

Fire retardant recyclable and bio-based polymer composites

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Abstract:

In this chapter, flame retardancy of recyclable and bio-based polymer composites is reviewed. Synthesis routes to obtain thermosetting bio-based polymer matrices are discussed and environmentally friendly flame retardancy solutions are proposed. Fire retardancy of thermoplastic biomatrices and fully recyclable self-reinforced composites made thereof are summarized. New methods to characterize the flame retardant biocomposites and understand their thermal degradation and flame retardant mechanisms are presented. After reviewing the chemical treatments to flame retard natural fibres, flame retardancy results of thermosetting and thermoplastic biocomposites are discussed. Green solutions utilizing synergistic effects, multifunctionality and integrated approaches are highlighted. Finally, application possibilities, future trends in the field of flame retarded biocomposites are indicated.

Keywords:

bio-based polymers, natural fibres, fibre treatment, biocomposites, self-reinforced composites, flame retardancy, phosphorus-based flame retardants, biodegradation, recycling

1. Introduction

There is a continuous increase in consumption of polymeric composites in growing range of application fields, which is mainly due to their prominent strength/weight ratio, corrosion resistance and low cost. From the enormous amount of the annually produced fibre reinforced polymeric composites about 35-40% is made of thermoplastics, generally reinforced by glass, carbon or natural fibres, while the rest is made of high-tech carbon or glass fibre reinforced thermosets, mainly applied in the transportation and E&E industries. Besides the indisputable advantages, however, the use of such multi-component polymeric composites is accompanied with several serious environmental, sustainability and safety issues:

- (1) The petrol-based polymer production contributes to the depletion of fossil fuel reserves.
- (2) The use of dissimilar materials in the reinforced composites largely encumbers their reprocessing and recycling. Enormous amount of end-of-life plastic (ELP) waste is being generated, the current treatment of which, due to the low volume/weight ratio and shortage of recycling, greatly burdens the landfills.
- (3) Extensive statistical researches show [1,2] that the number and danger of fire risk scenarios has been dramatically increased with the expansion of plastic usage endangering our everyday life.

Therefore, the industries will be forced by the increasingly strict environmental-focused legislation to replace their conventional (e.g. glass fibre reinforced) polymer composites by more environmental-friendly alternatives; the use of recyclable or biodegradable polymeric materials is urged. Therefore, developments toward recyclable and biodegradable polymer composites with good mechanical properties and a low environmental impact are nowadays extensively examined by researchers.

Depleting mineral oil sources initiated increasing environmental awareness and legislations aiming at fostering the use of renewable resources, which in turn is reflected in rapidly increasing need for bio-based polymers. The tendency towards replacement of mineral oil based polymers by bio-based ones has emerged also in polymer composite industry. By definition, bio-based composites are those composites, in which at least one of the components is originating from biological products issued from biomass [3]. This means that polymer composites, in which either the matrix or the reinforcement is bio-based can be already considered as bio-based. It is essential to distinguish these “partial bio-based” materials from the “completely bio-based” or “all-bio” composites. Bio-based polymer composites are not necessarily environmentally friendly, nor biodegradable. Thus the assignment of the environmentally friendly label can be done only on the base of a life cycle assessment, and not on the base of origin. Similarly, the ability of being degraded by biological activity depends not on the origin, but rather on the chemical structure. In case of polymer products the end of the use must be predictable, providing structural and functional stability during their entire service time, which requires controlled degradation even by biological activity. As the biodegradable feature is only relevant in case of all-bio composites, other end of life options have to be considered as well. Besides reuse and energy recovery, recycling should be addressed [4]. Obviously, composites with bio-based matrices and having similar structure to conventional mineral oil based ones, can be recycled the same way as the latter ones. The recycling routes greatly depend on the type of the polymer matrix (thermoplastic or thermosetting), as well as the type of the applied reinforcement (bio-based or conventional glass, carbon, etc. fibre reinforcement). From this point of view a special attention has to be paid to self-reinforced composites, where both the thermoplastic matrix and the thermoplastic reinforcement can be recycled in a single step, moreover, if prepared from a biodegradable matrix, they can be biodegraded at the end of their service time or after

several recycling loops. In case of polylactic acid, besides mechanical recycling, polymer feedstock recycling is also possible, as the polymer can be hydrolysed to lactic acid. Thermosetting bio-based composites require other recycling methods: if only the polymer matrix is bio-based, the conventional routes as mechanical and thermal (with energy and/or material recovery) recycling are available [5]. In case of natural fibre reinforcement the recovery of the fibres is not possible by thermal processes; however composites made from biofibres can be completely burnt, which is a clear advantage over conventional glass or carbon fibres. Furthermore, the use of biofibres offers the advantage of becoming fully biodegradable by combining natural fibres with a biodegradable thermosetting polymer matrix.

The main deficiency of these bio-based composites, similarly to mineral oil based ones, is their flammability during their use. In order to meet the strict safety requirements of more demanding sectors as automotive and aircraft industries, their flame retardant (FR) properties have to be improved by maintaining other important characteristics as mechanical and thermal properties, and also considering environmental issues as risks for human life and environment, waste treatment and recycling. The application of halogenated components is a highly effective method for the preparation of flame retarded systems. However, the increasing focus on health and environmental compatibility of flame retardants has resulted in a steady decline in the acceptance of such products. The sustainable development concept applied to this field implies that fire retardants should involve a low impact on health and environment during the entire life cycle including recycling and disposal. According to the directives of the European Parliament from July 2006 the most used halogenated flame retardants are banned from the market [6]. Considering the above mentioned drawbacks substantial amount of research and development has been focused on the replacement of these halogen-containing flame retardants by halogen-free products e.g. by phosphorus-containing

flame retardants (PFRs). Phosphorus, depending on the molecular structure of the flame retardant, can act both in gas phase, mainly at the beginning of degradation, and later in solid phase, providing advantageous FR effect for biopolymers by this combined mechanism. Environmental studies were carried out recently on additive-type PFRs [7]. The reactive-type FRs, being bonded to macromolecules, have probably no adverse effect. These do not migrate to the matrix surface either during high temperature processing or application and less FR, compared to the additive approach, is needed to achieve same level of flame retardancy, which in turn leads to reduction of toxic gas emission. Furthermore, reactive FRs can be cost-effectively integrated in the production process.

In the case of biocomposites, the use of natural reinforcement is an obvious solution. The natural fibre reinforcement represents a green and suitable alternative to the glass and carbon fibres (which are produced with high energy consumption) in several fields of application; however, their flammability represents a major drawback. In order to decrease their flammability, flame-retardant fibre treatments have to be applied, in such a way, that the achieved flame retardant properties do not entail with the decrease of the fibre–matrix adhesion and of the mechanical properties of the composites.

2. Flame retardancy of fully recyclable self-reinforced composites

The so-called self-reinforced composites represent an environmentally very favourable option for production of biocomposites [8,9]. The reinforcing fibres in such systems are made from the same polymer type as the matrix material. The preparation of well-designed self-reinforced composites (SRCs) is one possible way to improve the mechanical properties of polymers without any limitation regarding recycling. In the literature, there are several contributions reporting a comparison of conventional glass fibre reinforced (GF) and SR composites [10,11,12,13,14] revealing that besides recyclability the most important

advantages of SRCs are the achievable high strength and impact resistance, the excellent viscoelasticity and the potential of weight reduction, thus the SR composites represent increasing application potential. It is claimed that in automotives 20-30% reduction in weight can be achieved by using SRC parts (from PE, PP, PET, etc.) instead of conventional glass fibre reinforced parts of comparable mechanical properties [15].

