

Chapter 2

Biobased Flame Retardants

2.1 Issues and Objectives

A great part of commercially available flame retardants are oil-derived organic compounds (e.g. organo-halogenated, organo-phosphorous, organo-nitrogen compounds). As part of oil-based products, they face the same issues: growing scarcity of petroleum, geopolitical problems, impact on global warming. Moreover some of these compounds (i.e. the halogenated compounds) have received a bad press because they are suspected to provoke specific health and environment concerns. In the prospect to propose more environmentally friendly materials, it is necessary to go further in the application of the Green Chemistry principles as defined by Anastas and Warner [1] and thus to promote the development of biobased additives for polymers [2]. Compared to other additives, it must be said that flame retardants were not pioneers in that area. Indeed, most of the studies that will be presented in this chapter have been carried out for less than five years. Nevertheless times are changing and in the recent period the scientific community has produced a significant number of papers dedicated to the development of flame retardants from renewable resources. The ban of some halogenated compounds and the search for alternative solutions has been definitely an important driving force for the development of such new biobased additives. But another challenging insight is also to take advantage of the particular chemical structure of bio-resources to promote and emphasize specific flame retardant mechanisms.

This chapter will first describe the different biomolecules likely to be used as starting matter for flame retardants, highlighting their chemical structure and their intrinsic thermal properties. Then a review of biobased flame retardant systems studied in the literature will be proposed. Systems have been classified according to their expected mode of action. Finally, this chapter will close off with some thoughts about future industrial developments of biobased flame retardants.

2.2 Thermal Behavior of Biomass-Based Matter

Biobased compounds generally refer to compounds that can be obtained or derived from biomass which is defined as the biological matter that can be found on earth. It includes plants, animals and microorganisms. Apart from bacteria, the total biomass on land represents about 560 billion tons of carbon. Vassilev et al. [3] gave an overview of the chemical composition of biomass. Their analysis relies on the general classification of biomass in groups, sub-groups, varieties and species. Even if this composition is very variable depending on the group, they were able to identify the most abundant elements which in decreasing order are C, H, N, Ca, K, Si, Mg, Al, S, Fe, P, Cl, Na, Mn, and Ti. It is worthy to note that some of these elements are known to have a flame retardant effect.

In order to be used as raw matter for fuels, heat, power or chemicals, biomass has to be converted using various processes. This set of processes is the so-called biorefinery, a concept developed by analogy with the oil industry [4]. The purpose of a biorefinery is to extract, separate and modify the different biochemical compounds of biomass and to add value to these products and their intermediates. Therefore a better way of imaging how biomass can be used to develop flame retardants consists in considering its biochemical composition. Thus, four main families of compounds can be distinguished: carbohydrates, proteins, lipids and phenolic compounds (Fig. 2.1). These biomolecules can be used as such or

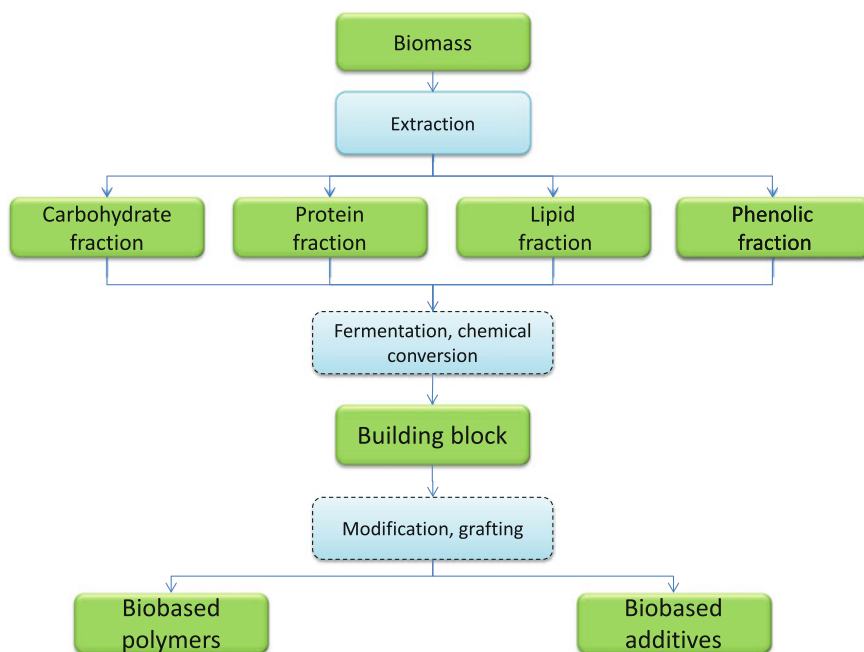


Fig. 2.1 From biomass to biobased additives for polymers

converted to derivatives by chemical or biological treatments. Thus biobased building blocks can be obtained and further modified to bring flame retardant functionalities.

2.2.1 Carbohydrates

Carbohydrates, also known in biochemistry as saccharides, are biological molecules containing carbon, hydrogen and oxygen atoms. They include low molecular weight compounds referred to as sugars (e.g. glucose, lactose) or more complex molecules such as oligo and polysaccharides. The compounds that got the more attention for flame retardant development were probably polysaccharides, and more particularly cellulose, starch and chitosan.

Cellulose is the main structural component of vegetal cell wall in plants. It is the most abundant source of organic matter on earth since it is estimated that plants synthesize 50 to 100 billion tons of cellulose each year. Cellulose is a linear homopolymer composed of D-glucose units linked by β 1-4 glycosidic bonds [5] (see Fig. 2.2). The degree of polymerization of native cellulose varies according to the source from 1000 to 30,000. The individual polysaccharide chains are bound together by hydrogen bonds into a fibrous structure called microfibrils whose diameter is about 25 nm. Parts of microfibrils called micelles are arranged in an orderly manner and give to cellulose its crystalline properties. Microfibrils are bundled together into fine threads that coil around one another to form macrofibrils. At a higher scale, arrangement of macrofibrils forms cellulose fibers that act as reinforcement in plant cell walls.

The thermal decomposition of cellulose occurs in one main step between 300 and 400 °C, the higher mass loss rate being observed around 370 °C (Fig. 2.3). Below 300 °C cellulose undergoes dehydration reactions that give rise to a small mass loss. Dehydration reactions may be intermolecular or intramolecular thus creating crosslinking and double bonds. This leads to the formation of an intermediary compound called active cellulose or anhydrocellulose. Above 300 °C the main degradation step corresponds to depolymerization that occurs via the breaking of the glycosidic linkage (transglycosylation). The decomposition of cellulose gives various kinds of anhydro-saccharides the main one being levoglucosan (1,6-anhydro- β -D-glucopyranose) that may represent up to 60 wt% of volatile yield. During this step, the amount of furan and benzene rings increases progressively in the condensed phase while aliphatic groups disappear. At high temperature (800 °C), a stable char representing 15 wt% of the initial mass is observed. This residue has a structure similar to that of lignin char. It should be added that the degradation pathway of cellulose may be modified depending on the heating conditions and the presence of other components in the surrounding. Thus at low heating rate, dehydration reactions are favored and the char yield is enhanced [6]. Similarly it was highlighted by Dorez et al. [7] that the presence of a low amount of lignin in flax fiber was likely to change the degradation pathway of cellulose due to

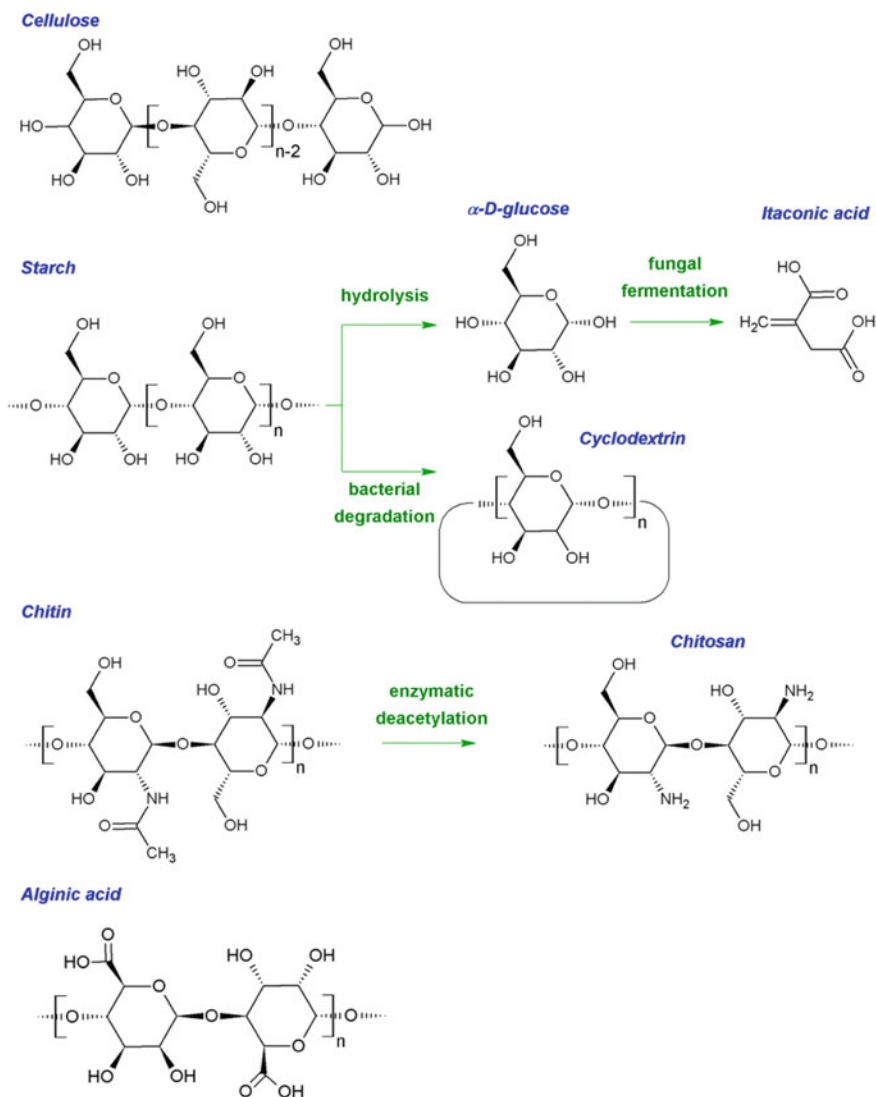
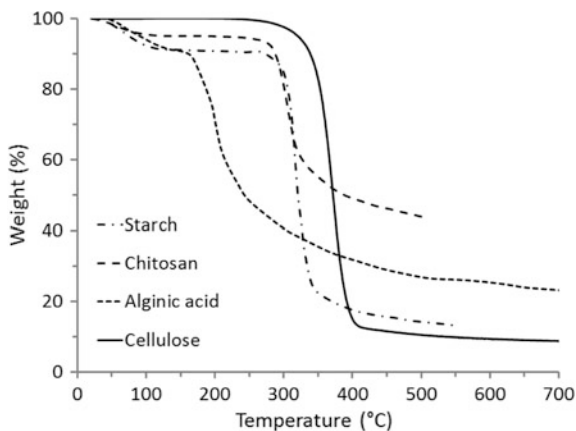


Fig. 2.2 Examples of carbohydrates used in flame retardant systems

the release of acidic compounds that promote dehydration and hence charring at the expense of depolymerization.

