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► **To cite this version:**

A. Taguet, Rodolphe Sonnier. Flame Retardancy of Natural Fibers Reinforced Composites. Towards Bio-based Flame Retardant Polymers, pp 73-98, 2018, 978-3-319-67083-6. 10.1007/978-3-319-67083-6\_3. hal-03282059

**HAL Id: hal-03282059**

**<https://hal.mines-ales.fr/hal-03282059>**

Submitted on 11 May 2023

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# Flame Retardancy of Natural Fibers Reinforced Composites

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Due to numerous advantages (high specific mechanical properties, low density, biosourcing, ...), natural fibers from plants are considered as credible alternatives to glass or carbon fibers for composites industry. Nevertheless, their relatively high flammability limits their potential applications. Many researches have been carried out to improve the flame retardancy of composites reinforced with natural fibers. This chapter attempts to establish the state-of-art of these researches.

There are already some reviews about the flammability of natural fibers and biocomposites [1–5]. Compared to these reviews, the specific objective of this chapter is to answer to the following questions: What are the differences in flammability between composites filled natural fibers and their counterparts reinforced with glass or carbon fibers? Is the treatment of natural fibers a viable solution for flame retarding biocomposites? The chapter is based on the literature available on biocomposites filled with natural fibers. The articles about the flammability of composites based on wood flour are not taken into account but reviews about this topic can be found elsewhere [6].

## 3.1 A Comparison Between Natural Fibers and Glass or Carbon Fibers

### 3.1.1 *Fire Behavior of Composites Filled with Glass or Carbon Fibers*

Since natural fibers should replace glass (GF) or carbon fibers (CF), it is important to list main issues specific to these latter. Due to their high stability, glass and carbon fibers do not directly participate to the heat release during burning. Carbon fibers start degrading only at high heat flux in cone calorimeter in presence of air, i.e. at the end of the test when flame is vanished [7]. Nevertheless, their presence

has an important influence (and sometimes negative influence) on the flammability. In particular, glass fibers lead generally to a decrease in limiting oxygen index for thermoplastic composites [8–10]. Casu et al. have explored the reasons for such a phenomenon [11]. They showed that the decrease in limiting oxygen index of glass fibers reinforced composites is not due to the seizing of fibers but mainly to the anti-dripping effect of glass fibers: fibers prevent the flowing of burning polymers away from the flame. Seizing may be another influent parameter [12]. Additional effect is due to wicking. Wicking corresponds to the flowing of polymer along the glass fiber surface from the bulk to the fire zone. Interfacial charring by grafting flame retardants on glass fiber surface can prevent efficiently the wicking [13]. Glass fibers also prevent dripping during UL94 test, another common fire test assessing the flammability of a small sample [14].

On the contrary, glass or carbon fibers have a positive effect in forced-flaming tests, for example in cone calorimeter test [7, 9–11, 14, 15]. Indeed, flowing is prevented in cone calorimeter test. Hence, the replacement of combustible by inert fibers decreases the fire load. High thermal conductivity of fibers allows delaying ignition [14, 15]. Perret et al. observed an increase of 20–25 s of time-to-ignition for epoxy reinforced with carbon fibers in cone calorimeter test at 35 kW/m<sup>2</sup> [15]. Liu et al. have measured the physical properties of flame retarded polystyrene containing various contents of glass fibers [14]. They showed that the incorporation of glass fibers enhances the thermal conductivity and the density but decreases the specific heat capacity. The net effect is an increase of the thermal inertia which influences the time-to-ignition [16]. Nevertheless Dao et al. noted that a small increase of carbon fiber in epoxy composites leads to a worse thermal resistance (decrease of time-to-ignition) but no explanation was proposed to explain this tendency [7].

A high thermal inertia generally delays ignition but increases the heating rate in the deeper layers. This was observed by Liu et al. in the case of polystyrene-based composites reinforced with glass fibers [14]. Usually, the fast heating of the bulk results in a higher heat release rate in a second time [17]. Nevertheless such a phenomenon is not observed for composites. Indeed, the accumulation of fibers at the top surface of samples promotes the formation of an insulating residue able to limit the gases and heat transfer, even if high thermal conductive fibers are probably not the best candidates for insulation. Consequently the heat release rate decreases.

Fibers can also modify more or less the modes-of-action of flame retardants. For example, Camino et al. noted that intumescence is hindered by the presence of carbon fibers in epoxy composites [18]. Braun et al. suggested that the impact of polymer charring promotion on heat release rate is limited in composites filled with high loadings of fibers [19]. Some authors have reported that the residue content of composites reinforced with glass or carbon fibers is higher than expected from a linear rule of mixtures. Kandola and Toqueer-Ul-Haq assumed that the presence of glass fibers allows increasing slightly char content in thermogravimetric analysis for PP flame retarded with some phosphate-based molecules [9]. They explained that glass fibers act as physical barrier and provide more chance for fire retardants to react with polymer. Zhao et al. [20] have incorporated small amount of carbon

fibers (up to 5 wt%) into thermoplastic polyurethane (TPU) flame retarded with ammonium polyphosphate (APP). They also noted that carbon fibers lead to a significant increase of char yield in thermogravimetric analysis: from 21 wt% for TPU-APP to 30–33 wt% for TPU-APP-CF. Carbon fibers also promote a dense and compact char in cone calorimeter test. Liu et al. noted that glass fibers incorporated into flame retarded polystyrene leads to higher char content than expected in cone calorimeter tests but not in thermogravimetric analysis [14]. The high residue content in cone calorimeter test may be probably assigned to the insulating character of the inert glass fibers accumulated at the top surface and limiting the degradation of the underlying polymer.

Orientation and aspect ratio of fibers in the composite are also important parameters influencing heat conductivity and flammability. Chai et al. have compared the flammability of epoxy composites containing different glass fabrics at the same volume fraction [21]. They pointed out significant differences in fire performances, for example in pHRR at cone calorimeter test. Levchik et al. showed that the limiting oxygen index of epoxy resin reinforced with carbon fibers is much higher if the fibers are oriented perpendicularly to the front of flame [18]. Milled glass fibers reduce the oxygen index of poly(butylene terephthalate) at a lower extent than long glass fibers because wicking effect was limited [11]. Kandola and Toqueer-UI-Haq observed that the residue content of polypropylene filled with glass fibers in cone calorimeter tests was much higher when the formulations were not compounded using extrusion but prepared directly by hot pressing [9]. Indeed, despite the non-uniform distribution of the fibers in the non-compounded composite filled with 20 wt% of glass fibers, the residue content was 29.5 wt% versus 19.1 wt% for the extruded formulation. The authors explained that the glass fibers were longer when not compounded and formed a better physical barrier at the top surface.

Finally, it must be noted that a small variation of fibers can modify greatly the fire performance of the composite. The change in fire properties is not linear with fiber content. Dao et al. [7] have studied epoxy composites reinforced with 56 or 59 vol.% of carbon fibers in cone calorimeter. The composite containing the highest amount of carbon fibers exhibits lower time-to-ignition but also lower mass loss rate and lower mass loss at the end of test. In particular at low heat flux (20 kW/m<sup>2</sup>, probably close to critical heat flux) the mass loss at the end of test is twice lower.