The importance of flame retardancy of these inherently highly flammable all-polymeric composites, especially in technical application fields, is indisputable. As polymer fibres are difficult to flame retard effectively [16], flame retardant modifications have been performed only in the embedding matrix materials so far. Bocz et al. investigated the use of intumescent flame retardant (IFR) system in the matrix layers of all-polypropylene composites and revealed a new synergism, namely the beneficial physical cooperation between the expansion of the intumescent flame retardant system and the shrinking of the reinforcing polymer tapes. As a result, UL-94 V-0 rating was achieved at IFR loading as low as 9 wt%, less than half amount of the additives needed in non-reinforced polypropylene blends [17]. Based on comprehensive analyses, performed in order to study the ignitability, char forming process, burning behaviour and postcombustion remains of flame retarded SRCs, important conclusions were drawn for better understanding of the phenomenon behind the outstanding flame retardant efficiency. They found that the significant shrinkage, exhibited by the highly-stretched reinforcing PP tapes when exposed to heat, is the key factor behind the self-extinguishing behaviour of the flame retarded SRCs with surprisingly low additive content. As a consequence of the shrinkage, which was fairly noticeable both during horizontal and vertical ignition (see in Figure 2.1), the elongation of the molten specimens, and thus the formation of virgin polymer surfaces, is hindered. In this case, the forming compact charred surface acts as a barrier of increased efficiency against heat and fuel transport resulting in immediate fire extinction. In a cone calorimeter, where the composites are exposed

perpendicularly to heat flux, further effects of the embedded PP tapes were confirmed. It was concluded that the embedded (additive-free) PP fabrics hinder the migration of flame retarding substances towards the top of the polymer bulk, resulting in somewhat higher initial rates of heat emission, but suppressed peak of heat release rates and higher amount of residual chars compared to their unreinforced counterparts of the same compositions. It was concluded that the embedding of additive-free, highly stretched (oriented) fibres into the polymer matrix changes the burning behaviour (ignitability, char forming process, migration effects, etc.) of an intumescent flame retarded polymer system substantially [18].

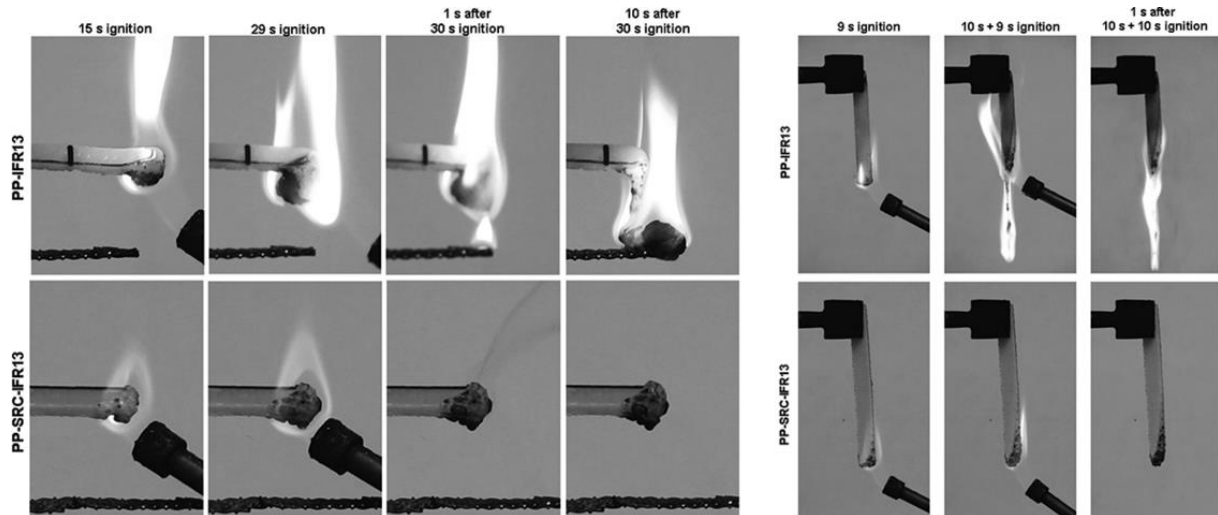


Figure 2.1 Vertical and horizontal burning test of PP compound (PP-IFR13) and SRC (PP-SRC-IFR13) with 13 wt% IFR content [18]

Nevertheless, the self-reinforced polypropylene composites exhibited prominent mechanical properties, even when flame retarded. Despite the flame retardant loading of the matrix layers, 4-times higher tensile strength and an 8-fold increase in impact energy absorption was measured for the SRCs compared to the non-reinforced PP samples. The presence of IFR additive did not influence the mechanical properties of the SRCs noticeably.

The approach of preparing high mechanical performance, recyclable all-polymer composites in flame retardant form was effectively utilized in other polymer systems, such as in recycled

self-reinforced composites [19] and also in fully biodegradable self-reinforced poly(lactic acid) composites [20]. Furthermore, Bocz et al. [18] proposed the feasibility of preparation of flame retarded all-polymer composites by high productivity injection moulding process [21,22].

Upgrading recycling of automotive shredder plastic waste was successfully accomplished by preparing flame retarded self-reinforced composites from secondary raw materials. Significantly reduced flammability was obtained by applying intumescent flame retardant additives and the prominent mechanical properties of the recycled multilayer composites have not been remarkably influenced by the FR content of their matrix layers. Comparable mechanical properties were achieved with conventional glass fabric reinforced composites. The special beneficial influence on the effectiveness of the applied phosphorus-based intumescent flame retardant additive was also evinced in the recycled self-reinforced system. At 18 wt% IFR loading, immediate flame extinguishing was observed during horizontal and vertical burning (UL-94) test and LOI of 30 v/v% was measured; furthermore peak of heat release rate was shifted in time and reduced by 75% during combustion in cone calorimeter. The use of polypropylene fabrics as reinforcement in recycled matrix supports the possibility of multiple recycling [19].

At the same time, preparation of flame retarded self-reinforced (polylactic acid) PLA composites proved to be a promising way to overcome two serious drawbacks, brittleness and flammability, of PLA simultaneously. Biodegradable self-reinforced PLA composites were successfully manufactured by film stacking of highly crystalline PLA multifilament yarns and fully amorphous PLA matrix films. Self-reinforcement provided PLA with outstanding impact resistance without compromising its strength, stiffness or biodegradability. The flammability of the self-reinforced PLA composites (PLA-SRCs) was effectively reduced by incorporating ammonium polyphosphate based flame retardant (FR) additive and montmorillonite clays in a

weight ratio of 10 to 1 into the matrix layers. As low as 16 wt% FR content proved to be sufficient for achieving self-extinguishing behaviour, i.e. UL-94 V-0 rating, and to achieve 50% and 40% reduction of peak of heat release rate and total heat emission, respectively. The introduction of FR additives improved also important mechanical properties compared to the reference (non-FR) PLA composite. The stiffness of the PLA-SRCs increased steadily with the FR contents of their matrix layers, furthermore, owing to the improved fibre–matrix bonding, prominent energy absorption capacity (impact perforation energy as high as 16 J/mm) was determined for the effectively flame retarded PLA-SRC (Figure 2.2). Besides their indisputable environmental benefits, such as renewable source and probable biodegradability, the manufactured self-reinforced PLA composites prove to have competitive mechanical characteristics with conventional petrol-based polymeric composites, both in respect to static (tensile and flexural strength and stiffness) and dynamic mechanical properties (impact resistance and temperature dependent storage modulus), especially when flame retarded. It was proposed that after several recycling loops the use of APP based FR additive may influence but not hinder the biodegradation of the developed all-PLA composites [20].