Starch is a polymer that is synthesized by plants as energy storage [8]. It takes the form of granules measuring 1–200 μm in diameter. Starch is very similar to cellulose in its chemical formula since it is also composed of D-glucose units. Actually starch contains two types of macromolecules: amylose which is a linear polymer constituted by glucose units bonded by a α 1-4 linkage and amylopectin

Fig. 2.3 Thermogravimetric curves of some carbohydrates



which is a branched polymer where branching occurs through α 1-6 linkage (see Fig. 2.2). Amylose whose fraction represents 15–25 wt% in starch exhibits molecular ranging from 0.2 to 2×10^6 g/mol while amylopectin which represents 75–85 wt% in starch has higher molecular weight ranging from 100 to 400×10^6 g/mol. Approximately 70 million tons of starch are produced per year world-wide.

The thermogravimetric curve of starch under inert atmosphere highlights two main weight losses (Fig. 2.3). The first weight loss occurring at low temperature up to 110 °C corresponds to evaporation/physical dehydration phenomena. As a matter of fact, starch is a highly hygroscopic material [9]. The second mass loss corresponds to chemical dehydration and thermal decomposition of starch and starts from 300 °C. In this range of temperature condensation between hydroxyl groups is observed leading to the formation of ether bonds. Condensation inside the glucose ring may also occur, leading to its breakdown. C–C bonds as well as aldehyde groups are formed. Above 500 °C carbonization occurs, leading to an increase of aromatic carbons at the expense of aliphatic carbons. The thermal decomposition of starch gives a 15–20 wt% residue at high temperature.

Starch industry not only includes the extraction and refinement of starches but also the production of starch derivatives. Starch can be hydrolyzed into simpler carbohydrates also called dextrans by acids or enzymes. As an example, *cyclodextrin* that will be cited later in the text as component of flame retardant systems was shown to be obtained via the degradation of starch by the bacillus amylobacter bacteria (see Fig. 2.2). Cyclodextrin is a cage molecule that may encapsulate other compounds and therefore appears as very attractive for the food and pharmaceutical sectors. Other polyols such as sorbitol or *isosorbide* may also be relevant to be used in flame retardant formulations. Fermentation is another process that enables to convert starch into derivatives. For example the use of fungi such as *Aspergillus itaconicus* or *Aspergillus terreus* allows for the conversion of glucose or molasses into *itaconic acid* (see Fig. 2.2). The fermentation of grape stock to make wine generates *tartaric acid*. These two organic acids have been used

as raw matter for the development of flame retardant. **Phytic acid** is a saturated cyclic acid and the main phosphorous storage molecule found in plant seeds. It is the most important iron uptake inhibitor contributing to iron deficiency. The biosynthesis of phytic acid starts from the D-glucose-6-phosphate. By the action of various enzymes hydroxyl groups of glucose are progressively substituted by phosphorus moieties.

Chitosan is a random copolymer of D-glucosamine and N-acetyl-D-glucosamine bonded by β 1-4 linkage [10]. It is obtained by chemical or enzymatic deacetylation of chitin which is the main component of shrimp (or other crustaceans) shells (see Fig. 2.2). For commercially available products, the acetylation degree varies from 60 to 100%. The global production of chitosan is around 20×10^3 tons per year. This is a growing market especially in Asia.

Under inert atmosphere, the thermal degradation of chitosan occurs in three steps (Fig. 2.3). Below 140 °C, the first weight loss corresponds to the release of water loosely bonded [11]. The second and main step of degradation occurring between 250 and 350 °C is assigned to further dehydration, deacetylation and depolymerization of chitosan. Above 400 °C a low mass loss rate attributed to residual decomposition reaction is observed. At 500 °C the char is as high as 40 wt%. As shown by Moussout et al. [12], this char is much lower (circa 20 wt%) when degradation occurs under air atmosphere. By comparing chitin and chitosan, these authors also evidenced that deacetylation degree modified both the hygroscopicity and thermal stability of the carbohydrate.

Alginates refer to the derivatives of alginic acid and alginic acid itself [13]. These are carbohydrates present in the cell wall of brown algae as calcium, magnesium and sodium salts of alginic acid. Alginic acid is a copolymer of mannuronic acid and guluronic acid, repeating units being bonded by a β 1-4 linkage (see Fig. 2.2). The proportion and distribution of comonomers are determining parameters to explain the physical and chemical properties of the polymer. Thus alginates could be considered as an anionic polysaccharide.

The thermal behavior of alginic acid and sodium alginate was studied by Soares et al. [14]. Under nitrogen, two main steps of degradation are highlighted (Fig. 2.3). At low temperature alginates exhibit a dehydration process. The moisture content was found to be higher for sodium alginate (15 wt%) than for alginic acid (10 wt%). The main decomposition step occurs between 150 and 300 °C. In the case of alginic acid, it leads to carbonaceous residue that was found to be between 21 and 26 wt% at 800 °C depending on the authors [15, 16]. In the case of sodium alginate, Soares et al. obtained a 22 wt% residue consisting mainly of sodium carbonate.

2.2.2 Proteins

Proteins are linear biological polymers found in living cells [17]. They are made of sequence of amino acids bonded by peptidic linkage (Fig. 2.4). There are only 20

naturally occurring amino acids that can be classified according to the polarity and the charge of the side chain that they bear. Proteins exhibit a very complex structure that can be described through 4 levels of organization. The primary structure corresponds to the sequence of amino acids in the macromolecule. The secondary structure corresponds to the local structure of the protein chain stabilized by hydrogen bonds. Hydrogen bonds are related to the presence of carbonyl and amine groups. It leads to structures such α -helix or β -sheet. The tertiary structure describes the folding of a single protein and defines its overall shape that is stabilized by different kinds of interactions. Globular, fibrous and membrane proteins are the most encountered tertiary structures. Finally the quaternary structure describes the structure formed by several proteins.

Proteins may play various roles in living cells. Enzymes which are a large family of proteins act as catalyst for biochemical reactions. Other proteins are involved as sensor in the communication system that governs the cell activities. They may also participate to the transport of smaller molecules. Finally, some polypeptides such as fibrous proteins play a structural role and bring stiffness to cell components.

It must be underlined that some proteins involved in signal transduction may undergo phosphorylation and dephosphorylation modification. Well known examples of phosphoproteins are casein (protein of milk) and phosvitine (protein of egg). The amino acids residues that may be modified by phosphate groups are usually serine, threonine or tyrosine (Fig. 2.5).

The thermal stability and the pyrolysis products of proteins tightly depend on their amino-acid composition [18]. As an example (Fig. 2.6), the thermal degradation of casein was studied by Mocanu et al. [19]. Their results indicate that casein undergoes a small weight loss below 170 °C that was assigned to the release of water physically retained within the proteins. Under nitrogen, the main degradation step occurs between 250 and 380 °C with the release of CO₂, CO, water, ammonia and isocyanic acid. The decomposition lets a thermally stable residue that can be as high as 25 wt% at 600 °C.

The primary structure of proteins i.e. the sequence of amino acids is given by the genetic information carried by deoxyribonucleic acid (DNA). Therefore it can be

Fig. 2.4 Chemical structure of proteins

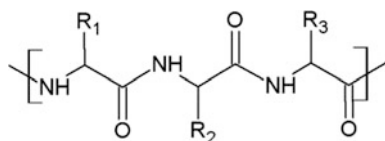


Fig. 2.5 Examples of phosphoprotein residues (phosphoserine and phosphothreonine)

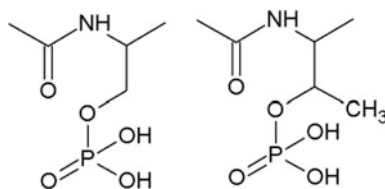


Fig. 2.6 Thermogravimetric curves of casein and DNA from [19, 21]

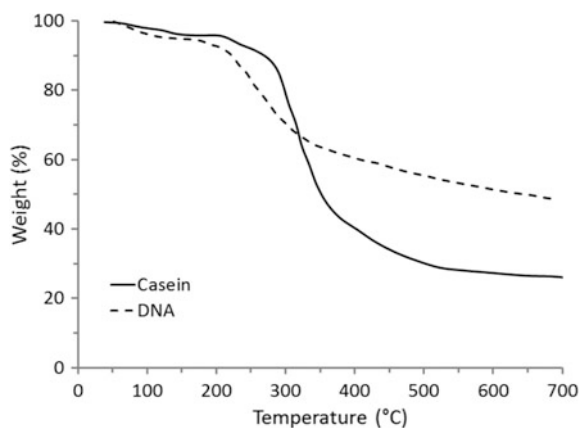
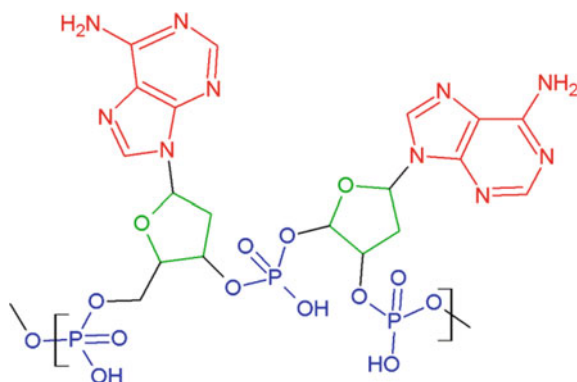


Fig. 2.7 Structure of DNA including sugar, phosphate and base units



said that proteins and DNA are closely tied in biosynthesis. As shown in Fig. 2.7, DNA exhibits a complex structure consisting of a phosphate-desoxyribose backbone with a base (adenine, cytosine, guanine or thymine) attached to the sugar ring [20]. This molecule has raised interest in the field of flame retardancy due to the simultaneous presence of nitrogen and phosphorus.

The thermal decomposition of DNA from herring sperm was studied in details by Alongi et al. [21]. The thermogravimetric curves are relatively similar in air and nitrogen atmosphere. A first weight loss is observed below 150 °C corresponding to the removal of absorbed moisture (Fig. 2.6). Some volatiles (e.g. isocyanic acid) are emitted around 160 °C however the main decomposition occurs between 200 and 400 °C with a maximal mass loss rate between 230 and 260 °C. Above 200 °C the main pyrolysis products are CO₂, water and ammonia. At still higher temperature the phosphate-desoxyribose backbone degrades producing 2,3 dihydrofuran 3,5 phosphate 5 exo-methylene that may further dimerize or polymerize. Above 400 °C crosslinking reactions take place creating a thermally stable P-N based structure. At 700 °C the stable residue represents circa 50% of the initial mass of DNA.

2.2.3 Lipids

Lipids are a group of naturally occurring molecules whose main biological functions are energy storing, signal transmission and structural material for cell walls. They are generally considered as hydrophobic or amphiphilic molecules indicating that at least one part of these molecules is non polar [22]. Taking into account the diversity of their chemical structure, there is no universal classification of lipids. In 2005 Fahy et al. [23] proposed a comprehensive classification of lipids in accordance with IUPAC rules including eight categories: fatty acids (e.g. ricinoleic acid), glycerol-lipids, glycerol-phospholipids (e.g. phosphatidylethanolamine), sphingolipids, sterol lipids, prenol lipids, saccharolipids, polyketides. To these true lipids, other compounds with a lipid character can be added: phenolic lipids (e.g. cardanol), terpenes (e.g. saponin), steroids. Some of the above-mentioned lipids are presented in Fig. 2.8.

