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## MINIREVIEW

# Molecular Firefighting – How Modern Phosphorus Chemistry Can Help Solve the Flame Retardancy Task

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**Abstract:** The ubiquity of polymeric materials in daily life comes at an increased fire risk, and enduring research into efficient flame retardants is the 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 halogenated variants 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 flame retarding polymeric materials. Phosphorus flame retardants can act in both the gas and condensed phase during a fire. This review investigates how current phosphorus chemistry helps in reducing flammability of polymers, and addresses the future of sustainable, efficient and safe phosphorus-based flame retardant chemistry from renewable sources.

## 1. The Flame Retardancy Task - Demands for 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. The enduring research of 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.

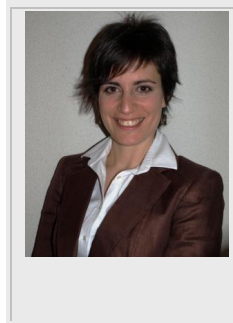
Halogenated flame retardants, widely applied in the past, have come under increased scrutiny, prompting increased research into halogen-free and especially phosphorus-based flame retardants (P-FRs).<sup>[1]</sup> This development is further attributed to legislation and decisive shifts in market demands, as increased attention has been brought to producing more sustainable FRs.

Now, P-FRs have become a prominent alternative to halogenated counterparts.<sup>[2]</sup> Phosphorus plays the key role in halogen-free flame retardancy due to 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 task? To more closely understand the task at hand, it's 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) FR properties must match polymer processing and pyrolysis specifics.
- 3) Following health regulations and market direction, formulations must become increasingly environmentally friendly, recyclable and sustainable.

In the following, these aspects are explored in detail. Then, state-of-the-art P-FRs and their modes of action are discussed, showing how these features are embraced. Finally, the authors highlight modern trends of P-FRs and their potential future application. To that end, representative examples for each section were chosen, however this minireview is not a comprehensive summary. For further reading, the authors recommend the reviews of Weil,<sup>[3]</sup> Malucelli,<sup>[4]</sup> and Bourbigot.<sup>[5]</sup>

**Dr. Maria M. Velencoso** got her M.Sc. in Chemical Engineering from the University of Castilla-La Mancha (Spain) in 2008. She earned her Ph.D. in 2014 from the same university for her work on synthesis and application of phosphorylated polyol as reactive flame retardant. For her research, she maintained a long-term collaboration with HUNTSMAN. Currently, she has joined a Marie Skłodowska-Curie Postdoctoral fellowship 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.



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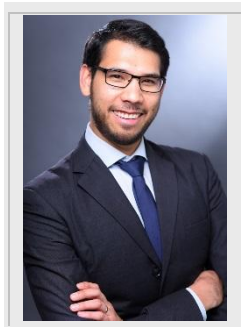
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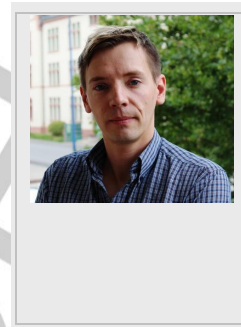
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**Alexander Battig** studied Chemistry (BSc) and Polymer Science (MSc) at the Free University Berlin, Germany. After establishing and running an own company, he joined the group of Bernhard Schartel at the Bundesanstalt für Materialforschung und -prüfung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



**Frederik R. Wurm** (Priv.-Doz. Dr. habil.) is currently heading the research group "Functional Polymers" at the Max Planck Institute for Polymer Research (MPIP), Mainz (D). In his interdisciplinary research, the group designs materials with molecular-defined functions for developing degradable polymers, nanocarriers with controlled blood interactions, adhesives, and phosphorus flame-retardants and published more than 130 research articles to date. He received his PhD in 2009 (JGU Mainz, D). After a two year stay at EPFL (CH) as a Humboldt fellow, he joined the department "Physical Chemistry of Polymers" at MPIP and finished his habilitation in Macromolecular Chemistry in 2016.



**Jens C. Markwart** studied Chemistry (MSc) at the Johannes Gutenberg-University of Mainz, Germany, where he received his master 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 PhD at the Max Planck Institute for Polymer Research, Mainz, Germany. His research focus is based 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).



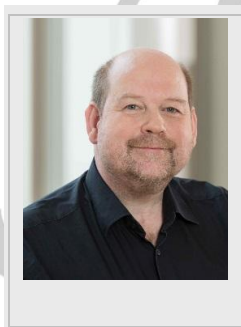
### 1.1. Retaining Material Properties: A Question of Price?

The polymer's chemical composition determines material properties, production means, application areas and bulk price, consequently (Figure 1). Thermoplastic polyolefins (e.g. polyethylene, 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, affecting material properties (e.g. coloration, opacity, tensile strength).<sup>[6]</sup> Commercially available P-FRs (e.g. ammonium polyphosphate, APP) require significantly lower loadings for similar effectivity, thereby retaining respective material properties.<sup>[7]</sup> Moreover, adjuvants and synergists (e.g. metal oxides, charring agents, nanofillers, additional P-FRs) increase efficacy and further lower required loadings.<sup>[8]</sup>

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

High-performance polymers (e.g. epoxy/ polyester resins, polyetherimides, polysulfones, polyaryletherketones) are used in specialized fields (e.g. adhesives, coatings, composites) due to their chemical resistance, temperature stability and high durability.<sup>[11]</sup> Here, performance outweighs production costs of materials and 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.<sup>[12]</sup> Notable formulations include 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO)-derivates and variations of P-species with synergistic moieties: nitrogen, silicon, sulfur and boron.<sup>[13]</sup>

**Bernhard Schartel** (Priv.-Doz. Dr. habil.) is head of the Technical Properties of Polymeric Materials division at the Bundesanstalt für Materialforschung und -prüfung (BAM). A polymer scientist with a broad background in different polymeric topics, materials, analysis and methods, he has been quite active in the area Flame Retardancy of Polymers for over 15 years, publishing more than 150 papers, serving on committees and the editorial boards of *Fire Mater.*, *J. Fire Sci.*, *Polym. Test.*, and *Fire Technol.* as well as editing *Polymer Degradation and Stability* for the topics Fire Retardants and Nanocomposites since 2012. His main interest is the understanding of the fire behavior and flame-retardancy mechanisms as a basis for future development.