### ***3.1.2 Flammability of Natural Fibers***

Natural fibers share some characteristics with glass or carbon fibers but exhibit also some important differences. Surely, they increase the viscosity and should prevent the flowing of polymers as do glass and carbon fibers. Similarly, intumescence should be limited in the presence of natural fibers. On the contrary, natural fibers may not promote high heat transfer. Thermal conductivity of natural fibers is close to that of polymers and much lower than glass or carbon fibers [3]. Annie Paul et al.

have measured the thermal conductivity of PP composites filled with banana fibers [22]. They found that the thermal conductivity decreases when incorporating 50 vol.% of fibers: from 0.240 to 0.157 W/m K. Similar results were found about polyester resins filled with sisal and banana fibers [23]. In both studies, various pretreatments of fibers allowed increasing the thermal conductivity due to a better compatibility with the matrix. Idicula et al. have also studied a composite with pineapple leaf fiber (PALF) and/or glass fibers [23]. They were able to estimate the thermal conductivity of the PALF fibers: 0.188 W/m K, i.e. much less than glass fibers (around 1–1.2 W/m K). Consequently, natural fibers do not allow transferring heat from the surface to the bulk. Insulating properties of the residue should be better than with high thermal conductive glass fibers. Note that some authors have claimed surprising and contradictory results: Du et al. observed a significant increase of thermal conductivity for PP filled with ramie fibers (from 0.22 to 0.41 W/m K with 27.5 wt% of ramie fibers [24]).

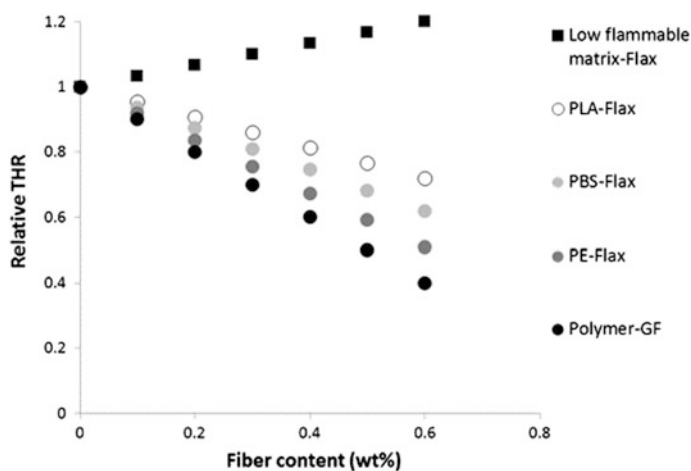
Obviously, the most relevant difference between natural fibers and glass or carbon fibers is their thermal decomposition. Natural fibers are ligno-cellulosic materials and then their flammability does not depend only on cellulose (the main component), but also on hemicellulose and lignin. The composition of a wide range of natural fibers can be found elsewhere [3, 5]. These three components have different thermal stability. Hemicellulose is the least thermally stable and starts decomposing at 200 °C. Cellulose is decomposing around 350 °C. Lignin is decomposing on a wide range of temperatures from 200 to 600 °C. Moreover the activation energy of pyrolysis is very different as recalled by Yao et al. [25]: 105–111, 195–213 and 35–65 kJ/mol, for hemicellulose, cellulose and lignin, respectively. The decomposition steps are largely overlapping.

The decomposition of cellulose, the main component in natural fibers, has been extensively studied. Briefly, after initial desorption of water, cellulose decomposes through two competitive routes. The first one corresponds to the formation of levoglucosan by depolymerisation. Then levoglucosan decomposes itself in high flammable low molecular weight molecules and char. It is well known that the formation of this levoglucosan during degradation of natural fibers leads to worse thermal and fire properties. The second route is the dehydration of cellulose giving more char [1, 4, 26].

An important point is that natural fibers are able to char. This char allows forming a barrier layer preventing the transfer of the heat from the flame to the underlying polymer. Even if the intrinsic char yield remains limited in some cases, it can be significantly enhanced by the use of additives, particularly phosphorus-based flame retardants. As polyaromatic compound, lignin is the main component promoting the fiber charring. Then its influence on flammability deserves to be discussed in greater details. As already noted, lignin is a minor component of natural fibers but its content varies in a large range (from 0 wt% for pure cellulose, less than 3 wt% for flax fibers [27], 20–30 wt% for bamboo fibers [28, 29] and up to 45–48 wt% for piassava fibers [30]). Dorez et al. have studied the properties of various natural fibers considering them as a mixture of three main components: cellulose, hemicellulose (i.e. xylan) and lignin [31]. Char yield increases when

lignin content increases but strong discrepancy can be found between experimental values and char yield calculated from a linear rule of mixtures. In particular, at low lignin content, experimental char yield is much higher than expected. The authors propose that lignin degradation releases acids able to dehydrate cellulose and to promote its charring. Lignin also increases the activation energy of combustion. Nevertheless other studies have already noted an opposite effect: lignin would prevent the thermal polymerization of levoglucosan, leading to a reduction of char fraction [32]. Yao et al. have studied a wide range of natural fibers by thermogravimetric analysis. They did not find any significant correlation between lignin content and char yield or apparent activation energy of pyrolysis (around 150–175 kJ/mol) [25]. To explain the apparently contradictory results about the role of lignin, it can be assumed that the composition and the structure of the fibers are much complex and may not be oversimplified using a linear rule of mixtures on the lignin content. Indeed, Lewin et al. have shown for a long time the influence of fine structure of cellulose (crystallinity, orientation, molecular weight, interchain distance and hydrogen bonds) on pyrolysis [33, 34]. It is obvious that the even more complex structure of natural fibers must also play a significant role on pyrolysis.

The heat released from the combustion of natural fibers releases around 8–12 kJ per gram of gases, which should contribute to the propagation of the flame [31, 35]. Nevertheless, this contribution is limited. Indeed, taking into account the relatively low effective heat of combustion and the char yield of many fibers, heat released by the burning of fibers is only around 8 kJ per gram of fibers. This is much lower than many polymers as PE, PP, PBS or PLA. Therefore the incorporation of natural fibers leads to a decrease in total heat release of many composites (Fig. 3.1). Of course, in the case of low flammable polymers like polyfurfuryl alcohol [36] or polybenzoxazine [37], the contribution of natural fibers to heat release becomes prominent.



**Fig. 3.1** Calculated relative total heat release of composites based on various polymers containing glass fibers or flax fibers—values are calculated according to a linear rule of mixtures

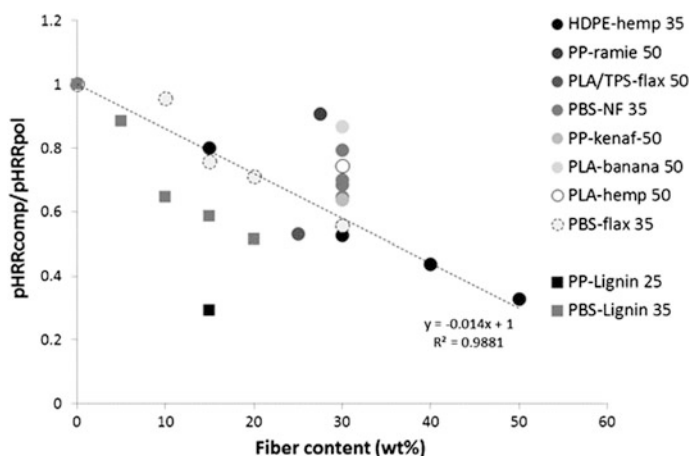
## 3.2 Fire Properties of Composites Reinforced by Natural Fibers