The thermal stability and the decomposition mechanisms of lipids tightly depend on their nature. Thus, no general scheme can be described. However the thermal analysis of some vegetable oils (sunflower, soybean, castor, jojoba) indicates that the decomposition occurs generally in the range 300–550 °C and leaves no residue at high temperature [24–26]. Considering the presence of hydrocarbon chains in their structure, the combustion of lipids is likely to be highly exothermic. Therefore lipids appear not to be the best candidates for being the basis of biobased flame retardants.

Nevertheless, for many years, plant oils and their derivatives have been used as building blocks in polymer chemistry with the aim to ensure a more sustainable production of macromolecular materials [27]. Due to the presence of various functional groups (hydroxyls, carboxylic acids, double bonds), a great variety of reactions may be envisaged. Hence some lipid derivatives such as undecylenic acid or cardanol have been used to prepare phosphorus containing monomers that can act as reactive flame retardant, especially in thermosets.

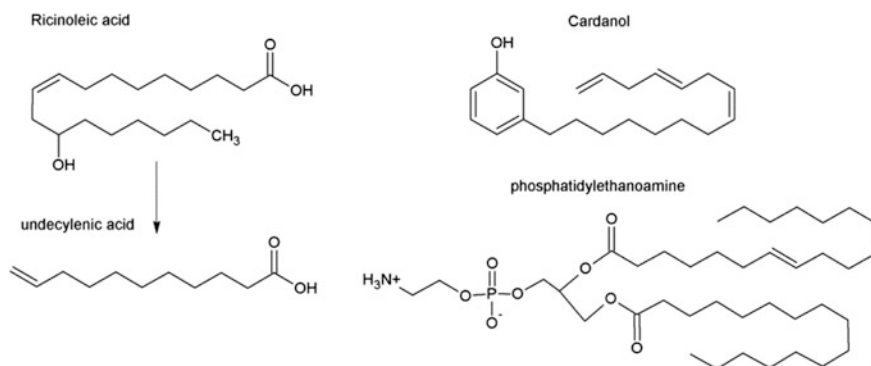


Fig. 2.8 Examples of lipids that may be used for biobased flame retardant synthesis

Besides, among the above-mentioned list of lipids, some may retain attention for prospective works owing to their chemical composition. Phospholipids and sphingolipids are two categories of lipids containing phosphorus and nitrogen atoms in their backbone. Considering the influence of these atoms in the fire behavior of polymers, these lipids may represent potential raw matter for new biobased flame retardants.

2.2.4 Phenolic Compounds

Natural polyphenols are a class of organic molecules found in plants and characterized by the presence of phenolic units bearing one or several hydroxyl groups associated in a high molecular weight complex structure. They result from the secondary metabolism of plants through the shikimate pathway [28]. They range from simple molecules such as hydroquinone to high polymerized structures such as tannins. Polyphenols can be classified according to the sequences in their carbon backbone. Thus simple phenols correspond to a C_6 sequence (e.g. phloroglucinol), phenolic acids correspond to a C_6-C_1 sequence, flavonoids correspond to a $C_6-C_3-C_6$ sequence (e.g. catechin), lignins correspond to $(C_6-C_3)_n$ sequences and condensed tannins correspond to $(C_6-C_3-C_6)_n$ sequences. The molecules that have raised the interest of researchers as raw matter for flame retardants belong mainly to simple phenols such as phloroglucinol or eugenol (Fig. 2.9) and to polymerized structures (tannins and lignins).

Lignin is the second most abundant natural polymer after cellulose and the first aromatic polymer. Lignins are mainly found in higher plants and in some algae.

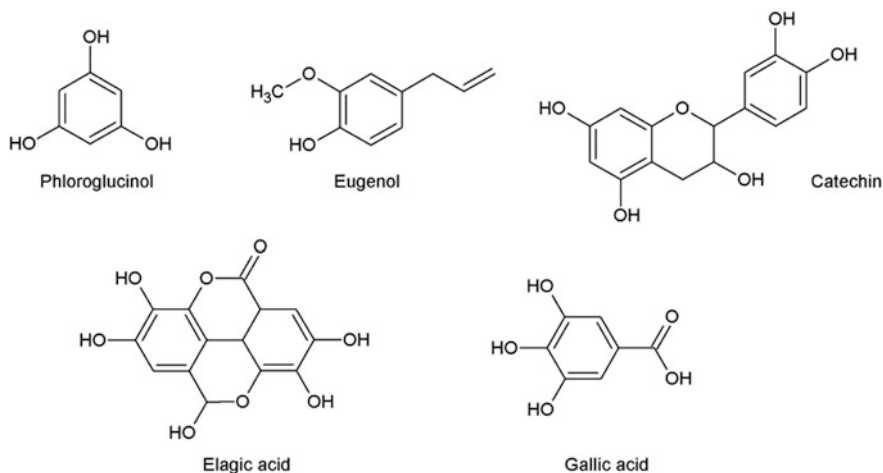
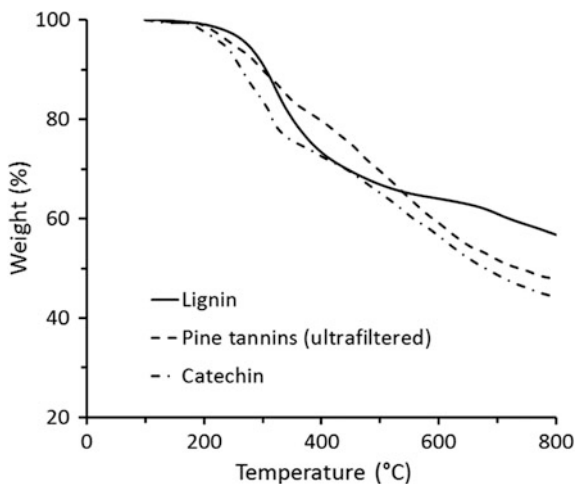


Fig. 2.9 Phenolic compounds

Fig. 2.10 TGA curves of lignin, pine tannins and catechin from [7, 30]



They play an important role in the mechanical properties of cell walls by bringing rigidity and in the protection against decomposition by giving waterproofness. On a chemical point of view lignins can be viewed as polymers of monolignols. They are based on three main monomers: coumarylic acid, coniferylic acid and sinapylic acid. The fraction of each monomer varies depending on the plant, the species, the organ and the tissue.

The thermal decomposition of lignin has been reviewed by Brebu and Vasile [29]. In comparison with other components of biomass, lignin degrades over a broader range of temperature between 200 and 500 °C (Fig. 2.10). The thermogravimetric curve generally shows a first weight loss between 100 and 180 °C that corresponds to the release of water physically bonded into the raw matter. Strictly speaking, the decomposition starts from circa 200 °C. In a first step (200–260 °C), low molecular weight products resulting from the propanoid side chain cleavage are released. Then the main degradation step (275–450 °C) corresponds to the cleavage of the main chain either by C–C and β -scission or by aryl-ether cleavage. At this point, a large quantity of methane is evolved. Above 500 °C, further rearrangements and condensation of the aromatic structure occur, leading to the formation of a significant char yield (57 wt% at 600 °C) and the release of dihydrogen in the gas phase.

Tannins are phenolic biomolecules that can be found in different parts of plants (bark, leaves, roots, leaves, fruits). They play a major role in the defense against pests. Two types of tannins can be distinguished: hydrolysable tannins which are based on gallic or ellagic acids and condensed tannins that are based on catechin or flavanol (Fig. 2.9). The thermal degradation of tannins extracted from pine bark was studied by Gaugler and Grigsby [30]. It was highlighted that the decomposition occurs over a wide range of temperature (180–800 °C) and was dependent on the mode of extraction and the degree of purification. Whatever the process, a high amount of char was formed at high temperature (>30 wt%). The largest char residue

(48 wt%) was obtained after ultra-filtration of tannins and was quite similar to that of pure catechin (Fig. 2.10).

To conclude it is difficult to predict what could be the interest of all the above-described biomolecules as flame retardant by simply examining their composition and thermal behavior. However some basic criteria may be supposed to be good indicators:

- A thermal stability sufficiently high to be compliant with polymer processing,
- A high charring ability,
- The presence of functional groups (hydroxyl, carboxylic acid, amine, double bonds) that enable chemical modification,
- The presence of elements known for their flame retardant activity (phosphorus, nitrogen, silicon...).

2.3 Strategies for Flame Retardancy with Biobased Compounds

The main strategies used for achieving flame retardancy of polymers have been reviewed in different papers [31, 32]. The modes of action of flame retardants are generally classified according to the nature of the involved mechanisms (physical or chemical action) and according to the location where these mechanisms take place (gas phase or condensed phase). Regarding all the biobased flame retardant systems that will be reported in the following, it is noteworthy that the improvement of the fire behavior was essentially achieved through one preferential mode of action the so-called charring effect. It means that the intended effect was to create at the sample surface and during combustion a charred layer. This char generates a double positive influence: (i) on one side a part of carbon atoms constituting the polymer structure is fixed within the residue thus decreasing the amount of volatile fuel and therefore the amount of heat released by the combustion reaction; (ii) on the other side the charred layer acts as a protective shield that slows down the heat transfer to the underlying polymer and modifies the kinetics of fuel diffusion to the flame. The effect of charring may be further enhanced if an expanded layer is formed; this is the so-called intumescence phenomenon. In this case it is necessary that a gas acting as blowing agent was released simultaneously with the charring process.

In the following the works will be presented according to the way renewable resources were used as flame retardants systems. It means (i) as unique component of flame retardant system, (ii) in combination with traditional phosphorus or nitrogen flame retardant, (iii) after chemical modification, (iv) after chemical modification and insertion in the polymer chain.

2.3.1 Bio-resources as Intrinsic Flame Retardant

2.3.1.1 Lignin

Among the renewable resources described in the preceding paragraph, lignin was probably the one giving the highest char yield at high temperature. That is surely the reason why lignin was tested as single additive to improve the fire behavior of polymers. Gallina et al. [33] studied the burning behavior of a polypropylene (PP) containing 20 wt% of lignin. Under a 25 kW/m² heat flux with cone calorimeter, this blend exhibits a peak of heat release rate (pHRR) three times lower than the pure PP (Fig. 2.11). The result was even better than those obtained with more classical flame retardant systems e.g. melamine or boric acid. This decrease was achieved with a final residue of only 6 wt%. The sole negative point was a decrease of time-to-ignition (Fig. 2.12) but it was also the case for nitrogen or phosphorus containing flame retardant. In a second paper [34], the same group obtained still interesting fire performance by decreasing the lignin content down to 15 wt% in PP. The reduction of pHRR was significant, moreover very low smoke opacity and CO yield were measured.

