc phosphate), and melamine poly(magnesium phosphate) in epoxy resins. Melamine poly(aluminum phosphate) reduced the peak heat release rate (PHRR) by about 50 %, whereas the other two melamine poly(metal phosphates) achieved a reduction of PHRR to less

than 30 % compared to the neat epoxy resin. All three materials reduced the fire load by 21–24 % and lowered the CO yield and smoke production. The improved fire behavior is explained by their main activity in the condensed phase, with minor signs of fuel dilution. The fire residue increased and, as a result of intumescence, a protective layer was formed. In addition, synergistic combinations with other flame retardants were also studied: here, melamine poly(zinc phosphate) with melamine polyphosphate showed the best overall FR results as a consequence of strong intumescence, with a low heat release rate (HRR) and the lowest PHRR, maximum average rate of heat emission, and fire growth rate index values.^[71]

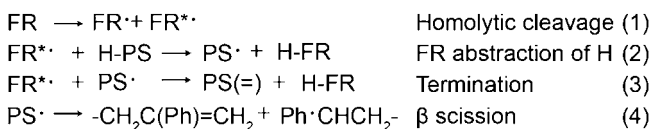
4.2. Organophosphorus Flame Retardants (OPFRs)

Organophosphorus compounds are currently discussed as substitutes for halogenated, mainly brominated, FRs. Most organophosphates are used as additives rather than being chemically bound to the polymer matrix.^[72] Besides their use as FRs, they work as plasticizers or antifoaming agents and are used in plastics, furniture, textiles, electronics, construction, vehicles, and the petroleum industry. In the following, some examples of these compounds—selected because of their importance to the field (more than 30 citations)—are discussed.

The influence of the chemical structure on the FR mechanism is not only important to small molecules, but also for organophosphorus polymers. Aromatic polyphosphonates exhibit higher thermal stability than aliphatic polyphosphonates, and, at the same time, they have a higher hydrolytic stability than the aromatic polyphosphates. This was explained by the presence of the stable P–C bond in phosphonates, while phosphates carry an additional hydrolyzable P–O–C linkage that results in lower degradation temperatures.^[73]

The influence of the chemical structure of the FR on its mechanism has been intensively studied. While Beach et al. suggested that the major FR mechanism for bromine- and sulfur-containing FR additives in polystyrene is through enhanced degradation of the polystyrene matrix,^[75] the phenomenon of radical generation together with flame inhibition was first investigated by Eichhorn in 1964.^[74] The mechanism of the condensed phase is as follows: a hydrogen atom is abstracted from the polystyrene backbone by the flame retardant, followed by β -scission of the polystyrene radical (Scheme 4).

P-FRs show no such enhanced degradation of polystyrene (PS) and, therefore, exhibit lower performance in LOI tests, the reason being the difference in bond dissociation energies. However, combining sulfur with triphenyl phosphate (TPP)



Scheme 4. Mechanism for enhanced degradation of polystyrene.^[75]

resulted in a performance comparable with that of hexabromocyclododecane (HBCD). Loosening of the polymer network by degradation is an important condensed-phase mechanism which allows mass transfer of gas-phase species to the surface and removes fuel and heat away from the pyrolysis zone via melt flow. According to the authors, the synergism between sulfur and TPP was achieved by the sulfur causing enhanced degradation of the PS network (Scheme 4), which resulted in an improved mass transfer of TPP to the surface.^[75] More recently, Wagner et al. investigated OPFRs with synergists containing disulfide bridges, further identifying the role of radical generators in the enhanced degradation of polystyrene.^[76]

As most additive monomeric and oligomeric OPFRs exhibit a plasticizing effect on the polymer matrix and may volatilize or migrate during the processing, alternative FRs are needed. Therefore, academic and industrial studies are increasingly turning to polymeric OPFRs which are designed to be completely miscible with the matrix and, therefore, less likely to migrate over time.^[73]

The importance of the FR molecular weight was investigated by comparing the monomeric FR TPP with the oligomeric FRs resorcinol bis(diphenyl phosphate) (RDP) and bisphenol A bis(diphenyl phosphate) (BDP) in polycarbonate/acrylonitrile-butadiene-styrene blends. All three compounds showed activity in the gas phase through flame poisoning, with TPP and RDP revealing a slightly better performance than BDP. However, TPP had almost no condensed-phase activity, while RDP showed some, and BDP demonstrated the highest activity. The behavior was explained by the fact that BDP and RDP catalyzed Fries rearrangements in the PC, while TPP volatilized before the decomposition of PC-ABS because of its low molecular weight, thus preventing chemical interaction.^[23c,77]

The phase separation of polymer blends must always be investigated with respect to the desired material properties. In this context, *hb* polymeric FRs are promising materials. Their key properties include many reactive end groups, a relative low intrinsic viscosity compared to linear polymers, and in most cases a high miscibility and solubility with other polymeric materials. In addition, their straightforward synthesis through “hyperbranching”, that is, statistical branching polymerization, makes them available on a large production scale. Furthermore, this class of polymers also has the potential to have a lower impact on material characteristics such as mechanical properties and T_g value.^[78]

Phosphorus combines chemical versatility and FR effectivity, thus allowing for enormous variety in FR formulations. These examples have shown that P shows different modes of action in FR formulations because of many various criteria: oxidation state, reactive or additive, inorganic or organic, low or high molecular weight, etc.

5. Modern Trends and the Future of Phosphorus-Based Flame Retardants

5.1. Synergistic Multicomponent Systems

Flame-retardant structures containing heteroatoms such as nitrogen, silicon, sulfur, and boron in combination with phosphorus provide a huge range of specific interactions, compared to the decomposition of phosphorus structures or the decomposition of these with pure hydrocarbons,^[26] thereby reducing the overall load of FRs in a material and maximizing effectivity (Figure 8).^[13d,58,79]

The combination of phosphorus–nitrogen (P–N) compounds is one of the most promising reported synergisms for halogen-free flame retardants. P–N synergism promotes the formation of cross-linked networks with polymer chains during a fire, thereby encouraging the retention of P in the condensed phase and yielding higher and more thermally stable char formation.^[81] Two of the most prominent P–N structures include phosphoramidates^[82] and cyclotriphosphazenes.^[83]

The main advantages of phosphoramidates over their analogous phosphates are their higher thermal stability,^[84] lower volatility,^[85] and higher viscosity as a result of hydrogen bonding.^[82c] These features can increase the density of the entire system and make them more likely to be retained in the matrix during combustion, thus contributing to a higher condensed-phase activity and affording higher char yields.

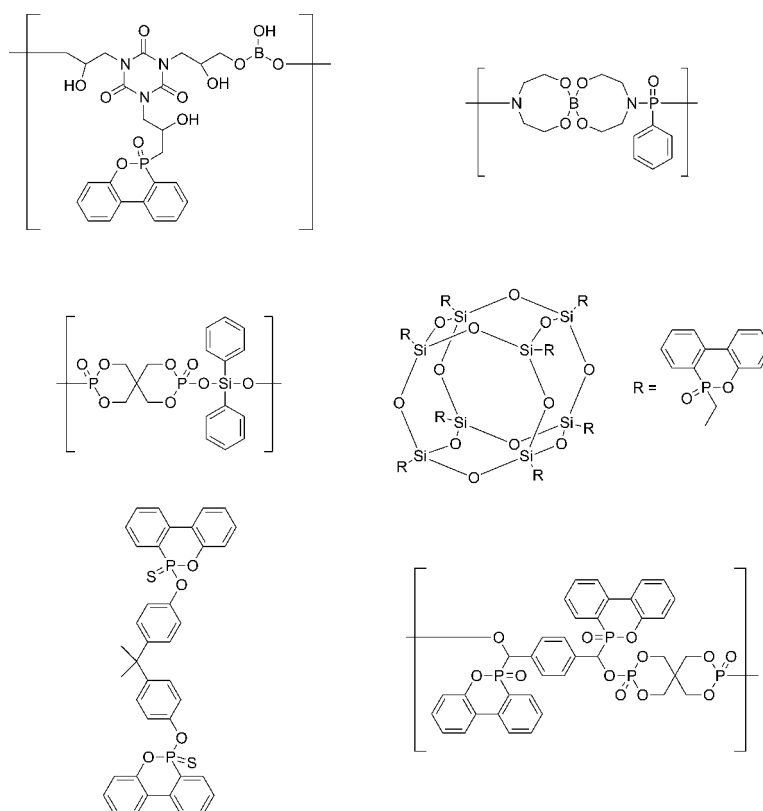
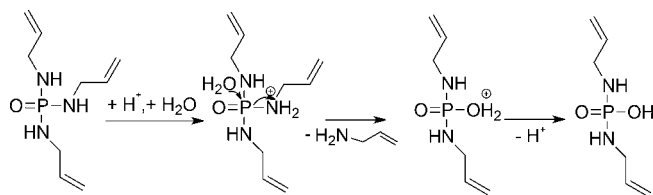