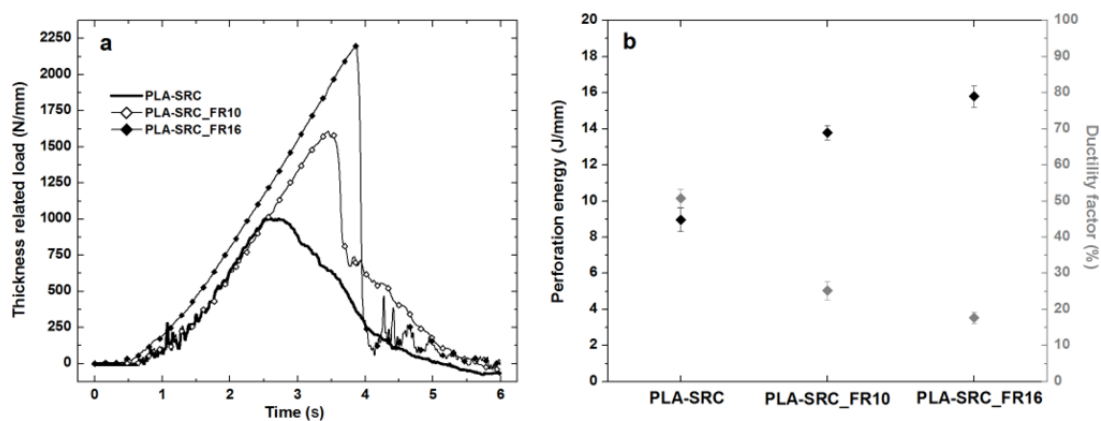


Figure 2.2 (a) Typical thickness related load–time curves recorded during instrumented falling weight instrument tests and (b) perforation energy and ductility factor of PLA-SRCs [20]

3. Synthesis and fire retardancy of thermosetting biomatrices

Thermosetting matrices, owing to their high strength, modulus, durability, and easily tailored properties by the choice of the reactants, represent an important group among the polymers for high-tech applications. The most important thermosetting matrices are epoxy resins, unsaturated polyester- or phenol/melamine-based resins and polyurethanes. In the followings, selected methods will be described for syntheses starting from bio-based building blocks.

For the preparation of phenolic resins, renewable compounds are available containing phenolic building blocks, such as lignin, tannins or cardanol. Lignin itself can be considered as a cross-linked polymeric structure, therefore, due to the steric hindrance, it cannot directly react with formaldehyde [23] to form phenolic resin. There are various thermochemical methods for the “depolymerisation” of lignin [24,25], such as fast or vacuum pyrolysis, liquefaction and solvolysis, leading to smaller phenolic molecules, which can be more easily converted to bio-based phenolic resin. During the solvolysis, the most commonly applied reagents are phenol [26,27,28], resorcinol [29,30] and the mixture of poly(ethyleneglycol) and glycerol [31,32]. Usually, these molecules are added to the lignin in 1:1 weight ratio, and the reaction takes place by applying 2-3% sulphuric acid. Once the smaller molecular phenolic compounds are formed, they can easily react with formaldehyde, to form lignin-based phenolic resin [33].

Tannins are natural polyphenolic materials, composed of flavan-3-ol repeating units, and bearing two aromatic (a resorcinolic and a pyrocatecholic) rings, joined by a heterocyclic ring [34]. These molecules are widely applied to form phenolic bioresins, by replacing partially [35] or fully [36] phenol or resorcinol [37] in the formulation. The main drawback of the application of tannins as phenol replacements is their restricted rotation around their backbone bonds, which leads to very fast gelation and thus to incomplete cross-linking [38].

Cardanol can be produced in large amount from cashew nut shell liquid (CNSL), of which about 1 million tons is produced annually [39]. As it includes both aromatic and aliphatic structures, cardanol is a promising substitute of petroleum-based phenols. Novolac resins prepared from cardanol and formaldehyde show higher flexibility than the conventional phenolic resins, due to the plasticization effect of the long side-chains, however, this phenomenon often results in decreased strength of the bioresin, compared to the petroleum-based ones [40].

Polybenzoxazines are a relatively new type of phenolic resins. They are produced *via* Mannich condensation from phenol, amine and formaldehyde [41]. The literature reports only few examples of renewable resources-based benzoxazine materials, among which cardanol represents the most investigated bio-based starting material [42,43,44]. It has been reacted with aqueous ammonia and formaldehyde to form bio-based benzoxazine monomer [43]. From the reaction of cardanol with paraformaldehyde and aniline, a low-viscosity monomer was obtained, which was then used as reactive diluent in the synthesis of BPA-based benzoxazines [44]. Recently, diphenolic acid (DPA)-based benzoxazine monomers have been synthesized [45]. The advantage of DPA as a starting material is that its chemical structure is similar to that of bisphenol A, and it's bio origin as it is derived from phenol and levulinic acid. Fully bio-based monomers have also been synthesized applying solvent-free method from eugenol, furfuryl or stearyl amine and paraformaldehyde, having wide processing window, and promising mechanical and thermal properties [46].

Considering unsaturated polyesters and polyurethanes as bioresins, it has to be mentioned that these are usually produced from renewable polyols, and petroleum-based dicarboxylic acids or isocyanates [47,48] resulting in partially bio-based resins. Among many known types of renewable polyols, vegetable oil-based polyols (such as castor oil pentaerythritol glyceride maleates) and 1,3-propanediol (prepared by certain micro-organisms) are mostly applied in

such formulations. Among the oils, one can find castor oil [49], palm oil [50], rapeseed oil [51,52], soybean oil [52,53] and sunflower oil [52], as well as oleic and undecylenic oils [54,55].

Some sugar-based polyurethanes have also been reported. Galbis et al. synthesized and characterized some new glutathione-mediated biodegradable sugar-based copolyurethanes [56]. These copolyurethanes were obtained by polyaddition reaction of mixtures of 2,2'-dithiodiethanol and 2,3,4-tri-O-benzyl-*D*-arabinitol or 2,3,4-tri-O-methyl-*D*-arabinitol to 1,6-hexamethylene diisocyanate. All the copolyurethanes were thermally stable (max. degradation temperatures above 220°C) and they proved to be biodegradable under the experimental conditions (pH = 7.02 and 37°C).

Aminoalditol 1-amino-1-deoxy-*D*-sorbitol was readily converted into 2,3,4,5-tetra-*O*-methyl derivative, a key precursor of a sugar-based [n]-polyurethane [57]. The resulting poly(1-amino-1-deoxy-2,3,4,5-tetra-*O*-methyl-*D*-sorbitol)urethane and cyclic oligomers had a moderate molecular weight and showed the presence of urea units.

Epoxy resins are widely used in different industries due to their favourable properties (e.g. stiffness, chemical, mechanical and electrical resistance), especially in those cases, where the technological advantages, provided by the epoxy resins can overcome their relatively high price (e.g. electronic industry, transportation).

To receive epoxy-functionalized vegetable oils, the carbon-carbon double bonds have to be epoxidized. There are four general methods for the epoxidization of oils: epoxidation with percarboxylic acids by acids or enzymes; epoxidation with inorganic or organic peroxides; epoxidation with halohydrines; or epoxidation with molecular oxygen [58].

According to the assumption of Rangarajan et al. [59], the mechanism of the epoxidation comprises three steps. The formation of the peracetic acid is the first step, followed by the

reaction between the percarboxylic acid and the double bonds, and, finally, hydrolysing side-reactions take place. The main reaction is the addition of the oxygen from the percarboxylic acid to the carbon-carbon double bond, which results in the formation of the oxirane group and is always accompanied by side-reactions. These reactions, which lead to the opening of the oxirane group, can be induced by several different compounds, including the percarboxylic acids present in the reaction mixture, the carboxylic acids formed from the percarboxylic acids during the epoxidation, traces of moisture, and the potentially produced hydrogen peroxide. All of these components can be nucleophiles, which can cause the opening of the oxirane ring, attacking the carbon atom of the three-membered ring.

Earls et al. used ω -unsaturated fatty acids as model compounds to investigate the mechanical properties of epoxidized triglycerides [60]. First, the esterification of glycerol took place with the eligible ω -unsaturated fatty acid, followed by the epoxidation with peracetic acid. Kim and Sharma proposed a solvent-free method for the preparation of several epoxidized plant oils [61]. The epoxidation of linseed oil, cottonseed oil, soybean oil, peanut oil and oilseed radish oil were carried out with good conversion and high selectivity.