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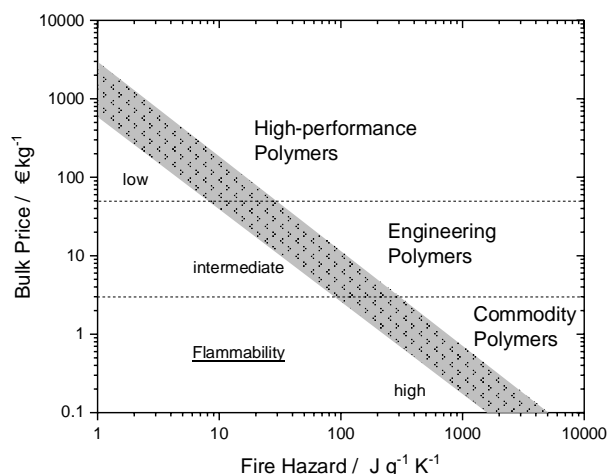


Figure 1. Fire hazard versus bulk price of various polymeric material classes.<sup>[14]</sup>

## 1.2. Production Specifics: Finding a Match

The FR's mode of action is key in tailoring suitable formulations for polymer materials. Effective flame retardancy depends strongly on the interaction between FR and polymer matrix and 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.<sup>[15]</sup> In the condensed phase, many P-FRs mediate the formation of char by inducing cyclization, cross-linking and aromatization/ graphitization *via* dehydration of the polymeric structure, and the formation of carbonaceous char reduces the release of volatiles, i.e. fuel.<sup>[16]</sup> Some P-FRs additionally act *via* intumescence: a multicellular residue acts as a protective layer, slowing down heat transfer to the underlying material.<sup>[17]</sup> Many FRs alter 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, e.g. *via* radical generators (non-flaming dripping UL-94 classification).<sup>[18]</sup> 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.<sup>[19]</sup> Gas phase modes of action, usually acting in parallel to condensed phase mechanisms, crucially increase FR effects: releasing non-combustible gases during decomposition reduces combustion efficiency (fuel dilution).<sup>[20]</sup> During the combustion of hydrocarbon fuels, H· and OH· radicals are formed, propagating the fuel combustion cycle most notably by the strong exothermic reaction  $\text{OH}\cdot + \text{CO} \rightarrow \text{H}\cdot + \text{CO}_2$ .<sup>[21]</sup> Many P-FRs decompose to form P-radicals which react with OH· and lower their concentration (flame poisoning).<sup>[22]</sup>

These mechanisms crucially depend on the decomposition temperatures of both matrix and 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 polymer and FR decomposition temperatures should be maximized.<sup>[23]</sup> 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.<sup>[24]</sup> For foams, FRs with good foamability are important to maintain mechanical properties, and fiber and textile FRs must undergo spinning, weaving and washing without loss of material or FR properties.<sup>[25]</sup>

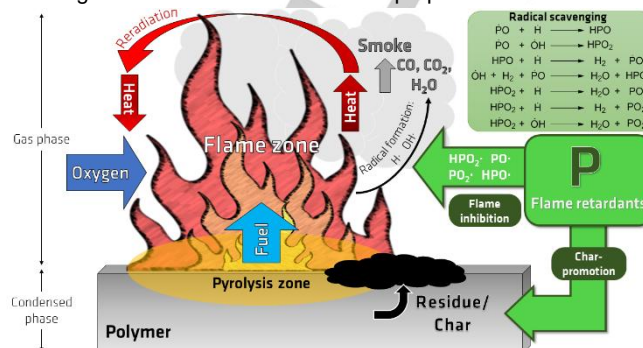


Figure 2. Schematic flaming combustion of polymeric material and the role of phosphorus-based flame retardants.<sup>[26]</sup>

Today, no single FR can be used for the wide range of polymers; a FR may work well for one matrix but not for another, as the structure-property relationship is specific to the polymer matrix.<sup>[26]</sup> This makes research for novel FRs with improved mechanism essential for all fields in polymer applications.

## 1.3. Sustainability: A Regulatory and Market Goal

Health, environment, and sustainability considerations play increasingly important roles in the development of novel FRs. Increased awareness has been paid to the "PBT" (i.e. persistence, bioaccumulation, toxicity) of FRs.<sup>[27]</sup> Studies on human exposure pathways and ecosystems have highlighted risks of some FRs, emphasizing the need for increased oversight and regulation.<sup>[28]</sup>

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), acting 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.<sup>[29]</sup> Notably, the use of penta-, octo- and decabromodiphenyl ethers was restricted under the Stockholm Convention on Persistent Organic Pollutants due to health risks, highlighting the need for halogen-free alternatives.<sup>[30]</sup>

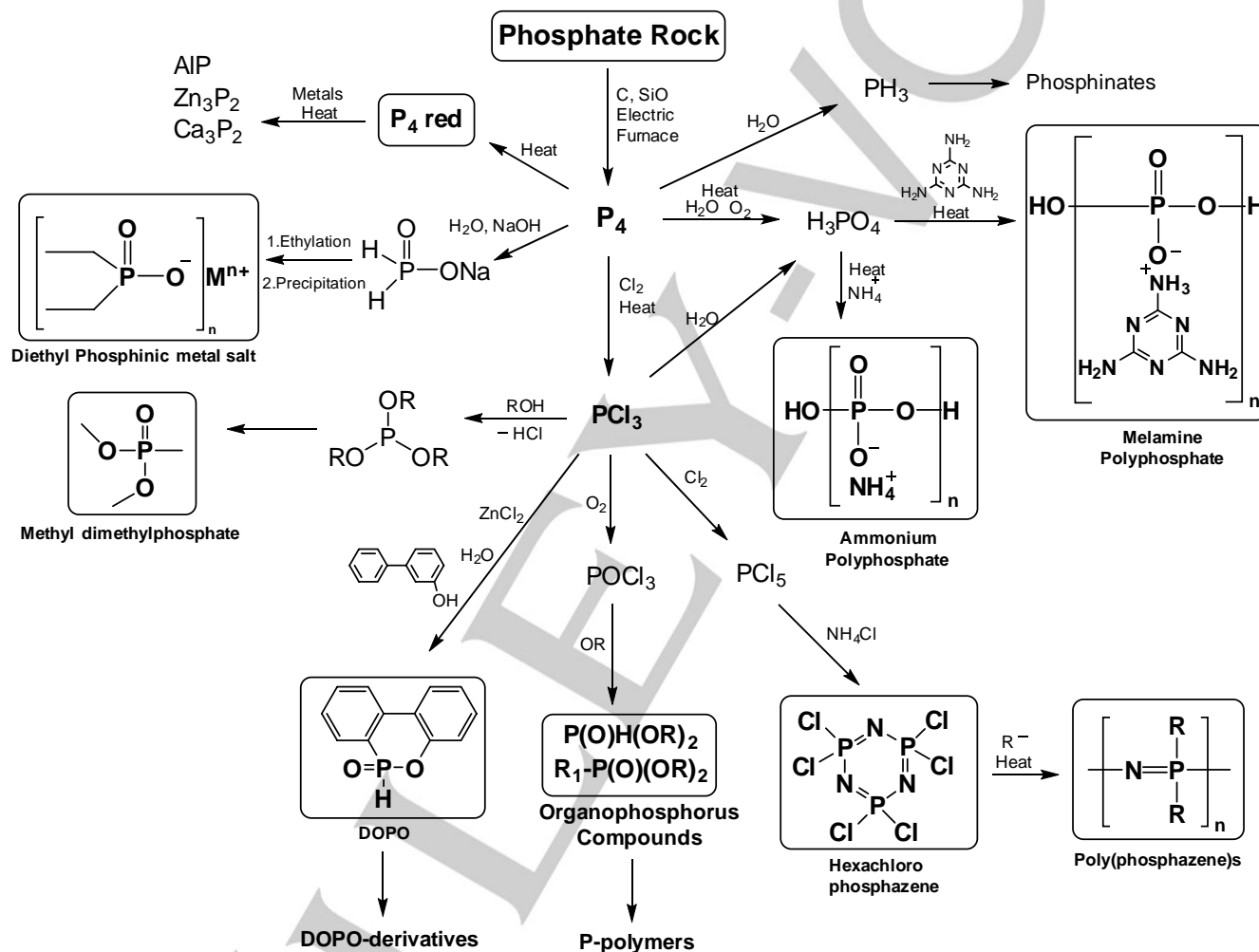
The voluntary ecolabels ISO introduced help prevent PBT-material circulation and raise awareness of sustainable, environmentally-aware production.<sup>[31]</sup> The "EU Ecolabel" serves to reduce the environmental impact and health risk of goods, services and the life cycle of products much like preexisting labels in Germany and the Nordic countries.<sup>[32]</sup> The Swedish TCO Certification specifically credits sustainability of IT products, a key industry for non-halogenated FRs. In suit, tech companies like HP and chemical companies like ICL-IP have implemented methods (GreenScreen®, SAFR®) to assess the chemical safety of their products.<sup>[33]</sup>

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

Three key aspects – cost-effective conservation of material properties; matching 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 play a pivotal role in future products: their chemical versatility makes them ideally suited, as will be showcased more closely in the following.