Figure 8. Various FR formulations with synergistic moieties. Top row: boron-containing formulations; middle row: silicon-containing formulations; bottom left: P-S-containing formulations; bottom right: formulation containing two types of P.^[13a, 80]

Neisius et al. suggested the hydrolysis of P–N bonds occurred under acidic conditions to form nonvolatile compounds (Scheme 5).^[82c] Interestingly, they showed that trisubstituted phosphoramidate displayed poor flame-retardant behavior on



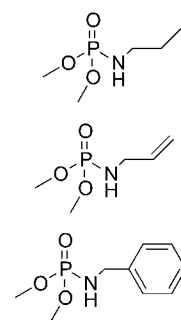
Scheme 5. P–N bond hydrolysis under acidic conditions.^[82c]

flexible polyurethane foams compared to the analogous monosubstituted phosphoramidate (Figure 9). The authors suggest that this is because the trisubstituted phosphoramidate decomposes thermally/hydrolytically to form nonvolatile structures that contribute only to condensed-phase activity. However, the monosubstituted phosphoramidate can decompose to form PO^\bullet radicals, which might prevent the oxidation of H^\bullet and OH^\bullet radicals.

Linear poly(phosphoramidate)s (PPAs) were also studied as FRs.^[86] The results indicated an enhanced thermal stability, increased formation of char yields at higher temperatures, and higher glass transition temperatures (T_g) with respect to the analogous poly(phosphate)s. Improvement in the flammability test (30% limiting oxygen index (LOI)) and dripping resistance (V-0 rating in UL-94) was achieved with a loading of about 30 wt % PPA.

In the last decade, a myriad of chemically and thermally stable phosphazene derivatives has been developed (Figure 10).^[83,86b,87] Cyclophosphazenes are reported to present even higher thermal stabilities than phosphoramidates: the thermal decomposition of the phosphazene-bound piperazine

Dimethyl mono-substituted
secondary phosphoramidates



Diphenyl mono-substituted
secondary phosphoramidates

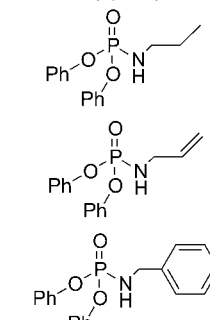


Figure 9. Monosubstituted dimethyl/diphenyl phosphoramidates.^[82c]

has been reported from 350 °C up to 500 °C (under N_2) with residues between 50 and 70 wt %, depending on the substituents. This large amount of char indicates cross-linking during pyrolysis, for example, through ring-opening polymerization.^[83a,88] The hydrolytic lability of P–N bonds limits their application in textiles (washing). Although, recent studies showed self-extinguishing in cotton/polyester blends grafted with allyloxypolyphosphazene.^[89]

Hexachlorophosphazene is the common starting material for polyphosphazenes, as it allows the introduction of various pendant groups after polymerization, for example, the fully inorganic polyaminophosphazene, or functional inorganic-organic hybrid polymers ranging from linear copolymers^[90] to branched polymeric structures.^[88] The cross-linked or *hb*-poly(phosphazene) structure not only acts as a good carbonization agent, but can also stop dripping and reduce the peak heat release rate (PHRR) by 55%, as reported by Tao et al.^[83a]

Polyphosphazenes usually exhibit low T_g values (from –100 °C to above room temperature).^[91] Qian et al. synthe-

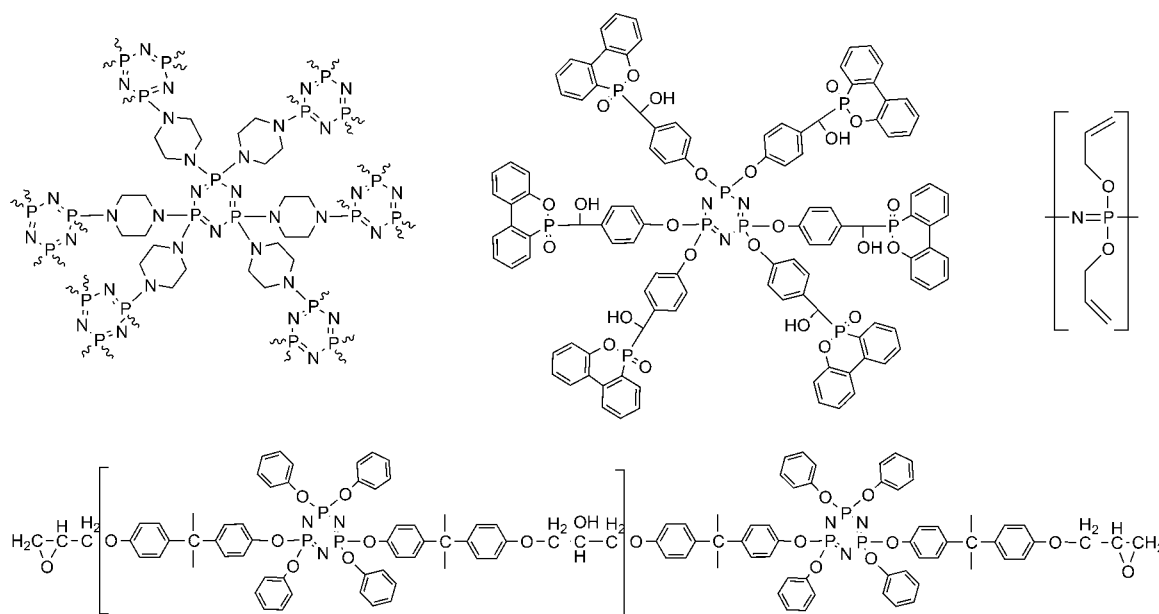


Figure 10. Low-molecular-weight and polymeric flame-retardant phosphazenes.^[87–90]

sized phosphaphenanthrene/cyclotriphosphazene FRs with practically the same T_g value as the neat diglycidyl ether of bisphenol A (DGEBA) epoxy resin.^[87] Recently, the Wu research group has been working on the synthesis of several cyclotriphosphazene-linked epoxy resins. T_g values of 160 °C or 145 °C were reached by using them as a matrix^[90a] or loading them into DGEBA resins (20 wt %), respectively.^[83b,90b] A self-extinguishing UL-94 V-0 rating was achieved with a loading of 30 wt % in the resulting thermosets.

