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Chapter 9

An Overview on the Use of Lignin and Its Derivatives in Fire Retardant Polymer Systems

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Additional information is available at the end of the chapter

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Abstract

Lignin is a highly abundant bio-polymeric material that constitutes cellulose one of major component in cell wall of woody plants. Alternatively, large quantity of lignin is yearly available from numerous pulping and paper industries; this is the key point that justifies its large use for industrial applications. Lignin could be one of the most essential and sustainable bio-resources as raw material for the development of environmentally friendly polymer composite. Owing to its huge chemical structure, lignin can provide additional functionality such as filler, reinforcing agent, compatibilizer, stabilizer, etc. In this study, the fire retardant functionality of lignin has been employed in polymeric materials. Due to high charring capability, lignin is effectively used as carbon source in combination with other flame retardants for designing the intumescent system for polymeric materials. Further in this, several articles related to lignin-based intumescent are reviewed and interesting work formulation as well as meaningful results achieved in the flame retardancy are discussed. More attention is given to the studies concerning the use of current intumescent systems for textile applications by means of coating on fabric/nonwoven and melt blending in bulk polymers.

Keywords: lignine, textile, flame retardancy

1. Introduction

Nowadays the growing interest about a green and sustainable development has contributed to recall attention to biomass and specifically to lignocellulosic feedstock as a promising, renewable and vast resource as chemical component, in this context, lignin represents a component of renewable raw material that is available in sufficient quantity and is not in direct competition with food production. After cellulose, lignin is the second most abundant polymer from

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biomass and the main one based on aromatic units [1–3]. It has been reported that worldwide more than 50 million tons of lignin is generated every year as a by-product from pulp and paper-making industries, however less than 2% is actually recovered for utilization as a chemical product and the rest is considered as waste and primarily burned for recovering energy [4, 5]. Therefore, the comprehensive utilization of lignin remains a big challenge. Many efforts have been done to increase the use of lignin into added value added applications [5–7].

In addition to the low-value lignin application, a wide diversity of high-value industrial applications has been industrially realized or demonstrated including uses as novel materials, polymeric, oligomeric and monomeric feed stock. Some of these opportunities, such as the use of lignin or its derivatives in animal feed additives, agriculture, construction, textile, oil drilling, binders, dispersants and composites, are today commercial realities but many others such as the production of carbon fibre precursors, the broad incorporation of lignin in synthetic polymeric blends and textiles or the production of BTX remain longer term opportunities with great value and market potential. In recent years, lignin has been exploited in various polymer composite applications, for example, stabilizing agents, lubricants, coatings, plasticizers, surfactants, carbon fibre, fire retardant (FR), etc. For example, Movil et al. [8] reported the generation of hydrogen through electrochemical oxidation of waste lignin from pulping mills for energy storage. Qin et al. [9] grafted hydrophilic side chains on the sulphonated alkali lignin with different molecular weights, and the resultant product could be used as dispersants for coal-water slurry. Thunga et al. [10] investigated lignin as a suitable precursor for carbon fibres. Yu et al. [11] modified lignin with phosphorus nitrogen molecules to improve thermal stability and fire retardancy of polypropylene.

In recent time, lignin has received great attention as bio-based flame retardant additive because of its high char yield after decomposition from its aromatic framework. It is investigated that the presence of lignin can effectively reduce the flammability of polymers such as polypropylene, PBS, ABS, PET, etc. Further, it is reported that thermal degradation of lignin generates very high amounts of char, around 35–40% [12]. It is well known that the ability to form char during the thermal degradation is a basic aspect of flame retardant intumescent systems. Upon heating, fire retardant (FR) intumescent materials form a foamed cellular charred layer, which protects the underlying material from the action of heat flux and flame. The proposed mechanism is based on the charred layer acting as a physical barrier, which slows down heat and mass transfer between the gas and the condensed phase [13, 14]. Generally, intumescent formulations contain an acid source, a carbon source and a blowing agent. Several studies have been demonstrated that compound like bio-based lignin act as carbon source blended with acidic source such as ammonium polyphosphate (APP), melamine polyphosphate (MPP), metal phosphinate, etc., can be used as intumescent systems for polymer to develop materials with enhanced fire retardant properties [15, 16].

In the pursuit of non-halogenated flame retardant textile, lignin-based intumescent could be considered an efficient system for textiles materials. To provide fire retardancy to textiles, it could be interesting to use lignin-based intumescent at different level of textile structure. In one approach, lignin could be incorporated with flame retardant additives in polymers before the processing of the fibres. In other approach, lignin-based fire retardant formulations could be used as surface treatments by the padding, layer by layer (LBL) and back-coating of on textile structures. Both these approaches are discussed in detail further in the literature.

The aim of this review is to investigate recent researches based on lignin as fire retardant additive for imparting flame retardancy to polymer composites. Intumescent systems based on lignin also have been investigated for textile materials when (1) used in bulk polymer matrix, (2) applied as thin coating or layer for fabrics, to confer fire retardancy. In addition, context also provides overview on different types of lignin, extraction processes and key player of global lignin market. Further different existing and emerging applications of lignin have been discussed briefly. Finally, the future perspective of lignin-based intumescent for imparting flame retardancy is also pointed out.

2. Chemical structure

Lignin plays a major role in woody plants, adding strength and structure to the cell walls, controlling fluid flow and protecting against biochemical stresses by inhibiting enzymatic degradation of other components [17]. It usually contributes between 15 and 40 wt.% of woody plants dry matter [18]. Its chemical structure consists of phenyl propane units, originating from three aromatic alcohol precursors (monolignols) such as p-coumaryl, coniferyl and sinapyl alcohols. The phenolic substructures that originate from these monolignols are called p-hydroxyphenyl (**H**, from coumaryl alcohol), guaiacyl (**G**, from coniferyl alcohol) and syringyl (**S**, from sinapylalcohol) moieties (**Figure 1**). Lignin composition and content are influenced by the species and also by the environment. Hardwood lignins consist principally of **G** and **S** units and traces of **H** units, whereas softwood lignins mostly comprise **G** units, with low levels of **H** units [19]. The variability of lignin composition is much greater in hardwoods than in softwoods.

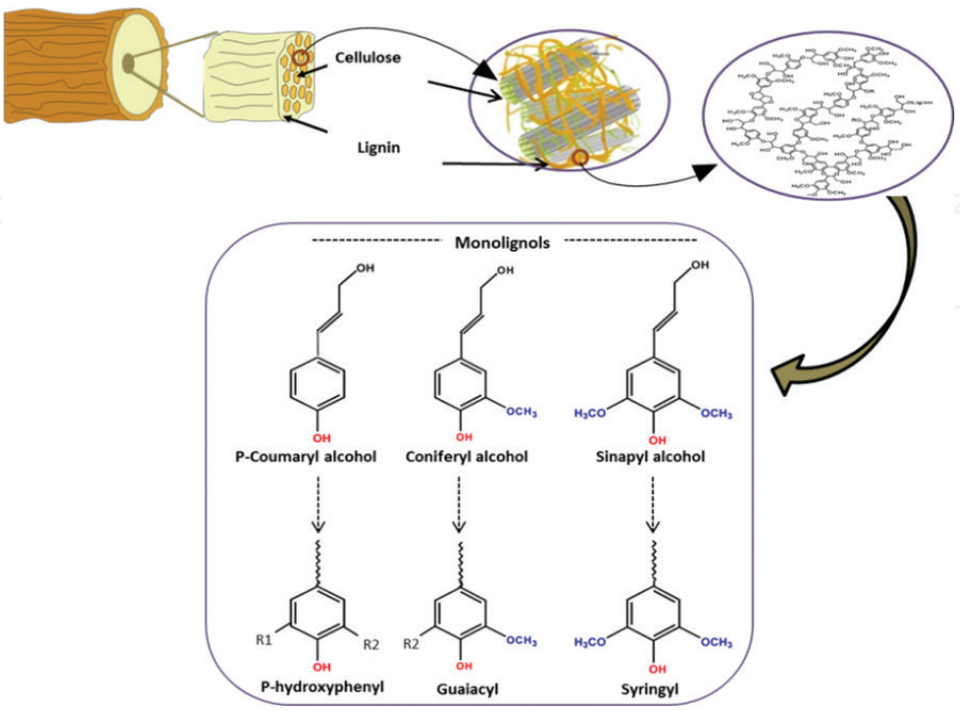


Figure 1. The three main precursors of lignin (monolignols) and their corresponding structures in lignin polymers [19].

Based on the first full lignin structure proposed by Adler in 1977 [20], lignin is recognized as a highly branched heteropolymer without any overall defined chemical structure (**Figure 2**). Lignin contains a variety of functional groups; the most common ones are aromatic methoxyl and phenolic hydroxyl, primary and secondary aliphatic hydroxyl and small amount of carbonyl group. The monomeric C9 unit is linked to form a polymer by C–O–C and C–C linkage. The most abundant lignin interunit linkage is the β-O-4 ether type of linkage, comprising about 50% of the interunit linkages in lignin (ca. 45% in softwoods and up to 60% in hardwoods). Other common lignin interunit linkages are α-O-4 type, resinol (β-β′), phenylcoumaran (β-5), 5-5′and 4-O-5 moieties (**Figure 2**). The number of these structures varies in different lignins.