In a later paper, Song et al. [35] investigated the effect of reactive compatibilization on the thermal and fire properties of acrylonitrile-butadiene-styrene (ABS)/lignin blends. Similarly to what was observed in PP, it was evidenced that lignin due to its lower thermal stability induces a slight decrease of the onset of degradation. In return, increasing the lignin content enables slowing down the degradation process and increasing the char residue. In cone calorimeter test, the presence of lignin leads to a 32% decrease of pHRR (Fig. 2.11). It was highlighted that compatibilization plays a positive role by reducing the mass loss rate and increasing the char residue. This was attributed to the cohesivity of the residue which is enhanced when lignin is well dispersed in the polymer matrix.

Fig. 2.11 Relative variation of pHRR versus char yield polymers containing biobased intrinsic flame retardant from [33, 34, 36, 38]

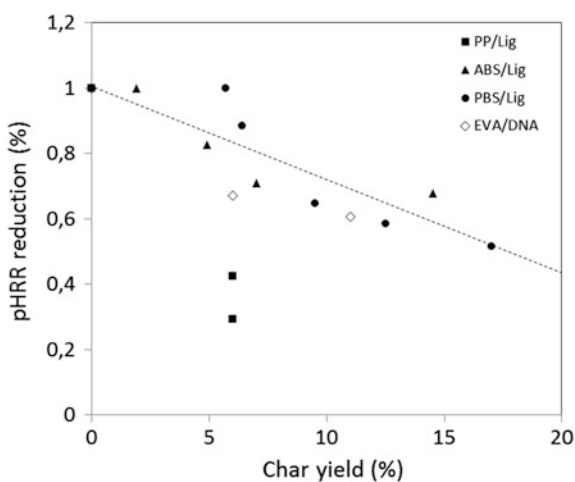
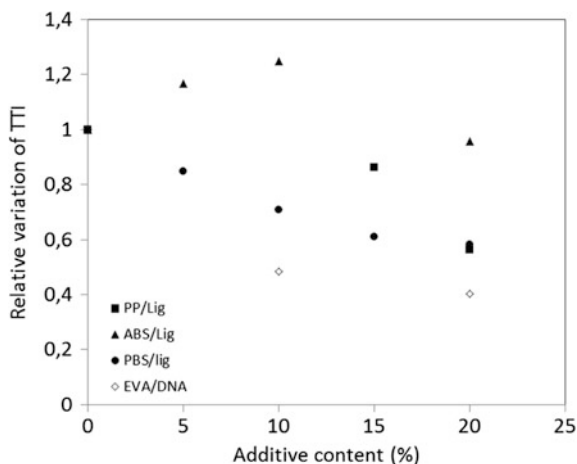


Fig. 2.12 Relative variation of time to ignition versus additive content of polymers containing biobased intrinsic flame retardant from [33, 34, 36, 38]



More recently Ferry et al. [36] compared the thermal and fire properties of two types of lignin differing by their extraction process (respectively kraft and organosolv process). The two lignins exhibit very similar thermogravimetric curves even if alkali lignin (kraft) gives a higher residue. More significant differences were evidenced when measuring the heat release rate during combustion either at small scale with micro-calorimeter of combustion (PCFC) or at bench scale with cone calorimeter. Alkali lignin shows lower pHRR and THR. This was assigned to the presence of sulfur resulting from the kraft process. It was assumed that sulfur containing moieties decomposed during lignin pyrolysis by releasing sulfur dioxide thus limiting the release of heat. The release of SO_2 was confirmed by using a FTIR/cone calorimeter coupling. Used at a 20 wt% content, alkali lignin induces an increase in polybutylene succinate (PBS) ignitability (Fig. 2.12) but also a significant decrease of pHRR (49%) as shown in Fig. 2.11. The most significant change concerns the shape of the HRR curve that turns from a non-charring behavior to a thick charring behavior. This result proves that lignin promotes a char residue that acts as protective layer that slows down the combustion. Comparing organosolv and kraft lignin in a poly(lactic acid) (PLA) matrix, Costes et al. [37] found better performance with lignin from the organosolv process, with a strong reduction of THR. Similar to the previous studies they observed a decrease of thermal stability leading to a decrease of time-to-ignition. All the studies presented here-above show that lignin tends to increase the ignitability of polymers what is penalizing in many classification tests. This encouraged the authors to turn to lignin modification.

2.3.1.2 Proteins and DNA

Since 2013, the group of Politecnico Torino has carried out several studies to assess the potential of proteins and deoxyribonucleic acid (DNA) as flame retardant [39].

There were several motivations for using such biomacromolecules: firstly some of them can be considered as waste or by-products from food industry and therefore are low cost raw matter; secondly DNA despite its current high cost might find prospective applications due to the development of large scale extraction methods; finally these biomacromolecules present the advantage to contain nitrogen and phosphorus, two elements of great interest for flame retardancy.

The main field of applications of proteins and DNA was the treatment of textiles and foams due to the ability of these macromolecules to make films [40]. Bosco et al. [41] studied whey protein isolate used as coating onto cotton fabrics. Whey proteins are polypeptides exhibiting a globular tertiary structure. They represent circa 20 wt% of proteins in milk. It was shown that whey proteins form a continuous and coherent film at the surface of cotton fibers. The authors demonstrated that the whey protein coating induced an enhancement of cotton charring during degradation under nitrogen atmosphere. Proteins retain a high water amount that provokes hydrolysis and thus amino acids are released. Carboxylic groups catalyze the cellulose decomposition favouring dehydration and thus charring to the detriment of depolymerization. With regard to fire properties, it was evidenced that protein coating enables to slow down the burning rate and hence to increase the burning time. The authors investigated also the influence of protein denaturation. It was noted that the effect on thermal and fire properties was the same whether the macromolecules were folded or unfolded. Alongi et al. [42] carried out a similar study using this time caseins and hydrophobins as coating deposited on cotton fabrics. Caseins are the main proteins of milk and belong to the phosphoprotein group meaning that some amino acid residues bear phosphate moieties as it was presented in Fig. 2.5. Hydrophobins are proteins produced by filamentous fungi, they exhibit an amphiphilic character and molar masses. Whatever the kind of proteins, the effects were similar to those obtained with whey proteins with catalysis of cellulose thermal decomposition and an increase of char residue at high temperature. Regarding to fire properties, the early degradation of cellulose induces a drastic decrease of time-to-ignition. On the other hand the formation of char layer enables a decrease of the pHRR and a slowdown of the burning rate.

In a similar way, Alongi et al. [43] used DNA from herring sperm as flame retardant and suppressant for cotton fabrics. The authors claimed that DNA was a natural intumescent flame retardant since the three main conditions for intumescence are met: a sugar unit acting as carbon source, a phosphate group able to release phosphoric acid and nitrogen-containing bases likely to release ammonia that plays the role of blowing agent [44]. After treatment, DNA forms a homogeneous and continuous coating at the cellulose fiber surface. This coating tends to accelerate the thermal decomposition of cellulose that starts from 200 °C. This early degradation was attributed to the release of phosphoric acid by DNA. Phosphoric acid catalyzes dehydration of cellulose and promotes the formation of an aromatic char thus limiting the production of fuel such as levoglucosan [45]. The authors assessed the flammability of the DNA-treated cotton fabrics using a horizontal burning test and cone calorimeter. Above a 10 wt% add-on, the DNA coating enabled the extinguishment of cotton as soon as the methane flame was

removed. In cone calorimeter a 19 wt% add-on prevents the ignition to occur [46]. In this latter case, it was proved that the DNA coating acts as a protective barrier that absorbs heat and releases inert gas. Thus the underlying cellulose undergoes pyrolysis instead of burning. It was also evidenced that the fire performance of coatings depends on the DNA molecular size and pH of the impregnation solution and number of impregnations [47]. Improving the fire behavior of cotton fabrics may also be achieved by using DNA in Layer by Layer (LbL) assemblies. Carosio et al. [48] proposed a bilayer composed of DNA as polyanion and chitosan as polycation. 5–20 bilayers were deposited onto the cotton fabrics. DNA layers promote the charring of chitosan. The obtained char is thermally stable and imparts a remarkable flame retardant character to cotton.

Carosio et al. [49] used DNA LbL assembly to improve the fire behavior of a polyethylene terephthalate (PET) foam. In this work, a DNA aqueous solution was prepared and was applied as one of the anionic layers in the LbL assembly, Poly (diallyldimethylammonium chloride) being the cationic layer and poly(acrylic acid) branched polyethylene imine being the other anionic layer. A LbL assembly containing ammonium polyphosphate (APP) instead of DNA was prepared for comparison. Flammability and cone calorimetry tests revealed that the LbL coatings containing APP induces superior performances. These results were ascribed to the fact that only APP-based architectures were able to suppress the melt dripping behavior typical of PET and hence to reduce the heat release rate peak.

DNA can also be utilized for the flame retardancy of thick polymers. For this application two strategies have been investigated. The first one consists in incorporating DNA in the bulk by melt-blending, in the second one DNA is deposited as coating onto the thick polymeric sample. When blended with EVA, DNA was proved to change the degradation pathway of the polymer leading to the formation of char, inhibiting the production of volatiles [38]. At a 20 wt% content DNA induces a 39% decrease of the pHRR (Fig. 2.11) and a strong reduction of CO and CO₂ production. It was concluded that DNA acts similarly to APP. When confined at EVA surface, the DNA coating was highlighted to block ignition when tested with cone calorimeter under a 35 kW/m² heat flux [50]. Hence ignition was greatly delayed and the combustion kinetics was drastically reduced. The coated EVA can also withstand the exposure to a butane/propane flame. Good results were obtained when DNA coating was applied onto other thermoplastic polymers (PP, polyamide 6 (PA6), ABS, polyethylene terephthalate (PET)) [51].

2.3.2 Bio-resources Combined with Phosphorus or Nitrogen Compounds

Considering the intrinsic charring ability of some bio-resources as described in paragraph 2, a very frequent strategy for developing performant flame retardant systems consisted in combining biomolecules with traditional flame retardant

known for their propensity to emphasize charring or to expand carbonaceous residues. That is probably why most of the studies presented hereafter deals with combination of renewable resources with phosphorus or nitrogen containing compounds.

2.3.2.1 Carbohydrates

Carbohydrates are oxygen containing polymers and therefore may be used as charring agent in flame retardant compositions. Among carbohydrates starch was more particularly studied as carbon source in intumescent systems. In 2008 Réti et al. [52] used potato starch as substituent to pentaerythritol (PER) in intumescent composition. 10 wt% starch was combined to 30 wt% ammonium polyphosphate (APP) in a polylactic acid (PLA) biopolymer. This enables to obtain a limiting oxygen index (LOI) of 40% and a V-0 rating at the UL94 test. This later rating was even better than that obtained with the PER containing composition (V-2). With regard to cone calorimeter test, the starch containing formulation enables to increase the time-to-ignition. The peak of heat release rate was also decreased but at lesser degree compared to the APP/PER system. The effect of starch was related to the high amount of charred residue (circa 50 wt%) generated by its interaction with APP. This char acts as a protective layer for the underlying polymer during the combustion.