As mentioned in Section 4, a current challenge in the development of new FRs is the retention of the mechanical performance of the matrix and effectiveness of the FR. This was achieved to some extent by reactive *hbPPEs* (see Section 3.2). Another, very promising approach to meeting this requirement is the combination of P compounds either by blending or covalent linkages to nanometric fillers, such as carbon nanotubes,^[92] graphene,^[93] polyhedral silsesquioxanes,^[94] halloysite nanotubes,^[95] montmorillonite, or metal oxide nanoparticles.^[96] In some cases, FRs which are covalently grafted onto the nanofillers have higher efficiency than additives at the same concentration.^[97] Acceptable grafted amounts of P compounds are between 10 and 30 wt %, which equate to less than 1 wt % phosphorus in the final nanocomposite.^[97] A UL-94 V-0 classification (Figure 11a) and an increase in the LOI value have been reported for polypropylene and epoxy resin using DOPO-grafted to SiO₂ nanoparticles,^[98] exfoliated graphene,^[99] or glass fabric.^[97a]

Typically, the synergistic effect of the nanofillers and P-grafted compounds occurs in the condensed phase. Phosphorus promotes the formation of cross-linked structures, which together with the effect of nanofillers of increasing the melt viscosity promotes intensive carbonization (Figure 11b). However, some studies have suggested that the grafting of chlorinated phosphorus compounds or DOPO-silane deriva-

tives to carbon nanotubes^[92b] and graphene^[99] also affected the gas phase. The combination of gas- and condensed-phase activity led to a reduction in the PHRR by around 35 % and an increase in the LOI values in polyamide 6 and epoxy resin, even achieving the V-0 classification in UL-94 tests.

However, the FR effect of the nanofillers depends not only on the formation of a compact network layer at high temperatures, but also on their ability to be dispersed in the nanocomposite (Figure 11). For example, several research groups focused on grafting P compounds such as diphenylphosphinic chloride,^[92a] hexachlorocyclotriphosphazene,^[92b] or an oligomeric diaminobisphosphonate^[100] to carbon nanotubes. These polymers cover the surface of the nanotubes with a thin layer, which impedes the formation of π - π interactions and promotes their individual dispersion in polystyrene (PS), polyamide 6 (PA6), or ethylene vinyl acetate (EVA), respectively. Stable dispersions in dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), or H₂O were achieved after ultrasonication. In addition, Qian et al. also obtained stable colloidal dispersions of graphene grafted with DOPO-silane in ethanol, tetrahydrofuran (THF), and DMF (Figure 11c).^[99] According to the authors, the introduction of compounds with polar groups on the surface of the carbon nanotubes favored their wettability and compatibility with polymer chains.

It is clear that research on synergistic systems is very active. P-N-based compounds have proved to be a robust alternative to the predominantly halogenated FRs in use today. As shown in Section 5.1, a condensed-phase mechanism is predominant for P-N compounds as well as for P nanocomposites. In the latter, the key role of P-FRs is to favor the dispersion of the nanofillers, thereby enhancing the formation of a protective char layer and lowering the heat release rate (HRR) during the combustion of the polymer.

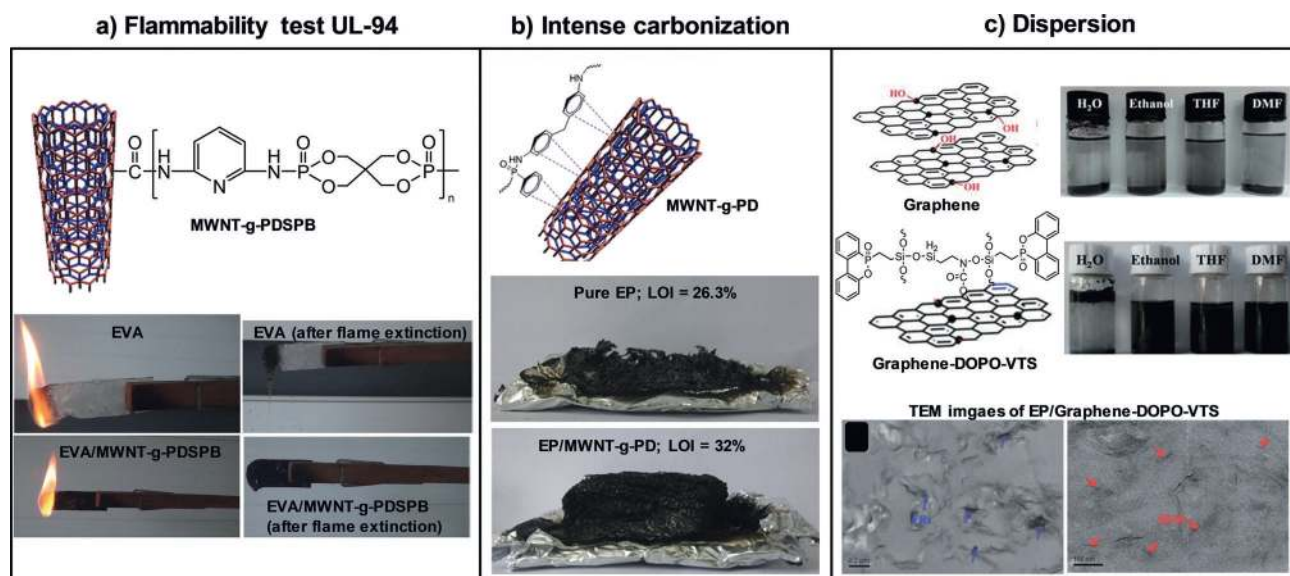


Figure 11. Effects of phosphorus-grafted nanofillers in an organic matrix.^[100,111] a) UL-94 test of ethylene vinyl acetate (EVA) with 1 wt % multiwalled carbon nanotubes (MWNTs) wrapped on the surface with poly(2,6-diaminopyridine spirocyclic pentaerythritol bisphosphonate) (PDSPB); b) carbonization after the cone calorimeter test of epoxy resin (EP) with 2 wt % of the MWNTs wrapped on the surface with poly(phenylphosphonic-4,4'-diaminodiphenylmethane) (PD); c) photographs of dispersions of graphene and graphene wrapped with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) modified vinyl trimethoxysilane (DOPO-VTS) in different solvents and transmission electron microscopy (TEM) images of EP with graphene-DOPO-VTS as a flame retardant.

5.2. Renewable Sources

Fractions of biomass from different industrial sectors (e.g. paper) are utilized to produce bio-based FRs, such as carbohydrate fractions (starch), oil fractions (triglycerides or fatty acids), and phenolic fractions (lignin).^[101,102] In some cases, these fractions are modified with P compounds to improve their FR potential.

Since 2006, the group of Cádiz, in particular, have made special efforts in this field.^[103] They reported new routes to obtain P-containing triglycerides or fatty acids from vegetable oils by cationic polymerization, by cross-metathesis reaction, or by Michael addition. An increase in the LOI values in the final material was detected. More recently, Howell et al.^[104] reported the esterification of isosorbide (from starch) with 10-undecenoic acid (from castor oil) to provide a difunctional ester which can be modified by a thiol-ene reaction to generate a series of phosphate, phosphonate, and phosphinate esters, which were later incorporated into epoxy resins. Howell et al. further synthesized diethyl esters of tartaric acid, a by-product of the wine industry, using diphenylphosphinic chloride, thereby producing an ester which may serve as a base for further FR agents.^[105]

Starch, chitin, and chitosan are polysaccharides that carry various chemical functionalities that can undergo reactions such as etherification, esterification, or graft polymerization to produce FRs.^[106] Cotton fabric is the matrix par excellence for the application of bio-based FRs and is the most commonly used. Polysaccharide cationic polyelectrolytes deposited through layer-by-layer (LbL) assembly can greatly enhance the char-forming ability of cellulose. 20–40 deposition steps are usually necessary to achieve significant flame-retardant properties, which limits the applicability of this technique. However, Carosio et al.^[107] recently achieved self-extinguishing during a flammability test after only two deposited bilayers (less than 5 wt % deposited on cotton) using a polyphosphoric acid as an anionic polyelectrolyte. The dehydration effect of the polyphosphoric acid promoted the formation of a protective layer from the starch. Xiao et al.^[108] reported the synergistic effect of a chitosan/urea compound based on a phosphonic acid melamine salt with melamine pyrophosphate and pentaerythritol in polypropylene, thereby accelerating the decomposition and promoting char formation.