### 3.2.1 Influence of Raw Natural Fibers

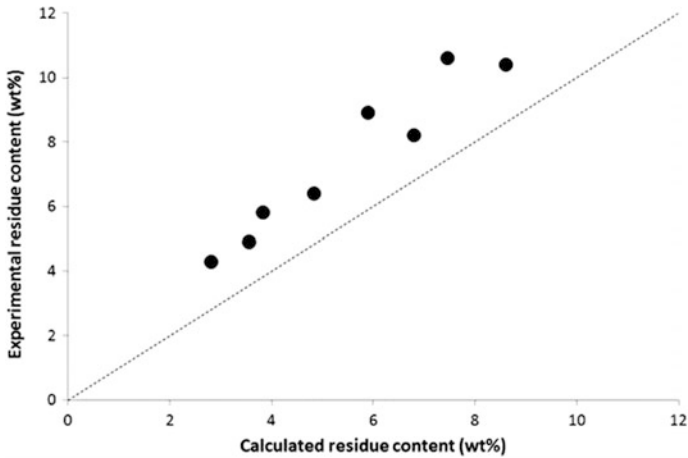
There are now consistent results about the influence of natural fibers on flammability of biocomposites. Natural fibers include at least flax, hemp, bamboo, banana, kenaf, sugar cane. Polymer matrices are mainly PE, PP, PLA and PBS. Attempts were made to incorporate natural fibers into engineering plastics as PA6 and PBT [37]. In all cases, natural fibers lead to a decrease of peak of heat release rate [35, 38–40] (Fig. 3.2). For a given series of composites, the decrease seems to be proportional to the fiber content. The best results indicate a decrease of pHRR around 14% for each addition of 10 wt% of fibers [35, 38]. One reference shows a slightly higher decrease of pHRR when 25 wt% of flax fibers are incorporated into a blend of PLA and thermoplastic starch (PLA/TPS) plasticized by glycerol [41]. A minimum content of natural fibers is required to form a protective barrier against fire. For example, Dorez et al. [35] evidenced that over 10 wt% of flax fibers, the HRR curves exhibit a plateau, typical of a barrier effect.

As expected from already discussed considerations, time-to-ignition is often reduced due to the presence of low thermally stable fibers [35, 38]. Nevertheless, this decrease is not systematic or sometimes is not significant [39–41].

Char yield of composites is quite often increasing when incorporating natural fibers, in particular when polymer is unable to char as polyolefins or aliphatic polyesters. In most articles, the experimental char yields are not compared to those calculated using a linear rule of mixtures. In the case of PBS filled with different



**Fig. 3.2** Evolution of relative pHRR versus fiber content for various non-flame retarded biocomposites. Figures on caption correspond to heat flux (plotted results from [24, 35, 38–41, 55, 56, 63, 65])



**Fig. 3.3** Experimental versus calculated residue contents of biocomposites PBS-flax fibers in anaerobic pyrolysis (from TGA results [35])

contents of various natural fibers, Dorez et al. observed the experimental char yield is systematically slightly higher than the expected values [35] (Fig. 3.3).

Apart from cone calorimeter, other fire characterizations were made on various biocomposites. We report here only results about the most common fire tests.

LOI is often slightly reduced in the presence of natural fibers [41–43] but it is not systematic [24, 44]. For example, Sain et al. have observed a slight increase in LOI for PP filled with 50 wt% of sawdust or rice husk (from 24 to 25–26) [45]. The decrease in LOI is assigned by some authors to the wicking effect [41, 43, 46]. This explanation is discussed in a further section. When a matrix is not rated at UL94 vertical burning test, the incorporation of natural fibers does not allow improving the rating [40–42, 47, 48]. Dripping is still observed in many cases. Glow wire flammability index of a PP copolymer drops from 725 to 675 °C when adding 30 wt% of kenaf fibers [40]. This last value is in good agreement with that found by Scharrel et al. for PP filled with 30 wt% of flax fibers (650 °C) [47]. Horizontal burning rates (ASTM D 635) are significantly increasing after incorporation of 50 wt% of sawdust or rice husk into PP [45]. Jeenchan et al. also observed an increase of horizontal burning rate for PP containing 30 wt% of sisal fibers using the same test [42]. This is not surprising considering the effect of a low thermal stability on propagation rate predicted by some models [49]. On the contrary, Suardana et al. noted a decrease in burning rate at the same test for PLA and PP after incorporation of jute or coconut fibers (volume fraction 35%) [50].

It is noteworthy that beyond the common tendencies listed just above, strong differences can be found depending on the type of natural fibers. There are relatively few studies comparing the fire performances of biocomposites (i.e. one polymer reinforced with various natural fibers). For example, Dorez et al. compared PBS composites filled with pure cellulose, flax, hemp, sugar cane and bamboo at a



weight content of 30 wt% [35]. The differences in terms of time-to-ignition or pHRR in cone calorimeter test are significant. Manfredi et al. observed even more variations for acrylic resins filled with jute, flax and sisal fibers (30% in volume) [51]. Time-to-ignition in cone calorimeter at 35 kW/m<sup>2</sup> is 110 s for flax but only 52 s for sisal. Peak of heat release rate is close to 500 and 900 kW/m<sup>2</sup> for sisal and jute, respectively.

Note that the performances of composites based on natural fibers do not depend only on the composition and content of fibers. Even if this point has been scarcely studied, the dispersion and length of short fibers in thermoplastics, or the fabric structure in thermoset composites must have a significant impact. Wang et al. have compared the flammability of two HDPE composites filled with 15 wt% of hemp short fibers using cone calorimeter [38]. The composite containing 2 wt% of maleic anhydride-grafted polyethylene (MAPE) exhibits a HRR plateau and a lower pHRR (around 2000 kW/m<sup>2</sup>) while the pHRR of the non-compatible composite is close to 2750 kW/m<sup>2</sup> without HRR plateau. The authors assigned this difference to the enhanced dispersion of fibers into the matrix due to MAPE allowing a more efficient barrier effect. Chai et al. have compared three epoxy composites based on flax fabrics with different structures using various fire tests [21]. For example, in cone calorimeter, the performances of the three composites are different in terms of time-to-ignition or peak of heat release rate. In vertical burning test, the burning duration and the mass loss also change according to the fabric structure.

### **3.2.2 Role of Lignin**

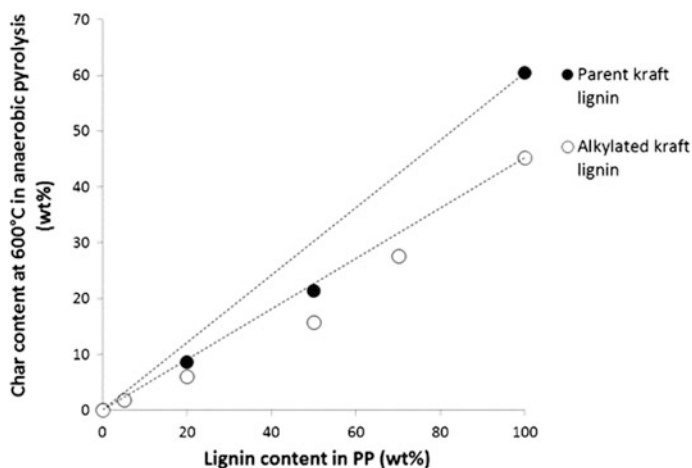
We have already discussed about the role of lignin on the flammability of natural fibers. Its influence on the fire behavior of biocomposites was highlighted by several studies.

Shukor et al. have studied biocomposites based on PLA and kenaf fibers using APP [52]. They compared raw and alkali treated kenaf fibers. Alkali treatment using different NaOH concentration allows removing lignin. Lignin content is not mentioned in this work but it is around 8–19 wt% in raw kenaf fibers [28, 53]. The thermal stability of composites is slightly enhanced when lignin is removed. But residue content and LOI are reduced. LOI decreases from 29.4 when raw kenaf fibers are used to 28.0 when fibers are treated with the highest concentration of NaOH. Similarly, residue content in anaerobic pyrolysis at 600 °C decreases from 19.4 to 16 wt%. Jute fibers were added to vinyl ester resin [54]. The decomposition temperature of both components (jute and resin) tends to increase by a few degrees (2–5 °C) after alkaline treatment of fibers (which reduces hemicellulose and lignin contents). But contrarily to Shukor's work, the residue content of the composite increases significantly when jute fibers are treated.