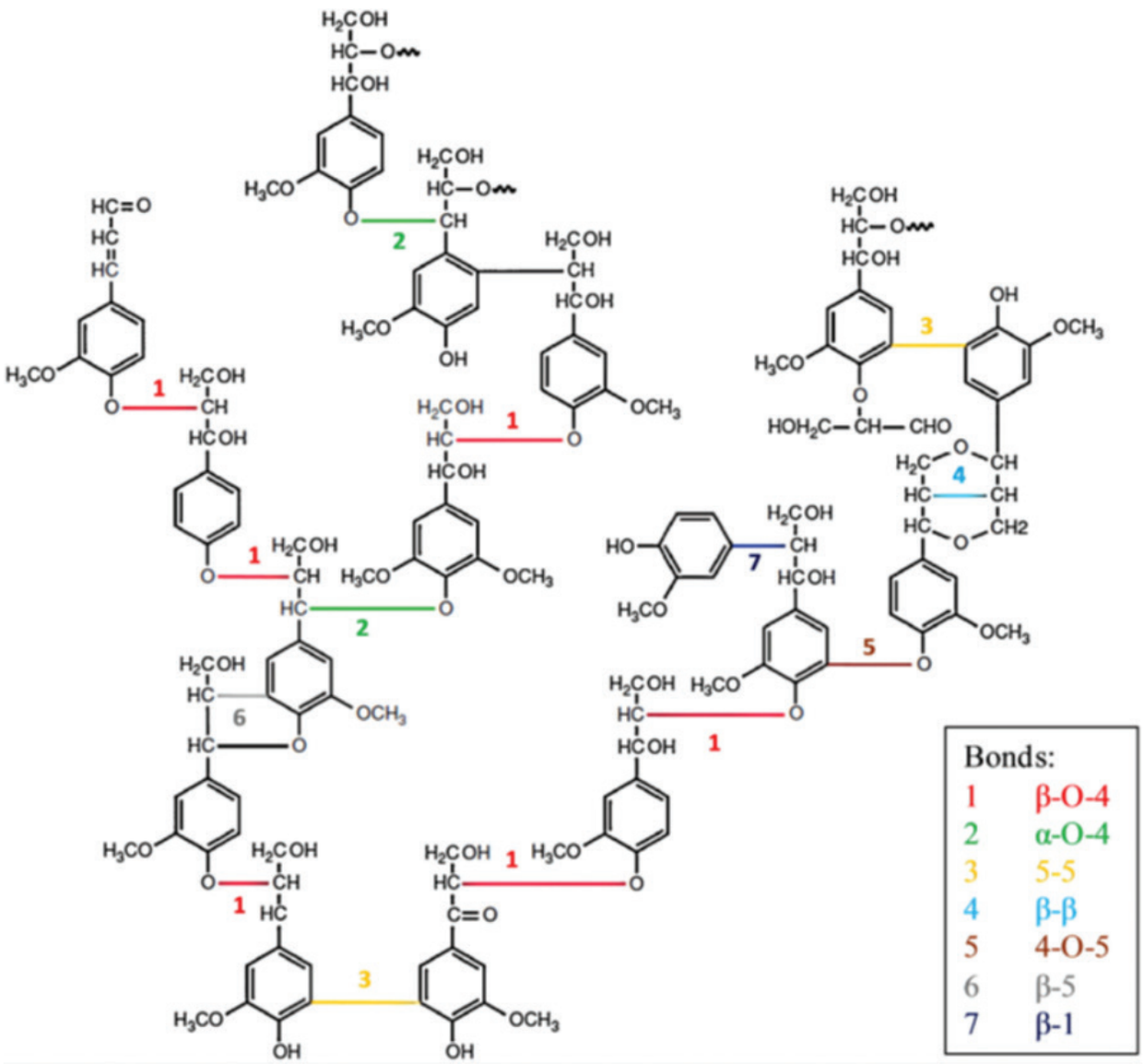


Figure 2. Main linkages in a softwood lignin.

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3. Extraction processes of lignin and their resulting technical lignin

Lignin is extracted from the other lignocellulosic parts by physical and/or chemical and biochemical treatments. Technical lignin can be classified based on different point of view (**Table 1**). Common pulping processes are based on the cleavage of ester and ether linkages. It is worth noticing that resulted technical lignin differ considerably from the plant lignin. In this part, different commercially available extraction processes are discussed, which are used to recover technical lignins. **Figure 3** shows the classification into two main categories such as sulphur-bearing and sulphur-free processes.

3.1. Sulphur-bearing process

Sulphur lignin includes kraft and lignosulphonates lignin, which are primarily produced by pulp and paper industries and mainly correspond to the lignin extraction from the cellulose.

Lignin type	Scale	Chemistry	Sulphur content	Purity
Kraft	Industrial	Alkaline	Low	High
Lignosulphonate	Industrial	Acidic	High	Low
Organosolv	Industrial/Pilot	Acidic	Free	High
Soda	Industrial/Pilot	Alkaline	Free	Moderate
Hydrolytic	Industrial/Pilot	Acidic	Low/Free	Moderate

Table 1. Classification of technical lignins.

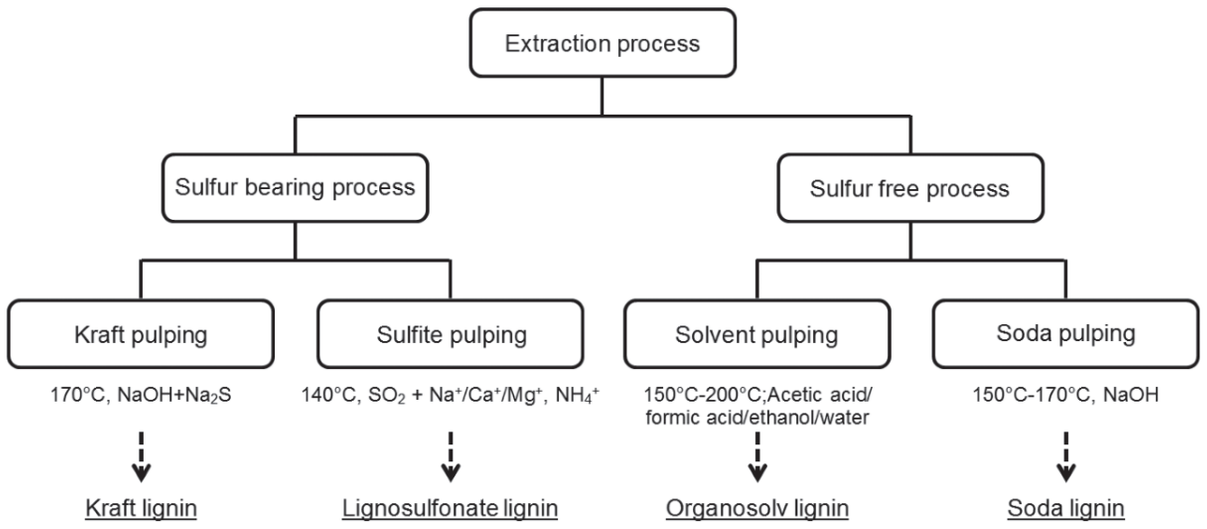


Figure 3. Different extraction processes to separate lignin from lignocellulosic biomass and the corresponding technical lignins.

3.1.1. Kraft process

The kraft process uses a mixture of chemicals including sodium hydroxide (NaOH) and sodium sulphide (Na_2S), known as white liquor, which breaks the bonds that link lignin to the cellulose. It basically converts wood or non-wood material into pulp and the generated black liquor that is then acidified to recover lignin. Considering the high sulphur environment used for kraft lignin extraction, it is quite surprising that the residual sulphur content is so low, typically below 2–3%. Moreover, it contains a high amount of condensed structures and a high level of phenolic hydroxyl groups [5], due to extensive cleavage of β-aryl bonds during cooking. The number-average molar mass (M_n) of kraft lignin is generally low, between 1000 and 3000 g mol^{-1} [21].

3.1.2. Sulphite process

The most abundant type of commercial lignin available is sulphite lignin because traditionally this was the most used type of pulping process. It is based on a cooking with an aqueous sulphur dioxide (SO_2) and a base calcium, sodium, magnesium or ammonium base. Lignosulphonates contain a considerable amount of sulphur in the form of sulphonate groups present on the aliphatic side chains. Lignosulphonates are water-soluble. They have a higher average molar mass than kraft lignin with a broad polydispersity index, around 6–8 [22]. However, they are generally contaminated by the cations used during pulp production and recovery. Their reactivity depends to some extent on the cation. Calcium- and ammonium-based products exhibit the lowest and the highest reactivity, respectively, while sodium- and magnesium-based lignosulphonates show a medium reactivity [23].

3.2. Sulphur-free process

Sulphur-free lignins are an emerging class of lignin products which have a low macromolecular size, after fractionation steps. The structure of these lignins is close to those of the native lignins. They show interesting properties that can make them an attractive source of low-molar mass phenol or aromatic compounds. Sulphur-free lignins can be divided into two main categories such as lignins from solvent pulping (organosolv lignin) and from alkaline pulping (soda lignin).

3.2.1. Organosolv process

Organosolv lignins are generally the purest ones, with the highest quality [24]. They show high solubility in organic solvents and practically insoluble in water, since they are very hydrophobic. They are recovered from the solvent by precipitation, which typically involves adjusting different parameters, such as concentration, pH and temperature. The most common organosolv processes are based on ethanol/water pulping (e.g., Alcell) and pulping with acetic acid, containing a small amount of mineral acid such as hydrochloric or sulphuric acid [25]. In addition, another extraction based on a mixture of formic acid, acetic acid and water was developed by CIMV Company (France). The lignin produced was called Bio-lignin© and is thought to be linear and have low molecular weight according to some published work [26, 27]. However, some of these isolation concepts, such as the Alcell process, using aqueous ethanol, are now being commercialized as a bio-refinery technology whereby the cellulose fraction is being used for ethanol production [28].

3.2.2. Soda process

Soda lignin originates from soda or soda-anthraquinone pulping processes. Soda-based cooking method are mainly used for annual plants such as straw, flax, bagasse, and to some extent hardwoods [29, 30] . Lignin extraction is based on hydrolytic cleavage of the native lignin but it results in a relatively chemically unmodified lignin compared to the others lignin types. A specific procedure for the precipitation of lignin in the black liquors of soda processes, which specially adapted from paper factories in the production of cellulose from annual plants or agricultural residual substances, is the Granit process, where the pH value of the liquor is lowered by acidification, typically with mineral acids. The recovery of spent cooking liquor from pulping of non-woods is not without problem, because of high content of silica which may co-precipitate with the lignin. So this lignin presents a low quality [31, 32]. In the meantime, companies have claimed to have solved this problem and to have obtained soda lignins with low ash and silica content [33].