Lignocellulosic materials are aromatic-rich polymers that exhibit high thermal stability and very high char yields. The high number of reactive functional groups in their structure allows their chemical functionalization with P to promote dehydration reactions, and with nitrogen compounds to release NH₃ gas. Liu et al.^[109] reported the modification of lignin by grafting polyethylene imine and diethyl phosphite as well as its incorporation in polypropylene/wood composites. Costes et al.^[110] modified lignin with PONH₄ to improve its FR action in poly(lactic acid). A V-0 classification in UL-94 fire tests was achieved through the incorporation of 20 wt % of the treated lignin.

Interestingly, the authors showed that the thermal stability of lignin is mainly dependent on the nature and the number of monomer units that constitute the plant, which is not only

affected by the plant origin but also by the extraction process used. Thus, Organosolv lignin was less thermally stable than Kraft lignin. The thermal degradation of lignin started around 230 °C with the cleavage of the phenylpropanoid side chain and continued with the further cleavage of the main chain (250 °C–450 °C), which produced a large quantity of methane. Above 500 °C, condensation reactions of the aromatic structure occur, promoting the formation of 50 wt % of a stable char up to 650 °C. Lignocellulosic derivatives such as coffee grounds^[112] in poly(butylene adipate-co-terephthalate) or vanillin^[113] in epoxy resins have also been reported as FR additives.

The use of phytic acid from cereal grains, beans, or seed oil (28 wt % P content) has been reported so far as a bio-based P-FR. Phytic acid (PA) decomposes around 200 °C, which ensures the dehydration of a carbon source and makes it a good candidate as an acid source for intumescent systems.^[114] Laufer et al. used LbL assembly to develop a fully renewable intumescent system which reduced the flammability of cotton.^[114] The combination of 30 bilayers of PA (anionic polyelectrolyte) with chitosan as a cationic polyelectrolyte succeeded in completely extinguishing the flame in a vertical flame test. Recently, Zheng et al.^[115] synthesized a melamine phytate (MPA) with a particle size around 1 μ m by the reaction of phytic acid with melamine. MPA starts to decompose at around 250 °C, releasing water and producing melamine polyphytate by self-cross-linking. At 400 °C, the s-triazine ring from melamine decomposes with generation of inert gases. The addition of a charring agent, dipentaerythritol, was necessary to reach 28.5 % in the LOI test and a V-0 rating in the UL-94 test (the dripping phenomenon of polypropylene needed to be suppressed).

5.3. Biopolymers

The groups of Malucelli and Alongi have recently introduced the use of phosphorylated biomacromolecules such as caseins (from milk products) and deoxyribonucleic acid (from the extraction of salmon milt and roe sacs) as inherent FRs; this was part of a strategy for the valorization of by-products from the agro-food industry.^[4,116]

α_{S1} -Caseins are phosphorylated proteins containing approximately nine bound phosphate groups per molecule. In cotton fabrics, caseins show thermal degradation profiles analogous to those of ammonium polyphosphate (APP) salts, except that the phosphoric acid is released at lower temperatures compared to the salts, because of the weaker covalent bonds of the phosphate groups in the main chain. The catalytic effect of the phosphoric acid in the dehydration of the cellulose promotes the formation of a thermally stable char at 600 °C. In flammability tests, a significant decrease of 35 % in the total burning rate and a reduction of the PHRR by 27 % were achieved. In polyester fabrics, the decrease in the burning rate was 67 %, but dripping was not suppressed.

The structure of deoxyribonucleic acid (DNA) makes it an ideal intumescent material as it carries 1) phosphates as an acid source, 2) deoxyribose units as a char source, and 3) nitrogen-containing aromatic groups as blowing agents.

However, DNA decomposes at lower temperatures (160–200 °C) than the typical intumescent additives (e.g. 300–350 °C).^[117] In cotton fabrics, the thermal degradation of DNA was similar to that of APP: the combustion data proved a significant decrease in the PHRR by 50 % combined with an intumescent effect.

The application of caseins and DNA to the fabric was carried out by impregnation or by LbL depositions. For significant results, 20 bilayers were necessary to reduce the burning rate and achieve self-extinguishment of the fabric as well as an increase of the final residue after burning. However, the major disadvantage of applying biomacromolecules to fabric is their poor resistance to washing treatments.

Recently, Alongi et al. investigated the potential of DNA coated on different matrices (EVA, PP, PA6) as a “universal” FR.^[118] Thicknesses of 3 mm (10 wt % DNA) showed good performances and a reduction in the PHRR of more than 50 % in all polymeric matrices (Figure 12).

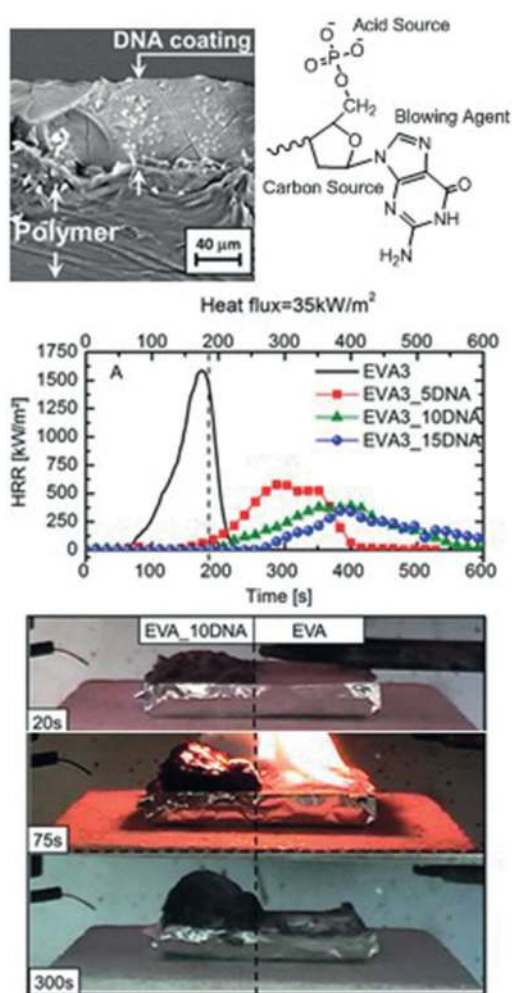


Figure 12. Top: DNA-coated polymer surface and chemical structure of a DNA segment and its different compounds acting together to form an intumescent flame retardant. Middle: Heat release rate plots at 35 kW m^{−2} for ethylene vinyl acetate (EVA) and EVA treated with 5, 10, and 15 wt% DNA. Bottom: Snapshots taken at different times during cone calorimetry tests on an EVA sample with only 50 % of the surface coated with DNA.^[118]

To summarize, the main mechanism of biopolymers in cotton fabrics is the release of phosphoric acid at lower temperatures to catalyze the formation of a thermally stable char. However, two current limitations to their use are their poor resistance to laundering and their expensive production on a large scale.

6. Conclusions

Phosphorus is pivotal to the development of novel efficient flame retardants, mainly because of its chemical versatility: it can act in both the condensed and gas phase, as an additive or as a reactive component, in various oxidation states, and in synergy with numerous adjuvant elements. With increased awareness towards nontoxic, recyclable, and bio-based (or even sustainable) materials, phosphorus has the potential to fulfill all the criteria for future flame retardants. Future FRs will be increasingly tailored to the polymer type and its application, especially for new polymers, including biopolymers. The trend towards high-molecular-weight FRs is apparent, and polymeric, complex, and multifunctional structures will aid in reducing flammability without a loss of valuable properties. Furthermore, investigations into combinations of P with various moieties (P-P, P-Si, P-B, etc.) and multicomponent systems will continue to reduce FR loading and improve FR performance. Finally, the use of renewable resources as effective FRs will ensure a more ecologically aware means of production, thereby increasing the longevity of research into the field of flame retardancy.