**Scheme 1.** Examples of industrial pathways of various P-based FRs from “phosphate rock”. (M is usually Zinc or Aluminum.)

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**Table 1.** Commercial P-FR alternatives to decabromodiphenyl ethers (d-PBDE) according to the United States (US) Environmental Protection Agency (released in January 2014).<sup>[36]</sup>

Commercial P-FR alternatives to deca-PBDE	Properties	Polymer applications	Mode of Action
Triphenyl phosphate; TPP	CAS: 115-86-6 M <sub>w</sub> : 326.29	PPE-HIPS PC-ABS	Chemical action in condensed phase + Char former
Bisphenol A bis(diphenyl phosphate); BAPP	CAS: 181028-79-5 M <sub>w</sub> : 693 (n=1); >1,000 (n=2)	PPE-HIPS PC PC-ABS	Chemical action in condensed phase + Char former
Resorcinol bis(diphenyl phosphate); RDP	CAS: 125997-21-9 M <sub>w</sub> : 574.46 (n=1; CASRN 57583-54-7); M <sub>w</sub> : 822.64 (n=2; CASRN 98165-92-5)	PPE-HIPS PC-ABS	Chemical action in condensed phase + Char former
Phosphonate Oligomer	CAS: 68664-06-2 M <sub>w</sub> : 1,000-5,000; 25 % M <sub>w</sub> <1,000	Thermosets	Chemical action in condensed phase + Char former
Polyphosphonate	CAS: 68664-06-2 M <sub>w</sub> : 10,000 to 50,000; <1 % M <sub>w</sub> <1,000	Elastomers Engineering Thermoplastic	Chemical action in condensed phase + Char former
Phosphoric acid, mixed esters with [1,1'-bisphenyl-4,4'-diol] and phenol; BPBP	CAS: 1003300-73-9 M <sub>w</sub> : 650.6 (n=1); 974.8 (n=2); >1000 (n≥3)	PPE-HIPS PC-ABS PC	Chemical action in condensed phase + Char former
Poly[phosphonate-co-carbonate]	CAS: 77226-90-5 M <sub>w</sub> : >1,000; <1 % <1,000	Elastomers Engineering Thermoplastic	Chemical action in condensed phase + Char former

## 2. Phosphate Rock – a Finite Natural Resource

Phosphorus chemistry is one of the oldest areas of chemistry, which is in the continuous development of new methods to improve the safety and sustainability of the chemical processes. P-FRs are versatile: i) the structure of P-FRs can vary from inorganic to organic; ii) the P content in these molecules can vary (e.g. from almost 100% for red P to 14.33 % for DOPO); iii) the P atom can have different oxidation states, from 0 to +5, resulting in different FR mechanisms (both gas and condensed phase). This architectural variation makes P unique for the design of FRs with tailored property profiles, such as density or glass transition temperatures ( $T_g$ s) 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. By an electro-thermal process, phosphate is

reduced to elemental phosphorus ( $P_4$ ),<sup>[37]</sup> which serves as a precursor to the production of the main intermediate compounds in industry such as red phosphorus, phosphoric acid ( $H_3PO_4$ ), phosphorus trichloride ( $PCl_3$ ), phosphorus pentachloride ( $PCl_5$ ), phosphine ( $PH_3$ ), or hypophosphite ( $H_2PO_2^-$ ). The exploitation of all these pathways for the synthesis of many FRs such as ammonium polyphosphate,<sup>[38]</sup> melamine polyphosphate,<sup>[39]</sup> phosphazenes,<sup>[40]</sup> diethyl phosphonic metal salts or DOPO<sup>[13b]</sup> validates the versatility of the phosphorus compounds used in FRs applications.

Although a large fraction of the production of  $P_4$  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), or bisphenol A bis(diphenyl phosphate) (BAPP), as well as for the production of oligomeric or polymeric FRs (Table 1). The common pathways for the synthesis of phosphorus-containing polymeric FRs is classical polycondensation (polytransesterification or *via* phosphoric acid chlorides)<sup>[41]</sup>, but also more modern strategies like olefin

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metathesis polycondensation<sup>[42]</sup> or ring-opening polymerization<sup>[43]</sup> (e.g. of cyclic phosphazene derivatives or cyclic phosphoric acid esters) were studied more recently.

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

Currently, there is no alternative for the replacement of this element; the phosphorus life cycle needs to be considered mainly for agriculture, 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.<sup>[46]</sup> 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 as global tasks. Possible technologies for phosphorus recovery include a wide range of strategies, such as phytoextraction (optimum annual P removal of Indian mustard seed equal to 114 kg P ha<sup>-1</sup>), biochar (near 10 g P kg<sup>-1</sup> biochar), or extraction from human urine and feces (recovery of over 80% of total P from urine with approximately 0.5 and 1.3 g capita<sup>-1</sup> d<sup>-1</sup>).<sup>[47]</sup> In addition, it is estimated that the extraction of P from manure in EU-27 may be near to 1.8 million t a<sup>-1</sup>, which would satisfy the annual demand of P required for EU-fertilizers<sup>[48]</sup>.

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 (compare Section 5 and Figure 3) and P-FRs can be a part of a sustainable phosphorus chemistry.

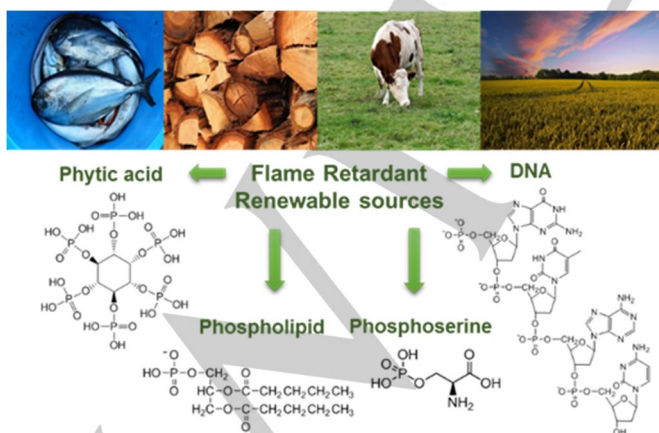


Figure 3. Renewable sources of P-FRs.