Various alternative pulping processes such as hydrothermal, steam explosion, ionic liquids (ILs), enzymatic, etc. have been developed but failed for industrial or large-scale implementation due to several reasons. There are many efforts and new approaches searching for new technologies and enhancing the value of lignin and lignin products [34].

4. Global lignin market scenario

It is excepted that depending on the plant source and the corresponding structure, lignin and lignin derivatives are offered in quite different qualities for a multitude of applications. Isolated lignin is currently used in a wide range of low volume, niche applications such as concrete additive, animal feed, dye stuff and other applications (including cosmetics and absorbents). In addition to this, lignin is a key intermediate for the production of activated carbon, carbon fibres, vanillin, sorbents, plastic materials, phenol, binders and motor fuel. These applications have tremendous scope in the future market. There is an increasing demand for lignin in developing countries such as China due to the country's expanding industrial base [35].

Globally, major companies active in the lignin and lignin-based products industry, with top 10 players accounting for over 90% share of the global lignin market in 2015 [36]. The lignin market is highly concentrated, with top five players accounting for more than 85% share of the global market in 2015. Key players operating in the lignin market include Borregaard LignoTech, MeadWestvaco Corporation, Tembec Inc., Domtar Corporation, Domsjö Fabriker AB, Changzhou Shanfeng Chemical Industry Co. Ltd, Nippon Paper Industries Co. Ltd., UPM-Kymmene Corporation, Asian Lignin Manufacturing Pvt. Ltd., Lignol Energy Corporation, Green Value and Liquid Lignin Company (LLC).

At present, lignosulphonates accounted for the largest share of the global lignin market due to rising demand for lignin on the building and construction industry, are produced majorly by Borregaard (Norway) and Tembac (Canada), but there are also minor suppliers, for example, Nippon paper Industries (Japan), ALMT (India) and Domsjo AB. Kraft lignin is manufactured by MeadWestvaco (MWV) corporation (USA) and Domtar (Canada). Organosolv lignin are produced based on ethanol/water pulping (Lignol©, Canada) [28, 37], another extraction

based on a mixture of formic acid, acetic acid and water (Bio-lignin©) was developed by CIMV Company (France) [38]. The degree of current utilization shows that at present only the potential of the lignin from sulphite pulping is utilized. The highest possible potential, however, has the lignin of the sulphate process due to the production volume.

The recent interest in lignin as renewable raw material feedstock is evidenced by the growing number of research documents containing the word "lignin application" which have been published in last 20 years (**Figure 4**). Especially during the last 10 years, more interest was developed on exploitation of lignin due to demand to promote "green concept". Several lignin market studies proposed high demand of lignin in forthcoming years. Zion Research has published a new report "Lignin Market" [39] for various applications; Global Industry Perspective, Comprehensive Analysis and Forecast 2014–2020. According to the report, global lignin market was valued at approximately USD 775 Million in 2014 and is expected to reach around USD 900 million in 2020, growing at a CAGR of slightly above 2.5% between 2015 and 2020. Global lignin market was dominated by the North America region followed by Europe. The lignin market in Europe region is expected to grow at a rapid pace in the years to come. The Europe region is followed by the Asia Pacific and Latin America, respectively. Asia Pacific is expected to be the fastest growing market for lignin during the forecast period

Most of the 70 million tons of lignin yearly occurring as a by-product in pulping is used for energy generation during sulphate pulping, because of the need to recover and recycle the inorganic cooking chemicals. For this reason, less than 2% of lignin and its by-products are materially utilized. Lignosulphonates accounted for the largest share of the global lignin market (1,000,000 tons per annum) [4, 40] due to rising demand for lignin on the building and construction industry. Demand for kraft lignin has increased (100,000 tap) due to growing demand for dye stuff in the paints and coatings and textile industries. Additionally, rising usage of kraft lignin as insecticides has contributed to the growth of global lignin market. Sulphur-free lignin is not yet commercialized in higher amounts (<5 kton).

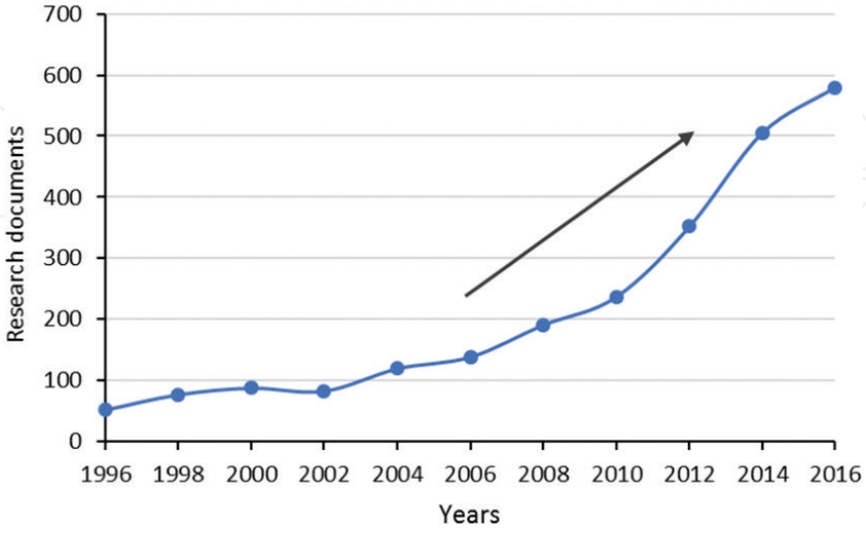


Figure 4. Research documents devoted to lignin applications in different areas published during 1996–2016 (Scopus® database with key word "lignin applications").

5. Industrial lignin applications

Lack of toxicity and versatility of lignin creates several potential industrial application routes. Stringent regulations, bulk availability, cost efficiency and growing need for bio-based and renewable chemicals are high-value lignin properties. Significant scope for diverse applications (**Figure 5**) principally segmented as power/energy, macromolecules and aromatics. Immense scope and opportunities to turn lignin into biofuel as companies are readily investing in the research and development for related applications. Overall, lignin applications can be divided into low or mid value and high-value applications. The low-value applications of lignosulphonates and sulphonated kraft lignins such as dust control, concrete admixtures and oil well drilling muds while most of the high-value applications target emerging applications, in which the chemical versatility of lignin could be fully utilized, or very large volume applications such as the production of BTX and other petrochemicals.

5.1. Low-value traditional applications

The traditional lignin applications include, primarily, lignin uses where lignin plays a replacement role for a relatively low-value chemical or material. As it was mentioned earlier, the largest current use of industrial lignin is fuel. However, there are several matured industrial

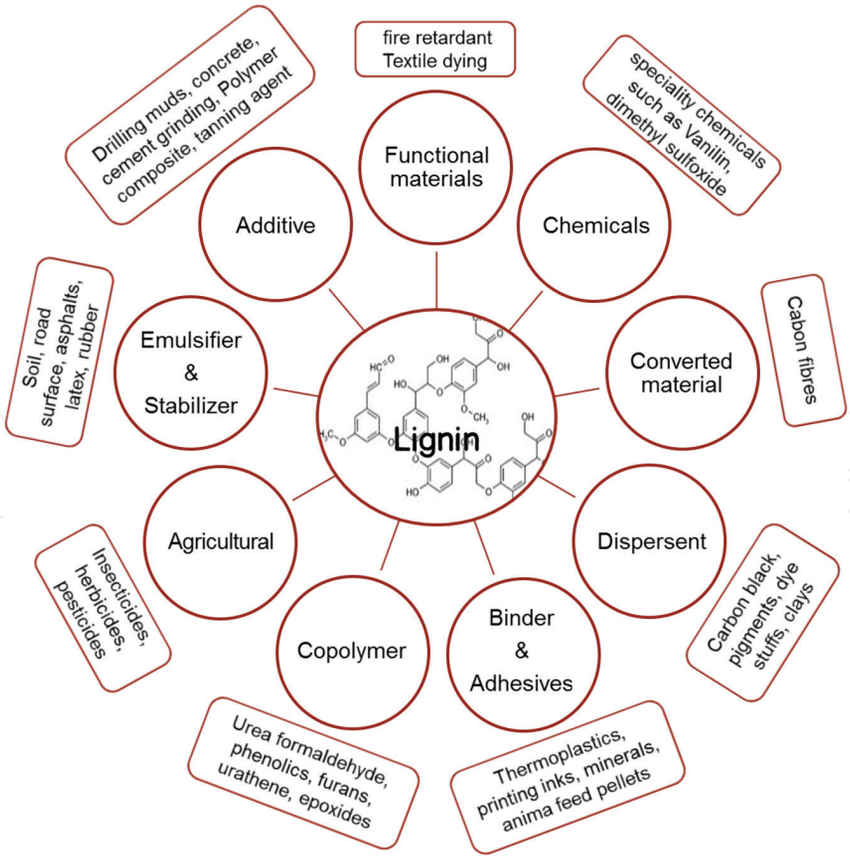


Figure 5. Current and potential applications of technical lignin.

lignin applications, constituting the bulk of the higher value lignin commercial chemical market, and this includes, primarily, lignosulphonates or sulphonated kraft lignins in large-medium-size markets such as additives for concrete admixtures, dust control, feed and food additives, dispersants, resin and binder compositions and oil well drilling. Examples of smaller market for technical lignins include carbon black, emulsifiers, water treatment, cleaning chemicals, leather tanning, battery expanders and rubber additives [41]. There are many reviews and literatures available, which cover traditional lignin applications [42] therefore, not discussed here.