“Molecular firefighting” demands the combined efforts of synthetic chemistry, an understanding of FR mechanisms, and knowledge of polymer processing. This interdisciplinary field continues to reveal new insight into the FR mechanisms, which we believe will drive toward a more sustainable P life-cycle for FRs and a new era of polymeric FR materials.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft (DFG WU 750/8-1; SCHA 730/15-1) for funding. M. M. V. thanks the Marie Skłodowska-Curie fellowship 705054-NOFLAME. J.C.M. is recipient of a fellowship through funding of the Excellence Initiative in the context of the graduate school of excellence “MAINZ” (Materials Science in Mainz; DFG/GSC 266). F.R.W., M.M.V., and J.C.M. thank Prof. Dr. Katharina Landfester (MPI-P, Germany) for support.

Conflict of interest

The authors declare no conflict of interest.

How to cite: *Angew. Chem. Int. Ed.* **2018**, *57*, 10450–10467
Angew. Chem. **2018**, *130*, 10608–10626

- [1] a) S. Shaw, *Rev. Environ. Health* **2010**, 25, 261–306; b) S.-Y. Lu, I. Hamerton, *Prog. Polym. Sci.* **2002**, 27, 1661–1712; c) S. V. Levchik, E. D. Weil, *J. Fire Sci.* **2006**, 24, 345–364.
- [2] a) Lucintel, Irving, TX, USA, **2016**; b) A. B. Morgan, J. W. Gilman, *Fire Mater.* **2013**, 37, 259–279.
- [3] E. D. Weil, S. V. Levchik, *Flame Retardants for Plastics and Textiles: Practical Applications*, 2nd ed., Carl Hanser, München, **2015**.
- [4] G. Malucelli, F. Bosco, J. Alongi, F. Carosio, A. Di Blasio, C. Mollea, F. Cuttica, A. Casale, *RSC Adv.* **2014**, 4, 46024–46039.
- [5] S. Bourbigot, S. Duquesne, *J. Mater. Chem.* **2007**, 17, 2283–2300.
- [6] a) P. R. Hornsby in *Macromolecular Symposia*, Vol. 108, Wiley Online Library, Chichester, **1996**, pp. 203–219; b) Lucintel, Irving, TX, USA, **2016**, p. 208.
- [7] a) R. W. Nalepa, D. J. Scharf, Hoechst Celanese Corp., **1993**; b) L. J. Chyall, H. A. Hodgen, F. J. Vyverberg, R. W. Chapman, Pabu Services, Inc., **2005**; c) A. Sut, S. Greiser, C. Jäger, B. Schartel, *Polym. Degrad. Stab.* **2015**, 121, 116–125.
- [8] a) E. D. Weil, *Fire Retard. Polym. Mater.* **2000**, 115–145; b) M. Lewin, *J. Fire Sci.* **1999**, 17, 3–19.
- [9] a) B. Schartel, R. Kunze, D. Neubert, *J. Appl. Polym. Sci.* **2002**, 83, 2060–2071; b) S. V. Levchik, G. F. Levchik, A. I. Balabanovich, E. D. Weil, M. Klatt, *Angew. Makromol. Chem.* **1999**, 264, 48–55; c) P. Catsman, L. C. Govaerts, R. Lucas, C08K 5/521 (2006.01), C08L 69/00 (2006.01) ed. (Ed.: G. E. Company), World Intellectual Property Organization (WIPO), USA, **2000**; d) D. K. Chattopadhyay, D. C. Webster, *Prog. Polym. Sci.* **2009**, 34, 1068–1133.
- [10] a) U. Braun, B. Schartel, M. A. Fichera, C. Jäger, *Polym. Degrad. Stab.* **2007**, 92, 1528–1545; b) Y. Liu, Q. Wang, *Polym. Degrad. Stab.* **2006**, 91, 3103–3109.
- [11] F. L. Jin, X. Li, S. J. Park, *J. Ind. Eng. Chem.* **2015**, 29, 1–11.
- [12] a) *Additives for Polymers* **2017**, 10–11; b) S. V. Levchik, E. D. Weil, *Polym. Int.* **2004**, 53, 1901–1929; c) M. Rakotomalala, S. Wagner, M. Döring, *Materials* **2010**, 3, 4300–4327; d) B. Schartel, A. I. Balabanovich, U. Braun, U. Knoll, J. Artner, M. Ciesielski, M. Döring, R. Perez, J. K. W. Sandler, V. Altstädt, T. Hoffmann, D. Pospiech, *J. Appl. Polym. Sci.* **2007**, 104, 2260–2269.
- [13] a) M. Ciesielski, B. Burk, C. Heinzmann, M. Döring in *Novel Fire Retardant Polymers and Composite Materials*, Woodhead, Sawston, **2017**, pp. 3–51; b) K. A. Salmeia, S. Gaan, *Polym. Degrad. Stab.* **2015**, 113, 119–134; c) X. Wang, Y. Hu, L. Song, W. Y. Xing, H. D. A. Lu, P. Lv, G. X. Jie, *Polymer* **2010**, 51, 2435–2445; d) S. Yang, Q. X. Zhang, Y. F. Hu, *Polym. Degrad. Stab.* **2016**, 133, 358–366; e) W. C. Zhang, X. M. Li, H. B. Fan, R. J. Yang, *Polym. Degrad. Stab.* **2012**, 97, 2241–2248.
- [14] R. E. Lyon, M. L. Janssens in *Encyclopedia of Polymer Science and Technology*, Wiley, Chichester, **2002**.
- [15] a) M. Lewin, E. Weil in *Fire retardant materials* (Eds.: A. R. Horrocks, D. Price), Woodhead, Sawston, **2001**, pp. 31–68; b) S. Rabe, Y. Chuenban, B. Schartel, *Materials* **2017**, 10, 23.
- [16] a) B. Schartel, B. Perret, B. Dittich, M. Ciesielski, J. Krämer, P. Müller, V. Altstädt, L. Zang, M. Döring, *Macromol. Mater. Eng.* **2016**, 301, 9–35; b) M. Lewin, *Spec. Publ. R. Soc. Chem.* **1998**, 224, 3–34; c) S. Levchik, C. A. Wilkie, *Fire Retard. Polym. Mater.* **2000**, 171–215.