### 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 a part of the material's constitution, 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.) allowing the incorporation into the polymer matrix during curing.<sup>[1b, 49]</sup> 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 ( $T_g$ s) and are prone to leaching (see below). The decreased leaching of reactive FRs also reduces 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 with a significant reformulation for the curing process. This presents a disadvantage of reactive FRs, i.e. each matrix needs a newly designed and formulated FR, while additives may be used for several polymer matrices.<sup>[50]</sup>

#### 3.1. Polyurethanes (PUs)

Due to the broad use of polyurethanes (PUs) in foams, coatings, etc. and their inherent flammability, FRs are necessary. However, not only the FR properties are important, but also their impact on the environment and physical properties. Biodegradable PUs are commonly synthesized by utilizing hydrolysable soft segments.<sup>[51]</sup> Using P-FRs could achieve both, since these materials demonstrate good FR properties, can be biocompatible and degradable.<sup>[52]</sup> Chiu et al.<sup>[51]</sup> synthesized PUs that achieve V-0 rating in the UL-94 test (classification for flammability of plastics) and presented efficient FR properties with limited oxygen indices (LOI, minimum oxygen concentration required to sustain combustion) higher than 27.7%. They 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 polycaprolactone diol (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% regarding MDI) in the PUs, the decomposition temperatures and the  $T_g$ s were reduced by several degrees.<sup>[51]</sup>

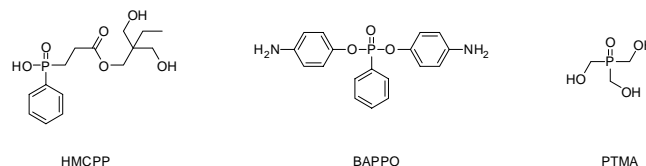


Figure 4. Examples for reactive P-FRs (HMCPP (5-hydroxy-3-(2-hydroxyethyl)-3-methylpentyl-3-[2-carboxyethylphenylphosphine]propanoate) – used in PU; BAPPO (bis(4-aminophenyl)-phenyl phosphine oxide) used in PU, PTMA (phosphoryltrimethanol) used in PU).<sup>[51, 53]</sup>

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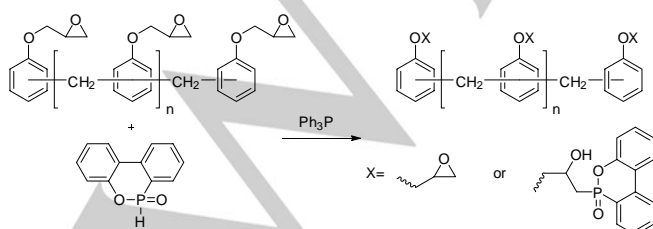
As a waterborne example, Çelebi et al.<sup>[53a]</sup> followed a similar approach to synthesis aqueous dispersions of FR PUs, but instead of incorporating the P-FR as a soft segment, they incorporated it in the chain-extension step. Waterborne PUs reduce the use of organic solvents and are therefore attractive from an environmental perspective. For the flame-retarded PU, bis(4-aminophenyl)-phenyl phosphine oxide (BAPPO, Figure 4) was used, and ethylene diamine for the non-flame retarded PU. As co-monomer, poly(propylene-co-ethylene) polyol was used. The physical properties of both PUs are almost identical, except the gloss properties. This was explained by the difference in chain conformation of both PUs. Furthermore, BAPPO increased the hard-segment crystallinity, due to its aromatic groups and longer chain length, which contribute to the higher packing capability of the hard segments.<sup>[53a]</sup>

The majority of reactive FRs rely on halogens or phosphorus. Due to toxicity and environmental concerns, halogenated FRs are substituted nowadays. It was reported that mainly P-containing polyols are the most appropriate reactive FR for rigid PU foams, but they are rarely used in flexible PU foams (FPUF).<sup>[54]</sup> Chen et al.<sup>[53b]</sup> 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 due to the cross-linking nature of PTMA, further influencing the mechanical properties. The FPUF containing 3.2 wt.-% PTMA showed an increase in tensile strength and elongation at break compared to the neat FPUF, due to change in the foam structure.<sup>[53b]</sup>

### 3.2. Epoxy Resins

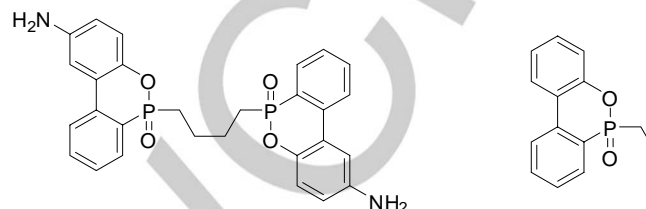
Copolymerization of FRs is not limited to PUs; also epoxy resins, often used for their thermo-mechanical properties and processability, exhibit high flammability and therefore require FRs. The FRs can be introduced to the epoxy- or nitrogen-containing compound.

Zhang et al.<sup>[55]</sup> proved that it is possible to achieve high  $T_g$ s, high thermal stability and UL-94 V-0/V-1 rating by 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 due to its high thermal stability, high reactivity on the P-H bond and flame-retarding efficiency.<sup>[56]</sup>



**Scheme 2.** FR-functionalized novolac resin for further use in epoxy resins.<sup>[55]</sup>

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.<sup>[57]</sup>, 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 a similar structure, but was an additive FR. They revealed that the reactive FR has the potential to be superior over the additive FR.



**Figure 5.** DOPO based hardener (left), non-reactive analog (right).<sup>[57]</sup>

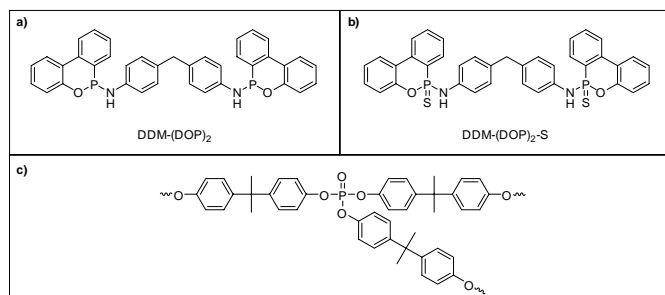
By attaching the amine groups directly to DOPO, the solubility of the hardener was increased in contrast to previous works. In comparison to the reference epoxy material, namely diglycidyl ether of bisphenol A with 4,4'-diaminodiphenylsulfon, the resin with the DOPO-based diamine hardener presented comparable thermal- and fracture-mechanical properties. In contrast to the reactive FR, the non-reactive additive showed a decrease of  $T_g$  by ca. 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 the application in composite materials due to the reduction in processing time.<sup>[57]</sup>

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)<sub>2</sub> and DDM-(DOP)<sub>2</sub>-S) (Figure 6 a and b), their epoxy resins achieved V-0 rating at 1% P in the resin without significantly lowering the  $T_g$ . It was reported that phosphoramides can ring-open epoxides,<sup>[58]</sup> 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  $T_g$ , which may be attributed to the flexibility of the P-O bond. However, Wang et al.<sup>[59]</sup> reported that reactive hyperbranched (*hb*) poly(phosphoester)s (PPEs) (Figure 6 c) - due to their branched structure - reduce the  $T_g$  to a lower extent. This was attributed to the higher cross-linking density of the *hb*PPE that was more noticeable than the P-O flexibility. The *hb*PPE was synthesized in an A<sub>2</sub> + B<sub>3</sub> approach *via* polycondensation of bisphenol-A and phosphoryl chloride. This *hb*PPE was used to cure a bisphenol-A-based epoxy resin *via* PPh<sub>3</sub> catalysis, which proved to have a higher  $T_g$  compared to the one cured with only bisphenol-A.<sup>[59]</sup>