Wang et al. [53] studied a similar starch based flame retardant system in PLA but this time APP was microencapsulated in polyurethane and associated with melamine. They observed the same trends than Reti et al. i.e. an increase of LOI, a V-0 rating in UL94 test and a decrease of pHRR measured with microscale combustion calorimeter (PCFC). It was evidenced that the FR system composed of microencapsulated APP melamine and starch has an excellent intumescent effect. The authors claimed that microencapsulation offers two main advantages: (i) an improved compatibility of APP with the polymer matrix, (ii) a retardation of the reaction between acid and carbon source during processing.

Another strategy to take benefit from starch in the improvement of fire properties was to use it as part of the polymer matrix. Gaialene is a polyolefin grafted starch developed by Roquette at the beginning of the 2010's with the aim to propose a lower carbon footprint polymer. Dupretz et al. [54, 55] investigated the fire behavior of Gaialene when associated with APP or APP and melamine. When used alone, APP improves very significantly the fire performance of Gaialene reaching a LOI of 30%, a V-0 rating at UL94 test and a 65% reduction of pHRR. The dehydrating effect of phosphoric acid released from APP provokes depolymerization and aromatization of starch leading to charring. The release of different gaseous products and the decrease of the viscosity generate the swelling of the structure giving rise to an efficient barrier effect. That makes it a good candidate for replacing PP/APP/PER intumescent formulation.

Starch can be also employed in flame retardant coating for textiles using the so-called layer by layer (LbL) technique. Carosio et al. [56] used a starch solution

as cationic electrolyte as well as carbon source and a solution containing poly (phosphoric acid) (PPA) was anionic electrolyte and acid source. 2 or 4 bilayers were deposited onto cotton fabrics of different densities. Despite the limited number of bilayers this FR system was likely to generate a strong charring that enables a self-extinguishing behavior. When exposed to the radiant heat of the cone calorimeter the total heat released by the FR fabrics was considerably reduced compared to the uncoated one.

Chitosan which is the deacetylated form of chitin, is another compound belonging to carbohydrates. Chitosan has raised a great interest in FR formulation during the last five years. The major part of papers dealing with chitosan is dedicated to the layer by layer (LbL) deposition technique. In acidic solution chitosan becomes a polycation, thus it may play the role of the positively charged layer. Chitosan was associated with various negatively charged layers. Carosio et al. [57] carried out the coating of PET-cotton fabrics using chitosan/APP bilayers that they compared with silica/APP bilayers. The LbL architectures was shown to enhance the overall flame retardancy of the fabric blend. The most significant result concerned the suppression of the afterglow phenomenon. This was associated with a significant increase of the residue after the test. Pursuing this work, Alongi et al. [58] used chitosan in bilayers (chitosan/APP) and quadlayers (chitosan/APP/silica/silica). Combination of bilayers was almost equivalent to quadlayers. The development of a coherent and homogeneous coating enables to slow down the thermal decomposition of the fabrics. The flame retardant mechanisms of APP/chitosan LbL assembly was studied in details by Jimenez et al. [59] when deposited on cotton fabrics. The LbL assembly promotes the formation of a protective char layer by dehydration of both chitosan and cotton. In the gas phase, the release of water tends to extinguish the flame while other volatiles favor a kind of “microintumescence” phenomenon. Hu’s team in Hefei developed various LbL assemblies involving chitosan to fireproof cotton fabrics. Hence chitosan was successively associated with phosphorylated cellulose (P-Cell) [60], phosphorylated chitin (P-Chit) [61], phosphorylated polyvinyl alcohol (P-PVA) [62], titanate nanotubes (TiNT) [63]. Generally speaking LbL assemblies tend to decrease the thermal stability of the fabrics except with titanate nanotubes (Fig. 2.13) but in return promote charring. The char yield increases with increasing bilayers and depends on the respective concentrations of the layers. Chitosan based coatings decrease the burning time of fabrics and suppress afterglow. pHRR and THR are significantly decreased (Fig. 2.14).

Chitosan based LbL assemblies were also used for the flame retardancy of polyurethane foams. Carosio et al. [64] developed a LbL chitosan/poly(allylamine diphosphonate) coating that was applied on an open cell PU foam. The coating enables preventing the melt dripping phenomenon while burning. It can also drastically reduce the heat release rate in cone calorimeter test. The assembly can efficiently hinder the foam structural collapsing during combustion. 2 bilayers were sufficient to reduce the pHRR by 48%. Pan et al. [65] realized by LbL method a fully biobased coating containing chitosan and lignosulfonate on the surface of flexible polyurethane foam. The main result concerns the reduction by 42% of the

Fig. 2.13 Temperature of the pHRR in PCFC versus char yield for cotton flame retarded by various LbL assemblies based on chitosan from [58, 60–63]

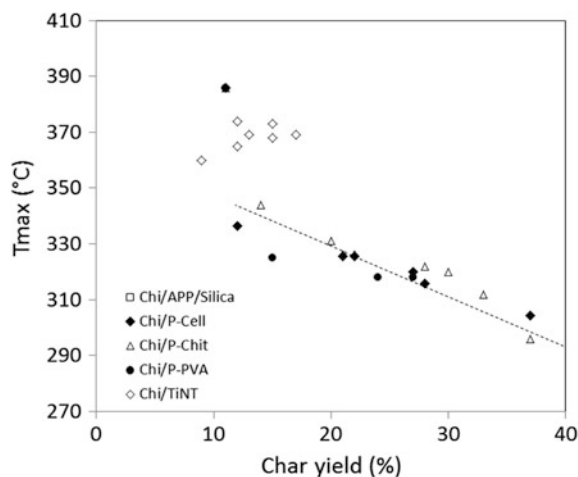
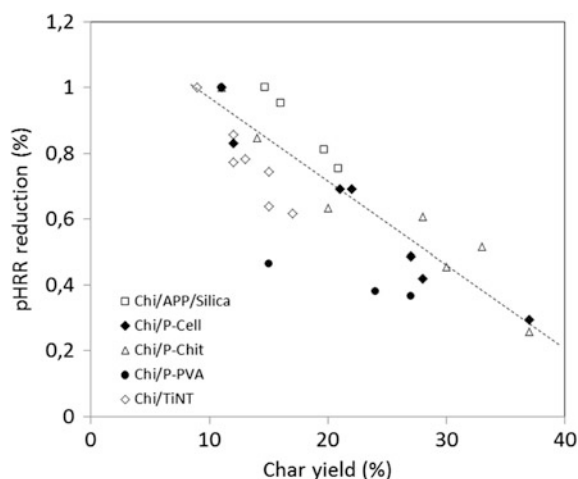


Fig. 2.14 Relative variation of pHRR versus char yield for cotton flame retarded by various LbL assemblies based on chitosan from [58, 60–63]



pHRR with 8 bilayers. Zhang et al. [66] used chitosan in combination with phytic acid in a polyelectrolyte complex (PEC) for the flame retardancy of ethylene vinyl acetate (EVA). Polyelectrolyte complexes differ from LbL assemblies in the sense that oppositely charged compounds are combined in a unique solution. After drying the PEC was incorporated in EVA at loading varying from 0 to 20 wt%. The presence of PEC enables increasing the char yield at high temperature. Furthermore, introduction of PEC leads to a reduction of the pHRR and THR measured by PCFC. Highly expanded and stable charred foam was formed generating an obvious barrier effect during combustion. By the same token Zhang et al. [67] prepared a PEC based on polyethylene imine and phytic acid for the flame retardancy of

polypropylene. At a 20 wt% loading this PEC allowed for a LOI of 25.1% and a decrease of pHRR and THR measured by PCFC.

With the aim to combine two strategies for flame retardancy, i.e. intumescence and use of nanoparticles, Alongi et al. [68] prepared a new flame retardant system containing a stable complex of cyclodextrin nanospices (NS) and a phosphorous compound. NS was synthesized from β -cyclodextrin a starch derivative. β -cyclodextrin units were crosslinked by an organic carbonate thus forming a porous structure including two types of cavities. Grinding of NS and phosphorous compounds enabled the phosphorous moieties to be entrapped either in internal cavities of cyclodextrin or in external cavities of NS. The resulting complex exhibits all features of an intumescent flame retardant system. Different phosphorous compounds were tested triethyl phosphate (TEP), triphenyl phosphate (TPP), ammonium polyphosphate (APP), dibasic ammonium phosphate (APb), diethyl phosphoramidate (PhEt). NS-P was incorporated in EVA and the fire properties were assessed. Regarding UL94 vertical test, NS-P confers a V-2 rating whatever its content and the source of phosphorus. In cone calorimeter test, NS-P enables a strong decrease of both pHRR and THR. Alongi et al. evaluated the interest of NS-P in other polymers, i.e. PP, LLDPE (linear low density polyethylene) and PA6. The results are contrasted depending on the matrix. Enescu et al. [69] compared the efficiency of β -cyclodextrin NS to that of other nanofillers such as montmorillonite (MMT), carbon nanotube (CNT) and zirconium dihydrogen phosphate in a PA6,6 matrix. Even if some improvements were noticed, NS was supplanted by MMT and CNT. Wang et al. [70] prepared an inclusion complex between β -cyclodextrin and poly(propylene glycol) that they used as carbon in intumescent flame retardant composed of APP and melamine. Once incorporated in PLA, this intumescent flame retardant revealed a good efficiency, increasing the LOI up to 34%, conferring V-0 rating and significantly decreasing pHRR and THR. Later on Wang et al. [71] proposed to use β -cyclodextrin to microencapsulate APP with the final goal to improve its resistance against water. Microencapsulation was achieved by using toluene-2,4 diisocyanate as crosslinking agent between β -cyclodextrin units. The microencapsulated APP was incorporated in EVA at 35 and 40 wt% loading. The samples were aged in distilled water at 70 °C during various periods of time. Cyclodextrin capsules were highlighted to increase the durability of APP since V-0 rating was retained after 96 h of ageing while the composite with non-protected APP was non-rated after 24 h of ageing.

Saponins are a class of biomolecules found in various plants that belong to amphiphilic glycosides. They arise from the condensation of a sugar and another functional group. In saponins sugars are bonded to cyclic triterpene. Recently tea saponin extracted from the nutshell of camelia was used as both blowing agent and carbon source in an intumescent flame retardant formulation [72]. Tea saponin was mixed with APP and pentaerythritol (PER) to give an intumescent flame retardant (IFR) that was thereafter blended with an alkyd varnish and deposited onto wood boards. During combustion an intumescent layer was formed that enabled a decrease of pHRR and THR measured by cone calorimeter. In the same manner tea saponin was associated to APP and melamine to form a new intumescent flame

retardant system for natural rubber [73]. This system was of interest because it enabled to combine both good fire properties and reinforced mechanical properties.

2.3.2.2 Phenolic Compounds

It was shown in a preceding section that lignin by itself can bring flame retardant properties to polymers. However some weak points e.g. low thermal stability, poor cohesion of char residue can be pointed out. That is why lignin has often been used in synergy with traditional flame retardant. De Chirico et al. [34] used lignin in combination with aluminum hydroxide (ATH), melamine phosphate, mono-ammonium phosphate and APP in a polypropylene (PP) matrix. These combinations led generally to increase the thermal degradation temperature, the combustion time and the char yield of PP, and decrease the rate of heat release and the weight loss rate during combustion. Réti et al. used lignin as substituent for pentaerythritol in APP based intumescent composition. PLA loaded with 30 wt% APP and 10 wt% lignin reached a V-0 rating at UL94 test instead of V-2 for the PER containing formulation. Nevertheless the APP/PER system remained more performant in cone calorimeter and LOI tests. More recently the same flame retardant system (APP/lignin) was utilized by Cayla et al. [74] for fireproofing PLA fabrics. An optimization of formulation was performed in order to obtain both good spinnability and satisfying fire properties. It was evidenced that 5 wt% of lignin and 5 wt% of APP were sufficient to obtain an efficient FR effect in PLA fabric.