Due to the high char yield of lignin, several authors have attempted to use it directly alone or in combination with other flame retardants [55–58]. De Chirico et al. have incorporated 15 wt% of lignin into non-charring polypropylene [55]. The

peak of heat release rate is reduced from 1400 to 410 kW/m<sup>2</sup>. Such a drop (−70%) is much more impressive than for composites filled with natural fibers (around −20, −25% at the same content). Ferry et al. have also observed a significant decrease in pHRR for PBS composites containing various contents of alkali lignin (−40% for 15 wt% of lignin) [56] (Fig. 3.2). In De Chirico’s work, the formation of char is only due to lignin (15 wt% of lignin leading to 6 wt% of char) but it is enough to observe a strong decrease of pHRR. Chen et al. have also observed that the char yield of composites PP filled with alkylated or raw kraft lignin increases when more lignin is incorporated [59]. Nevertheless the char yields are always below the values calculated from a linear rule of mixtures (Fig. 3.4). On the contrary, Ferry et al. have concluded about some interactions between lignin and PBS because the experimental char contents in thermogravimetric analysis are slightly higher (around +2 wt%) than the values calculated from a linear rule of mixtures [56]. Actually, the explanation may be more complicated as the experimental char contents of PBS filled with lignin-free fibers (pure cellulose) are also higher than expected [35].

Different types of lignin exist and exhibit various compositions and charring capacity. De Chirico et al. measured a char content of 40 wt% at 700 °C [55] while Ferry et al. noted that alkali and organosolv lignin exhibit a char yield of 53.5 and 58.7 wt% at 750 °C, respectively [56]. Moreover, the latter authors have attempted to enhance the char yield by grafting phosphorus molecules onto lignin. No significant increase in char yield was noted. Moreover, the fire behavior of PBS containing 20 wt% of lignin is unchanged in cone calorimeter after modifying lignin. But the authors note that the residues of PBS composites with modified lignin are more homogeneous and cohesive with fewer cracks.



**Fig. 3.4** Char content in anaerobic pyrolysis versus lignin content for PP-lignin biocomposites (from [59]). Dotted lines represent the values calculated from a linear rule of mixtures

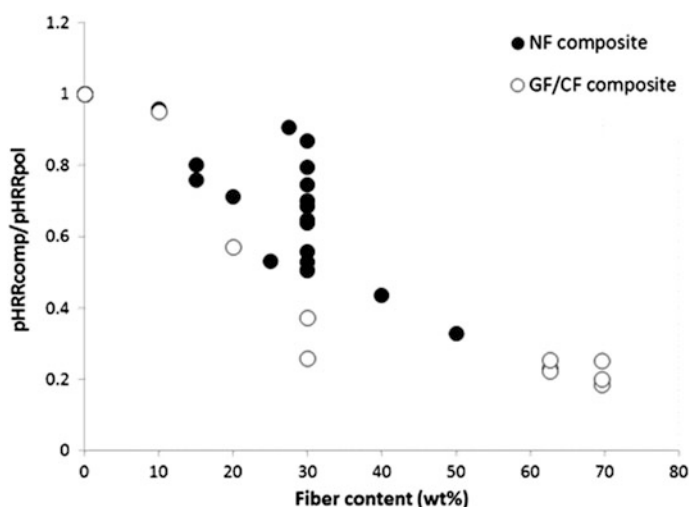
Most generally, the incorporation of lignin into a polymer leads to a reduction of thermal stability and time-to-ignition [55, 56]. Nevertheless it is not always the case. Hence, Chen et al. have studied PP composites filled with kraft lignin [59]. The temperatures for 10 and 50 wt% of mass loss increase from 406 to 443 °C for pure PP to 433 and 472 °C for PP containing 5 wt% of alkylated lignin. At higher content, the degradation starts earlier.

Zhang et al. pointed out another effect of lignin on flammability of composites [57]. The authors have prepared flame retarded silicones filled with high amount of lignin. The best ranking at UL94 test (V-0) can be reached if thermal and chemical post-treatments are applied to remove Si-H groups on silicones. They observed that the decomposition rate of composites is slowed down above 450 °C and explained that lignin acts as phenolic antioxidant trapping radicals and then protecting silicone from radical degradation.

The presence of lignin may also change the capacity of natural fibers to be grafted by some molecules as revealed by Dorez et al. [60] and discussed in the following.

### 3.2.3 Comparison with CF or GF Composites

When the influence of natural fibers is compared to that of glass or carbon fibers in terms of pHRR reduction, it seems that glass or carbon fibers may perform slightly better (Fig. 3.5). But a systematic comparison rather than a compilation of results from various articles would give more reliable conclusions.



**Fig. 3.5** Evolution of relative pHRR versus fiber content for various biocomposites and composites (plotted results from [9–11, 15, 24, 35, 39–41, 63, 65])

Some articles deal with the comparison of the flammability of composites reinforced with glass fibers or alternatively natural fibers. But systematic comparison is scarce. El Sabbagh et al. have studied PA6 and PBT composites filled with flax or glass fibers using a cone calorimeter [61]. Some composites were flame retarded with organic phosphate and/or boehmite. The fiber content was fixed at 30 wt%. There is no clear tendency when comparing similar composites reinforced with flax or glass fibers. In some cases, the glass fibers-reinforced composite performs better (lower pHRR). But similar results are obtained in several cases. Non-flame retarded PA6 composite filled with flax fibers exhibit a lower pHRR than its counterpart reinforced by glass fibers. Same conclusions may be drawn considering THR.

Same results can be drawn from the work of Hapuarachchi et al. [62]. The authors have compared flammability of sheet moulding compounds (SMC) reinforced with hemp or glass fibers using cone calorimeter at various heat fluxes. Some SMC were flame retarded with aluminum trihydrate. SMC filled with hemp fibers exhibit higher THR than SMC filled with glass fibers with or without flame retardant. pHRR was lower for non-flame retarded SMC filled with glass fibers. But when aluminum trihydrate was added, SMC reinforced with hemp fibers performed better. More surprisingly, SMC filled with hemp fibers ignited later than their counterparts, particularly at low heat flux ( $25 \text{ kW/m}^2$ ).

Glass fibers are denser than natural fibers. Then when composites reinforced with glass or natural fibers are compared at the same weight loading of fibers, the amount of matrix is higher in the composite reinforced with glass fibers. Another (more valuable?) comparison is to study composites filled with the same volume fraction of fibers. Hence the amount of matrix is kept constant. This was the choice of Chai et al. [21]. The authors have compared different epoxy composites based on flax and glass fabrics. The volume fraction of fibers was fixed at 40%. Characterizations include horizontal and vertical burning tests and cone calorimeter tests. The structure of glass fabrics is similar to that of flax fabrics. Results show clearly that glass fibers-reinforced composites perform better. They exhibit higher time-to-ignition, lower peak of heat release rate, lower mass loss (and consequently lower total heat release). Indeed, at same volume fraction, the same amount of polymer can burn but flax fibers also contribute to heat release in composites filled with natural fibers. Moreover, the authors noted that glass-reinforced composites maintain their initial shape. On the contrary flax fibers-reinforced composites deform with delamination and bulging. Hapuarachchi and Peijs have also reported such a phenomenon [63]. Manfredi et al. have compared various composites based on unsaturated polyester or acrylic resin and reinforced with natural or glass fibers at a same volume fraction (30%) [51]. Based on cone calorimeter test, the authors confirmed that glass fibers-filled composites exhibit better performances, and in particular a lower heat release as expected.