5.2. High-value emerging lignin applications

From 1990 to 2010, several novel lignin applications have been proposed and described in the scientific and patent literature. Some of these novel applications have been demonstrated at larger than laboratory scale. For instance, the production of lignin-based carbon fibre (LCF) [10, 43, 44] is one of the brightest examples of successful lignin upgrading technology which has been scaled up to pilot scale. Another example of nontraditional lignin application is the use of upgraded technical lignins in polymers composites. For instance, depolymerization of lignins to produce valuable oxygenated aromatic compounds, and possibly olefins too, in replacement of petrochemicals [45, 46]. This section briefly summarizes these three relevant examples of emerging nontraditional lignin applications which in our opinion present the largest potential, in terms of volume and value, for commercialization of technical lignins in the future. Among all the emerging lignin applications, utilization of lignin's functionality in polymer composites is perhaps one with the large market potential in future lignin demand.

6. Fire retardant applications in polymer composite

For environmental concerns, halogen-free flame retardant (HFFR) has stimulated great attention in recent years due to the evolution of corrosive and toxic gases during the combustion of halogen-containing flame retardant materials [47]. The presence of lignin gives peculiar properties to the composite. Lignin can act as a stabilizer preventing polymer aging due to its antioxidant activity [48–50]. Lignin has the advantage of being a bio-based compound and can be effectively used as carbon source for the design of intumescent systems in combination with other flame retardant additives. Owing to the presence of highly aromatic structure lignin is able to produce a large amount of char residue upon heating at elevated temperature [12, 51], which reduces the combustion heat and heat release rate (HRR) of polymeric materials and thus enhances the fire retardancy. All forthcoming reviewed study have demonstrated that lignin-based intumescent could be a worthy alternative that represents a great advantage in comparison with the other proposed fire retardant system.

6.1. Lignin-based intumescence in synthetic polymers

Polypropylene is one of those most versatile polymers available with applications, both as a plastic and as a fibre. Its low density, low cost and easy processability makes it suitable for

applications in automobiles, packaging and textile industry. However, PP has some drawbacks such as thermal stability, high flammability, thermal oxidation, etc. There are several ways to improve fire and thermal properties but incorporation of fillers into the polymer matrix has been extensively used to improve the mentioned properties. About decade ago in first study, A. De Chirico et al. [16] used lignin as charring agent with other traditional phosphorus flame retardants for improving the flame retardancy of polypropylene, each formulation containing 14 wt.% lignin and 6 wt.% of other flame retardants. TGA and cone calorimetry study showed that combination of lignin in intumescent formulation could prolong the combustion time, enhance the char residue and reduces the heat release rate during burning. Further, the same research group utilized direct lignin in polypropylene matrix to study thermal stability and fire performance of PP composite [52]. Polypropylene blends containing 5 and 15 wt.% of lignin was prepared by mixing in a screw mixer. Thermogravimetric analysis presented, increase in the thermal degradation temperature of the blends as a function of lignin content. The increase is more pronounced for the experiments carried out in air atmosphere, where the interactions between the PP and the charring lignin lead to the formation of a protective surface shield able to reduce the oxygen diffusion towards the polymer bulk. Another different study proposed by Yu et al. [11], wherein alkali lignin was modified by chemical grafting of flame retardant phosphorous and nitrogen-containing macromolecules, modified lignin (PN-lignin) blended with polypropylene polymer matrix to give enhanced fire property. Cone calorimetry study showed PN-lignin further reduces the peak heat release rate (−45%) and slows the combustion process, modified lignin (PN-lignin) also exhibits a much higher char-forming ability with a char of 61.4 wt.% (40.7 wt.% for lignin) at 600°C in N_2. Similar strategy is used by Liu et al. [53] to fabricate flame retardant wood plastic PP composite (WPC). Lignin was chemically modified by grafting of N-P then coordinated with metal ions. Wood-PP (WP/PP) and wood-PP-lignin (WP/PP/lignin) composites were fabricated via melt compounding using a rheomix at 180°C for 10 min. Flammability of samples was tested using UL94: the obtained results reported that adding 15 wt.% F-lignin resulted in a V-1 rating showing better FR properties than PP/WP composite. Compared with pure lignin incorporation of equal loading of F-lignin into WPC can further increase the thermal stability of PP/WP composite. Cone tests showed that optimum content of F-lignin in PP/WP shows 15 wt.%, which gave the best FR result by reducing PHRR, THR and MARHE. Moreover, smoke production was also reduced by 30 wt.%. The study by Acha et al. [54] present combination of lignin and jute fabric for impart fire retardancy and toughening to PP matrix. Different formulation of kraft lignin blended with PP in mixer at 180°C for 10 min and film were obtained by compression moulding and then jute fabric was sandwiched between the film and compression moulded PP at 180°C for 25 min. The blends showed higher degradation temperature compared to neat PP and with increased char residue. Char residue produced at degradation was directly related to lignin content in blend. With increasing lignin content time to ignition (TTI) decreases, but with increased char yield. Addition of jute fabric to PP leads to significant increase in stiffness of composite due to higher modulus of jute fibre. Jute fabric also improves tensile strength and impact behaviour. In different study Song et al. [55] investigated the synergistic effect of lignin for acrylonitrile-butadiene-styrene copolymer (ABS): improved flame retardancy was revealed with 20 wt.% of lignin. Cone calorimetry test demonstrated 20 wt.% lignin causing

a 32% reduction in peak heat release rate. Further addition of styrene ethylene-co-butadiene styrene-grafted maleic anhydride (SEBS-g-MA) as in situ reactive compatibilizer for ABS/lignin composite further reduces peak heat release rate (PHRR), indicating enhanced flame retardancy due to the improved interfacial adhesion. The *in situ* reactive compatibilization with SEBS-g-MA also contributes protective char layer formation. Thermal degradation and melting behaviour of PET was investigated by Canetti and Bertini [56]. Hydrolytic lignin was directly blended with PET thermoplastic using a single screw extruder. Thermal decomposition, melting behaviour and crystallinity of the resulting blend was studied by thermogravimetry, differential scanning calorimetry and X-ray diffraction, respectively. TG analysis results show that the introduction of lignin leads char formation and effective char layer (~27 wt.%) formed with 20 wt.% lignin content, evidenced of barrier effect. Further presence of lignin in blends promotes the crystallization process and induces a faster crystalline reorganization than that of the pure PET. The reduction in the entropy of melting due to a modification of the amorphous phase must be considered as responsible of the melting behaviour. Research group from China studies lignin-modified PU foam as a single component with excellent flame retardancy [57]. Corn straw lignin was first grafted with phosphate-melamine containing group to prepare a compound named as LPMC and then different wt.% ratio (5, 10, 15 and 20 wt.%) of LPMC were copolymerized with isocyanate to produce lignin-modified PU foam. TGA study showed initial degradation temperature of modified PU-LPMC foam that is slightly lower than that of pure PU, which accelerates intumescent action. In addition, the presence of LPMC could promote the generation of non-flammable gases during PU degradation, inhibiting the flame propagation and dehydration of PU to form compact char layer. Further char formation greatly increases with increasing LPMC content. Furthermore, flame retardancy assessed by limiting oxygen index (LOI) and UL-94 flame spread test illustrate, self-extinguishment and inhibition from melt dripping with small amount of LPMC and V-1 rating could be achieved for PU-$LPMC_{15}$ foam.

6.2. Lignin-based intumescence in bio-polymers

Recent years have seen the development of polymer made from renewable resources (bio-polymers). These materials represent an interesting alternative to traditional polymers due to their independence towards petroleum and, in some cases, they offer a different end of life scenario (bio-degradation). In previous years, bio-polymers were essentially used for short life products, for example, packaging. Now durable applications can be visualized. However, to penetrate some industrial sectors, functional properties, like thermal stability and flame retardant properties must be improved. Few studies have been proposed to use lignin as an additive for bio-polymers to modify flame retardant properties and thermal stability and to get a completely "green" material. In this regard Zhang et al. [58] reported a novel intumescent flame retardant (IFR) consisting of microencapsulated ammonium polyphosphate (MCAPP) and lignin to confer fire retardancy to poly lactic acid (PLA). The IFRs formulation was made up of MCAPP, lignin and organic modified montmorillonites (OMMTs). The ratio of MCAPP to lignin was fixed at 3:1, and the loading of OMMTs were kept at 0.5, 1.0 and 2.0 wt.%, the total content of IFR in PLA composites

was kept at 23 wt.%. PLA composite containing 21 wt.% MCAPP/lignin and 2 wt.% OMMT showed the best LOI value of 35.3 and UL-94 V-0 classification, and exhibited a remarkable enhancement of the flame retardancy. For the same blend, the reduction of PHRR was 79% and that of THR was 60% as assessed in cone calorimetry test. In addition, the char residue analysis clearly showed that the incorporation of OMMTs can improve the char quality with a much more compact and continuous morphology. Alternatively, Reti et al. [59] studied lignin-based intumescent to provide flame retardant PLA. 10 wt.% kraft lignin and 30 wt.% ammonium polyphosphate (APP) were blended with PLA and compared with same composition of PLA/APP/starch and PLA/APP/PER systems. Further flammability properties were assessed by limiting oxygen index (LOI) and UL-94 vertical flame test. Blends containing lignin exhibited LOI value as high as 32 vol.%, slightly lower than starch containing blends (40 vol.%) but acceptable to achieve self-extinction. However, UL-94 test revealed that the presence of lignin and starch leads to superior fire properties and V-0 rating was achieved. Cone calorimeter results demonstrate that lignin-based formulation under test condition form an efficient intumescent protective char layer structure, which further reduces the heat release rate (HRR) besides, the observed 47% reduction in peak HRR is higher than that of the starch containing (PHRR, −41%) blend. However, the best cone test results were obtained for PLA/APP/PER system. In other study, Bertini et al. [60] exploited rice husk lignin, isolated by means of acidolytic (AL) and alkaline enzymatic (AEL) extraction methods. The isolation methods provides lignin samples with significant differences among their molecular, thermal and chemical features. Bio-composites of poly(3-hydroxybutyrate) (PHB) with AL and AEL lignin were prepared by weight ratios of 97.5/2.5, 95/5, 90/10 and 85/15%. The morphological, structural and thermal characteristics of the bio-composites were extensively studied. TG analysis of the PHB-AL bio-composites showed an enhancement of the thermal resistance, being the thermal degradation process shifted to higher temperatures. The increase of thermal stability was observed as a function of the lignin amount in PHB-AL bio-composites. Further, Ferry et al. [61] used lignins (alkali and organosolv) as flame retardant to improve the fire behaviour polybutylene succinate (PBS) bio-polyester. Lignin was successfully modified by grafting of macromolecular phosphate molecule. 20% loading of modified lignin in PBS matrix, alkali lignin significantly reduces heat release rate, promotes thick charring behaviour and was proved to be more interesting than organosolv lignin due to the release of sulphur dioxide during decomposition. A study by Liu and coworker [62] explains modification of alkali lignin by grafting of phosphorus-nitrogen-zinc-containing macromolecule and blending of modified lignin (PNZn-lignin) with bio-degradable polybutylene succinate (PBS) to impart flame retardancy. Incorporation of PNZn-lignin can effectively increase to some extent the thermal stability of PBS composites by gradual shift of T_{max}. Adding 10 wt.% of PNZn-lignin, PHRR and THR are remarkably reduced by 51 and 68%, respectively. Meanwhile, the AMLR and TSR are also decreased, respectively, by 54 and 55% as compared with pure PBS. Impressively, the char residue is enhanced from 9 wt.% for pure PBS to 55 wt.% with 10 wt.% of PNZn-lignin content. The prescence of Zn (II) ions leads to a compact, thick and strong char layer and makes PBS to show reduced flammability and smoke release. **Tables 2** and **3** collect the most significant results based on these attempts.