- [17] a) G. Camino, S. Lomakin in *Fire retardant materials* (Eds.: A. R. Horrocks, D. Price), Woodhead, Cambridge, **2001**, pp. 318–336; b) J. Alongi, Z. D. Han, S. Bourbigot, *Prog. Polym. Sci.* **2015**, 51, 28–73; c) S. Bourbigot, M. Le Bras, S. Duquesne, M. Rochery, *Macromol. Mater. Eng.* **2004**, 289, 499–511.
- [18] a) M. Matzen, B. Kandola, C. Huth, B. Schartel, *Materials* **2015**, 8, 5621–5646; b) K. Shibuya, H. Hachiya, N. Nanba, (Ed.: J. Asashi Kasei Kabushiki Kaisha), **2002**; c) F. Kempel, B. Schartel, J. M. Marti, K. M. Butler, R. Rossi, S. R. Idelsohn, E. Oñate, A. Hofmann, *Fire Mater.* **2015**, 39, 570–584.
- [19] S. Bourbigot, M. Le Bras, R. Leeuwendal, K. K. Shen, D. Schubert, *Polym. Degrad. Stab.* **1999**, 64, 419–425.
- [20] S. Duquesne, M. Le Bras, S. Bourbigot, R. Delobel, F. Poutch, G. Camino, B. Eling, C. Lindsay, T. Roels, *J. Fire Sci.* **2000**, 18, 456–482.
- [21] G. J. Minkoff, *Chemistry of combustion reactions*, Butterworths, London, **1962**.
- [22] J. Green, *J. Fire Sci.* **1996**, 14, 426–442.
- [23] a) S. K. Brauman, *J. Fire Retard. Chem.* **1977**, 4, 38–58; b) G. Camino, L. Costa, M. P. L. di Cortemiglia, *Polym. Degrad. Stab.* **1991**, 33, 131–154; c) B. Perret, K. H. Pawlowski, B. Schartel, *J. Therm. Anal. Calorim.* **2009**, 97, 949–958.
- [24] S. V. Levchik, E. D. Weil, *Polym. Int.* **2005**, 54, 11–35.
- [25] a) M. Modesti, A. Lorenzetti, *Polym. Degrad. Stab.* **2002**, 78, 167–173; b) K. A. Salmeia, S. Gaan, G. Malucelli, *Polymer* **2016**, 8, 319; c) A. R. Horrocks, *Polym. Degrad. Stab.* **2011**, 96, 377–392.
- [26] B. Schartel, *Materials* **2010**, 3, 4710–4745.
- [27] a) T. Marzi, A. Beard in *Flame Retardants*, Vol. 12, Interscience, London, **2006**, p. 21; b) I. van der Veen, J. de Boer, *Chemosphere* **2012**, 88, 1119–1153.
- [28] a) J. D. Meeker, H. M. Stapleton, *Environ. Health Perspect.* **2010**, 118, 318–323; b) A. M. Sundkvist, U. Olofsson, P. Haglund, *J. Environ. Monit.* **2010**, 12, 943–951; c) G. L. Wei, D. Q. Li, M. N. Zhuo, Y. S. Liao, Z. Y. Xie, T. L. Guo, J. J. Li, S. Y. Zhang, Z. Q. Liang, *Environ. Pollut.* **2015**, 196, 29–46.
- [29] A. Beard, T. Marzi in Proceedings of Going Green CARE Innovation 2006 Conference. Vienna, Austria, **2006**.
- [30] P. L. Lallas, *Am. J. Int. Law* **2001**, 95, 692–708.
- [31] I. ISO, International Org. for Standardization, Geneva **2000**.
- [32] a) U. Landmann, Freie Universität Berlin **1999**; b) T. B. Bjørner, L. G. Hansen, C. S. Russell, *J. Environ. Econ. Manag.* **2004**, 47, 411–434.
- [33] a) A. Beard, M. Klimes, U. Wietschorke, *2012 Electronics Goes Green 2012 + (Egg)* **2012**; b) H. Wendschlag, H. Holder, C. Robertson, C. Wray in *2nd International Conference on ICT for Sustainability (ICT4S 2014)*, Atlantis Press, **2014**, pp. 306–310; c) G. Ondrey, *Chem. Eng.* **2015**, 122, 19–23.
- [34] a) G. Marosi, B. Szolnoki, K. Bocs, A. Toldy in *Polymer Green Flame Retardants*, 1st ed. (Eds.: C. Papaspyrides, P. Kiliaris), Elsevier, Amsterdam, **2014**, pp. 181–220; b) A. Sakharov, P. Sakharov, S. Lomakin, G. Zaikov in *AIP Conf. Proc.*, Vol. 1459, AIP, **2012**, pp. 316–318; c) M. Zammarano, D. M. Fox, S. Matko, T. Kashiwagi, J. W. Gilman, R. D. Davis, *Fire Mater.* **2011**, 337–342.
- [35] a) P. F. Sommerhuber, J. L. Wenker, S. Ruter, A. Krause, *Resour. Conserv. Recycl.* **2017**, 117, 235–248; b) D. Hoang, T. Nguyen, H. An, J. Kim, *Macromol. Res.* **2016**, 24, 537–546; c) M. Schlummer, A. Maurer, T. Leitner, W. Spruzina, *Waste Manage. Res.* **2006**, 24, 573–583.
- [36] EPA, in *An Alternatives Assessment for the Flame Retardant Decabromodiphenyl ether (DecaBDE)*, https://www.epa.gov/sites/production/files/2014-05/documents/decabde_final.pdf, **2014**.
- [37] J.-L. Montchamp, *Acc. Chem. Res.* **2014**, 47, 77–87.
- [38] K. T. Carter, Vol. US3464808 A (Ed.: S. Co), **1969**.
- [39] J. D. Leman, A. J. Robertson, Vol. US4117200 (Ed.: A. C. Company), **1978**.
- [40] N. Fukuoka, H. Yasuda, M. Nishimatsu, Y. Ohmae, Vol. EP1403273 A1 (Ed.: L. Chemipro Kasei Kaisha), **2004**.
- [41] L. K. Müller, T. Steinbach, F. R. Wurm, *RSC Adv.* **2015**, 5, 42881–42888.
- [42] a) F. Marsico, A. Turshatov, R. Peköz, Y. Avlasevich, M. Wagner, K. Weber, D. Donadio, K. Landfester, S. Balushev,