The lignin-based epoxy monomers are prepared from liquefied lignin, as described above. The received liquefied lignin is reacted with epichlorohydrin in strong basic conditions. Hofmann et al. [62] reacted the pre-treated lignin first with propylene oxide, in order to improve the solubility, and then the product was reacted with ethylene oxide, resulting in primary hydroxyl groups instead of the former secondary ones. These primary –OH groups were then reacted with epichlorohydrin, resulting in lignin-based epoxy monomer. The prepared phenolated lignin-based epoxy monomer was mixed with DGEBA (diglycidyl ether of bisphenol A) in 10-50 weight%, and then cured with triethylene-tetramine (TETA) [27]. By increasing the lignin-content, the water uptake of the cured resins increased. When the solvolysis was carried out using resorcinol, the resulting epoxy resins showed similar

mechanical properties to DGEBA, both when cured with DDS (4,4'-diaminodiphenylsulphone) [29] or with DDM (4,4'-diaminodiphenylmethane) [30] .

Epoxy monomers have been synthesized from green tea extract [63], tara tannins [64] and catechol [65,66] by the reaction with epichlorohydrin. However, due to the different reactivity of the hydroxyl groups and some side reactions, no fully alkylated product could be obtained. Another approach for the preparation of glycidyl ether function is to react the –OH groups with allyl bromide, followed by the epoxidation of the carbon-carbon double bonds. By applying this method, the side reactions can be avoided, and fully alkylated products can be obtained, leading to higher functionality, thus higher cross-link density, and higher T_g [67].

From the cardanol-based novolac resin, epoxy monomer can be synthesized by reacting the free phenolic –OH groups with epichlorohydrin. In a two-step reaction, diepoxy monomer can be synthesized from cardanol. First, phenol was reacted with the double bonds of the unsaturated side chain in the presence of a strong acid (HBF_4), and then a received diphenol was converted to the corresponding bifunctional epoxy molecule with epichlorohydrin [68]. With the application of *Candida Antarctica* lipase enzyme, the double bonds of the side chain can also be epoxidized using H_2O_2 as oxidizing agent [69].

Cellulose and starch are biopolymers composing of D-glucose units. Examples for the epoxidation of both starch [70,71] and cellulose [72] can be found in the literature, applying different epoxidizing reagents. By enzymatic [73], acetic [74] or hydrothermal hydrolysis [75] of cellulose and starch, D-glucose can be prepared [76]. Sorbitol is formed by the hydrogenation of glucose, and by the didehydration of sorbitol, the resulting products are dianhydrohexitols (Figure 3.1).

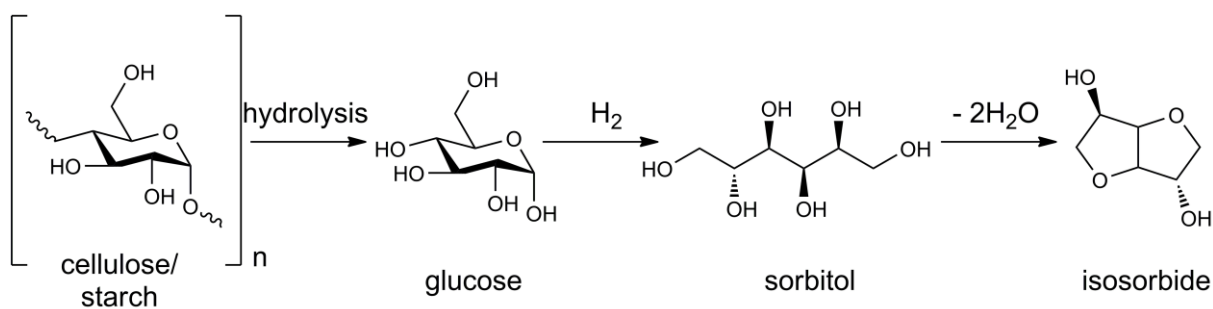


Figure 3.1 Synthesis of isosorbide

From the molecules depicted on Figure 3.1, the epoxy monomer prepared from sorbitol is already a commercial product (sorbitol polyglycidyl ether, SPE), as well as the glycidyl ethers prepared from glycerol. Japanese researchers reacted SPE with different renewable curing agents to receive fully bio-based epoxy resins. With the application of quercetin as hardener, the highest glass transition temperature reached was 85°C, while with the application of DGEBA as epoxy monomer under the same circumstances, they reached 145°C [77]. When tannic acid was applied as hardener, the T_g increased to 90°C [78], while with the use of a calixarene, synthesized from pyrogallol and vanillin, the T_g increased to nearly 150°C [79].

One of the most promising sugar-based starting material to form engineering plastics is the group of dianhydrohexitols (isosorbide, isomannide and isoidide) [80], which are produced from D-glucose, D-mannose, and L-fructose, respectively. Several research groups synthesized epoxy monomers from isosorbide and its diastereomers, both by the reaction with epichlorohydrin and by allylation followed by epoxidation [81,82,83].

Glucose-based epoxy monomers have been recently synthesized by the reaction of glucose, methyl-glycoside and isopropylidene glucofuranoside with allyl bromide, followed by the epoxidation of the double bonds. The synthesized trifunctional glucofuranoside-based epoxy monomer ensures high T_g when cured with aromatic amine [84].

As the synthesis of bio-based thermosetting polymers is a relatively new research area in the field of polymer chemistry, only a few articles deal with the flame retardancy of such biopolymers. Das and Karak [85] determined the flame retardant properties of vegetable oil-based epoxy formulations applying tetrabromobisphenol A (TBBPA)-based epoxy monomer as flame retardant. In their work, they reached high LOI values (up to 45 V/V%) and UL-94 V-0 rating. Similarly, TBBPA was applied as flame retardant together with melamine polyphosphate in the study of Zhan and Wool [86], reaching V-0 rating. However, the application of brominated flame retardants deteriorates the environmentally friendly character of the bio-based polymers, since HBr is released during combustion, which is corrosive and toxic. As a greener alternative, silicon-containing vegetable oil-based polyurethanes have been synthesized in order to enhance the flame retardant properties of the biopolymer [87]. With the incorporation of 9% of Si into the matrix by the reaction between methyl 10-undecenoate and phenyl tris(dimethylsiloxy)silane, the LOI value increased from 18.2 V/V% of the reference system to 23.6 V/V%.

Pillai et al. reacted the free hydroxyl group of cardanol with orthophosphoric acid, in order to prepare a flame retardant starting material [88]. Based on their experience, oligomerization of cardanol occurred by the reaction of the carbon-carbon double bonds present in the side chain, proposing new potential fields of application.

Lligadas et al. synthesized phosphorus-containing flame retarded epoxidized fatty acids [89,90]. ω -Unsaturated undecenoyl chloride was used as a model fatty acid precursor, which can be later exchanged to natural-based unsaturated fatty acids. The phosphorus-content of the prepared system was provided by using 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), which is an extensively used commercially available flame retardant for epoxy resins. DOPO was reacted with hydroquinone by its active hydrogen. The product of this

reaction was then reacted with undecenyl chloride, followed by epoxidation with *m*-Cl-perbenzoic acid (Figure 3.2).