As noted above, some authors consider that natural fibers promote wicking effect as glass fibers. Nevertheless, it is doubtful that the flowing of polymer is favored along the natural fibers. Indeed, natural fibers have a lower thermal conductivity and are much rougher than smooth glass fibers. Moreover, they are able to char

even without flame retardant. In other words, the interfacial charring proposed by some authors for composites filled with glass fibers [13] can improve the flame retardancy of biocomposites by reducing the heat release and increasing the char yield but not by preventing the irrelevant wicking effect.

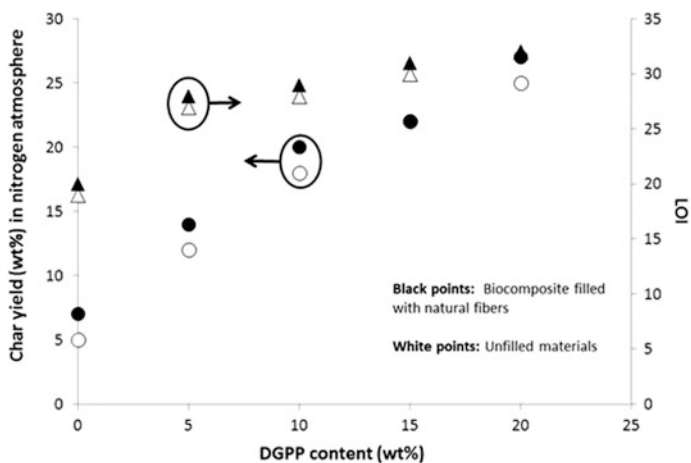
### **3.3 Flame Retardancy of Biocomposites**

In most cases, the flame retardancy of natural fibers reinforced composites was provided by the incorporation of flame retardant additives into the matrix. In many articles it is not specified if the addition of the FR system is expected to have an effect on the natural fibers or on the matrix thermal degradation pathways or on both. Another strategy could be to modify specifically the degradation pathway of NF by grafting or adsorbing or encapsulating the fibers with appropriate species (molecules or particles). The modification of the chemistry of the fiber is often performed in order to avoid the formation of levoglucosan [64].

#### ***3.3.1 Incorporation of Flame Retardants into the Matrix***

The most used FR additive is surely ammonium polyphosphate, which is well known as char promoter in presence of a carbonization agent [35, 47, 48, 52, 65, 66]. While natural fibers are rich in polyhydric compounds, ammonium polyphosphate can be very effective even in composites based on polyolefin matrix as polypropylene for example. In that case, natural fibers can be considered as a part of a multicomponent FR system. Other phosphorus compounds as 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), phosphoric acid or dihydrogen ammonium can act similarly to APP [67, 68].

Le Bras et al. have prepared PP/flax fibers composites flame retarded with APP and with a complex intumescent system (IFR—based on APP, melamine and pentaerythritol) [66]. The ratio PP/fibers is fixed to 1.5. The authors observed that both flame retarded composites perform similarly in cone calorimeter test. In other words, APP and flax react to form a charred layer protecting the underlying material similarly to an intumescent system, confirming that flax can be used as a charring source. Nevertheless, the PP/flax/APP composite is not rated at UL94 test (too long combustion time and formation of burning drops) while the PP/flax/IFR composite is V-0 rated. Schartel et al. [47] have also observed that APP and flax react to form a charred layer. Moreover, APP allows to increase the LOI from 21 (only PP with 30% of flax) to 26 (when 25% of PP was replaced by APP). A V-0 rated was obtained by Nie et al. [48] using 20% of microencapsulated APP (MCAPP) in a PBS/bamboo fiber (30/50) composite. Similarly, Reti et al. tried to replace the typical pentaerythritol (PER) with 10% of lignin (replacement of petroleum sources with natural renewable resources) used as charring source into intumescent flame



**Fig. 3.6** Influence of diglycidylphenylphosphate on the flame retardancy of materials based on DGEBA and natural fibers (from [44])

retarded PLA (containing 30 wt% APP) [69]. Lignin does not perform as well as PER in terms of LOI and pHRR in cone calorimeter. On the contrary, lignin allows reaching V0 rating at UL94 test while the formulation with PER is only V2 rated.

It is noteworthy that the combination of phosphorus flame retardants and natural fibers does not lead systematically to a synergy. For example, Sudhakara et al. have studied composites based on DGEBA and Borassus fruit fibers [44]. The composites were flame retarded with various contents of diglycidylphenylphosphate (DGPP). This flame retardant improves the flame retardancy of the composites, in terms of char yield, LOI or burning rate. But the improvement is the same with or without 5 wt% of fibers (Fig. 3.6). This may be assigned to the low content of fibers.

Other flame retardants have been used. A detailed list of flame retardants can be found elsewhere [1, 5]. Sain et al. used magnesium dihydroxide and boron-based compounds to improve the flame retardancy of PP filled with sawdust and rice husk [45]. Hapuarachchi et al. incorporated mineral filler (aluminum trihydrate) into SMC filled with hemp fibers [62]. Jeenchan et al. have attempted to flame retard PP/sisal using zinc borate or magnesium hydroxide [42]. But when mineral flame retardants and phosphorus compounds have been compared at same contents, it seems that the former were not as efficient as the latter [42, 48, 70]. It may be due to the fact that mineral fillers like magnesium or aluminum hydroxide are efficient only at very high loadings. But the main reason is probably that natural fibers and phosphorus compounds cooperate as already explained: phosphorus flame retardant is the acid source reacting with the hydroxyl groups of the fiber leading to dehydration and charring of cellulose [71].

Nanoparticles are scarcely used alone to improve fire retardancy because they are not able to improve all the aspects of the fire behavior. Indeed, they are mainly

efficient to only reduce the heat release rate. When they are used alone in biocomposites, it has been reported that the presence of natural fibers can increase the pHRR probably by disturbing the protective layer formed by the accumulation of nanoparticles at the top surface. The incorporation of banana fibers into a PP matrix flame retarded with nanoclays leads to a linear increase of the peak of heat release rate in cone calorimeter test (heat flux 50 kW/m<sup>2</sup>) [72]. The pHRR increases from 748 to 1256 kW/m<sup>2</sup> when 30 wt% of fibers are incorporated. Hapuarachchi and Peijs have also observed that hemp fibers increase the pHRR of PLA flame retarded with nanoparticles (sepiolite and multiwalled carbon nanotubes) in cone calorimeter test [63]. The authors noted that hemp fibers provoke severe delamination during the test. Interestingly, when nanoparticles are adequately modified, they can be highly efficient on flame retardancy of biocomposites. For example Yu et al. [68] proved the efficiency of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) functionalized MWCNTs to improve UL94 test and limiting oxygen index (LOI) of ramie/poly(lactic acid) (PLA) composites. The char improvement is allowed thanks to a high dispersion of the functionalized MWCNTs and the interaction between DOPO and ramie fibers (that acts as a charring agent).