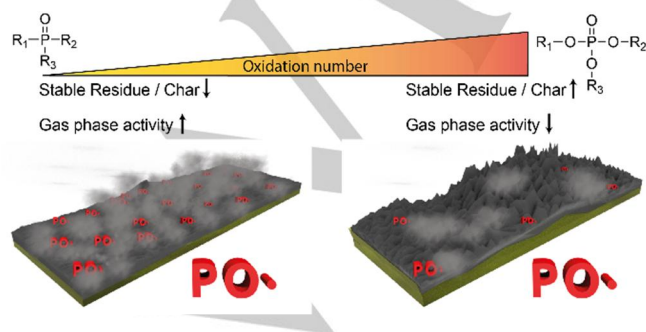
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**Figure 6.** a) and b) DOPO based derivatives FR achieved V-0 rating at 1 % P in the epoxy resin; c) *hbPPE* FR for epoxy resins with lower impact on  $T_g$ .<sup>[58-59]</sup>

### 3.3. Phosphorus oxidation state

The reduction of the  $T_g$  from the flexible P-O bonds was also reported by Jeng et al. In addition, they stated that the introduction of sterically demanding groups like P-O-Ph-O-P can reduce the cross-linking density, resulting in a further lowering of the  $T_g$ . In contrast, when they used a FR with a more rigid P-Ph group, the  $T_g$  was reduced to a lower extent. However, by exchanging a P-O bond with a P-C bond, the FR mechanism was influenced also. 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.<sup>[60]</sup> The higher gas phase activity for phosphine oxides was also reported by Braun et al. who investigated the impact of the P oxidation state on its FR behavior in epoxy resin composites. They reported, in alignment with previous reports<sup>[60b]</sup>, that the stable residue increased and the release of volatiles containing phosphorus decreased with increasing oxidation state of P (Figure 7). However, in previous reports it was concluded that phosphates are the more efficient FRs, due to their high efficiency as char promoter, compared to phosphine oxides.<sup>[60b]</sup> This conclusion differs from Braun et al., who ranked phosphine oxide as the best FR and phosphate as the worst FR, by observing an increase in charring and decreasing flame inhibition for the phosphates, which was significantly accountable to 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.<sup>[12d, 61]</sup> They showed that the key role of oxidation state was in the interaction during pyrolysis. The authors explained the greater role of the gas phase activity for composite materials with the high content of carbon fiber, decreasing the relative charring impact.<sup>[60b, 62]</sup>



**Figure 7.** The char residue increases and the gas phase activity decreases with increasing oxidation state.

## 4. Recent Developments in Additive Phosphorus Compounds

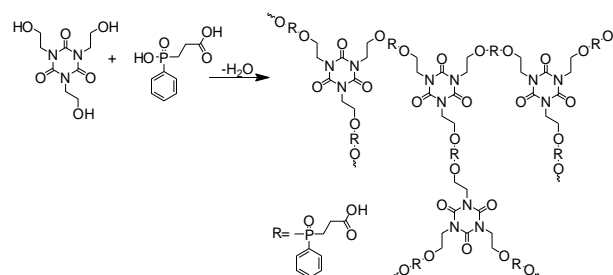
A majority of FRs are added as additives during polymer processing steps instead of implemented into the polymer backbone.

The major advantage of additive FRs is their cost-effectivity (i.e. performance value of the material) and ease of application in various matrices, making them widely used in industry.<sup>[2b, 63]</sup> Despite these obvious advantages, additive FRs also exhibit several drawbacks, most notably the impact on physical properties like  $T_g$  or mechanical stability. Leaching of the FR 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.<sup>[64]</sup> The biggest challenge for additive FRs is therefore to find the optimal balance between FR and mechanical properties.<sup>[50a, 50b]</sup>

### 4.1. Inorganic Phosphorus Flame Retardants

The “classic” example of inorganic P-FRs is red phosphorus, yet in practice it is only used as an encapsulated substance to process FR thermoplasts, e.g. glass-fiber (GF) reinforced PA 6,6, or in all manner of multicomponent FR systems.<sup>[9a, 65]</sup> 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.-% were 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 e.g. in P + inorganic filler, or P-P mixtures combined with intumescent ammonium polyphosphate (APP) - based systems.<sup>[10b, 66]</sup>

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



**Scheme 3.** Synthesis of the *hb* phosphorus/ nitrogen containing FR polymer.<sup>[68]</sup>

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

Braun et al. showed that the reactivity of the P-additive with the polymer matrix (here: GF-reinforced PA 6,6) has great influence on its interaction with other additives and the main activity in the condensed or gas phase. The work illustrated that melamine polyphosphate's (MPP) main mechanism is fuel-dilution and the creation of a P-based protective layer. Aluminum phosphinate (AlPi), another currently widely applied FR, on the other hand, acts mainly in the gas phase. The combination of both additives changes the dominant FR mechanism by the formation of a strong protective layer consisting of aluminum phosphate. By adding zinc borate, a boron-aluminum phosphate layer formed, which showed a better protective layer performance in comparison to that of aluminum phosphate, resulting in the best cone calorimeter (most significant instrument in fire testing, measuring heat release rate by the amount of oxygen consumed during combustion) performance of the samples, showing hardly any ignition.<sup>[10a, 69]</sup>

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 modification of AlPi (e.g. encapsulation, particle size, etc.).<sup>[13a]</sup>

Gallo et al. investigated the synergism between AlPi and nanometric iron oxide or antimony oxide, and a different FR behavior between the two was detected: in a redox cycle,  $\text{Fe}_2\text{O}_3$ , oxidized P to inorganic phosphates and was reduced to magnetite, increasing the amount of P in the condensed phase. However, for  $\text{Sb}_2\text{O}_3$ , a non-reducible oxide, a catalytic effect on the cross-linking was postulated as no hint of the same mechanism was detected. They proposed that the surfaces of the metal oxides stabilize the oxygen-containing intermediate structures and therefore promote cross-linking reactions between polymer chains and interaction with P-based intermediates.<sup>[70]</sup>

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 ca. 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 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, due to intumescence, a protective layer was formed. In addition, synergistic combinations with other flame retardants were also studied: here, melamine poly(zinc phosphate) with

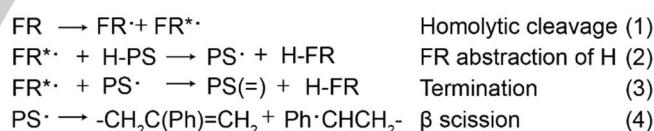
melamine polyphosphate showed the overall best FR results due to strong intumescence, resulting in a low heat release rate (HRR) and the lowest PHRR, maximum average rate of heat emission and fire growth rate index values.<sup>[71]</sup>

## 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.<sup>[72]</sup> Beside their use as FRs, they work as plasticizers or anti-foaming agents and are used in plastics, furniture, textiles, electronics, construction, vehicles, and the petroleum industry. In the following, some examples for these compounds, selected due to 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. Especially aromatic polyphosphonates exhibit higher thermal stability compared to 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, resulting in lower degradation temperatures.<sup>[73]</sup>

The influence of the chemical structure of the FR on its mechanism has been intensely 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, the phenomenon of radical generation together with flame inhibition was first investigated by Eichhorn in 1964.<sup>[74]</sup> The condensed phase mechanism is as follows: a hydrogen is abstracted from the polystyrene backbone by the flame retardant, followed by  $\beta$ -scission of the polystyrene radical (Scheme 4).