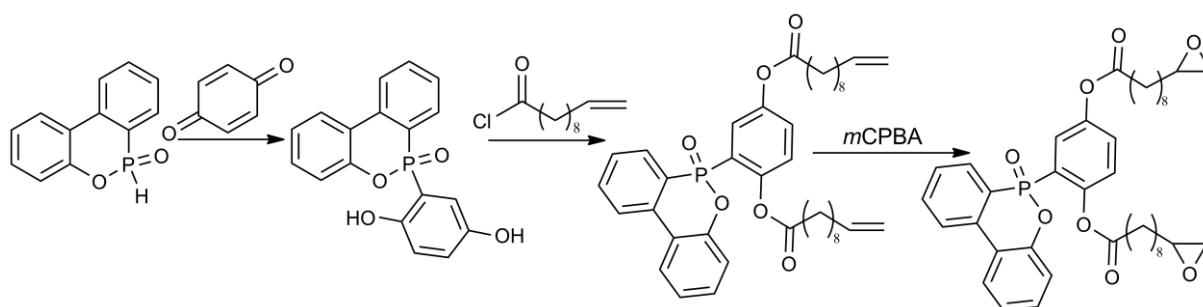


Figure 3.2 Preparation of flame retarded epoxidized fatty acids [89]

The epoxy component produced was cured with 4,4'-diaminodiphenylmethane (DDM) and bis(*m*-aminophenyl)methylphosphine oxide (BAMPO), respectively. The cured samples were analysed by DSC and DMA measurements, and tested to determine their limiting oxygen index (LOI) (Table 3.1).

Table 3.1 Properties of the flame retarded epoxidized fatty acid-based epoxy resins [89]

	Glass transition temperature (°C)		LOI (%)
	from storage modulus	from tan δ	
DDM-cured resin	88	108	31
BAMPO-cured resin	78	95	32

Based on the results presented in Table 3.1, it was found that, contrary to expectations, the application of phosphorus-containing curing agent (BAMPO) did not notably increase the LOI of the resin, and that the glass transition temperature decreased compared to the DDM-cured sample.

Itaconic acid was reacted with DOPO to form a phosphorus-containing dicarboxylic acid [91]. In a second step, diglycidyl esters of this molecule were prepared two ways. On the one hand, the acid was reacted directly with epichlorohydrin, and on the other hand, allyl bromide was added to form allyl ester, followed by the epoxidation of the double bonds with *meta*-chloroperbenzoic acid. The received epoxy monomer was then cured with methyl hexahydrophthalic anhydride. The cured samples having 4.4% phosphorus content, reached V-0 rating in the UL-94 test, however, the LOI of this sample was only 22.8 V/V%. When DGEBA was added to the system, decreasing the P-content to 2%, a LOI of 31.4 V/V% was reached.

A possible interpenetrating polymer network (IPN) structure was proposed by Alagar et al. [92] for the flame retardancy of soy-based epoxy resins. Several bismaleimides (BMIs) were synthesized, which compounds were then admixed to the bio-based epoxy resin before curing. Besides the crosslinking of the epoxy resin, the homopolymerization of the BMI molecules also took place through their carbon-carbon double bonds. The resulted IPN system provided improved thermal stability, and when the P-containing BMI was applied in 20 phr concentration, the LOI value of the reference system increased from 21 V/V% to 30.2 V/V%.

A new class of phosphorus-containing renewable thermosetting polymers was synthesized through aza- and phospho-Michael additions on α,β -unsaturated carbonyl groups established on high oleic vegetable oils [93,94]. When the phospho-Michael addition was carried out with the monofunctional diphenyl phosphine oxide [93], a LOI of 35 V/V% was reached, however, the crosslink density of the polymer decreased. To overcome this negative effect, a bifunctional phosphine (1,3-bis(phenylphosphino)propane oxide) was applied [94], and in this case the LOI further increased to 38 V/V%.

4. Fire retardancy of thermoplastic biomatrices

Bio-based polymers have been defined as man-made or man-processed macromolecules derived from biological resources for plastic or fibre applications. Various types of partially or completely bio-based thermosetting and thermoplastic polymers are already commercially available. Among the thermoplastics mainly polyesters and polysaccharide derivatives can be found; these include bio-based polyethylene terephthalate (bio-PET), PLA, bio-based polyethylene (bio-PE), starch blends, polyhydroxy alkanate (PHA) and bio-based polyamide (bio-PA), cellulose acetate (CA), cellulose acetate propionate (CAP), cellulose acetate butyrate (CAB) and poly ϵ -caprolactone (PCL). PCL is compatible with many polymers and thus it is used in many formulations as compatibilizer, or it provides water resistance in starch-based formulations. The packaging industry is the most important user of thermoplastic bioplastics, followed by the automotive and electronic sectors, where these would be needed also in flame retarded form.

As PLA has already found applications not only in packaging but some examples appeared even in engineering fields (such as in construction, electronics and automotive industry), the possibilities of its flame retardancy have been extensively investigated. In 2010, a comprehensive review on the flame retardancy of PLA was published by Bourbigot and Fontaine [95]. Besides the widespread additive methods, however, several possible inherent flame retardations of PLA have been also described. The copolymerization of D,L-lactic acid (LA) with 3,3'-diaminobenzidine (DAB) *via* melt polycondensation resulted in a copolymer with improved thermal stability [96]. By chain extension with P-containing moieties, the flame retardant can inherently be incorporated into the polymer backbone. Wang et al. developed different chain extended structures from dihydroxyl-terminated pre-PLA, on the one hand by the application of ethyl phosphorodichloridate [97], while on the other hand they used hydroquinone-modified DOPO and 1,6-hexamethylene diisocyanate [98]. In the first case, the synthesized P-containing PLA (PPLA) showed significantly lower peak of heat

release in microscale combustion calorimeter than the neat PLA, and the peak appeared at 60°C higher temperature. The PPLA has also been used as additive flame retardant in PLA. At 10% PPLA loading, a LOI value of 34 V/V% and UL-94 V-0 rating was reached [97]. The DOPO-modified PLA itself reached UL-94 V-0 rating and high, around 30 V/V% LOI values, independently of the applied diol-diisocyanate ratio [98].

In contrast, the flame retardancy of other bio-based thermoplastics, such as PHA, PBS PCL and TPS have been barely studied yet. The researchers strive generally for non-toxic and green (bio-based) solutions to flame retard biopolymers in order to keep the environmentally friendly character of the final product. As for an example, lignin, chemically modified with phosphorus compounds, was found to be an effective bio-based flame retardant when applied in polybutylene succinate (PBS) [99]. The known flame-retardant synergism between phosphorus-based additives and metal oxides, used earlier for petroleum-based plastics, has been extended recently to bio-based materials (PHBV/PBAT blends) by Gallo et al. [100]. Bocz et al [101,102] proposed the use of phosphorous polyols, as multifunctional plasticizers with flame retardant effect to obtain FR-TPS blends. Such multifunctional additives can be utilized to flame retard bio-based thermoplastic polymers in an economic way.

5. Fire retardant modification of biofibres

Natural fibres represent an obvious choice as reinforcement for bio-based polymer matrix materials, as with their combination all-bio composites can be prepared. Lower density, renewability and biodegradability, as well as lower price and composite processing costs make them promising alternatives to the commonly applied synthetic carbon, glass or aramid fibres [103]. Kenaf, hemp, flax, jute, and sisal have attained commercial success in designing biocomposites. Among their disadvantages, such as fluctuating fibre quality, high moisture uptake, limited processing temperature range, low impact strength and durability, their

flammability represents a major drawback, especially in more demanding sectors as automotive, aircraft and electronic industries.

The flammability of bio-based fibres depends mainly on their chemical composition (determining their thermal degradation), but also on their structure, degree of polymerization and fibrillar orientation. The thermal degradation of the natural fibres is a well-described phenomenon [104,105,106]. It involves several processes as desorption of absorbed water, depolymerisation of cellulose leading to dehydrocellulose and water, decomposition of the formed dehydrocellulose to char and volatiles, formation of levoglucosan and its decomposition to flammable and non-flammable volatiles and gases, tar and char. The main characteristics of the thermal degradation behaviour of the major natural fibre components and their effect on flammability are summarized in Table 5.1.