On the whole, phosphorous compounds seem to be the most efficient FR in NF based biocomposites. As they are incorporated by additive way, a high amount is usually needed that can induce a significant degradation of mechanical properties and may provoke processing troubles [61, 73]. For example, Zhang et al. have studied PP composites filled with APP and silica. Both fillers lead to a decrease in mechanical properties, particularly impact strength. Moreover, the authors note that these fillers have a certain impact during foaming using CO<sub>2</sub> as blowing agent [73]. One alternative that can be used for laminates is to protect the composite by a fire retardant layer (multilayer composites) as proposed by several authors [74, 75]. The geometry as well the choice of the composition for each layer has a great influence on properties, including fire properties [74, 76]. Another alternative is to incorporate the FR in reactive way, in order to flame retard the reinforcement. Therefore, the question is: Is it possible to reach the same fire performances by flame retarding only the natural fibers? A less ambitious (but more realistic) objective may be to combine both approaches in order to reduce the FR amount in the matrix: the incorporation of FR additives into the matrix and the chemical grafting of FR on the natural fibers.

### ***3.3.2 Is to Flame Retard Natural Fibers Enough to Impart Fire Performances to Composites?***

Natural fibers are sometimes functionalized to improve their compatibility with the matrix. Even if these treatments are not intended to improve the flame retardancy, some authors have noted that the fiber modifications have an impact on the fire behavior, especially on LOI [77–80]. Hence, Nair et al. [78] found that PS

composites filled with modified (benzoylated and acetylated) sisal fibers exhibit a better thermal stability than the composite containing unmodified fibers. According to the authors, this is explained by the improved stability of modified fibers themselves but also by the interactions between the modified fibers and the matrix. Silanated *Grewia optiva* fibers increase the thermal stability and the residue content of unsaturated polyester filled with 30 wt% of fibers [77]. The limiting oxygen index is also slightly enhanced from 19 to 22 when fibers are silanated. VP et al. [39] have not observed that silanization of banana fibers does improve the thermal stability of PLA biocomposites. But the burning rate is reduced in UL-94 horizontal test, dripping is limited and drips do not ignite cotton. Moreover the pHRR in cone calorimeter decreases from 398 kW/m<sup>2</sup> for PLA containing 30 wt% of untreated banana fibers to 340 kW/m<sup>2</sup> for PLA filled with silanated fibers at the same loading.

The strategies to flame retard natural reinforcements can be directly inspired from techniques used in textile industry. There is a huge literature about the flame retardancy of plant-based textiles, mainly cotton. Alongi et al. [81] have recently reviewed the innovative methods to impart flame retardancy to fabrics. Among the reviewed methods, layer-by-layer (LbL) assembly process has attracted the interest of several researchers. Flame retardancy was imparted mainly to cotton fabrics [82–85], but also ramie fabrics [86] or delignified wood fibers [87]. In most cases, phosphorus-based compounds were used to promote the charring. To the best of our knowledge, LbL has rarely been used to flame retard a natural reinforcement for composite applications. Li et al. [37] have coated a ramie fabric using this method and incorporated it into a polybenzoxazine composite. The coating is constituted by ammonium polyphosphate (APP) and polyethyleneimine. The fabric content was around 65–70 wt%. The LbL treatment strongly increases the LOI: from 26.5 for the composite containing the uncoated fabric to 38.9. The coating also allows reaching V-0 rating at UL94 test. The thermal stability is enhanced above 300 °C under nitrogen and air and the residue content is significantly increased (by 15% under nitrogen). In this case, due to the high amount of ramie fibers and to the intrinsic good behavior of the matrix, the flame retardancy of fibers allows dramatically improving the performances of the composite.

Some authors have modified natural fibers by adsorbing or absorbing some phosphorous flame retardants as DAP, APP or phosphoric acid without washing fibers after modification [43, 46, 50]. For example, Suardana et al. have treated coconut and jute fibers with diammonium phosphate and incorporated them into PLA or PP at a volume fraction of 35% [50]. The phosphorus content into fibers was not measured. The flammability of composites is reduced as proved by the decrease in burning rate (horizontal propagation) and the increase in char yield.

Grafting of FR is another strategy. In most cases, it is involved through hydroxyl groups of cellulose or lignin. Dorez et al. used molecules (cellulose, xylan and lignin) to study the reactivity of natural fibers toward phosphonic acid molecules (such as octadecylphosphonic acid, ODPA) [60]. They proved that ODPA reacts strongly with lignin and at a lower degree with xylan (model for hemicellulose) whereas no reaction with cellulose was evidenced. These results mean that in soft conditions used in this study, phosphonic acid preferentially reacts with aromatic



hydroxyl groups rather than with aliphatic ones. Then the modification may be much more effective for lignin-rich natural fibers.

Du et al. have chemically wrapped via in situ condensation reaction a phosphorus and nitrogen containing flame retardant onto ramie fibers [24]. The authors have firstly carried out an alkali treatment on fibers to “activate” hydroxyl groups, i.e. to remove hemicellulose and lignin but also surface impurities (other treatments may be used as ethanol to remove waxes and pectins ensuring the cohesion of fibers beam [67]). The phosphorus content was not precised but the char yield under nitrogen increased from 8 to more than 40 wt% for the fibers. Fibers were incorporated at 40 phr into PP (containing a small part of maleated polypropylene). The char yield of composites was 0 wt% for PP and PP filled with unmodified ramie fibers, but 12.6 wt% for PP filled with phosphorylated fibers. As expected, the thermal stability of modified fibers was reduced leading to a lower time-to-ignition in cone calorimeter test. The peak of heat release rate decreased from 714 kW/m<sup>2</sup> for PP containing unmodified ramie fibers to 548 kW/m<sup>2</sup> when fibers were phosphorylated. LOI was also slightly enhanced (from 18 to 20).

Dorez et al. have compared the phosphorylation of flax fibers using molecular (dihydrogen ammonium phosphate—DAP) or macromolecular (poly(methacryloyloxy)methyl phosphonic acid homopolymer and poly(methacryloyloxy)methyl phosphonic acid methylmethacrylate copolymer) flame retardants [88]. For similar phosphorus content, thermal stability is more reduced and charring is more enhanced with DAP. According to the authors, it is due to the fact that phosphorus from DAP is covalently directly bonded to flax while only a fraction of phosphorus from macromolecular flame retardants is involved in the grafting. In other words, the phosphorus fraction not directly bonded to flax is less efficient to promote dehydration of cellulose (maybe because a less close proximity). When the authors incorporate the phosphorylated flax fibers onto PBS matrix, they observe that the degradation of PBS is not affected by the presence of fibers. Phosphorus acts as char promoter only for the fibers and not for the matrix. It seems that DAP does not perform better than macromolecular flame retardants when composites are tested using cone calorimeter. The authors explain that these phosphonated macromolecules are able to char themselves leading to the formation of a sheath that acts as a barrier effect. This effect is not highlighted in thermogravimetric analysis because barrier effect is not efficient at microscale.

While phosphorus directly bonded to flax fibers seems to be more effective to promote charring, the same authors have compared in deeper details the grafting of octadecylphosphonic acid (ODPA) and dimethyl(octadecyl)phosphonate on the different components of flax [60]. The authors have shown that only phosphonic acid function is able to be grafted and not phosphonate group.