**Scheme 4.** Mechanism for enhanced polystyrene degradation.<sup>[75]</sup>

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) resulted in a performance comparable with that of hexabromocyclododecane (HBCD). Loosening 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.<sup>[75]</sup> More recently, Wagner et al. investigated OPFRs with synergists

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containing disulfide bridges, further identifying the role of radical generators in the enhanced degradation of polystyrene.<sup>[76]</sup>

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.<sup>[73]</sup>

The importance of FR molecular weight was reported 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 PC, while TPP volatilized before the decomposition of PC/ABS due to its low molecular weight, thus avoiding chemical interaction.<sup>[23c, 77]</sup>

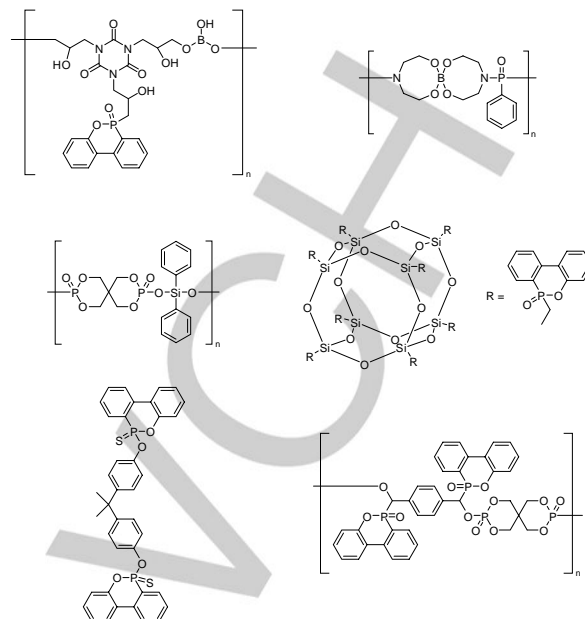
Phase separation of polymer blends must always be investigated with respect to the desired material properties. In this context, *hb* polymeric FRs are promising materials. Their key properties include many reactive end groups, a relative low intrinsic viscosity compared to linear polymers, and in most cases a high miscibility and solubility with other polymeric materials. In addition, their straightforward synthesis *via* "hyperbranching", i.e. 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 like mechanical properties and  $T_g$ .<sup>[78]</sup>

Phosphorus combines chemical versatility and FR effectivity, allowing for an enormous variety in FR formulations. These examples have shown that P shows different modes of action in FR formulations based on many varying 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

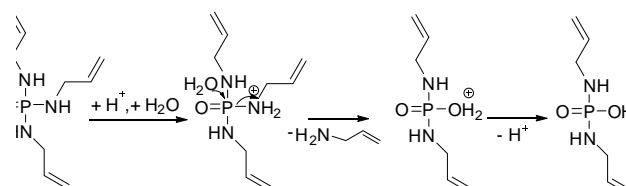
Flame retardant structures containing hetero-atoms like nitrogen, silicon, sulfur and boron in combination with phosphorus provide a huge range of specific interactions, compared to the decomposition of the phosphorus structures or the decomposition of these with pure hydrocarbons<sup>[26]</sup>, reducing the overall load of FRs in a material and maximize effectivity (Figure 8).<sup>[13d, 58, 79]</sup>



**Figure 8.** Various FR formulations implementing synergistic moieties. Top row: boron-containing formulations; middle row: silicone-containing formulations; bottom left: P-S-containing formulation; bottom right: formulation containing two types of P.<sup>[13a, 80]</sup>

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

The main advantages of phosphoramidates over their analogous phosphates are their higher thermal stability,<sup>[84]</sup> lower volatility,<sup>[85]</sup> and higher viscosity due to hydrogen bonding.<sup>[82c]</sup> 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, affording higher char yields. Neisius et al. suggested the hydrolysis of P-N bonds under acidic conditions to form non-volatile compounds (Scheme 5)<sup>[82c]</sup>.

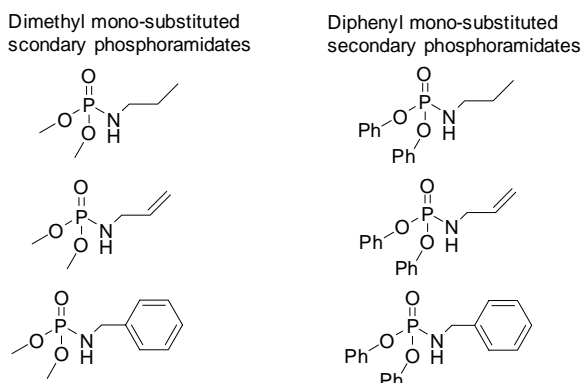


**Scheme 5.** P-N bond hydrolysis under acidic conditions.<sup>[82c]</sup>

Interestingly, they showed that tri-substituted phosphoramidate displayed poor flame retardant behavior on flexible polyurethane foams compared to the analogous mono-substituted phosphoramidate (Figure 9). They suggest that this is because the tri-substituted phosphoramidate decomposes thermally/ hydrolytically to form non-volatile structures, contributing only to condensed phase activity. However, the

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mono-substituted phosphoramidate can decompose to form PO-radicals which might prevent the oxidation of H· and OH· radicals.



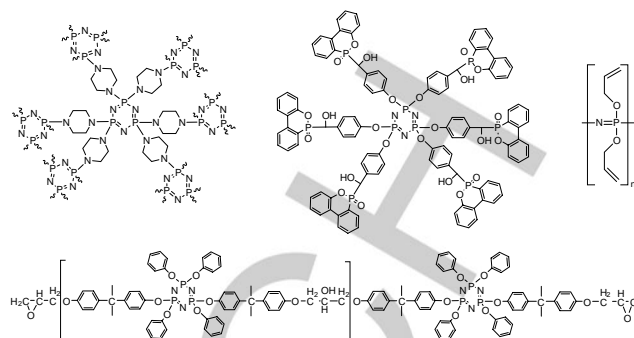
**Figure 9.** Mono-substituted Dimethyl/Diphenyl Phosphoramidates.<sup>[82c]</sup>

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

In the last decade, a myriad of chemically and thermally stable phosphazene derivatives has been developed,<sup>[87]</sup> (Figure 10).<sup>[83, 86b]</sup> Cyclophosphazenes are reported to present even higher thermal stabilities than phosphoramidates: the thermal decomposition of the phosphazene-bound piperazine has been reported from 350 °C until 500 °C (under  $N_2$ ) with residues between 50 – 70 wt.-%, depending on the substituents. This high amount of char indicates cross-linking during pyrolysis, e.g. *via* ring-opening polymerization.<sup>[83a, 88]</sup> The hydrolytic lability of P-N bonds limits their application in textiles (washing). Although, recent studies showed self-extinguishing in cotton/polyester blends grafting with allyl-oxy-polyphosphazene.<sup>[89]</sup>