Table 5.1 Thermal degradation characteristics of natural fibre main components

main component	temperature range of thermal degradation	major decomposition products	effect on flammability
cellulose	260-350°C	flammable volatiles, gases incombustible gases tars less char	increased flammability
hemicellulose	200-260°C	incombustible gases less tar	decreased flammability
lignin	160-400°C	aromatic char	higher decomposition temperature lower resistance to oxidation

As for the chemical composition of fibres, lower cellulose content and higher lignin content reduce their flammability. Concerning the fine structure of fibres, the high crystallinity of cellulose leads to formation of high amount of levoglucosan during pyrolysis and consequently to increased flammability, so from this point of view lower cellulose content is preferred. On the other hand, as more activation energy is required to decompose the crystalline structure of the cellulose, it results in higher ignition temperature. As for the degree of polymerization and orientation of the fibrillar structure higher molecular weight and orientation (resulting in lower oxygen permeability) is favourable.

The flammability of natural fibres and composites made thereof can be decreased with flame-retardant fibre treatments. Inorganic phosphorous compounds (such as phosphoric acid (PA), monoammonium phosphate (MAP) and diammonium phosphate (DAP)), tributyl phosphate (TBP), triallyl phosphate (TAP), triallyl phosphoric triamide (TPT), have been used to flame retard cellulose based fibres [107,108,109,110]. Phosphorus-containing flame retardants can efficiently initiate the charring of fibres, which is favourable in terms of flame retardancy [101,107], however, the application of these treatments decreases the initial decomposition temperature of natural fibres significantly (even by 90°C) [101,111]. The reduced thermal stability can be a major issue, both from mechanical and aesthetic point of view, when the natural fibres are intended to be used as fillers or reinforcements in polymer composites. Presence of water, acids and oxygen catalyses the thermal degradation of cellulose, therefore natural fibres usually turn brown during fibre treatments. Low thermal stability is critical in case of thermoplastic matrices with processing temperatures above 140°C (such as PP, PA, PET and also PLA), but also in case of high glass temperature thermosetting matrices requiring elevated curing temperature (e.g. high-tech epoxy resins, cyanate esters). Surface treatment with silane compounds is a possible solution to increase the thermal stability of

cellulosic fibres [112,113]. Recently, the layer by layer assembly came to the forefront for rendering textiles flame retardant [114,115].

According to the literature, when bio-based fibres are used as reinforcements (without adding flame retardants to the polymer matrix) in polymer matrices to form biocomposites, the heat conductivity increases while the apparent stability of the polymer decreases, therefore the ignition of the composite is facilitated [116]. This, so-called candlewick effect of natural fibres makes the flame retardancy of the natural fibre reinforced biocomposites rather challenging [117,118]. Thus the flame retardant treatment of biofibres was found to be essential from this respect as well.

Bocz et al. elaborated a novel one-step reactive flame-retardant treatment for natural fibres: Phosphorus-containing silanes were synthesized from commercial phosphorus-containing polyol and 3-(triethoxysilyl)-propyl isocyanate, and the adduct was used to treat flax fibres used for the reinforcement of PLA/thermoplastic starch composites [102]. These phosphorus-containing silanes did not decrease the initial temperature of thermal degradation as the treatment with diammonium phosphate, and lead to improved fire retardant properties. These results can be explained by the known synergistic effect of P and Si atoms [119,120]. Figure 5.1 presents a comparison between the TG and DTG curves of neat flax fibres, conventional diammonium phosphate (DAP)-treated fibres, and the referred PSil-treated flax fibres. The highest amount (47%) of residual char (at 500°C) clearly belongs to the PSil-treated fibres. Furthermore, in each cited work, the phosphorus-containing species, being present both on the surface of the reinforcing biofibres and in the biodegradable matrix material, provided improved mechanical performance to the effectively flame retarded biocomposites [101,102,121] emphasizing the key importance of combined strategy of flame retardancy for natural fibre reinforced bio-based thermoplastics.

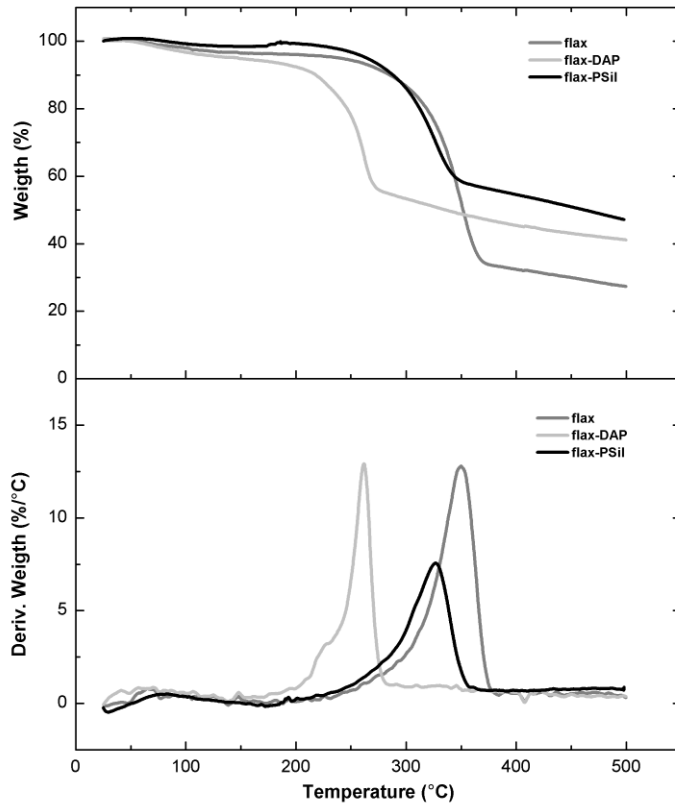


Figure 5.1 .TG and DTG curves of neat, DAP-treated and PSil treated flax fibres [102]

In order to improve the fibre-matrix adhesion in natural fibre composites several ways of surface modifications like dewaxing, alkali treatment, vinyl grafting, cyanoethylation, acetylation, bleaching, peroxide treatment, sizing with polymeric isocyanates, treatment with silane and other coupling agents have been applied [122]. In case of thermosetting matrices, e.g. in epoxy resins, the silane treatment can be combined with the alkali surface treatment of the natural fibres [123], aiming at improving the relatively poor interaction at the fibre - matrix interphase [124,125]. Fibre treatment with silanes having reactive functionalities (e.g. amine) leads to covalent bonds between the fibre and the matrix resulting in improved mechanical properties as well [126]. However, it has to be taken into account that the surface treatment of the reinforcement with reactive species can influence the curing kinetics of the applied epoxy resin [127].

Szolnoki et al. compared the effects of thermotex procedure (i.e. removal of adsorbed water from the capillaries and then filling the micro/nano-voids) with phosphoric acid [128] and sol-gel treatment with amine-type silanes followed by thermotex treatment on the flammability of hemp fibres used for the reinforcement of epoxy resins [129]. The thermotex treatment decreased the initial degradation temperature of hemp fabrics by more than 60°C, as expected [101,111], while the combined silane-phosphoric acid treatment increased the decomposition temperature by 30°C compared to thermotex-treated fibres, as the sol-gel treatment of the fabrics partially protected the cellulose structure from the acidic hydrolysis [130,131]. The combined treatment increased the time to ignition from 3 s to 15 s, decreased the heat release rate from 68 kW/m² to 9 kW/m² and led to the formation of consistent char instead of fluffy, light ash in case of untreated fabrics (Figure 5.2). A possible synergistic effect was described in terms of composite mechanical properties: when both the matrix and the reinforcement contained phosphorus, despite the inferior mechanical performance of the FR matrix itself and the decreased strength of the surface treated fabrics, the mechanical properties for the FR samples reached the level of the reference composite almost in all cases.