Polymer	Formulation	Flame retardancy	Ref.
PP	20 wt.% total add-on (14 wt.% lignin + 6 wt.% $Al(OH)_3$/PVA/MeP/AHP/APP)	Synergism with other FRs, longer combustion time and reduced PHRR with phosphate FRs	[16]
PP	Lignin 5 and 15 wt.% add-on	Higher char yield with increased lignin content, protective char layer formed	[52]
PP/WPC	Up to 20 wt.% total add-ons of chemically functionalized lignin and wood	PHRR decreased by 9%, THR by 25%, AMLR by 19% and char residue increased by 30%	[53]
PP	Lignin up to 20 wt.% and jute fabric	Char yield increases with increasing lignin content which leads to improved FR properties	[54]
PP	Soda lignin grafted with N-P containing macromolecule up to 30 wt.%	PHRR reduction 45%, char residue 21% increased, compact char layer formation	[11]
ABS	Wheat straw alkali lignin up to 20 wt.% with SEBS-g-MA up to15 wt.%	PHRR reduction 32%, protective char layer formation increased	[55]
PET	Hydrolytic lignin up to 20 wt.%	Formation of protective char layer, degradation temperature increases	[56]
PU	Corn straw lignin grafted phosphate melamine compound up to 20 wt.%	Improvement in thermal stability, increased charring, self-extinguishment, inhibition of melt dripping and smoke production	[57]

Table 2. Lignin-based fire retardant system to improve fire retardancy.

Polymer	Formulation	Flame retardancy	Ref.
PLA	Alkali lignin + MCAPP 23 wt.% with OMMTs 0.5, 1 and 2 wt.%	LOI 35%, PHRR reduction 79%, UL94 V0 classification, THR reduction 60%	[58]
PLA	Kraft lignin/starch 10 wt.% + APP 30 wt.%	PHRR reduced to 47%, UL94 V0 classification LOI improved to 32%, protective layer formed	[59]
PHB	Lignin isolated by alkali enzymatic (AEL) and acidolytic (AL) process up to 15 wt.%	PHB-AL bio-composite showed higher thermal resistance than PHB-AEL bio-composite	[60]
PBS	Alkali lignin 10 wt.% + macromolecular phosphate-modified alkali lignin 10 wt.%	Significant drop of PHRR and THR promotes thick charring behaviour	[61]
PBS	Alkali lignin grafted with N-P-Zn containing macromolecule (PNZn-lignin) up to 10 wt.%	Reduction in PHRR 51% and TSR 55%, char residue enhanced by 54% from pure PBS	[62]

Table 3. Lignin-based fire retardant system to improve fire retardancy of biopolymers.

7. Fire retardant textile applications

The development of flame retardant material is very crucial research topic and even more when it is related to textile material (**Figure 6**). Textiles are everywhere in our day today life and serve not only as clothes, curtains, bedding, seat covers and carpets but also in public transports and cinema halls. Different countries like UK, US, Canada, Australia and some EU countries have some stringent flammability requirement for textiles used in home appliances, public transport and public places. These textiles are made of natural or synthetic fibres show

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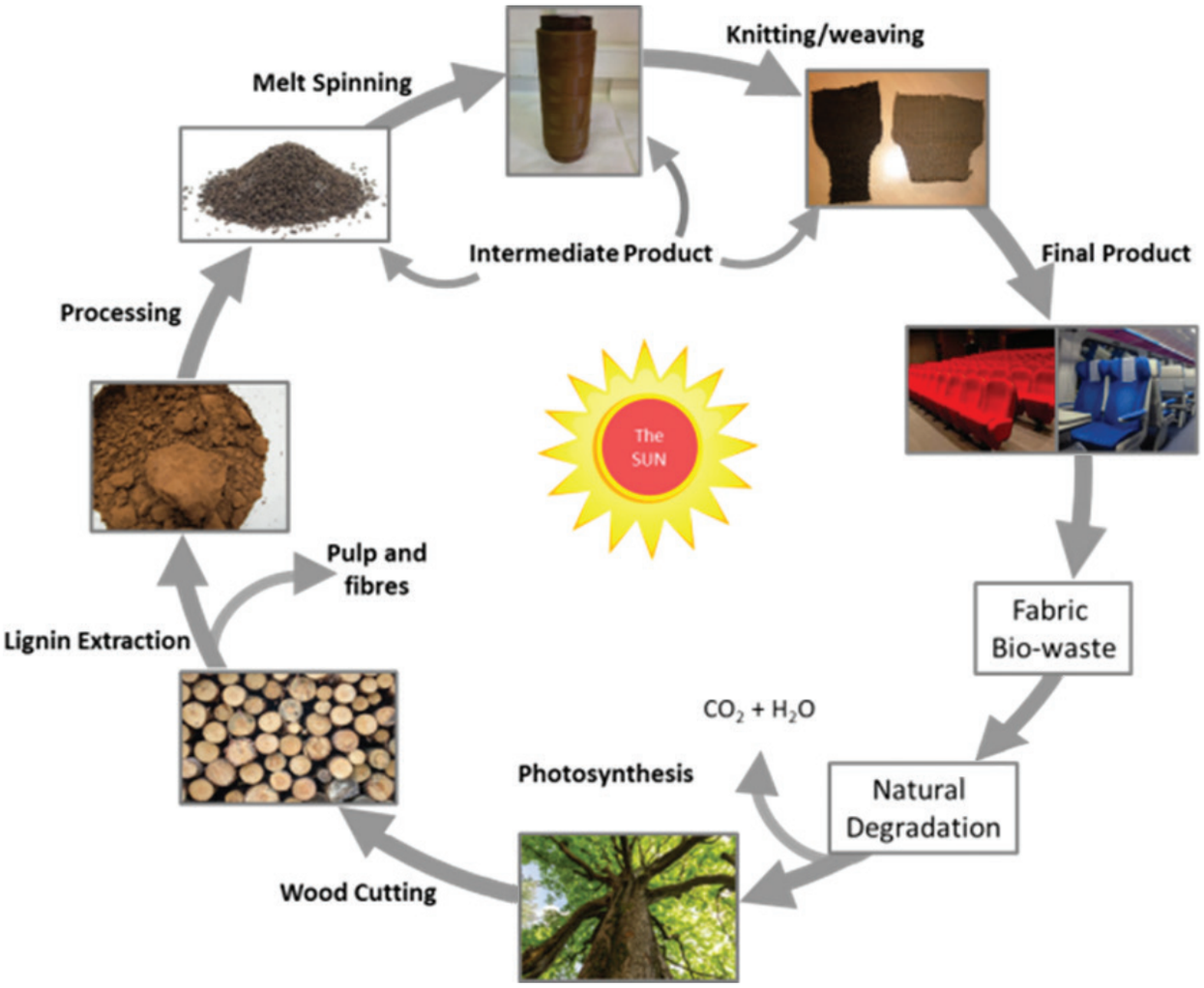


Figure 6. Life cycle of bio-based textile.

high burning rate due to their organic nature and the high specific surface further dripping effect make it more hazardous material. Therefore, a constant demand on fire protection is observed and even more since the toxicity of halogenated additives was highlighted [63]. As previously emphasized in this article, in the recent years researchers in the field of fire retardancy of polymeric substrates have geared up to find a sustainable approach to reduce the carbon foot print. In this connection, efforts have been extended, especially from the last 10 years, to use different eco-friendly bio-based extracted plant resources and other natural resources due to the desire to promote a "green concept". In this approach, a few researchers have started exploratory work to use a sustainable way to make the materials fire retardant and came out with good research findings where they used different bio-macromolecules as fire retardant alternatives instead of synthetic chemicals. The exciting results are documented in the scientific published articles [64–66]. In this direction, Alongi et al. used DNA bio-molecule to impart flame retardancy to cotton fabric [67]. Very recently, Basak et al. reported use of different bio-molecule such as banana pseudostem sap (BPS), spinach juice and hydrophobin for improving thermal stability and subsequent fire retardancy [68]. In another study, Wang et al.

developed novel eco-friendly chicken feather-based protein bio-molecule for imparting fire retardancy to cotton fabric [69]. In a different approach, the use of bio-based ingredients for the formulation of intumescent flame retardant system (IFR) has been proposed. Few studies proposed to replace the acid source by bio-based component: more specifically, fumaric acid and phytic acid were proposed as suitable candidates to develop intumescent system with PLA [70]. Bio-based carbonizing agents such as starch [71], cyclodextrin [72] and chitosan [73] have been proposed and showed high efficiency. Among those entirely bio-based carbonizing agents, lignin has also been considered by some researchers due to its abundance in nature and high charring capacity. Thus, very recently Cayla et al. have prepared fire retardant PLA fibres containing IFR composed of lignin and ammonium polyphosphate (APP) [74].