Natural fibers differ from synthetic fibers by their high porosity. Therefore the natural fibers can be flame retarded in bulk and high amounts of FR can be grafted while synthetic fibers are flame retarded only on their surface (except if a flame retardant is added directly during processing). Nevertheless, in many articles, the location of flame retardants onto (or into) the fibers is not specified. This point has been addressed by Sonnier et al. [27]. These authors have used ionizing radiations

to graft phosphorus flame retardants into flax fibers. Ionizing radiations allow grafting FR to ligno-cellulosic materials without involving hydroxyl groups. The main drawback of this method is that cellulose is highly sensitive to irradiation and its molecular weight decreases drastically even at moderate dose (above 20 kGy). Nevertheless the authors have shown that it is possible to graft high amounts of phosphorus onto flax fibers at low doses (more than 3 wt% of phosphorus at 10 kGy) when molecules (dimethylvinyl phosphonate—MVP) diffuse into the fiber bulk. On the contrary the grafting content is low (<0.5 wt% of phosphorus) when the flame retardant (dimethyl(methacryloxy)methyl phosphonate—MAPC1) remains on the fiber surface. In this work, it was not possible to determine if flame retardants were grafted to cellulose or homopolymerized and trapped into the fiber core. Self-extinguishing flax fabrics are obtained when the phosphorus content exceeds 1 wt%. Char content is roughly proportional to the phosphorus content. When modified flax fabrics are incorporated into unsaturated polyester, the fire behavior of the composite is slightly improved (using cone calorimeter test) (Fig. 3.7). Nevertheless, phosphorous flame retardants act mainly as char promoter and then do not modify the pyrolysis of the matrix. It results only on the charring of the fabric (representing around 30 wt% of the total weight of the composite). Then this strategy does not allow the composite to reach the highest level of flame retardancy.

If the flame retardancy of natural fibers is most often carried out by using phosphorous flame retardants, other possibilities exist. As an example, Zhang et al. have flame retarded cellulose fibers by grafting zinc ion [20]. Maleic anhydride is first grafted on cellulose by reacting with hydroxyl groups. Then zinc ions were grafted onto modified fibers using zinc carbonate. Strong decrease of flammability is measured using cone calorimeter and LOI. LOI is improved from 19 to 30 when zinc content increases to 4.96 wt%. The authors consider that zinc ion catalyzes the

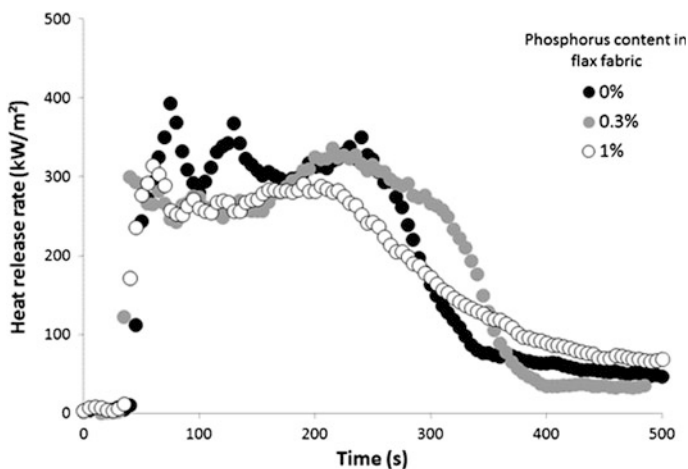


Fig. 3.7 Heat release rate curves of composites containing flax fabrics (unpublished data)

dehydration of cellulose, inhibiting its depolymerization and promoting its charring. Moreover, metal compounds are generated, covering the fibers surface to stop the oxygen penetration and the release of pyrolytic gases.

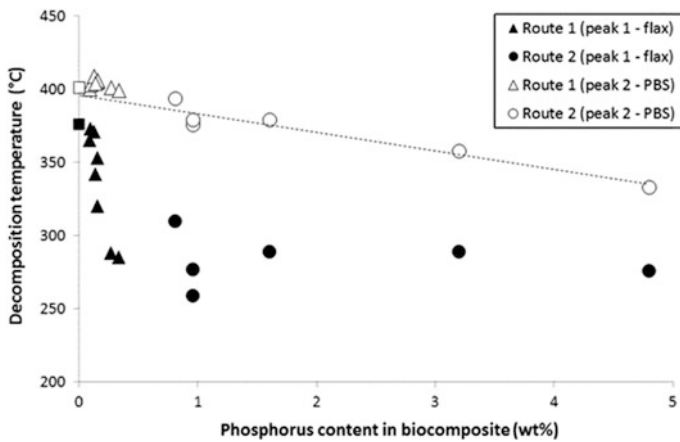
Combined strategies may also be considered. Zhou et al. have coated kenaf fibers with zinc oxide [89]. The objective of these authors is to partially replace a phosphorus-based flame retardant (resorcinol di(phenyl phosphate)—RDP) by these modified fibers into flame retarded PLA. The ZnO coating allows RDP to be adsorbed onto kenaf fibers. Therefore, the dispersion of fibers is improved and a better flame retardant effect is claimed by the authors. Indeed, PLA is V-0 rated at UL94 test with only 9 wt% of RDP and 6 wt% of modified kenaf fibers. Nevertheless, no comparison was performed with similar composites containing unmodified fibers and thermogravimetric analyses do not support any enhancement of char formation.

Composites based on natural fibers have become attracted for ten or fifteen years, i.e. more or less when halogenated flame retardants are gradually replaced by other alternatives. Then there are very few studies about the use of halogenated compounds to flame retard biocomposites. Misra et al. have brominated coir fibers to improve the LOI of epoxy composites [90]. Nevertheless, the coir content is only 5 wt% and fibers are used as filler rather than as reinforcement.

### **3.3.3 Comparison of Both Approaches**

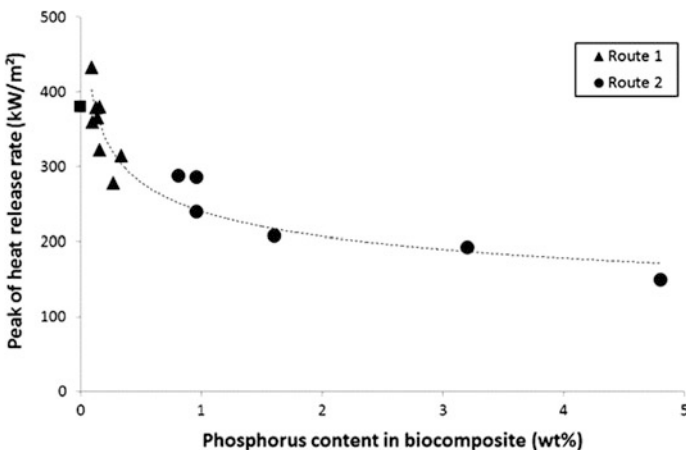
Some researchers have compared both approaches cited above, i.e. the incorporation of FR additives and the functionalization of natural reinforcement to flame retard biocomposites.

Dorez et al. have treated flax fibers with two different flame retardants (dihydrogen ammonium polyphosphate—DAP and phosphoric acid—PA) [67]. They incorporated these treated fibers into PBS matrix (route 1) and compared the performances of these biocomposites to PBS-flax fibers composites filled with additive flame retardants (route 2): DAP, PA but also APP. The fiber content is fixed at 30 wt%. The authors noted that the decomposition peak temperatures measured in thermogravimetric analysis decrease with the amount of phosphorus (Fig. 3.8). The decrease is fast for the first peak corresponding to flax degradation. The second peak corresponds to the PBS decomposition. Its temperature remains stable around 400 °C for biocomposites prepared with modified flax fibers but decreases for biocomposites flame retarded with additives. The authors explained that FR additives present in the matrix promote the hot hydrolysis of PBS while this phenomenon is inhibited when FR are present on the fibers. Nevertheless, the difference between results obtained with additive and reactive strategies may also be related to the higher content of phosphorus into biocomposites filled with phosphorous additives or to the specific role of APP (phosphorus contents higher than 1 wt% were reached only with APP).