- F. R. Wurm, *J. Am. Chem. Soc.* **2014**, *136*, 11057–11064; b) M. Steinmann, J. Markwart, F. R. Wurm, *Macromolecules* **2014**, *47*, 8506–8513; c) G. Becker, L. Vlaminc, M. M. Velencoso, F. E. Du Prez, F. R. Wurm, *Polym. Chem.* **2017**, *8*, 4074–4078.
- [43] a) T. Wolf, T. Steinbach, F. R. Wurm, *Macromolecules* **2015**, *48*, 3853–3863; b) T. Steinbach, S. Ritz, F. R. Wurm, *ACS Macro Lett.* **2014**, *3*, 244–248.
- [44] R. W. Scholz, A. H. Roy, F. S. Brand, D. T. Hellums, A. E. Ulrich, *Sustainable Phosphorus Management: A Global Transdisciplinary Roadmap*, Springer, Dordrecht, Heidelberg, New York, London, **2014**.
- [45] J. Cooper, R. Lombardi, D. Boardman, C. Carliell-Marquet, *Resour. Conserv. Recycl.* **2011**, *57*, 78–86.
- [46] EU, http://ec.europa.eu/growth/sectors/raw-materials/specific-interest/critical_es, **2017**.
- [47] E. D. Roy, *Ecol. Eng.* **2017**, *98*, 213–227.
- [48] A. Ehmann, I.-M. Bach, S. Laoeamthong, J. Bilbao, I. Lewandowski, *Agriculture* **2017**, *7*, 1.
- [49] A. H. Landrock, *Handbook of Plastic Foams: Types, Properties, Manufacture and Applications*, Noyes Publications, Park Ridge, **1995**.
- [50] a) G. Marosi, B. Szolnoki, K. Bocz, A. Toldy in *Polymer Green Flame Retardants*, Elsevier, Amsterdam, **2014**, pp. 181–220; b) B. Szolnoki, A. Toldy, P. Konrád, G. Szebenyi, G. Marosi, *Period. Polytech. Chem. Eng.* **2013**, *57*, 85–91; c) S. V. Levchik, *J. Fire Sci.* **2006**, *24*, 345–364.
- [51] S.-H. Chiu, C.-L. Wu, H.-T. Lee, J.-H. Gu, M.-C. Suen, *J. Polym. Res.* **2016**, *23*, 205.
- [52] M. Steinmann, M. Wagner, F. R. Wurm, *Chem. Eur. J.* **2016**, *22*, 17329–17338.
- [53] a) F. Çelebi, O. Polat, L. Aras, G. Gündüz, I. M. Akhmedov, *J. Appl. Polym. Sci.* **2004**, *91*, 1314–1321; b) M.-J. Chen, C.-R. Chen, Y. Tan, J.-Q. Huang, X.-L. Wang, L. Chen, Y.-Z. Wang, *Ind. Eng. Chem. Res.* **2014**, *53*, 1160–1171.
- [54] L. Chen, C. Ruan, R. Yang, Y.-Z. Wang, *Polym. Chem.* **2014**, *5*, 3737–3749.
- [55] X.-H. Zhang, F. Liu, S. Chen, G.-R. Qi, *J. Appl. Polym. Sci.* **2007**, *106*, 2391–2397.
- [56] a) C. Klinkowski, L. Zang, M. Döring, *Mater. China* **2013**, *32*, 144–158; b) M. Rakotomalala, S. Wagner, M. Döring, *Materials* **2010**, *3*, 4300.
- [57] J. Artner, M. Ciesielski, O. Walter, M. Döring, R. M. Perez, J. K. W. Sandler, V. Altstädt, B. Scharrel, *Macromol. Mater. Eng.* **2008**, *293*, 503–514.
- [58] M. Ciesielski, A. Schäfer, M. Döring, *Polym. Adv. Technol.* **2008**, *19*, 507–515.
- [59] Q. F. Wang, W. F. Shi, *Polym. Degrad. Stab.* **2006**, *91*, 1289–1294.
- [60] a) P. M. Hergenrother, C. M. Thompson, J. G. Smith, J. W. Connell, J. A. Hinkley, R. E. Lyon, R. Moulton, *Polymer* **2005**, *46*, 5012–5024; b) S. Monge, G. David, B. Z. Tang, A. S. Abdel-Aziz, S. Craig, J. Dong, T. Masuda, C. Weder, *Phosphorus-Based Polymers: From Synthesis to Applications*, Royal Society of Chemistry, London, **2014**; c) R.-J. Jeng, J.-R. Wang, J.-J. Lin, Y.-L. Liu, Y.-S. Chiu, W.-C. Su, *J. Appl. Polym. Sci.* **2001**, *82*, 3526–3538.
- [61] a) U. Braun, B. Scharrel, *Macromol. Mater. Eng.* **2008**, *293*, 206–217; b) B. Perret, B. Scharrel, K. Stoss, M. Ciesielski, J. Diederichs, M. Döring, J. Krämer, V. Altstädt, *Macromol. Mater. Eng.* **2011**, *296*, 14–30.
- [62] U. Braun, A. I. Balabanovich, B. Scharrel, U. Knoll, J. Artner, M. Ciesielski, M. Döring, R. Perez, J. K. W. Sandler, V. Altstädt, T. Hoffmann, D. Pospiech, *Polymer* **2006**, *47*, 8495–8508.
- [63] J. H. Song, *J. Vinyl Addit. Technol.* **1995**, *1*, 46–50.
- [64] C. Vasile, *Handbook of Polyolefins, 2nd ed.*, CRC, Boca Raton, **2000**.
- [65] U. Braun, B. Scharrel, *Macromol. Chem. Phys.* **2004**, *205*, 2185–2196.
- [66] H. Q. Yin, D. D. Yuan, X. F. Cai, *J. Therm. Anal. Calorim.* **2013**, *111*, 499–506.
- [67] Y. Tan, Z.-B. Shao, L.-X. Yu, J.-W. Long, M. Qi, L. Chen, Y.-Z. Wang, *Polym. Chem.* **2016**, *7*, 3003–3012.
- [68] L. J. Duan, H. Y. Yang, L. Song, Y. B. Hou, W. Wang, Z. Gui, Y. Hu, *Polym. Degrad. Stab.* **2016**, *134*, 179–185.
- [69] E. Gallo, U. Braun, B. Scharrel, P. Russo, D. Acierno, *Polym. Degrad. Stab.* **2009**, *94*, 1245–1253.
- [70] E. Gallo, B. Scharrel, D. Acierno, P. Russo, *Eur. Polym. J.* **2011**, *47*, 1390–1401.
- [71] a) A. D. Naik, G. Fontaine, F. Samyn, X. Delva, Y. Bourgeois, S. Bourbigot, *Polym. Degrad. Stab.* **2013**, *98*, 2653–2662; b) A. D. Naik, G. Fontaine, F. Samyn, X. Delva, J. Louisy, S. Bellayer, Y. Bourgeois, S. Bourbigot, *Fire Saf. J.* **2014**, *70*, 46–60; c) A. D. Naik, G. Fontaine, F. Samyn, X. Delva, J. Louisy, S. Bellayer, Y. Bourgeois, S. Bourbigot, *RSC Adv.* **2014**, *4*, 18406–18418; d) P. Müller, B. Scharrel, *J. Appl. Polym. Sci.* **2016**, *133*, 43549; e) P. Müller, M. Morys, A. Sut, C. Jäger, B. Illerhaus, B. Scharrel, *Polym. Degrad. Stab.* **2016**, *130*, 307–319.
- [72] G.-L. Wei, D.-Q. Li, M.-N. Zhuo, Y.-S. Liao, Z.-Y. Xie, T.-L. Guo, J.-J. Li, S.-Y. Zhang, Z.-Q. Liang, *Environ. Pollut.* **2015**, *196*, 29–46.
- [73] L. Chen, Y.-Z. Wang, *Materials* **2010**, *3*, 4746–4760.
- [74] J. Eichhorn, *J. Appl. Polym. Sci.* **1964**, *8*, 2497–2524.
- [75] M. W. Beach, N. G. Rondan, R. D. Froese, B. B. Gerhart, J. G. Green, B. G. Stobby, A. G. Shmakov, V. M. Shvartsberg, O. P. Korobeinichev, *Polym. Degrad. Stab.* **2008**, *93*, 1664–1673.
- [76] J. Wagner, P. Deglmann, S. Fuchs, M. Ciesielski, C. A. Fleckenstein, M. Doring, *Polym. Degrad. Stab.* **2016**, *129*, 63–76.
- [77] K. H. Pawlowski, B. Scharrel, *Polym. Int.* **2007**, *56*, 1404–1414.
- [78] K. Täuber, F. Marsico, F. R. Wurm, B. Scharrel, *Polym. Chem.* **2014**, *5*, 7042–7053.
- [79] a) B. Liang, X. D. Hong, M. Zhu, C. J. Gao, C. S. Wang, N. Tsubaki, *Polym. Bull.* **2015**, *72*, 2967–2978; b) S. Q. Song, J. J. Ma, K. Cao, G. J. Chang, Y. W. Huang, J. X. Yang, *Polym. Degrad. Stab.* **2014**, *99*, 43–52; c) W. C. Zhang, X. M. Li, R. J. Yang, *Polym. Degrad. Stab.* **2011**, *96*, 2167–2173; d) X. Wang, Y. Hu, L. Song, H. Y. Yang, W. Y. Xing, H. D. Lu, *Prog. Org. Coat.* **2011**, *71*, 72–82.
- [80] S. Hörold in *Polymer Green Flame Retardants, 1st ed.* (Eds.: C. Papaspyrides, P. Kiliaris), Elsevier, Amsterdam, Oxford, Waltham, **2014**, pp. 221–254.
- [81] F. Laoutid, L. Bonnaud, M. Alexandre, J. M. Lopez-Cuesta, P. Dubois, *Mater. Sci. Eng. R* **2009**, *63*, 100–125.
- [82] a) A. Toldy, B. Szolnoki, I. Csontos, G. Marosi, *J. Appl. Polym. Sci.* **2014**, *131*, 40105; b) B. Edwards, S. Rudolf, P. Hauser, A. El-Shafei, *Ind. Eng. Chem. Res.* **2015**, *54*, 577–584; c) M. Neisius, S. Liang, H. Mispereuve, S. Gaan, *Ind. Eng. Chem. Res.* **2013**, *52*, 9752–9762; d) X. Zhao, F. R. Guerrero, J. Llorca, D.-Y. Wang, *ACS Sustainable Chem. Eng.* **2016**, *4*, 202–209.
- [83] a) K. Tao, J. Li, L. Xu, X. Zhao, L. Xue, X. Fan, Q. Yan, *Polym. Degrad. Stab.* **2011**, *96*, 1248–1254; b) H. Liu, X. Wang, D. Wu, *Polym. Degrad. Stab.* **2014**, *103*, 96–112.
- [84] K. N. Bauer, H. T. Tee, M. M. Velencoso, F. R. Wurm, *Prog. Polym. Sci.* **2017**, *73*, 61–122.
- [85] S. Gaan, G. Sun, K. Hutches, M. H. Engelhard, *Polym. Degrad. Stab.* **2008**, *93*, 99–108.
- [86] a) B. Li, Z. Zhan, H. Zhang, C. Sun, *J. Vinyl Addit. Technol.* **2014**, *20*, 10–15; b) D. Freitag, P. Go, Y. JEONG, L. Kagumba, Google Patents, WO2013071230A1, **2013**; c) W. Zhao, J. Liu, H. Peng, J. Liao, X. Wang, *Polym. Degrad. Stab.* **2015**, *118*, 120–129.
- [87] L. J. Qian, L. J. Ye, G. Z. Xu, J. Liu, J. Q. Guo, *Polym. Degrad. Stab.* **2011**, *96*, 1118–1124.