Hexachlorophosphazene is the common starting material for polyphosphazenes, as it allows the introduction of various pendant groups after polymerization, e.g. the fully inorganic polyaminophosphazene, or functional inorganic-organic hybrid polymers ranging from linear copolymers<sup>[90]</sup> to branched polymeric structures<sup>[88]</sup>. 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.<sup>[83a]</sup>

Polyphosphazenes usually exhibit a low  $T_g$  (from -100 °C to above room temperature).<sup>[91]</sup> Qian et al. synthesized a phosphaphenanthrene/cyclotriphosphazene FRs with practically the same  $T_g$  as the neat diglycidyl ether of bisphenol A (DGEBA) epoxy resin.<sup>[87]</sup> Recently, Wu's group has been working on the synthesis of several cyclotriphosphazene-linked epoxy resins.  $T_g$  values of 160 °C or 145 °C were reached using them as a matrix<sup>[90a]</sup> or loading them into DGEBA resins (20 wt.-%), respectively.<sup>[83b, 90b]</sup> Self-extinguishing UL-94 V-0 rating was achieved with a loading of 30 wt.-% in the resulting thermosets.



**Figure 10.** Low molecular weight and polymeric flame retardant phosphazenes.<sup>[87-90]</sup>

As mentioned earlier, 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 *hb*PPEs (*vide supra*). Another, very promising approach to meeting this requirement is the combination of P-compounds either by blending or covalently linkages to nanometric fillers, such as carbon nanotubes,<sup>[92]</sup> graphene,<sup>[93]</sup> polyhedral silsesquioxanes,<sup>[94]</sup> halloysite nanotubes,<sup>[95]</sup> montmorillonite, or metal oxide nanoparticles.<sup>[96]</sup> In some cases, FRs which are covalently grafted onto the nanofillers have higher efficiency than additives at the same concentration.<sup>[97]</sup> Acceptable grafted amounts of P-compounds are between 10 – 30 wt.-%, which involve less than 1 wt.-% of phosphorus in the final nanocomposite. UL-94 V-0 classification (Figure 11a) and an increase of LOI have been reported in polypropylene and epoxy resin using DOPO-grafted to  $SiO_2$  nanoparticles<sup>[98]</sup>, exfoliated graphene<sup>[99]</sup>, or glass fabric.<sup>[97a]</sup>

Typically, the synergistic effect of the nanofillers and P-grafted compounds occurs in the condensed phase. P promotes the formation of cross-linked structures, that together with the effect of nanofillers of increasing melt viscosity, promoting the formation of an intense carbonization (Figure 11b). However, some studies suggested that grafting of chlorinated phosphorus compounds or DOPO-silane derivatives to carbon nanotubes<sup>[92b]</sup> and graphene<sup>[99]</sup> also effected the gas phase. The combination of gas and condensed phase activity led to a reduction of PHRR of around 35% and an increase of 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 diphenyl-phosphinic chloride,<sup>[92a]</sup> hexachlorocyclotriphosphazene,<sup>[92b]</sup> or an oligomeric diamino-bisphosphonate<sup>[100]</sup> to carbon nanotubes. These polymers cover the surface of the nanotubes with a thin layer, which impedes the formation of  $\pi$ - $\pi$  interaction and promotes the individual dispersion of them in polystyrene (PS), polyamide 6 (PA6), or ethylene-vinyl acetate (EVA), respectively. Stable dispersions in dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), or  $H_2O$  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

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11c)<sup>[99]</sup>. 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's clear that research in 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 above, 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 heat release rate (HRR) during the combustion of the polymer.

## 5.2. Renewable Sources.

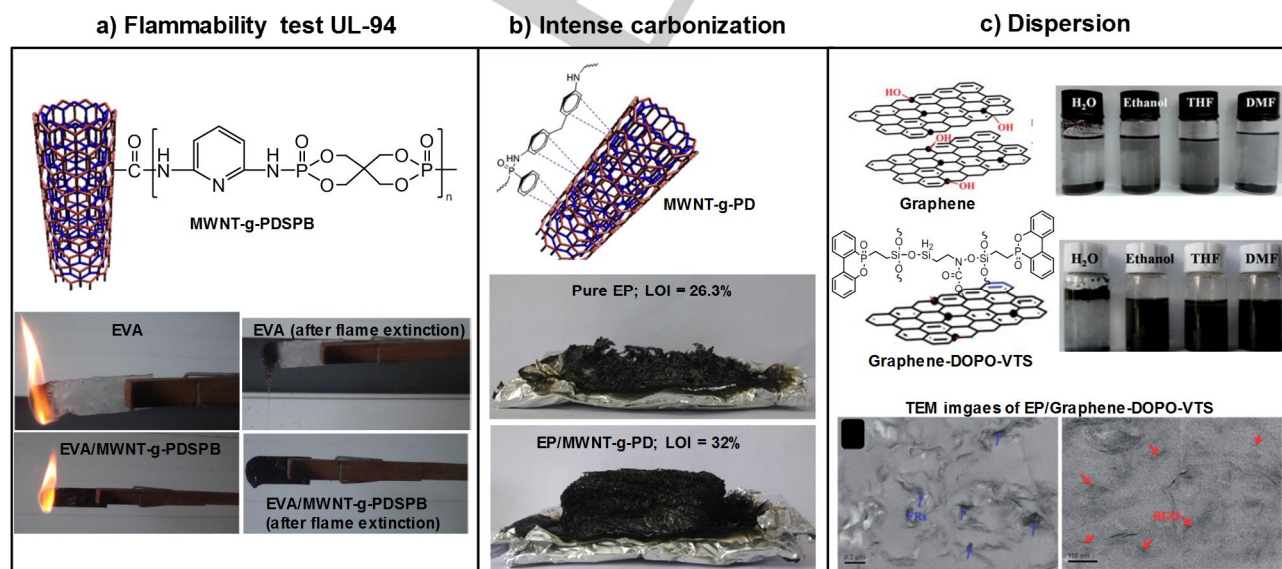
Fractions of biomass from different industrial sectors (e.g. paper) are utilized to produce bio-based FRs, such as carbohydrate fractions (starch), oil fractions (triglycerides or fatty acids) and phenolic fractions (lignin), among others.<sup>[101] [102]</sup> In some cases, these fractions are modified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

Since 2006, special effort has been placed in this field by the group of Cadiz.<sup>[103]</sup> 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 LOI values in the final material was detected. More recently, Howell et al.<sup>[104]</sup> reported the esterification of isosorbide (from starch) with 10-undecenoic acid (from castor oil) to provide a difunctional ester which can be modified by 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, producing an ester which may serve as a base for further FR agents.<sup>[105]</sup>

Starch, chitin, or chitosan are polysaccharides, carrying various chemical functionalities that can undergo reactions such as etherification, esterification, or graft polymerization to produce FRs.<sup>[106]</sup> Cotton fabric is the matrix par excellence for the application of bio-based FRs and the most commonly used. Polysaccharide cationic polyelectrolytes deposited *via* 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.<sup>[107]</sup> recently achieved self-extinguishing during flammability test after only 2 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 achieved from the starch. On the other hand, Xiao et al.<sup>[108]</sup> reported the synergistic effect of a chitosan/ urea compound based on phosphonic acid melamine salt with melamine pyrophosphate and pentaerythritol in polypropylene, accelerating decomposition and promoting char formation.