Two different well-known methods are discussed to confer flame retardancy to textile materials. These approaches are evidently easier to process as compared to synthesizing fire retardant fibres by copolymerization.

7.1. Fire retardant coating on textile surface

The first approach, which is widely used to provide low flammability to textiles, concerns the surface treatments such as padding, layer by layer (LBL) and back-coating of fire retardant intumescent formulation on textile structures during the finishing step. In the field of textile coating market, the standard formulation based on antimony III oxide (ATO) and brominated hydrocarbons, notably decabromodiphynyl ether (decaDBE) and hexabromocyclododecane (HBCD) are most commercially successful flame retardant formulations due to their low cost and durable flame retardancy effect. However, during the last 20 years environmental concerns have been raised to reduce their usage. The challenge of replacing these system by phosphorus-nitrogen-containing fire retardant system have been investigated [75, 76]. Consequently, phosphorous- and nitrogen-based fire retardant chemicals became dominant in the market because some of the phosphorous-/nitrogen-based species have high wash durability (even more than 50 washes). As a result, durable flame retardants based on the composition of phosphorous, nitrogen-like Tetrakis phosphonium chloride salt [proban® process] and N-alkyl phosphopropionamide [pyrovatex® and similar processes] derivatives are widely used commercially [77]. In fact, these chemical treatments bring stiffness in fabric due to high add-on%, are hazardous due to toxic chemical release, are expensive also because of a larger use of chemicals. Challenges associated to developments of flame retardant textile have been highlighted by Horrocks et al. in detail [77]. From that extensive review, it is quite clear that the major challenges for the flame retardant researchers are to develop more cost effective, environmental friendly and sustainable fire retardant chemicals. The first attempt to apply a bio-based intumescent coating to textile was carried out by Srikulkit et al. in 2006 [78], depositing multilayer of polyelectrolyte consisting of chitosan and poly(phosphoric acid) on silk. The results showed that an assembly consisting of 60 bilayers promotes the formation of a highly thermally stable char. Alternatively Laufer et al. [79] proposed fully bio-based intumescent based on phytic acid and chitosan applied to impart fire retardancy and reduced cotton PHRR by 50%. In the same scenario Alongi et al. reported DNA as an effective intumescent flame retardant for cotton fabrics as it contains all three components typical of an IFR formulation [67, 80]. Further by combining DNA with chitosan, the resulting assemblies (10 and 20 Bls) applied to cotton extinguished

flame in horizontal flame spread tests and under a 35 kW/m^2 heat flux, produced a significant decrease of cotton PHRR and THR (−41 and −32%, respectively) [81]. Among those bio-based IFR components, lignin has also been considered as carbonizing agent by some researchers due to its abundant availability as raw material from pulp and paper making industries. In this context, Reti et al. [82] showed that intumescent films based on lignin are able to confer flame retardancy to nonwovens composed of hemp/wool. Films are elaborated with the formulations PLA/APP/LIG used as a potential flame retardant treatment on nonwoven. Intumescent film of about 250 μm thickness was applied on nonwoven using moulding press at 180°C. Horizontal and vertical flame spread measurements have shown no combustion when PLA FR films are coated on nonwovens. Self-extinguishable materials were obtained. In cone calorimetry, nonwoven covered with PLA/APP/Lignin film increased TTI by 50%, nonwoven treated with these coatings have around 40% of PHRR reduction. In the same scenario, work was performed in our lab as PET fabric was coated with intumescent solution [83]. Intumescent flame retardant coating based on lignin and APP in polyurethane (PU) were prepared by dispersing lignin (10 wt.%) and APP (10 wt.%) in PU solution. The dispersions were applied onto PET fabrics using a K Control Coater with a specific threaded rod to obtain a wet film of 100 μm at 2 m s^{-1}. The coated textile was then cured at 155°C for 4 min for crosslinking. Fire test performed using cone calorimetry with 25 kW/m^2 revealed that intumescent coating of APP/lignin/PU on PET fabric shows good result with increasing the number of coating layers. Reduction of peak heat release rate (PHRR) of ~59% was observed with eight coating layers.

7.2. Melt blending and spinning with fire retardant additives

Apart from the use of back coating, which may be applied to any textile comprising any type of fibres, flame retardant can also be applied to fusible fibre forming polymer during processing stage. There are two established viable ways to embed a flame retardant component in polymeric textiles. The first method deals with synthesizing fire retardant fibres by copolymerizing a FR component in thermoplastic macromolecular chain, where the flame retardant properties are firmly anchored in the fibre such as Trevira® CS a fire retardant copolyester fibres [84]. Despite their interesting fire performance, processing these materials is a costly and challenging task which often stops at laboratory scale, besides melt dripping issue is also addressed to PET. Therefore, there is a need for fire retardants that reduces melt dripping and promote the char formation. The second method deals with melt blending of FR additives and polymers. This method is discussed further in this review. Phosphorus-based compounds are widely investigated as FR additive in intumescent system by melt blending to impart flame retardancy to bulk polymer. Most of studies have been carried out on plates and composites. This section is not aimed to review all of them, as two detailed studies have been already published [85, 86]. In this context efforts have been extended, especially from the last 10 years, to use different eco-friendly bio-based extracted plant resources and other natural resources due to the desire to promote a "green concept". Thus, the formulation of intumescent flame retardant (IFR) systems may be based on bio-based acidic source such as phytic acid [87], metallic phytates [64], different bio-based carbonization agents like chitosan [73], cyclodextrin [72] and starch [71] exploiting melt blending processes. Among bio-based carbonizing agents, lignin has also been considered as an effective char former due to its highly aromatic

structure. As reviewed in a previous section, lignin has been studied as a bio-based carbon source in intumescent system for various thermoplastic polymers to develop thermally stable and flame retardant composites.

As observed for bulk polymer, the combination of lignin with conventional flame retardants may enhance the overall flame retardant properties [16, 52]. Very recently, Cayla et al. [74] have used the same melt blending and spinning approach to develop flame retardant textile of PLA by using kraft lignin (LK) as carbon source with ammonium polyphosphate (APP) flame retardant additive, blended prior to the extrusion process. Several blends based on PLA/LK/APP were prepared to determine the possibility of melt spinning. Kraft lignin at 5 and 10 wt% with same proportion of APP was blended with PLA. TGA study showed that the combination of PLA/LK/APP exhibits single stage decomposition and degradation of PLA/LK/APP composites starts at a lower temperature than PLA. UL94 vertical flame tests performed on fabric samples showed that all the PLA/LK/APP ternary composites achieved V-0 rating with lowering the sample burning length. The combustion behaviour of fabric specimen was studied by cone calorimetry at heat flux 25 kW/m^2. The presence of lignin only in PLA does not improve the fire properties, but the combination of PLA/LK/APP exhibits good enhancement of fire retardant properties: in fact, t_{ign} is closer to that of the neat PLA and overall THR & MARHE values are lower than 56% and 43%, respectively. Besides, the combination of LK/APP allows increasing the charring effect that leads to the maximum residue at the end of combination.

In the same line, another work presents [88] intumescent formulations of lignin and APP with bio-based Polyamide 11 (Rilsan® PA11) prepared and extruded at 220°C. Blends were prepared by taking different weight ratios of intumescent formulation, keeping as high as 20 wt.% the total add on. TGA analysis shows an increase of char residue in the lignin-containing blends. Sheets of the different formulations were tested under the cone, using a heat flux of $25kWm^{-2}$. Based on cone calorimetry results some of selected formulations were spindrawn by melt spinning to produce multifilament and finally knitted textile structures were preferred to woven fabrics. Cone calorimetry tests performed on the fabrics containing 10 wt.% lignin and 10 wt.% of OP1230 showed reduction of PHRR and THR of about 50 and 30%, respectively and an increase of time to ignition. In another work by Gaan et al. [89], flammability of cellulose-based textiles obtained from cotton fibre (Cot-Cell) and peat fibres (P-Cell), this latter is rich source of lignin (about 30 wt.%) are studied. Fibres are pretreated to make them a similar contraction. Both fibres were knitted in single jersey pattern. In a first step, flammability of knitted textile was evaluated for their flammability using the vertical fabric strip, BKZ-VB Swiss standard test. To further improve the flammability, a series of phosphoramidate was synthesized and Cot-Cell and P-Cell textile were treated with the FR compound normal by soaking in solution followed by drying in air. TGA and pyrolysis combustion flow calorimeter (PCFC) were used as screening tools.

8. Conclusion and future perspectives

The pursuit of sustainable development are the driving forces for increasing the interest in the use of material derived from renewable and bio-based sources. As indicated in this review, lignin is a promising component as carbon source in intumescent flame retardant systems due to its high charring capacity and abundancy in nature. In recent years, novel emerging

applications of lignin have been explored: among them, it is worthy to mention the production of chemicals by depolymerization, manufacturing of lignin-based carbon fibres (LCF) and their use in polymer composites are the examples some niche areas. As presented in this review, the highly aromatic structure of lignin makes it suitable candidate as char former (carbon source) for intumescent system to improve flame retardant properties of polymer. Further, lignin-based intumescent have been studied extensively in bulk polymer including a wide range of synthetic thermoplastic and with bio-based polymers. In the same scenario, few researcher extended the lignin utilization to develop flame retardant textile. Furthermore, lignin-based intumescent are applied to textile by mean of textile coating and to bulk polymers through melt blending. Very few literature studies are available related to lignin as additive for intumescent systems in combination with other flame retardant to use as intumescent coating material for textiles. On the other side, very recently lignin-based intumescent systems have been used in bulk polymer to develop flame retardant PLA multifilament fibres and textile structures. Therefore, lignin-based intumescent are a possible way to develop 'green' flame retardant materials that could design the formulation of an intumescent system for future. The number of increasing scientific articles involving lignin is the indication of the growing lignin utilization in various niche areas. As far as flame retardancy is concerned, we expect more and more scientific and industrial research exploring flame retardancy specifically for textile applications.