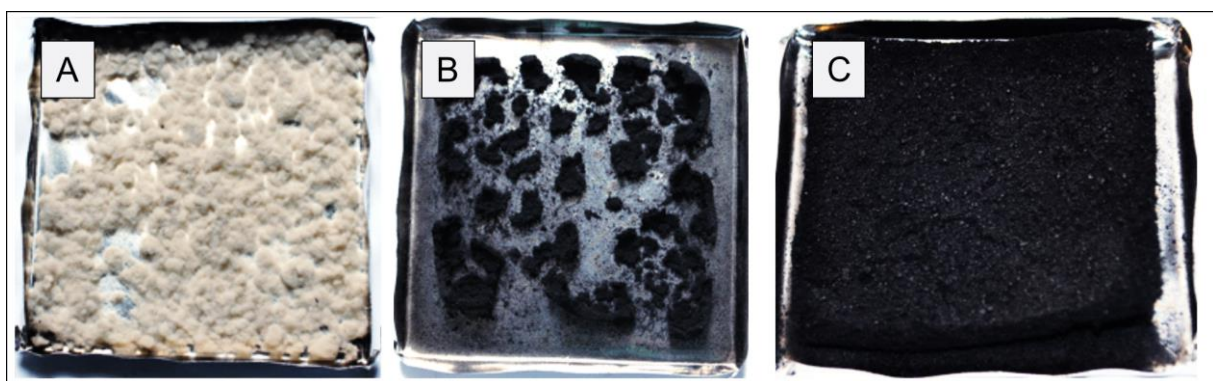


Figure 5.2 Cone calorimetry residues of untreated (A), thermotex-treated (B), silane and thermotex-treated (C) hemp fabric [129]

6. Flame retardancy of bio-based composites

Thermoplastic green composites increasingly find applications in a range of widely different fields such as in cars, buildings, furniture, cases for electronic devices, etc.; however, their poor fire resistance often represents a critical limitation for their widespread use in structural engineering applications. The flame retardancy of the thermosetting biocomposites, comprising both the matrix and the reinforcement of renewable resources, is a future challenge. Only a few papers deal with the preparation of thermosetting all-bio composites [29,35,77,78,79], and none of them investigated the flammability properties yet.

Until now, a limited number of papers have been published on flame retardancy of biocomposites. Most of them are dedicated to materials using PLA as matrix [132], but the flame retardant possibilities of PBS [133] and TPS [134] based green composites have also been studied. As described earlier, the flame retardants can be either incorporated into the polymer matrix or used on the surface of the reinforcing natural fibres by means of impregnation or grafting, but the best results were obtained when both strategies were combined. The most commonly used flame retardants in green composites are the phosphorus-based compounds [109,117,135]. Shumao et al. compared the flammability properties of ramie fibre reinforced PLA composites flame retarded with APP by three different processes: (1) PLA was blended with APP and combined with neat ramie fibres, (2) ramie fibres were treated with APP and then compounded with PLA and (3) both PLA and ramie fibres were flame retarded using APP and blended together. In contrast to the identical APP loadings (10.5 wt%), significantly better flame retardancy was evinced for the composites where APP was present in both phases, which they explained by the successful elimination of the candlewick effect of the ramie fibres [121]. Similarly, in natural fibre reinforced TPS composites UL-94 V-0 rating was achieved only when phosphorus compounds were used both on the surface of the natural fibres and in the matrix polymer [101]. In both cases, the non-toxic phosphorus-based compounds initiated effectively the

charring of the biofibres; however, the initial decomposition temperature of the natural fibres decreased significantly due to the treatments. To overcome this, Bocz et al. proposed the use of a phosphorus and silicon containing compound for flame retardant modification of reinforcing natural fibres. In their study, the candle-wick effect of flax fibres was effectively counterbalanced by their flame retardant treatment with the newly synthesized phosphorus-silane compound prior to embedding in PLA/TPS biopolymer blend matrix and without causing noticeable decrease in the thermal stability of the reinforcing cellulosic fibres [102].

7. Characterization of fire retarded biocomposites

Besides the well-known and widely applied thermal degradation and flammability characterization methods, such as thermogravimetric analysis (TGA), UL-94 test, limiting oxygen index (LOI) measurements, cone calorimeter test, Bunsen burner test, microscale combustion calorimeter (MCC) tests, glow wire flammability index, etc., several other techniques can be applied to fully characterize green composites.

A major drawback of natural fibre reinforced composites is the relatively poor interaction at the fibre–matrix interphase [124]. Microbond test is a suitable method for the determination of the adhesion between the composite parts. Matrix droplets are placed on elemental fibres prepared from the reinforcing fabric, and the interfacial shear strength is measured using a microbond device fixed onto a universal tester [129,136].

Laser pyrolysis-FTIR (LP-FTIR) method is a fast way to investigate the pyrolytic degradation products of biocomposite samples [101]. When compared with the TG-FTIR coupled method, where some higher molecular weight gaseous degradation products can condense between the TG and FTIR equipments, in the case of LP-FTIR the direct connection between the pyrolysis zone and the analysing unit allows the immediate and in situ analysis of the degradation products without loss of any component. It has to be also highlighted that, in contrast to the

much more time-consuming TG-FTIR method, the LP-FTIR experiments take only about a minute per samples [137].

The migration of the flame retardant components often plays a crucial role in the char formation process. By elemental analysis using e.g. energy-dispersive X-ray spectroscopy (EDS), of the samples and chars at different points of the burning process, the migration of the FR additives can be described (Figure 7.1), and important conclusions about the charring process can also be drawn [18].

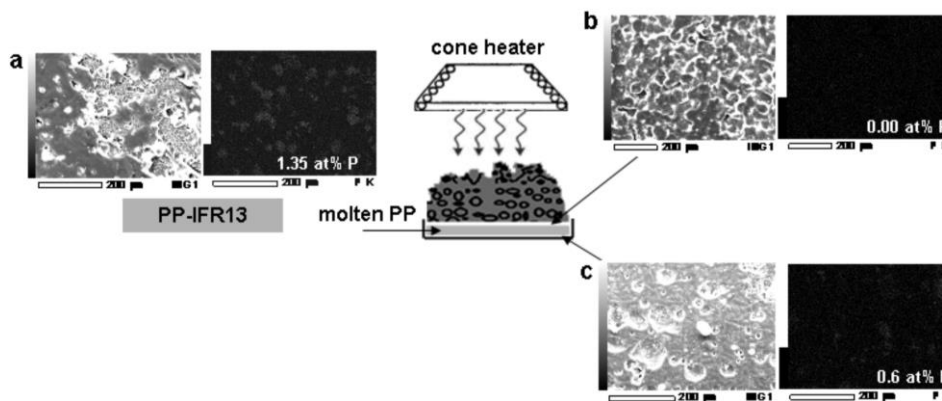


Figure 7.1 EDS imaging of the P content of a) the prepared PP-IFR13 compounded sample, b) upper layer of the molten PP and c) lower layer of the molten PP (obtained after 180 s combustion in cone calorimeter) [18]

The foaming processes of different intumescent flame retarded environmentally friendly composites can be investigated by compression tests of the charred residues, as different foaming processes lead to different char structures. The steepness of the curves can be interpreted as the characteristic resistance of char layers or cell structures of the formed foams against deformation [18].

8. Applications

Parallel with the intense research at the academic level of green composites their large-scale commercialization has also begun. The widespread application of the first green composites appeared in the automotive sector in the early 2000's, and the automotive applications represent the largest market for natural fibre reinforced bioplastics. The biocomposites with polypropylene or unsaturated polyester matrices and biofibres, used as "partially biodegradable" interior or exterior parts in vehicles, are in fact pseudo-environmental approaches. Real solutions are offered by "completely recyclable" self-reinforced composites and by the "completely biodegradable" types thus the spreading of such systems is expected in the near future. New environmental regulations and societal concern have triggered the search for these new products and processes that are compatible with the environment. However, in most cases modification is required because of disadvantages such as limited water resistance, low impact resistance and poor fire safety.