**Fig. 3.8** Decomposition temperatures of PBS and flax fibers in biocomposites PBS-flax fibers (from [67])

Flammability of biocomposites was assessed using cone calorimeter at  $35 \text{ kW/m}^2$  (Fig. 3.9). DAP on fibers is more effective to promote charring than into PBS matrix. Nevertheless, only the incorporation of APP at higher contents allows reaching high char yields (up to 30 wt%). The peak of heat release rate decreases when phosphorus content increases. But this tendency is not linear. On the one hand, the incorporation of additives into PBS matrix leads to lower pHRR because this route leads to higher phosphorus contents. But on the other hand the proximity of the phosphorous compound with the flax fibers may allow the formation of an efficient barrier layer even at low phosphorus content. It is not possible to determine



**Fig. 3.9** Peak of heat release rate (in cone calorimeter) of biocomposites PBS-flax fibers (from [67])

which route is more effective at similar phosphorus content because the phosphorus content in composite remains low ( $<0.4$  wt%) when flax fibers were modified.

Szolnoki et al. have modified hemp fabric using different methods: absorption of phosphoric acid (called Thermotex treatment), modification using an aminosilane coupling agent and a combination of both treatments [43]. The thermal stability of fibers is reduced by Thermotex but not by silanization. All treatments improve the residue content in nitrogen atmosphere from around 30 to 40–45 wt%. The flammability of epoxy composites containing 30 wt% of these fabrics has been studied. The modification of fabrics allows increasing LOI from 22 to 26–28 but all composites fail to UL94 vertical burning test. Residue increases from 1.8 to 7.4–9.6 wt% in cone calorimeter (at  $50 \text{ kW/m}^2$ ) but the improvement of flame retardancy is moderate. When a phosphorus curing agent is added into the matrix, the performances are much better. Even without any modification of hemp fabric, LOI is 32, the composite is V-1 rated at UL94 test and pHRR in cone calorimeter is significantly reduced. Char residue increases up to 20.1 wt%. When modified fabric is combined with flame retarded epoxy resin, LOI remains equal to 32 but V-0 rating is reached. Residue content in cone calorimeter is not further improved (around 20 wt%) but peak of heat release rate is reduced and delayed. Then, the phosphorylation of the matrix is much efficient than the modification of fabric. This result can be basically related to the dispersion of phosphorus (present in matrix bulk and not only on the fabric) but also to the phosphorus content. When only fabric is modified, the phosphorus content in the biocomposite does not exceed 0.5 wt%. Biocomposite based on flame retarded epoxy is 1.75 wt% even without any phosphorylation of the fabric.

Bocz et al. have studied the flammability of various PLA/TPS plasticized with glycerol and containing 25 wt% of flax fibers [41]. In their study and contrarily to the previous ones, the phosphorus content is higher by modifying the fibers using a phosphorus silane than by modifying the matrix through the replacement of glycerol by glycerol-phosphate. In the first case, the phosphorus content into the composite was 0.5 wt% (versus 0.2 wt% for the second approach). The results depend on the fire test. LOI increases from 20 to 23 with modified flax fibers, and only to 21 with glycerol-phosphate. On the contrary, pHRR in cone calorimeter test is lower with this latter approach ( $270 \text{ kW/m}^2$  versus  $310 \text{ kW/m}^2$  when fibers are modified). Combining both approaches does not provide much better performances. LOI is equal to 24 but pHRR is  $285 \text{ kW/m}^2$ , i.e. slightly higher than for the composite only flame retarded with glycerol-phosphate.

Shumao et al. have also compared different biocomposites based on PLA and ramie fibers and flame retarded according to different approaches [46]. Three composites were prepared: (i) APP was adsorbed on the ramie fibers and then the modified fibers were incorporated into PLA (composite called PLA-FNF). (ii) APP was added directly into PLA matrix (FPLA-NF). (iii) Ramie fibers were modified and APP was also added directly into PLA matrix (FPLA-FNF). Fiber content was fixed at 30 wt%. APP content is 10.5 wt% for FPLA-NF and FPLA-FNF but only 5.3 wt% for PLA-FNF composite. Therefore the latter composite has poor fire performances: LOI increases from 19.1 (for unmodified composite) to 25 and no rating is reached at

UL94 test. Char residue under air increases from 8.9 to 13.3 wt%. Both other composites (with 10.5 wt% of APP) perform much better. Residue content reaches 19.5–21.9 wt% and V-0 rating is obtained. Moreover FPLA-FNF allows reaching a LOI value of 35.6 versus only 28.1 for FPLA-NF. These results show that it is more efficient to flame retard the fibers in addition to the matrix. According to the authors, it may be due to the candlewick effect which is inhibited when the fibers are treated but we have already discussed this assumption. Note that mechanical tests on biocomposites confirm that modification of fibers allow maintaining better mechanical performances. This may be related to the presence of APP in matrix for FPLA-NF and FPLA-FNF which deteriorates the mechanical properties but the authors also noted from SEM observations that interfacial adhesion between PLA and fibers is better when APP is adsorbed onto ramie.

The main issue of these studies is that both approaches (flame retarded matrix or flame retarded fibers) are compared while the phosphorus content is not the same. With the exception of the study of Bocz et al. [41], the phosphorus content is always higher when an additive phosphorous flame retardant is added into the matrix. This is explained by the fact that the phosphorus content provided by this last method can be (almost) as high as desired. On the contrary, the phosphorus content provided by the modification of fibers is often limited. However, as already discussed, it exists some works allowing to graft high phosphorus content (up to 4 wt%) into a natural reinforcement [27].

### 3.4 Conclusions

Biocomposites filled with natural fibers are nowadays very attractive. In order to extend their application fields, their fire behavior needs to be studied. A quite large but recent literature has been focused on the flame retardancy of these biocomposites. From the results reviewed above, it is possible to draw some main conclusions, even if some specific points are still controversial.

Despite their combustible nature, natural fibers have been very soon considered by researchers as a potential component of flame retardant systems due to their capacity to charring in the presence of phosphorus additives. Ammonium polyphosphate is used in a considerable number of research works to reach flame retarded biocomposites.

Nevertheless, FR additives impact negatively mechanical properties and processing of biocomposites as for all polymeric materials. Therefore, efforts have been made to provide flame retardancy through the modification of the natural reinforcement. From this point of view, the porosity and the surface functions of natural fibers offer more opportunities than synthetic fibers. This strategy has also involved mainly phosphorous flame retardants.

Flame retarded reinforcements have been incorporated into composites. Even if the flammability is reduced, the highest level of flame retardancy cannot be reached without adding flame retardants into the matrix. The main reason of such limited

performances is twofold. First, the phosphorus content grafted onto fibers remains most often limited. Second, the flame retardants are located only on the reinforcement and not dispersed into the matrix. As explained above, most of articles dealt with charring promoters (based on phosphorus) to improve the flame retardancy of natural fibers. In such a case, flame retardants act only on the fibers but the matrix (representing generally more than 50% of the weight) remains unaffected. Due to their high porosity, it should be possible to incorporate high amounts of flame inhibitors able to slowdown the combustion of pyrolytic gases released from the degradation of fibers but also of the matrix. This strategy alone or in combination with charring promoters may be more efficient.

Other aspects deserve to be further investigated. Let us quote two among them. There is very little knowledge about the influence of the fiber structure on the grafting efficiency. At best, the grafting was studied on the separated main components of the fibers, i.e. cellulose, hemicellulose and lignin but the organization of all the components including minor ones can be very complex. The formation of the barrier char layer when natural fibers are decomposing is a main parameter to reach high flame retardancy. Not only the composition and the content of the fibers must be taken into account but also the fabric structure, or in case of thermoplastic matrix filled with short fibers, or the length, entanglement and orientation of fibers. Only few studies have provided some data about these issues.

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