In summary, there are many interesting application investigated: some are novel applications but for this purpose lignin quality standard must be developed, because at present available lignin types differ substantially in composition, structure, purity, etc., depending on the plant source, extraction process and many other factor. It is generally excepted that intumescent systems appeared to be very efficient when used as coatings, regardless of the underlying substrate since no interference may occur, and their efficiency can be assured. In contrast, the situation becomes more difficult when lignins are employed in bulk; in fact, at processing temperature chemical and physical interactions may occur. At the same time, lignins must be highly compatible with the polymer matrix; certainly, a homogenous distribution and uniform dispersion are mandatory. On the other hand, the possibility to create an expanded char layer that can protect polymer during combustion is primarily depends on coherency and consistency of the char layer; in fact, it must be mechanically strong and compact, hence strongly increasing its efficiency.

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References

[1] White JF, Werpy T, Petersen G, Holladay JE, Program USD of EO of the B, Aden A, et al. Top Value Added Chemicals From Biomass: I. Results of Screening for Potential Candidates from Sugars and Synthesis Gas [Internet]. Department of Energy Report. U.S. Department of Energy [Office of] Energy Efficiency and Renewable Energy; 2004

[2] Cazacu G, Pascu MC, Profire L, Kowarski AI, Mihaes M, Vasile C. Lignin role in a complex polyolefin blend. Industrial Crops and Products. 2004;**20**(2):261-273

[3] Sahoo S, Seydibeyoğlu MÖ, Mohanty AK, Misra M. Characterization of industrial lignins for their utilization in future value added applications. Biomass and Bioenergy. Oct 2011;**35**(10):4230-4237

[4] Gosselink RJA, de Jong E, Guran B, Abächerli A. Co-ordination network for lignin—standardisation, production and applications adapted to market requirements (EUROLIGNIN). Industrial Crops and Products. 2004;**20**(2):121-129

[5] Laurichesse S, Avérous L. Chemical modification of lignins: Towards biobased polymers. Progress in Polymer Science. 2014;**39**(7):1266-1290

[6] Thakur VK, Thakur MK, Raghavan P, Kessler MR. Progress in green polymer composites from lignin for multifunctional applications: A review. ACS Sustainable Chemistry and Engineering. 2014;**2**:1072-1092

[7] Naseem A, Tabasum S, Zia KM, Zuber M, Ali M, Noreen A. Lignin-derivatives based polymers, blends and composites: A review. International Journal of Biological Macromolecules. 2016;**93**:296-313

[8] Movil O, Garlock M, Staser JA. Non-precious metal nanoparticle electrocatalysts for electrochemical modification of lignin for low-energy and cost-effective production of hydrogen. International Journal of Hydrogen Energy. 2015;**40**(13):4519-4530

[9] Qin Y, Yang D, Guo W, Qiu X. Investigation of grafted sulfonated alkali lignin polymer as dispersant in coal-water slurry. Journal of Industrial and Engineering Chemistry. 2015;**27**:192-200

[10] Thunga M, Chen K, Grewell D, Kessler MR. Bio-renewable precursor fibers from lignin/polylactide blends for conversion to carbon fibers. Carbon NY. 2014;**68**:159-166

[11] Yu Y et al. Functionalized lignin by grafting phosphorus-nitrogen improves the thermal stability and flame retardancy of polypropylene. Polymer Degradation and Stability. 2012;**97**(4):541-546

[12] Li B, Zhang X, Su R. An investigation of thermal degradation and charring of larch lignin in the condensed phase: The effects of boric acid, guanyl urea phosphate, ammonium dihydrogen phosphate and ammonium polyphosphate. Polymer Degradation and Stability. 2002;**75**(1):35-44

[13] Chen C, Gu X, Jin X, Sun J, Zhang S. The effect of chitosan on the flammability and thermal stability of polylactic acid/ammonium polyphosphate biocomposites. Carbohydrate Polymers. 2017;**157**:1586-1593

[14] Feng J et al. Syntheses of metallic cyclodextrins and their use as synergists in a poly(vinyl alcohol)/intumescent flame retardant system. Industrial & Engineering Chemistry Research. 2013;**52**(8):2784-2792

[15] Réti C, Casetta M, Duquesne S, Bourbigot S, Delobel R. Flammability properties of intumescent PLA including starch and lignin. Polymers for Advanced Technologies. Jun 2008;**19**(6):628-635

[16] De Chirico A, Armanini M, Chini P, Cioccolo G, Provasoli F, Audisio G. Flame retardants for PP based on lignin. Polymer Degradation and Stability. 2003;**79**:139-145

[17] Boerjan W, Ralph J, Baucher M. Lignin B iosynthesis. Annual Review of Plant Biology. Jun 2003;**54**(1):519-546

[18] Lin SY, Dence CW. Methods in Lignin Chemistry. Vol. 53. Berlin Heidelberg: Springer; 1989

[19] Doherty WOS, Mousavioun P, Fellows CM. Value-adding to cellulosic ethanol: Lignin polymers. Industrial Crops and Products. 2011;**33**(2):259-276

[20] Adler E. Lignin chemistry? Past, present and future. Wood Science and Technology. 1977;**11**(3):169-218

[21] Marton J, Marton T. Molecular weight of kraft lignin. TAPPI Journal. 1964;**47**(8):471-476

[22] Vishtal A, Kraslawski A. Challenges in industrial applications of technical lignins. BioResources. 2011;**6**(3):3547-3568

[23] El Mansouri N, Pizzi A, Salvadó J. Lignin-based wood panel adhesives without formaldehyde. Holz als Roh- und Werkst. Feb 2007;**65**(1):65-70

[24] Sannigrahi P, Ragauskas AJ, Miller SJ. Lignin structural modifications resulting from ethanol organosolv treatment of Loblolly pine. Energy and Fuels. 2010;**24**(1):683-689

[25] Shukry N, Fadel SM, Agblevor FA, El-Kalyoubi SF. Some physical properties of acetosolv lignins from bagasse. Journal of Applied Polymer Science. Jul 2008;**109**(1):434-444

[26] Kham L, Le Bigot Y, Delmas M, Avignon G. Delignification of wheat straw using a mixture of carboxylic acids and peroxoacids. Industrial Crops and Products. 2005;**21**:9-15

[27] Delmas M. Vegetal refining and agrichemistry. Chemical Engineering and Technology. 2008;**31**(5):792-797

[28] Lignol Innovations Ltd. | Sustainable Development Technology Canada. [Online]. Available from: https://www.sdtc.ca/en/organizations/lignol-innovations-ltd. [Accessed: Feb 13, 2017]

[29] Saake B, Lehnen R, Saake B, Lehnen R. Lignin. In: Ullmann's Encyclopedia of Industrial Chemistry. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA; 2007

[30] Rodríguez A, Sánchez R, Requejo A, Ferrer A. Feasibility of rice straw as a raw material for the production of soda cellulose pulp. Journal of Cleaner Production. 2010;**18**(10):1084-1091

[31] Lora J. Chapter 10 – Industrial commercial lignins: Sources, properties and applications. In: Belgacem MN, Gandini A, editors. Polymers and Composites from Renewable Resources ABT-M. Amsterdam: Elsevier; 2008. pp. 225-241

[32] Gellerstedt G, Henriksson G. Chapter 9 – Lignins: Major sources, structure and properties. In: Belgacem MN, Gandini A, editors. Polymers and Composites from Renewable Resources ABT-M. Amsterdam: Elsevier; 2008. pp. 201-224

[33] Gosselink RJA et al. Analytical protocols for characterisation of sulphur-free lignin. Industrial Crops and Products. 2004;**19**:271-281

[34] Adorjan I, Zhou Z, Jaaskelainen AS, Influence of carbonyl groups on the brightness reversion of eucalyptus kraft pulp. European Workshop on Lignocellulosics and Pulp, Vienne, Austria. 2006

[35] Market Research Store. Global Lignin Market – Industry Analysis, Size, Growth, Trends, Statistics, Segment and Forecast 2014-2020. 2015. [Online]. Available from: http://www.marketresearchstore.com/report/lignin-market-for-z36379

[36] Mordor Intelligence. Global Lignin Products Market – Segmented By Product Type, Source, Application, and Geography – Trends And Forecasts (2015-2020). 2016. [Online]. Available from: http://www.mordorintelligence.com/industry-reports/global-lignin-products-market-industry?gclid=CjwKEAjwrIa9BRD5_dvqqazMrFESJACdv27GeNb_zoHSY_-SAKQPrE1UG3nOjo7Qm6uvQ2yaFtiO5xoCNwjw_wcB.