The current application of environmentally promising polymer systems in FR form is very limited and is accompanied with several open questions. The need for flame retardancy in the medical, textile and packaging industries (traditional consumers of biopolymers) is not common yet. Although the nature shows examples for reducing the flammability (by extensive water uptake of hydrophilic polymers in living organisms, by the sudden increase of water in vesicle at flash burns, by proteins of limited flammability and DNA of complete intumescent FR structure) only very limited examples of such inspirations went through to the industrial practice. The possibility offered by the nature is utilized in the textile industry when hardly flammable fabrics are made from mixture of wool and cotton [138].

The relationship between environment and fire-safety is clearly visible in the field of E&E industry, where the printed circuit boards (PCB) are made of thermosetting epoxy composites, which are neither recyclable nor biodegradable, and the halogenous FRs, banned from this area, are still present in the instrument housing wastes. In order to avoid damages caused by

FRs, the new E&E parts contain mostly P-containing FRs. The cables made of recyclable poly(ethylene-co-vinyl acetate) filled with metal hydroxides are considered to be the most environmentally friendly, but the recent restrictions of the authorities mean major challenges even at this area as well.

The application of biopolymers in the construction industry is limited due to the severe fire safety regulations. The memory of huge fires of buildings, caused by the widespread use of wood in the Middle Ages, is probably still working in the collective mind. Nevertheless significant increase can be seen in the application of wood fibre reinforced PE and PP, which means a big challenge towards the developers of flame retardant systems. The insulation of heat and sound, the service parts of buildings and the household industry requires the use of polymers in flame retarded form. The spread of economic and recyclable biopolymer-based solutions for these purposes is expected only after the development of their efficient flame retardancy.

In 2013, the bio-based polymer production of 3.5 million tons per year was reported to share about 1.5% of the total polymer production, which is expected to increase to 3%, reaching nearly 12 million tons by 2020 [139]. The most significant drivers to move from fossil based polymers to bio-based polymers are the limited fossil fuel resources, the concerns about climate change and the important breakthroughs in biotechnology aiming sustainable development. The cost/performance ratio of many bio-based polymers is quite competitive already, furthermore it is suggested that bio-based polymers have the potential not only to replace existing polymers in a number of applications, but also to provide new combinations of properties for new applications [140]. The main advantage of using renewable materials is that the global CO₂ balance is kept at a stable level. The biocomposites are prone to integrate into natural cycle.

9. Future trends

The relatively expensive biopolymers can become competitive when applied (with low cost biofibres) in biocomposite form. Furthermore, larger-scale production can reduce the costs providing attractive alternative in the near future to the currently used polymer composites. However, in order to promote the application of environmentally advantageous types of FR biomaterials several questions have to be answered, just to mention the most important ones: What is the optimal relationship between the recyclability and biodegradability? How to design the lifetime accurately? How to perform the process control accurately? Is there a special health issue if the common stabilizers are applied in biodegradable polymers? Is there a special environmental issue if the common FR types are applied in biodegradable polymers? What is the optimal FR mechanism (solid/gas phase effect) in each biopolymer? How to produce the biocomposites in an eco-efficient way? Answering these questions means real challenge of research.

It is worth to learn from the nature e.g. DNA, even if not economic and stable enough as a FR additive, it can serve as an example for the development of new IFR types [141,142]. The current relatively low cost of mineral oil is predicted to increase again and by that time feasible new solutions have to be available. The biggest challenge is the replacement of the thermosetting composites with alternatives of controlled biodegradability. For this purpose sugar-based monomers are the most promising. The choice of the thermoplastic biocomposites will be enriched by further flame retarded types and their price will decrease with the application of multifunctional additives. Elaboration of self-reinforced polymers in FR form on industrial scale will promote the rate of recycling. Development of commercial non-flammable bio-based reinforcements is required for both bio-thermosets and bio-thermoplastics.

The end of life vehicles directive (ELV) gave a new motivation for the development of new biocomposites for transportation industry, which is reflected in relevant project calls (e.g. Clean Sky Eco Design [143] or ‘Advanced electric vehicle concepts’ [144] FP 7 programmes). As ~75% of a vehicle’s energy consumption is directly related to factors associated with vehicle’s weight, extensive work is foreseen in order to elaborate a more eco-friendly concept in the automotive industry. The request for fire-safe design will be much more severe for the electric and hybrid cars, as the risk of electric fire is higher in these types. A low cost multilayer biodegradable composite approach with fire bearing design is needed in this field.

Environmental awareness and the level fire-safety regulations in textile and packaging industry will increase requiring new FR biopolymer approaches.

In the field of E&E industry the development of flame retarded and flexible, recyclable/biodegradable PCBs, the use of phosphorus FR in the instrument housings and the application of ceramizing FR systems in the cable coatings (preventing short circuit even at severe fires) is foreseen.

In the construction industry the efficient fire retardancy of wood and its woodlike alternatives will be an increasing request in order to widen the available material choice for architecture. The need for new indoor design elements will also initiate research for further FR biocomposites. Especially challenging is the fire retardancy of biofoams with reactive FR modifiers.

If the research activities for the development of new multifunctional additives, new efficient controlled processing technologies and new testing methods, suitable for modelling and predicting of the properties, will be successful, the biocomposites can become the novel key materials of the 21st century.

10. Sources of further information and advice

Further information is available at relevant homepages [143,145,146,147,148,149].

The authors believe that it is advisable to spread the message that no contradiction exists between serving the matter of fire safety and environmental protection at the same time. Biocomposites are already available, at least at laboratory scale, and they are economically competitive and more attractive in respect of environmental features and fire safety than the currently applied polymer composites. This message serves the competitiveness by itself through increasing the demand for scaling up of the experimental approaches and initiating relevant R+D projects that can define the exact role and ratio of completely recyclable and completely bio-based polymer systems.

11. List of abbreviations

APP: ammonium polyphosphate

BAMPO: bis(*m*-aminophenyl)methylphosphine oxide

BMI: bismaleimide

CA: cellulose acetate

CAB: cellulose acetate butyrate

CAP: cellulose acetate propionate

CNSL: cashew nut shell liquid

DAB: 3,3'-diaminobenzidine

DAP: diammonium phosphate

DDM: 4,4'-diaminodiphenylmethane

DGEBA: diglycidyl ether of bisphenol A

DMA: dynamic mechanical analysis

DNA: deoxyribonucleic acid

DOPO: 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide

DPA: diphenolic acid

DSC: differential scanning calorimetry

DTG: derivative thermogram

E&E: electrical & electronics

EDS: energy-dispersive X-ray spectroscopy

ELP: end-of-life plastic

ELV: end-of-life vehicle

FR: flame retardant

GF: glass fibre

IFR: intumescent flame retardant

IPN: interpenetrating polymer network

LA: D,L-lactic acid

LOI: limiting oxygen index

LP-FTIR: laser pyrolysis coupled with Fourier-transform infrared spectrometry

MAP: monoammonium phosphate

MCC: microscale combustion calorimeter

PA: phosphoric acid

PA: polyamide

PBS: polybutylene succinate

PCB: printed circuit board

PCL: poly ϵ -caprolactone

PE: polyethylene

PET: polyethylene terephthalate

PFR: phosphorus-containing flame retardant

PHA: polyhydroxy alkanate

PLA: polylactic acid

PP: polypropylene

PPLA: phosphorus-containing PLA

SPE: sorbitol polyglycidyl ether, SPE

SRC: self-reinforced composite

TAP: triallyl phosphate

TBP: tributyl phosphate

TETA: triethylene-tetramine

TGA: thermogravimetric analysis

TG-FTIR: thermogravimetric analysis coupled with Fourier-transform infrared spectrometry

TPS: thermoplastic starch

TPT: triallyl phosphoric triamide

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