Tannins are other polyphenolic compounds that may be of relevance for flame retardancy. However this is so far an almost unexplored area. Tondi et al. [75] used mimosa tannin extract combined with hexamine as hardener for the impregnation of wood. Boric acid and phosphoric acid were added as synergist in the tannin based solution. Fire behavior was assessed by exposure to the flame of Bunsen burner. It was highlighted that ignition of wood was strongly delayed after treatment. Very close results were obtained whatever the synergist used with tannin.

2.3.3 *Modified Bio-resources with Enhanced Charring Effect*

The preceding paragraph has shown that natural raw matter may advantageously be combined with phosphorus or nitrogen compounds to enhance charring. Following the same objective, many studies have been devoted to the chemical modification of bio-resources with the aim to build new all-in-one biobased flame retardant molecules. Among the possible chemical modification, phosphorylation was probably the most frequently investigated. Phosphorylation of biobased compounds was the subject of a review by Illy et al. [76] that described very completely all the

synthetic routes than can be used. Nevertheless other types of chemical modification may also be encountered.

2.3.3.1 Carbohydrates

Numerous works deal with phosphorylation of cellulose within the framework of textiles flame retardancy. However cellulose has rarely been modified with the specific aim to build a biobased flame retardant. In 2010 Aoki and Nishio [77] modified a cellulose ester derivative with various phosphoryl groups. Depending on the moiety, they observed a significant increase of the char yield at 700 °C under nitrogen atmosphere up to 29 wt% for diethylphosphoryl group. The phosphorylated cellulose derivatives were incorporated in polylactic acid (PLA) and polyethylene terephthalate (PET) and a V-2 ranking was obtained at the UL94 vertical test. Pan et al. [78] prepared a cellulose derivative containing both phosphorus and nitrogen. Firstly the microcrystalline cellulose (MCC) was phosphorylated by phosphorous acid in molten urea and then the phosphorylated cellulose was reacted with ammonia water to obtain the final product (CPA). The biobased flame retardant was incorporated into polyvinyl alcohol (PVA) at contents varying from 0 to 15 wt%. The presence of CPA lowered the thermal stability of composites and the early emission of phosphoric acid favored dehydration of cellulose at the expense of depolymerization. Thus, the char yield was enhanced up to 19.4 wt% for the highest loading. Microcalorimetry of combustion revealed that pHRR as well as THR were reduced. At 15 wt% loading PCA enabled PVA to obtain V-0 rating at UL94 test and LOI of 30%. More recently Costes et al. [79] prepared a phosphorylated MCC using the same procedure than Pan et al. This modified cellulose was introduced at 20 wt% loading for PLA fireproofing. Despite a V-0 ranking at vertical burning test, the cone calorimeter quantities (pHRR and THR) were only slightly reduced. Thereafter the authors decided to substitute a part of phosphorylated MCC by aluminum phytate a derivative of the biobased phytic acid. This time the results were much more convincing. It was assigned to the charring effect of aluminum phytate that leads to the fast formation of the charred layer. Phosphorylated cellulose can also be combined with other biobased compounds via the layer by layer (LbL) process. Pan et al. [60] proposed a LbL assembly composed of chitosan as polycation and phosphorylated cellulose as polyanion. The ionic character was given by adjusting the pH of the solutions. This LbL assembly was used for the fireproofing of cotton fabrics. It was noticed that the char yield depended on the proportion of the two components and the number of bilayers. When coated with 20 bilayers the cotton fabrics was self-extinguishing and the pHRR and THR measured by PCFC were drastically reduced. A similar study was done by substituting phosphorylated cellulose by phosphorylated chitin (another carbohydrate) [61]. In both cases, the high fire performance was attributed to the insulating properties of the phosphorus containing char formed at the cotton surface. Among the various ways to achieve cellulose phosphorylation, one is of particular interest within the frame of green chemistry. Božič et al. [80] studied the

enzyme-mediated phosphorylation of cellulose nanofibers (CNF) by using hexokinase and adenosine-50-triphosphate in the presence of Mg-ions. Depending on the operating conditions, up to 8.8 wt% of phosphorus may be added to cellulose. In this latter case the char residue of phosphorylated CNF is circa 57 wt% at 600 °C which is remarkable. This offers potential applications for cellulose modified by enzymatic means to be used as flame retardant.

Hu and his coworkers carried out several studies involving modified chitosan. The first step of all modifications consisted in the esterification of chitosan by phosphorous pentoxide (P_2O_5). In a second step different modifications of the phosphorylated chitosan (PCS) were envisaged. In a first paper PCS was reacted with nickel nitrate hexahydrate to give a nickel chitosan phosphate (NiPCS) [83]. In a second article a urea salt of chitosan phosphate was prepared (UPCS) [82]. In a third article a melamine salt of chitosan phosphate was synthesized (MPCS) [81]. Finally in a last paper, PCS was reacted with glycidyl methacrylate to obtain a chitosan phosphate acrylate (GPCS) [84]. In the first three studies the chitosan based flame retardants were incorporated in PVA while in the last case, the chitosan phosphate methacrylate was used in an epoxy acrylate resin. Whatever the system, the conclusions were roughly the same. The presence of the phosphorous moieties accelerates the dehydration of chitosan and therefore promotes charring (Fig. 2.15). The char yield were significantly increased while the quantities (pHRR and THR) measured by micro-calorimetry of combustion were decreased (Fig. 2.16).

Howell et al. [85, 86] investigated the potential of low cost by-products from the wine industry as raw materials for flame retardant. Hence tartaric acid was converted into its diethyl ester form. The phosphorylation of diethyl tartrate was then achieved using diphenyl phosphinic chloride. The resulting diethyl 2,3-diphenylphosphinato-1,4-butanedioate may be used as flame retardant since its thermal decomposition is likely to liberate diphenylphosphinic acid to promote char formation, at the combustion temperature of several common polymers.

Fig. 2.15 Char yield versus phosphorus content for PVA and EA flame retarded by various phosphorylated chitosan from [81–84]

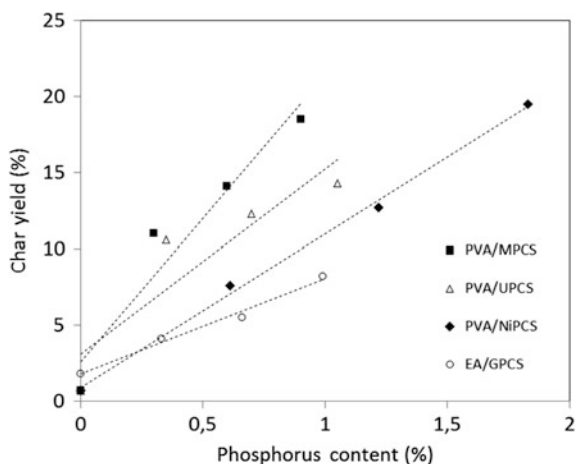
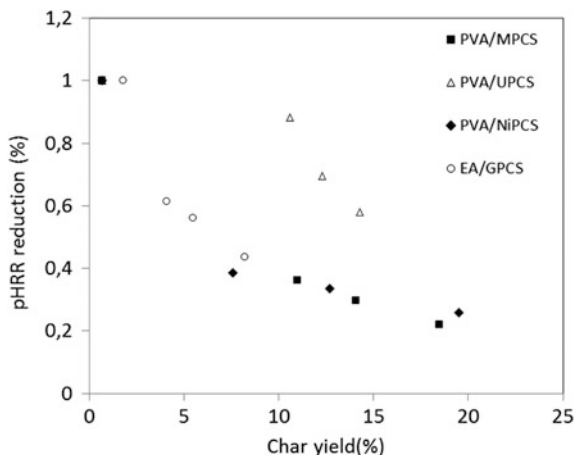


Fig. 2.16 Relative variation of pHRR versus char yield for PVA flame retarded by various phosphorylated chitosan from [81–84]



Howell and Daniel [87] also investigated the thermal degradation of a series of phosphorus esters derived from a diol generated by the esterification of isosorbide (from starch) with 10-undecenoic acid (from castor oil) followed by thiol-ene reaction with 2-hydroxyethanethiol. The diol could thereafter be converted to phosphorus esters either by treatment with phosphoryl chloride in the presence of an acid acceptor or by treatment with a phosphite in carbon tetrachloride. It was evidenced that the thermal stability of the esters was extremely dependent on their chain ends. The diethyl phosphate-terminated ester exhibits a very low degradation onset while the DOPO-terminated ester was very stable (DOPO: 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide). The char yield was also dependent on the structure and with regard to this parameter the diphenyl phosphate terminated-ester was the most performant. Isosorbide was also used by Mauldin et al. [88] to prepare biobased flame retardant system. In this work, a polyphosphonate was synthesized by melt condensation polymerization of isosorbide and a phosphonic dichloride. This polyphosphonate was then blended with PLA at loadings varying from 0 to 15 wt%. The authors showed that the isosorbide derived flame retardant enables to reach the V-0 rating at UL94 test although no major change was observed by cone calorimetry.

As mentioned previously, alginates are a class of carbohydrates that can be extracted from algae. Most of them are water soluble and thus can be used as hydrogel or as film after casting process. Sodium alginate is the common form of alginic acid salt obtained after extraction. It is likely to form a large amount of char at high temperature (between 20 to 25 wt%). Several works evidenced that the thermal and flammability properties of alginate may be improved by exchanging the sodium cation by other cations like calcium, barium, copper or zinc [89–91]. As an example Liu et al. [92] prepared barium alginate films by a facile ion exchange route. It was highlighted that barium alginate film exhibits very high LOI value (52.0%) compared to sodium alginate film (24.5%). The biobased film obtained the V-0 rating at UL-94 test, while the sodium alginate film was not rated.

Moreover PCFC tests revealed a strong decrease of pHRR for barium alginate film. It is suggested that the barium ion considerably modified the degradation pathway of alginate by catalytic effect that promotes the formation of more stable products.

Phytic acid or phytates are the phosphorous containing biomolecules naturally found in plant tissues. Sodium phytate is the most common commercial form of phytates. Costes et al. [93] investigated the flame retardant effect of various metallic phytates in PLA. Following an approach close to that above-described for alginates the authors have substituted the sodium cation by aluminum, iron and lanthanum cations using a solubilization/precipitation procedure. Metallic phytates were incorporated in PLA at loading varying from 0 to 30 wt%. Blends of phytates were also tested. Phytates were shown to promote the rapid formation of a charred layer during combustion. This layer induced a significant reduction of pHRR. The best results were obtained with aluminum phytate. Unfortunately this compound was proved to be responsible for the degradation of PLA during melt processing. A solution to this issue was found by combining two phytates.