Lignocellulosic materials are rich-aromatic 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 nitrogen compounds to release NH<sub>3</sub> gas. Liu et al.<sup>[109]</sup> reported the modification of lignin by grafting polyethylene imine and diethyl phosphite and its incorporation in polypropylene/ wood composites. Costes et al.<sup>[110]</sup> modified lignin with PONH<sub>4</sub> in order to improve its FR action in poly(lactic acid). V-0 classification in UL-94 fire tests was achieved with the incorporation of 20 wt.-% of the treated lignin.



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

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Interestingly, they showed that the thermal stability of lignin is mainly dependent on the nature and the amount of the 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) that 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 until 650 °C. Lignin-cellulosic derivatives such as coffee grounds<sup>[112]</sup> in poly(butylene adipate-co-terephthalate) or vanillin<sup>[113]</sup> in epoxy resins have been also 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 ensuring the dehydration of a carbon source, which makes it a good candidate as an acid source for intumescent systems.<sup>[114]</sup> Via LbL assembly, a fully renewable intumescent system which reduced the flammability of cotton was reported by Laufer et al. The combination of 30 bilayers of PA (anionic polyelectrolyte) with chitosan as a cationic polyelectrolyte succeeded in completely extinguishing the flame in vertical flame test. Recently, Zheng et al.<sup>[115]</sup> synthesized a melamine phytate (MPA) with a particle size around 1 μm via the reaction of the phytic acid with melamine. MPA starts to decompose at around 250 °C, releasing water and producing melamine polyphosphate by self-cross-linking. At 400 °C, the s-triazine ring from melamine decomposes, generating inert gases. The addition of a charring agent, dipentaerythritol, was necessary to reach 28.5% in the LOI test and V-0 rating in UL-94 test in order to suppress the dripping phenomenon of polypropylene.

### 5.3. Biopolymers.

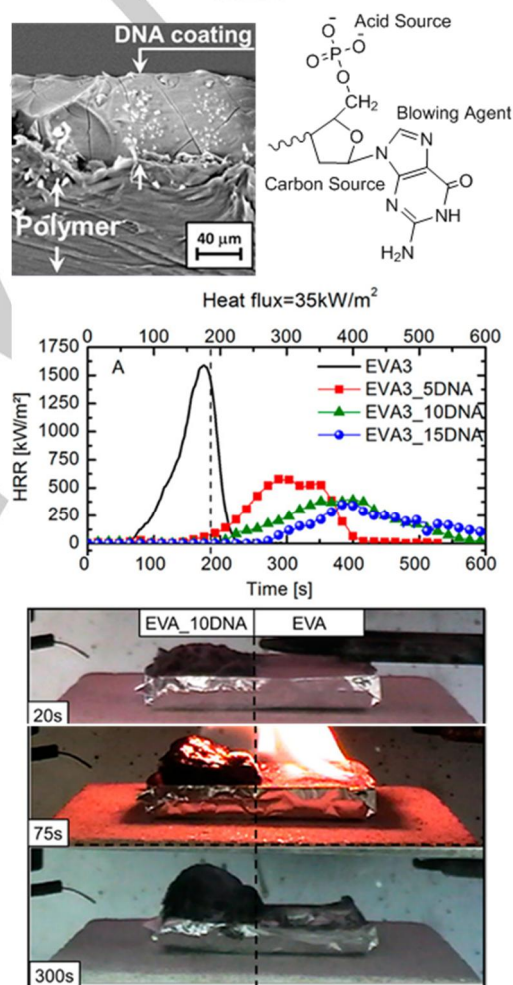
The groups of Malucelli and Alongi have recently introduced the use of phosphorylated biomacromolecules such as caseins (from milk products) and deoxyribonucleic acid (from the extraction of salmon milt and roe sacs) as inherent FRs as a strategy for the valorization of by-products from the agro-food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

$\alpha_{S1}$ -Caseins are phosphorylated proteins containing approximately nine bound phosphate groups per molecule. In cotton fabrics, caseins present 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, due to 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 the total burning rate of 35% and a reduction of the PHRR by 27% were achieved. In polyester fabrics, the decrease of the burning rate was 67%, but dripping was not suppressed.

The structure of deoxyribonucleic acid (DNA) makes it to an ideal intumescent material as it carries i) phosphates as an acid

source, ii) deoxyribose units as a char source, and iii) nitrogen-containing aromatics as blowing agents. However, DNA decomposes at lower temperatures (160 – 200 °C) than the typical intumescent additives (e.g. 300 – 350 °C).<sup>[117]</sup> In cotton fabrics, the thermal degradation of DNA was similar to that of APP: the combustion data proved a significant decrease of PHRR by 50% combined with an intumescent effect.

The application of caseins and DNA onto the fabric was carried out by impregnation or by LbL depositions. For significant results, 20 bi-Layers 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 biomacromolecules applied to fabric is their poor resistance to washing treatments.



**Figure 12.** Heat release rate plots at 35 kW m<sup>-2</sup> for ethylene-vinyl acetate (EVA) and EVA treated with 5, 10, and 15 wt.-% DNA and snapshots taken at different times during cone calorimetry tests of an EVA sample with only 50 % of the surface coated with DNA.<sup>[118]</sup>

Recently, Alongi et al. investigated the potential of DNA coated on different matrices (EVA, PP, PA6) as an “universal” FR.<sup>[118]</sup> Thicknesses of 3 mm (10 wt.-% of DNA) showed good

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performances and a reduction of PHRR greater than 50% in all polymeric matrices (Figure 12).

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 in the 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, due mainly to its chemical versatility: it can act in both the condensed and gas phase, as additive or reactive components, in various oxidization states, and in synergy with numerous adjuvant elements. With increased awareness towards non-toxic, recyclable and bio-based (or even sustainable) materials, phosphorus has the potential to fulfill all 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 clear, and polymeric, complex, and multifunctional structures will aid in reducing flammability without 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, use of renewable resources as effective FRs will ensure a more ecologically aware means of production, 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 the authors believe will drive toward a more sustainable P life-cycle for FRs and a new era of FR polymeric materials.

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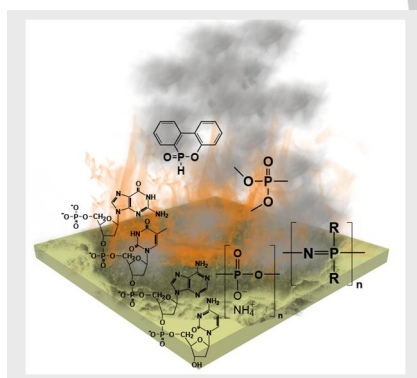
## MINIREVIEW

## Entry for the Table of Contents (Please choose one layout)

Layout 1:

## MINIREVIEW

Phosphorus-based flame retardants are discussed as attractive and versatile alternatives to halogenated compounds. Aspects of sustainable sources are discussed.



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

**Molecular Firefighting – How Modern Phosphorus Chemistry Can Help Solve the Flame Retardancy Task**