[37] Wang M, Leitch M, Xu C. Synthesis of phenol-formaldehyde resol resins using organo-solv pine lignins. European Polymer Journal. 2009;**45**(12):3380-3388

[38] Delmas G-H, Benjelloun-Mlayah B, Bigot Y Le, Delmas M. Biolignin TM based epoxy resins. Journal of Applied Polymer Science. 2013;**127**:1863-1872

[39] Global Lignin Market – Industry Analysis, Size, Growth, Trends, Statistics, Segment and Forecast 2014-2020. 2015. [Online]. Available from: http://www.marketresearchstore.com/report/lignin-market-for-z36379

[40] von Lignin SN. [Online]. Available from: https://mediathek.fnr.de/downloadable/download/sample/sample_id/285/ [Accessed: Feb 13, 2017]

[41] Agrawal A, Kaushik N, Biswas S. Derivatives and applications of lignin – An insight. The Scitech Journal. 2014;**1**:30-36

[42] Glasser WG, Northey RA, Schultz TP, editors. Lignin: Historical, Biological, and Materials Perspectives. Vol. 742. Washington, DC: American Chemical Society; 1999

[43] Maradur SP, Kim CH, Kim SY, Kim BH, Kim WC, Yang KS. Preparation of carbon fibers from a lignin copolymer with polyacrylonitrile. Synthetic Metals. 2012;**162**(5-6):453-459

[44] Baker DA, Rials TG. Recent advances in low-cost carbon fiber manufacture from lignin. Journal of Applied Polymer Science. Oct 2013;**130**(2):713-728

[45] Pandey MP, Kim CS. Lignin depolymerization and conversion: A review of thermochemical methods. Chemical Engineering and Technology. Jan 2011;**34**(1):29-41

[46] Galkin MV, Samec JSM. Lignin valorization through catalytic lignocellulose fractionation: A fundamental platform for the future biorefinery. ChemSusChem. Jul 2016;**9**(13):1544-1558

[47] Segev O, Kushmaro A, Brenner A. Environmental impact of flame retardants (persistence and biodegradability). International Journal of Environmental Research and Public Health. 2009;**6**(2):478-491

[48] Gregorová A, Košíková B, Moravčík R. Stabilization effect of lignin in natural rubber. Polymer Degradation and Stability. 2006;**91**(2):229-233

[49] Pouteau C, Dole P, Cathala B, Averous L, Boquillon N. Antioxidant properties of lignin in polypropylene. Polymer Degradation and Stability. 2003;**81**:9-18

[50] Pucciariello R, Villani V, Bonini C, D'Auria M, Vetere T. Physical properties of straw lignin-based polymer blends. Polymer (Guildf). 2004;**45**(12):4159-4169

[51] Hu J, Xiao R, Shen D, Zhang H. Structural analysis of lignin residue from black liquor and its thermal performance in thermogravimetric-Fourier transform infrared spectroscopy. Bioresource Technology. Jan 2013;**128**:633-639

[52] Canetti M, Bertini F, De Chirico A, Audisio G. Thermal degradation behaviour of isotactic polypropylene blended with lignin. Polymer Degradation and Stability. 2006;**91**:494-498

[53] Liu L, Qian M, Song P, Huang G, Yu Y, Fu S. Fabrication of green lignin-based flame retardants for enhancing the thermal and fire retardancy properties of polypropylene/wood composites. ACS Sustainable Chemistry & Engineering. 2016;**4**(4):2422-2431

[54] Acha BA, Marcovich NE, Reboredo MM. Lignin in jute fabric–polypropylene composites. Journal of Applied Polymer Science. 2009;**113**:1480-1487

[55] Song P, Cao Z, Fu S, Fang Z, Wu Q, Ye J. Thermal degradation and flame retardancy properties of ABS/lignin: Effects of lignin content and reactive compatibilization. Thermochimica Acta. 2011;**518**(1-2):59-65

[56] Canetti M, Bertini F. Influence of the lignin on thermal degradation and melting behaviour of poly(ethylene terephthalate) based composites. E-Polymers. 2009;**49**:1-10

[57] Zhu H et al. Preparation and characterization of flame retardant polyurethane foams containing phosphorus–nitrogen-functionalized lignin. RSC Advances. 2014;**4**(98):55271-55279

[58] Zhang R, Xiao X, Tai Q, Huang H, Yang J, Hu Y. The effect of different organic modified montmorillonites (OMMTs) on the thermal properties and flammability of PLA/MCAPP/lignin systems. Journal of Applied Polymer Science. 2013;**127**(6):4967-4973

[59] Reti C, Casetta M, Duquesne S, Bourbigot S, Delobel R. Flammability properties of intumescent PLA including starch and lignin. Polymers for Advanced Technologies. 2008;**19**:628-635

[60] Bertini F, Canetti M, Cacciamani A, Elegir G, Orlandi M, Zoia L. Effect of ligno-derivatives on thermal properties and degradation behavior of poly(3-hydroxybutyrate)-based biocomposites. Polymer Degradation and Stability. 2012;**97**(10):1979-1987

[61] Ferry L, Dorez G, Taguet A, Otazaghine B, Lopez-Cuesta JM. Chemical modification of lignin by phosphorus molecules to improve the fire behavior of polybutylene succinate. Polymer Degradation and Stability. 2015;**113**:135-143

[62] Liu L, Huang G, Song P, Yu Y, Fu S. Converting industrial alkali lignin to biobased functional additives for improving fire behavior and smoke suppression of polybutylene succinate. ACS Sustainable Chemistry & Engineering. 2016;**4**(9):4732-4742

[63] Darnerud PO. Toxic effects of brominated flame retardants in man and in wildlife. Environment International. 2003;**29**:841-853

[64] Costes L et al. Metallic phytates as efficient bio-based phosphorous flame retardant additives for poly(lactic acid). Polymer Degradation and Stability. 2015;**119**:217-227

[65] Basak S, Samanta KK, Chattopadhyay SK. Fire retardant property of cotton fabric treated with herbal extract. Journal of Textile Institute. Dec 2015;**106**(12):1338-1347

[66] Malucelli G et al. Biomacromolecules as novel green flame retardant systems for textiles: an overview. RSC Advances. Sep 2014;**4**(86):46024-46039

[67] Alongi J et al. Intrinsic intumescent-like flame retardant properties of DNA-treated cotton fabrics. Carbohydrate Polymers. 2013;**96**(1):296-304

[68] Basak S, Ali SW. Sustainable fire retardancy of textiles using bio-macromolecules. Polymer Degradation and Stability. 2016;**133**:47-64

[69] Wang X, Lu C, Chen C. Effect of chicken-feather protein-based flame retardant on flame retarding performance of cotton fabric. Journal of Applied Polymer Science. 2014;**131**:n/a-n/a

[70] Bourbigot S, Fontaine G, Duquesne S. Intumescence for the flame retardancy of polylactide, 21th BCC Conference – Recent Advances in Flame Retardancy of Polymeric Materials, Stamford, États-Unis, Mai. 2010

[71] Wang J, Ren Q, Zheng W, Zhai W. Improved flame-retardant properties of poly(lactic acid) foams using starch as a natural charring agent. Industrial and Engineering Chemistry Research. 2014;**53**:1422-1430

[72] Feng J-X, Su S-P, Zhu J. An intumescent flame retardant system using β-cyclodextrin as a carbon source in polylactic acid (PLA). Polymers for Advanced Technologies. Jul 2011;**22**(7): 1115-1122

[73] Xiao Y, Zheng Y, Wang X, Chen Z, Xu Z. Preparation of a chitosan-based flame-retardant synergist and its application in flame-retardant polypropylene. Journal of Applied Polymer Science. 2014;**131**(19):1-8

[74] Cayla A, Rault F, Giraud S, Salaün F, Fierro V, Celzard A. PLA with intumescent system containing lignin and ammonium polyphosphate for flame retardant textile. Polymers. 2016;**8**:331-346

[75] Wang MY, Horrocks AR, Horrocks S, Hall ME, Pearson JS, Clegg S. Flame retardant textile back-coatings. Part 1: Antimony-halogen system interactions and the effect of replacement by phosphorus-containing agents. Journal of Fire Sciences. Jul 2000;**18**(4):265-294

[76] Horrocks AR, Wang MY, Hall ME, Sunmonu F, Pearson JS. Flame retardant textile back-coatings. Part 2. Effectiveness of phosphorus-containing flame retardants in textile back-coating formulations. Polymer International. Oct 2000;**49**(10):1079-1091

[77] Horrocks AR. Flame retardant challenges for textiles and fibres: New chemistry versus innovatory solutions. Polymer Degradation and Stability. 2011;**96**(3):377-392

[78] Srikulkit K, Iamsamai C, Dubas ST. Development of flame retardant polyphosphoric acid coating based on the polyelectrolyte multilayers technique. Journal of Metals Materials and Minerals. 2006;**16**(2):41-45

[79] Laufer G, Kirkland C, Morgan AB, Grunlan JC. Intumescent multilayer nanocoating, made with renewable polyelectrolytes, for flame-retardant cotton. Biomacromolecules. Sep 2012;**13**(9):2843-2848

[80] Alongi J et al. DNA: a novel, green, natural flame retardant and suppressant for cotton. Journal of Materials Chemistry A. 2013;**1**(15):4779

[81] Carosio F, Di Blasio A, Alongi J, Malucelli G. Green DNA-based flame retardant coatings assembled through Layer by Layer. Polymer (Guildf). 2013;**54**(19):5148-5153

[82] Réti C, Casetta M, Duquesne S, Delobel R, Soulestin J. Intumescent biobased-Polylactide films to flame retard nonwovens. Journal of Engineered Fibers and Fabrics. 2009;**4**(2):33-39

[83] Giraud S, Rault F, Rochery M, Gacquere L. Use of bio-based carbon source to develop intumescent flame retardant polyurethane coating for polyester textile fabric. 14th European Meeting on Fire Retardant Polymers, FRPM13. Lille, France. 2013

[84] Black S. The development of Trevira CS (comfort and safety). Journal of the Society of Dyers and Colourists. Oct 2008;**108**(9):372-373

[85] Alongi J, Han Z, Bourbigot S. Intumescence: Tradition versus novelty. A comprehensive review. Progress in Polymer Science. 2014;**51**:28-73

[86] Richard Horrocks A. Textile flammability research since 1980 – Personal challenges and partial solutions. Polymer Degradation and Stability. 2013;**98**(12):2813-2824

[87] Cheng X-W, Guan J-P, Tang R-C, Liu K-Q. Phytic acid as a bio-based phosphorus flame retardant for poly(lactic acid) nonwoven fabric. Journal of Cleaner Production. 2016;**124**:114-119

[88] Cayla A, Rault F, Giraud S, Salaün F, Campagne C, Fierro V. Interest of wood wastes (lignin) as flame retardant fillers in bio-based polymers (PA11 and PLA). Eurofillers and Polymer Blends, Montpellier, France. 2015

[89] Salmeia AK, Jovic M, Ragaisiene A, Rukuiziene Z, Milasius R, Mikucioniene D, et al. Flammability of cellulose-based fibers and the effect of structure of phosphorus compounds on their flame retardancy. Vol. 8. In: Polymers. 2016

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