- [88] P. Wen, Q. Tai, Y. Hu, R. K. K. Yuen, *Ind. Eng. Chem. Res.* **2016**, *55*, 8018–8024.
- [89] T. Mayer-Gall, D. Knittel, J. S. Gutmann, K. Opwis, *ACS Appl. Mater. Interfaces* **2015**, *7*, 9349–9363.
- [90] a) Y. Bai, X. Wang, D. Wu, *Ind. Eng. Chem. Res.* **2012**, *51*, 15064–15074; b) H. Liu, X. Wang, D. Wu, *Polym. Degrad. Stab.* **2015**, *118*, 45–58.
- [91] S. Rothmund, I. Teasdale, *Chem. Soc. Rev.* **2016**, *45*, 5200–5215.
- [92] a) W. Xing, W. Yang, W. Yang, Q. Hu, J. Si, H. Lu, B. Yang, L. Song, Y. Hu, R. K. K. Yuen, *ACS Appl. Mater. Interfaces* **2016**, *8*, 26266–26274; b) J. Sun, X. Gu, S. Zhang, M. Coquelle, S. Bourbigot, S. Duquesne, M. Casetta, *Polym. Adv. Technol.* **2014**, *25*, 1099–1107; c) S. Qiu, X. Wang, B. Yu, X. Feng, X. Mu, R. K. K. Yuen, Y. Hu, *J. Hazard. Mater.* **2017**, *325*, 327–339.
- [93] B. Yu, Y. Shi, B. Yuan, S. Qiu, W. Xing, W. Hu, L. Song, S. Lo, Y. Hu, *J. Mater. Chem.* **2015**, *3*, 8034–8044.
- [94] a) M. Raimondo, S. Russo, L. Guadagno, P. Longo, S. Chirico, A. Mariconda, L. Bonnaud, O. Murariu, P. Dubois, *RSC Adv.* **2015**, *5*, 10974–10986; b) A. Lorenzetti, S. Besco, D. Hrelja, M. Roso, E. Gallo, B. Schartel, M. Modesti, *Polym. Degrad. Stab.* **2013**, *98*, 2366–2374.
- [95] D. C. O. Marney, W. Yang, L. J. Russell, S. Z. Shen, T. Nguyen, Q. Yuan, R. Varley, S. Li, *Polym. Adv. Technol.* **2012**, *23*, 1564–1571.
- [96] E. Gallo, B. Schartel, U. Braun, P. Russo, D. Acierno, *Polym. Adv. Technol.* **2011**, *22*, 2382–2391.
- [97] a) J. Jiang, Y. Cheng, Y. Liu, Q. Wang, Y. He, B. Wang, *J. Mater. Chem.* **2015**, *3*, 4284–4290; b) S. Pappalardo, P. Russo, D. Acierno, S. Rabe, B. Schartel, *Eur. Polym. J.* **2016**, *76*, 196–207.
- [98] Q. Dong, M. Liu, Y. Ding, F. Wang, C. Gao, P. Liu, B. Wen, S. Zhang, M. Yang, *Polym. Adv. Technol.* **2013**, *24*, 732–739.
- [99] X. Qian, L. Song, B. Yu, B. Wang, B. Yuan, Y. Shi, Y. Hu, R. K. K. Yuen, *J. Mater. Chem.* **2013**, *1*, 6822–6830.
- [100] G. Xu, J. Cheng, H. Wu, Z. Lin, Y. Zhang, H. Wang, *Polym. Compos.* **2013**, *34*, 109–121.
- [101] R. Ménard, C. Negrell, M. Fache, L. Ferry, R. Sonnier, G. David, *RSC Adv.* **2015**, *5*, 70856–70867.
- [102] P. Jia, L. Hu, M. Zhang, G. Feng, Y. Zhou, *Eur. Polym. J.* **2017**, *87*, 209–220.
- [103] a) M. Sacristán, J. C. Ronda, M. Galià, V. Cádiz, *J. Appl. Polym. Sci.* **2011**, *122*, 1649–1658; b) M. Moreno, G. Lligadas, J. C. Ronda, M. Galià, V. Cádiz, *J. Polym. Sci. Part A* **2012**, *50*, 3206–3213.
- [104] B. A. Howell, Y. G. Daniel, *J. Therm. Anal. Calorim.* **2015**, *121*, 411–419.
- [105] B. A. Howell, K. E. Carter, *J. Therm. Anal. Calorim.* **2010**, *102*, 493–498.
- [106] H. Pan, W. Wang, Y. Pan, L. Song, Y. Hu, K. M. Liew, *Carbohydr. Polym.* **2015**, *115*, 516–524.
- [107] F. Carosio, G. Fontaine, J. Alongi, S. Bourbigot, *ACS Appl. Mater. Interfaces* **2015**, *7*, 12158–12167.
- [108] Y. Xiao, Y. Zheng, X. Wang, Z. Chen, Z. Xu, *J. Appl. Polym. Sci.* **2014**, *131*, 40845.
- [109] L. Liu, M. Qian, P. A. Song, G. Huang, Y. Yu, S. Fu, *ACS Sustainable Chem. Eng.* **2016**, *4*, 2422–2431.
- [110] L. Costes, F. Laoutid, M. Aguedo, A. Richel, S. Brohez, C. Delvosalle, P. Dubois, *Eur. Polym. J.* **2016**, *84*, 652–667.
- [111] a) C. Bao, Y. Guo, B. Yuan, Y. Hu, L. Song, *J. Mater. Chem.* **2012**, *22*, 23057–23063; b) S. Wang, F. Xin, Y. Chen, L. Qian, Y. Chen, *Polym. Degrad. Stab.* **2016**, *129*, 133–141.
- [112] H. Moustafa, C. Guizani, A. Dufresne, *J. Appl. Polym. Sci.* **2017**, *134*, 44498.
- [113] S. Wang, S. Ma, C. Xu, Y. Liu, J. Dai, Z. Wang, X. Liu, J. Chen, X. Shen, J. Wei, J. Zhu, *Macromolecules* **2017**, *50*, 1892–1901.
- [114] G. Laufer, C. Kirkland, A. B. Morgan, J. C. Grunlan, *Biomacromolecules* **2012**, *13*, 2843–2848.
- [115] Z. Zheng, S. Liu, B. Wang, T. Yang, X. Cui, H. Wang, *Polym. Compos.* **2015**, *36*, 1606–1619.
- [116] J. Alongi, F. Carosio, G. Malucelli, *Polym. Degrad. Stab.* **2014**, *106*, 138–149.
- [117] J. Alongi, A. Di Blasio, J. Milnes, G. Malucelli, S. Bourbigot, B. Kandola, G. Camino, *Polym. Degrad. Stab.* **2015**, *113*, 110–118.
- [118] J. Alongi, F. Cuttica, F. Carosio, *ACS Sustainable Chem. Eng.* **2016**, *4*, 3544–3551.

Manuscript received: November 15, 2017

Revised manuscript received: January 8, 2019

Accepted manuscript online: January 9, 2018

Version of record online: June 29, 2018