2.3.3.2 Phenolic Compounds

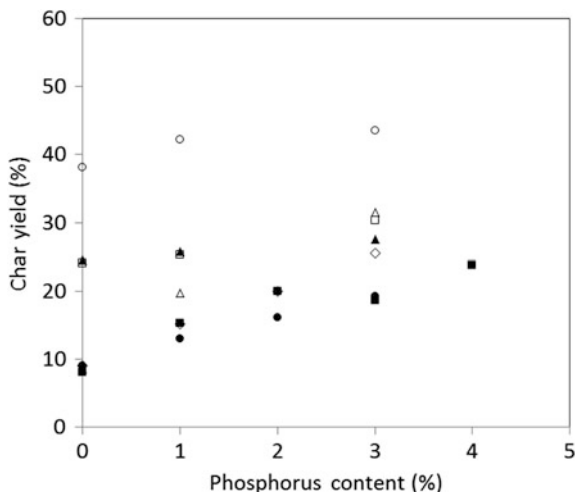
Lignin was highlighted to be interesting raw material for biobased flame retardant since it is a low cost and intrinsically high charring product. Hence many attempts were made to modify polyaromatic biomolecule with the aim to enhance its fire-proofing efficiency. In 2012 Yu et al. [94] performed the grafting of a phosphorus-nitrogen compound onto lignin. The first step of the modification consists in the hydroxymethylation of lignin using formaldehyde. The hydroxymethylated lignin was then reacted with a phosphoryl dichloride imidazole to obtain PN-lignin. This modified lignin was incorporated into polypropylene at loading up to 30 wt%. An increase of both the thermal stability and the char yield was proved by thermogravimetric analysis. In the cone calorimeter test, the increase of the residue was associated to a decrease of pHRR and THR. The better fire performance of PN-lignin compared to unmodified lignin was assigned to the quality of the charred layer that was shown to be more continuous and compact. Ferry et al. [36] studied the grafting of different molecular or macromolecular phosphorous compounds onto kraft lignin. Thus dihydrogen ammonium phosphate, a homopolymer of (methacryloyloxy) methyl phosphonic acid and a copolymer of (methacryloyloxy) methyl phosphonic acid and methyl methacrylate were used as grafting agents. The grafted lignin was blended with polybutylene succinate (PBS) at content varying from 0 to 20 wt%. The modification of lignin did not impart enhancement of char yield. Nevertheless slight improvement in cone calorimeter quantities (pHRR and MAHRE) was observed. As did Yu et al., this was attributed to the higher quality of the char layer which was more homogeneous and cohesive. A simple route to achieve the phosphorylation of lignin was proposed by Prieur et al. [95]. Lignin was reacted with phosphorous pentoxide (P_2O_5) in tetrahydrofuran (THF). The phosphorylated lignin (P-Lig) was incorporated in Acrylonitrile Butadiene Styrene (ABS) at 30 wt% loading. The phosphorus content

in P-Lig was measured to be 4.1 wt%. P-Lig induced a huge increase of char yield which was as high as 55 wt%. In cone calorimeter test, despite a decrease of time-to-ignition, the results were satisfying with a decrease of pHRR and THR stronger than with pure lignin. More recently Costes et al. [37] studied a two-step phosphorus/nitrogen chemical modification of lignin to enhance the fire behavior of PLA. This approach was applied to both kraft and organosolv lignins. The modified lignin was blended with PLA at a 20 wt% loading. Thermal analysis revealed that modified lignin increases the temperature of the maximum mass loss rate. However the char yield was lower than that obtained with unmodified lignin. The modified lignins were proved to be highly effective to reduce the flammability of PLA composites and V-0 rating was reached at UL-94 test. The most interesting result was probably the fact that phosphorus-nitrogen grafting enables to counterbalance the thermal destabilization generally induced by lignin and to maintain a high time-to-ignition. Liu et al. [96, 97] performed the modification of lignin using polyethyleneimine (PEI) diethyl phosphite and metal acetate. This enables binding phosphorus and nitrogen atoms as well as metallic cations (Zn^{2+} or Cu^{2+}) to lignin. The functionalized lignin was used either in PBS at loading varying from 0 to 10 wt % or in PP/wood composite at content up to 15 wt%. The results were much probative in PBS with a large increase of char yield and decrease of pHRR and THR. Metal cations were supposed to catalyze the carbonization of polymer and lignin leading to higher residue and better flame retardancy.

Phosphorylation is not the only pathway for conferring to lignin enhanced flame retardant properties. Zhang et al. [98] prepared a urea-modified lignin (UM-Lig) according to the Mannich reaction. This nitrogen containing lignin was combined with ammonium polyphosphate (APP) and used as a novel intumescent flame-retardant for PLA. Depending on the proportion between APP and UM-Lig it was possible to reach V-0 rating in vertical burning test and a LOI of 34.5%. pHRR and THR were drastically reduced due to the formation of a thick intumescent char that represents up to 35% of the initial sample mass. A second strategy tested by Zhang et al. consists in preparing a lignin-silica hybrid (LSH) by the sol-gel method [99]. Combined with APP, LSH gives a very performant intumescent flame retardant system for PLA that leads to effects very similar to those obtained with UM-Lig.

Apart from lignin other natural phenolic compounds may be used to prepared flame retardant additives. In 2002 Marosi et al. [100] demonstrated the possibility to achieve phosphorylation or phosphinylation of phloroglucinol and hydroquinone, two biobased hydroxyphenols. Phosphorylation involved the reaction with chlorophosphates while phosphinylation implies phosphinyl chloride. Later Vothi et al. [101] achieved the phosphorylation of phloroglucinol and resorcinol by various chlorophosphates. The obtained cyclic phosphates were introduced at 30 wt % loading in ABS and 5 wt% loading in polycarbonate (PC). The phosphorous flame retardant promotes polymer charring. The best results were obtained with the phloroglucinol triphenyl phosphate with a V-0 rating when used at only 3 wt% in PC. More recently Ménard et al. [102] synthesized various phloroglucinol phosphates according to a protocol similar to that of Vothi et al. These biobased flame

Fig. 2.17 Char yield versus phosphorus content for epoxy resins flame retarded by additive or reactive flame retardant based phosphorus modified phloroglucinol from [102–104], ■ DGEBA-IPDA-P3P(OEt), △ DGEBA-IPDA-P2EP1P, ● DGEBA-IPDA-P3SP, ◇ DGEBA-IPDA-P2EP1SP, □ P3EP-IPDA-P2EP1P, ▲ P3EP-DA10-P2EP1P, ○ P3EP-DIFFA-P2EP1P



retardants were introduced in an epoxy resin (bisphenol A diglycidyl ether/isophorone diamine hereinafter DGEBA/IPDA) and the global phosphorus content was varied between 0 and 3 wt%. Whatever the molecule the char yield was shown to increase with increasing phosphorus content (Fig. 2.17).

In cone calorimeter test a spectacular decrease of pHRR and THR was observed with the phloroglucinol diethyl phosphate (P3P(OEt)). This was associated with a huge expansion of the char residue during the combustion forming a highly thermally insulating layer at the sample surface. Ménard et al. [104] prepared also phosphonate flame retardant from phloroglucinol. The synthesis consists firstly in the glycidylation of phloroglucinol and secondly in the reaction of epoxydized phloroglucinol with diethyl(3-mercaptopropyl) phosphonate. The interest of the study lies in the comparison of additive (P3SP) and reactive (P2EP1SP) flame retardants with similar structure. It was concluded that both approaches are very efficient in reducing pHRR and THR (Fig. 2.18). The reactive flame retardant was shown to enable a higher charring effect and a higher intumescence.

2.3.4 Reactive Biobased Flame Retardants

There are various motivations to use reactive rather than additive flame retardants. In their review about the effects of ageing on the fire behavior of flame retarded polymers Vahabi et al. [105] mentioned several situations where ageing induces migration of the flame retardant additive out of the polymer matrix onto the sample surface. The so-called blooming or exudation mechanism may be due to the low solubility and/or the small size of the additive and results generally in a decrease of the fire performance. Therefore, a way to counteract this effect consists in inserting

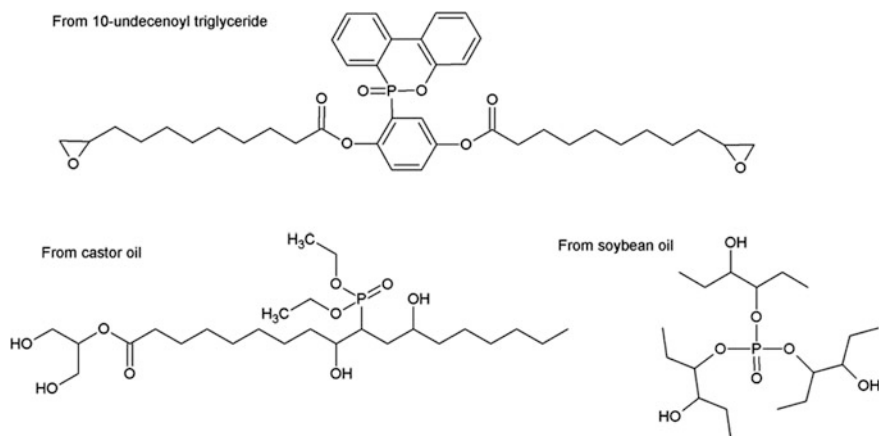


Fig. 2.19 Oil-based reactive flame retardants

monomer was synthesized from the ω -unsaturated fatty acid derivative and from a DOPO derivative [108]. The presence of phosphorus moieties enabled to increase the char residue (at 800 °C) up to 18 wt% for 5.7 wt% phosphorus content. Flammability was significantly improved and a tight correlation was evidenced between LOI and the phosphorus content into the epoxy resin [109].

Heinen et al. [110] developed oil-based rigid polyurethanes with enhanced fire properties. In order to obtain phosphorylated polyols (Fig. 2.19), an epoxidized soybean oil was reacted with phosphoric acid. Polyurethane foams were then prepared by reacting the above-mentioned polyols (after neutralization with triethanolamine) with polymeric diphenylmethane diisocyanate (MDI) while pentane was used as blowing agent. Light foams with homogeneous cell size distribution were obtained. LOI was shown to increase with increasing phosphorus content in the foam. The best performance measured with reactive biobased monomer was comparable to that obtained with a commercial phosphorous flame retardant. It was evidenced that the fireproofing action took place mainly in the condensed phase by increasing the char residue. An approach similar to that of Heinen et al. was used by Zhang et al. [111] to obtain flame retarded polyurethane foams. This time castor oil was used as raw matter. It was alcoholized with glycerol (GCO) and then epoxidized to obtain a polyol that was further reacted with diethyl phosphate (see Fig. 2.19). The resulting phosphorylated polyol (COFPL) was mixed with GCO and reacted to methylene diphenyl 4,4'-diisocyanate to form a rigid polyurethane foam containing various amount of phosphorus. It was highlighted that LOI increases with increasing phosphorus content up to 24.5 wt% when COPFL was used as unique polyol. The cone calorimeter test revealed that the phosphorylated polyol enabled a slight decrease of pHRR and more particularly a significant decrease of THR that was attributed to the promotion of a thick and compact char.

2.3.4.2 Bio-phenol Derivatives

Bio-phenolic compounds have been used for a long time to obtain reactive monomers. In 1990, Pillai et al. [112] mentioned the simultaneous phosphorylation and oligomerization of cardanol to prepare flame retardant prepolymers. Cardanol is a phenolic lipid that comes from anacardic acid which is contained in cashew nutshell liquid. Phosphorylated cardanol was obtained by reaction between cardanol and orthophosphoric acid at 175 °C under vacuum. Oligomeric species were formed (Fig. 2.20). The phosphorylated cardanol prepolymer (PCP) was then cured with formaldehyde to obtain a Novolac type resin. The PCP containing resin was shown to exhibit a LOI of 33% compared to only 21% for the cardanol based resin. Later on, Menard et al. prepared phosphorus containing biobased epoxy using phloroglucinol as raw matter. Phloroglucinol is a benzenetriol that occurs naturally in certain plants e.g. in the bark of fruit trees, it can be also produced by brown algae or bacteria. In a first step epoxydization of phloroglucinol was achieved by reaction with epichlorhydrin. It leads to the triglycidyl phloroglucinol (P3EP) that can be further used as epoxy monomer. In a second step P3EP was reacted with triethyl phosphite with zinc chloride as catalyst to obtain the diglycidyl mono-phosphonated phloroglucinol P2EP1P (see Fig. 2.20) which can be considered as a reactive phosphorous flame retardant [103]. Another method consists in reacting P3EP with the diethyl(3-mercaptopropyl)phosphonate to obtain the diglycidyl thiophosphonated phloroglucinol which is a sulfur and phosphorus containing reactive flame retardant [104]. The two reactive monomers were used for fireproofing a DGEBA/IPDA epoxy resin. In both cases it was shown that the use of reactive flame retardants induces a strong increase of char residue that was almost proportional to the phosphorus content in the resin (Fig. 2.17). Moreover, a huge

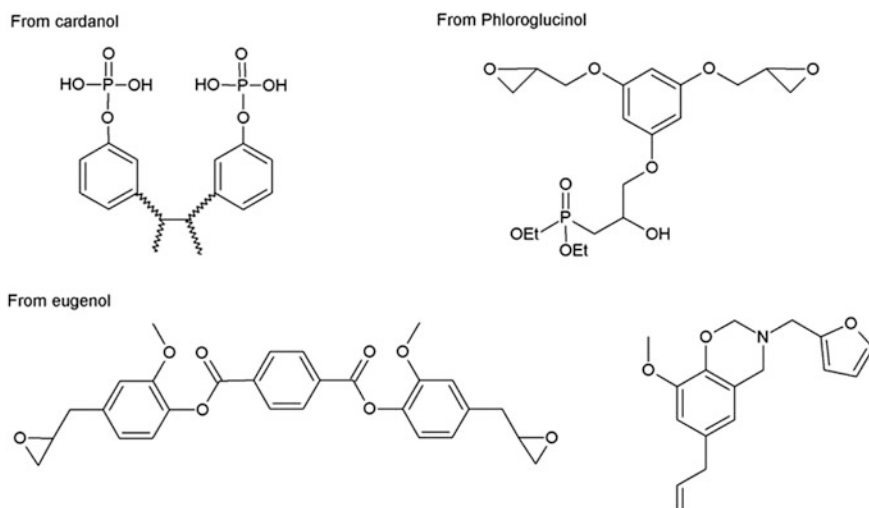


Fig. 2.20 Biophenol-based reactive flame retardants

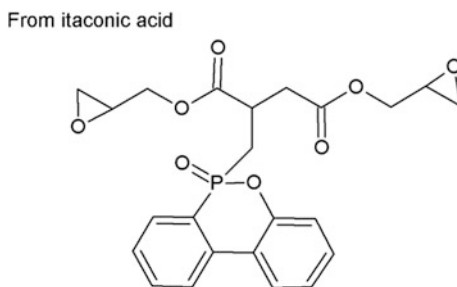
intumescent effect was highlighted. This results not only in a decrease of pHRR (Fig. 2.18) but also in a reduction of THR. By combining P3EP as epoxy monomer, P2EP1P as reactive flame retardant and difurfurylamine a commercial biobased diamine the authors succeeded in preparing a fully biobased flame retarded epoxy resin.

Eugenol is another biophenol naturally found in cloves that has been used as raw matter for developing reactive flame retardant. Eugenol was reacted with terephthaloyl chloride to obtain a diene intermediate [113]. Thereafter this diene was epoxidized by reaction with a peracid. Thus an aromatic-ester type eugenol based epoxy monomer was obtained (Fig. 2.20). This monomer was formulated in a DGEBA-DDS resin. It was highlighted that the eugenol based monomer enables an increase of LOI from 23.5 to 26.8. Moreover, it provokes the rapid extinguishment of flame in a vertical burning test. In cone calorimeter test, despite a lower time-to-ignition, the eugenol monomer allows a decrease of pHRR as well as THR. This set of performance was ascribed to the ability of the aromatic monomer to promote a char layer that acts as protective shield during fire tests. Eugenol was also used by Thirukumaran et al. [114] as raw material to synthesize benzoxazine monomers. In this case eugenol was first reacted with furfurylamine (Fig. 2.20) or stearylamine and then polymerized or copolymerized by ring opening polymerization. The resulting polymers were evidenced to exhibit very high char yield (up to 53.8 wt%) and very high LOI (up to 39%) depending on the comonomer content. The two latter examples show that fire properties may be enhanced by the introduction of aromatic monomer in their structure without addition of active elements like phosphorus or nitrogen.

2.3.4.3 Carbohydrate Derivatives

Ma et al. [115] used itaconic acid produced by fermentation of carbohydrates to synthesize phosphorus containing monomers with flame retardant activities. In a first step itaconic acid was reacted with DOPO in xylene at 120 °C to obtain DOPO containing itaconic acid (DI). In a second step two synthetic routes were envisaged to achieve the glycidylation of DI. Hence a DOPO containing monomer (EADI) with two epoxy functions was obtained (Fig. 2.21). This reactive flame retardant

Fig. 2.21 Carbohydrate derivative based reactive flame retardant



was incorporated in an epoxy/anhydride resin. The fire behavior was assessed through UL94 vertical burning test and LOI. Even if the V-0 rating was not reached, the self-extinguishing time was considerably reduced as the phosphorus content increases. LOI increases from 19.6 to 31.4% as phosphorus increases from 0 to 2 wt%. When DGEBA monomer was completely replaced by EADI, the fire behavior was less performant. In this latter case, EADI strongly decreases the thermal stability of the resin that was not counterbalanced by the increase of char yield. In 2013, Kim et al. [15] used directly the alginic acid as polyol to react with 2,4-toluene di-isocyanate (TDI) for the synthesis of a polyurethane. Even if no fire properties were assessed, the thermal analysis of this alginate polyurethane hybrid reveals slow degradation kinetics and a high amount of residue at high temperature (circa 30 wt%) that seems promising with regard to flame retardancy.

2.4 Opportunities for the Industrial Scale-up of Biobased FR Systems

The preceding section has highlighted that a great number of research works has been carried out for the last few years to develop and assess new biobased flame retardants. Many biomolecules and green processes are available and each application is likely to find an appropriate fireproofing solution. Obviously, all the solutions studied for research purpose will not be scaled up and produced at industrial level. It is difficult to predict among the different proposals what products could be a success story in the coming years. However it seems that three main criteria could be considered: technical performance, health and environmental impact and economic efficiency.

2.4.1 Fire Performance Criteria

The first criterion to be considered is the fire performance. Do the new biobased flame retardants enable to fulfill the specifications of the fire regulation? In most of the scientific papers previously mentioned, four main types of tests have been carried out to characterize flammability properties: LOI, UL94, cone calorimeter and micro-calorimeter of combustion. The main parameters that can be extracted from these tests refer to ignitability, burning rate, char yield and self-extinguishing. It is complex to compare the various flame retardant systems because they are often implemented in different polymers, according to different processes and assessed by different tests. However some broad lines may be drawn up. As it was previously explained, the main strategy envisaged when using biobased compounds is the so-called barrier effect that is achieved through the promotion of a charred layer. Therefore the char yield is a key element of comparison. Char yield depends not

only on the additive content but also on the presence of active element such as phosphorus in the formulation. Figures 2.15 and 2.17 show that char yield increases almost linearly with increasing phosphorus content in the material. Nevertheless the slope of the curve depends on the molecule bearing the phosphorus atoms and on the host matrix. Charring was generally related to lower pHRR and THR. Whatever the flame retardant and whatever the polymer, a linear decrease of pHRR with increasing char yield was evidenced as revealed by Figs. 2.11, 2.14, 2.16 and 2.18. A counterpart of charring is often an increase of ignitability that results in a decrease of the onset of degradation (Fig. 2.13) and a decrease of the time-to ignition (TTI). In the case of biobased intrinsic flame retardant Fig. 2.12 shows that TTI tends to decrease with increasing content of additive. However some points were out of this trend. In the case of chitosan based LbL assemblies, it was highlighted in Fig. 2.14 that the temperature of degradation decreases with increasing char yield, i.e. with increasing additive content. Succeeding in decreasing the ignitability of polymers containing biobased flame retardant is very challenging for the coming years.

Apart fire performance, it is also important to check that the new biobased flame retardants do not impinge upon processability and other functional properties of polymers (e.g. mechanical properties, ageing resistance...).

2.4.2 *Environmental and Health Criteria*

For the last ten years some of the most widespread flame retardants have been phased out due to health and environmental issues. Some of the so-called halogenated compounds were proved to be bio-accumulative, some of them are considered to be endocrine disruptors, neurotoxic and carcinogenic. The development of new biobased flame retardants must of course avoid falling back into these issues. This is the objective of the REACH regulation and the role of the European Chemical Agency (ECHA) to promote the protection of human health and environment. Natural product does not mean safe product. Most of the biobased compounds mentioned in this review are harmless. However innocuousness must always be checked. As an example, some naturally found biophenols like catechol or hydroquinone may exhibited some toxicity [116]. Beside the intrinsic health and environmental properties of products, all the precepts of green chemistry must be favored when synthesizing new biobased flame retardants and a life cycle assessment approach should be used to determine the effective impact of these products.

2.4.3 *Economic Criteria*

Last but not least, economic criteria are probably those which could definitely impede the development of biobased flame retardants. A universal panacea would be low cost raw matter and low cost processes. With regard to the raw matters that

were developed in this chapter, the most promising are probably the ones that derived from well-established industries. For example the wood industry supplies various biomolecules such as cellulose, lignin, lignosulfonate, vanillin that are of great interest for flame retardancy as described previously. Lignin can also be extracted from different other plants, especially in by-products. The world annual production of lignin is estimated to be higher than 50 million tons. Chitosan is another biomolecules presenting positive outlooks. There is a growing interest for crustacean shell-derived chitin and chitosan in biomedicine, nutrition and food processing. The global market for chitosan was estimated to be 21.4 thousand metric tons in 2015. A major issue impacting the chitosan is its high production cost. Nevertheless flame retardancy may take benefit of this growing market to constitute a new application of chitosan.

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