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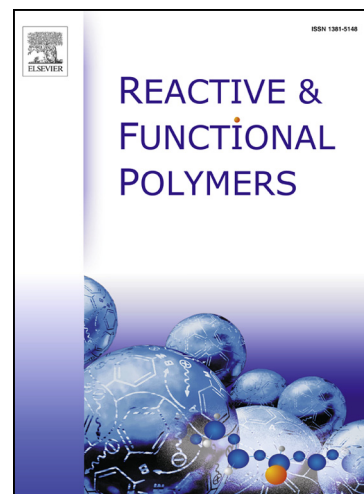Please cite this article as: A. Duval, M. Lawoko, A review on lignin-based polymeric, micro- and nano-structured materials, *Reactive & Functional Polymers* (2014), doi: http://dx.doi.org/10.1016/j.reactfunctpolym.2014.09.017

A review on lignin-based polymeric, micro- and nano-structured materials

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Abstract (200 words)

Next to cellulose, lignin is the second most abundant biopolymer, and the main source of aromatic structures on earth. It is a phenolic macromolecule, with a complex structure which considerably varies depending on the plant species and the isolation process. Lignin has long been obtained as a by-product of cellulose in the paper pulp production, but had rather low added-value applications. Changes in the paper market have however stimulated the need to focus on other applications for lignins. In addition, the emergence of biorefinery projects to develop biofuels, bio-based materials and chemicals from carbohydrate polymers should also generate large amounts of lignin with the potential for value addition.

These developments have brought about renewed interest in the last decade for lignin and its potential use in polymer materials. This review covers both the topics of the direct use of lignin in polymer applications, and of the chemical modifications of lignin, in a polymer chemistry perspective. The future trend toward micro- and nanostructured lignin-based materials is then addressed.

Keywords: lignin, copolymer, functionalization, chemical modification, materials

List of abbreviations: ATRP: atom transfer radical polymerization, CEL: cellulolytic enzyme lignin, CL: ε-caprolactone, EMAL: enzymatic mild acidolysis lignin, HDI: hexamethylene diisocyanate, KL: Kraft lignin, LA: lactide, LS: lignosulfonates, MAL: mild acidolysis lignin, (P)MDI: (poly)methylene diphenyl diisocyanate, MWL: milled wood lignin, OSL: organosolv lignin, PA: polyacrylamide, PAA: poly(acrylic acid), PBG: polybutylene

glycol, PCL: polycaprolactone, (LD)PE: (low density) polyethylene, PEG: polyethylene glycol, PET: polyethylene terephthalate, PF: phenol-formaldehyde, PHB: polyhydroxybutyrate, PHBV: polyhydroxybutyrate-*co*-hydorxyvalerate, PLA: poly(lactic acid), PMMA: poly(methyl methacrylate), PNIPAM: poly(N-isopropylacrylamide), PP: polypropylene, PS: polystyrene, PU: polyurethane, PVA: poly(vinyl alcohol), PVAc: poly(vinyl acetate), PVC: poly(vinyl chloride), PVP: poly(N-vinyl pyrrolidone), ROP: ring opening polymerization, SC: sebacoyl chloride, SL: soda lignin, TC: terephtaloyl chloride, TDI: 2,4-toluene diisocyanate

1. Introduction

Environmental concerns and depletion of fossil-based raw materials for fuels, chemicals, functional polymers and materials have prompted the necessity for alternatives based on renewable resources [1]. Biomass presents one of the candidates and solutions based on several crops, such as corn or soy, have been extensively studied and industrially applied. However, the competition with human feeding as well as the considerable water consumption associated to their production are problematic [2]. Forest-based biorefinery thus appears as a promising alternative, and currently attracts a lot of attention [3].

The main polymers in woody biomass are cellulose, hemicelluloses and lignin, all with great potential to serve as raw materials for production of fuels, functional polymers and materials. While progress is being made in the research areas for applicability of cellulose as raw material source for bio-based functional polymers and materials [4], lignin polymer presents a few hurdles that require further investigations to unlock its full potential [5].

Lignin is the main renewable source of aromatic structures on Earth. In addition to its potential use as polymer, it is also expected to play a major role for the sustainable production of aromatic chemicals, monomers or building blocks, such as phenol, vanillin, ferulic acid… However, for the sake of concision, this review will only focus on the use of lignin as a polymer. The whole field of lignin depolymerization to produce chemicals or fuels will thus not be addressed herein. For detailed information, the reader is referred to several recently published reviews dealing with pyrolysis [6–8], hydrogenolysis [8], hydrothermal treatments [9], oxidative methods [10,11] or supercritical solvent treatments [7,8] for the production of lignin-based chemicals, monomers, building blocks and fuels.

The potential of lignin to be used in polymer materials has been studied for about 30 years. Its wide availability, its aromatic structure, as well as the variety of potential modifications offered by its chemical nature, have long been very attractive for polymer scientists. However, the use of lignin in polymer applications is a challenge due to its complex macromolecular structure, which is known to be highly dependent on both the botanic origin and the isolation procedure. Heterogeneities at a molecular level can exist within a same batch, because of a complex distribution of inter-unit linkages, whose full quantification remains challenging. The first part of this review sheds some light on some of those challenges inherent in the lignin structural characterization. The different extraction processes will then be shortly addressed, keeping the focus on their influence on the lignin structure and reactivity, rather than on technological issues.

The use of lignin in polymer applications will then be discussed. Some potential applications can afford a direct use of lignin, without any need for chemical modifications. However, many applications in polymer science require the functionalization of the lignin macromolecule. An overview of the different types of chemical reactions that have been applied to lignin derivatization will thus be given. Finally, the global trend in polymer science toward the elaboration of materials with a controlled structure down to the nanometer scale will be discussed for lignin-based materials, pointing at some recent developments in the field of nanoporous materials, nanoparticles and nanocarriers.

2. The lignin structure and its characterization
2.1. Lignin biosynthesis and structure

The lignin structure varies considerably among plant species, due to the different proportions of the monomers of lignin, so called monolignols. They are phenylpropane units, which differs only from the degree of substitution by methoxyl groups on the aromatic ring (Figure 1). Softwood lignins are comprised almost solely of coniferyl alcohol, hardwood lignins of both coniferyl and sinapyl alcohol and grass lignins of all 3 types [12].

Fig. 1. The three main monolignols, with the associated nomenclature for C atoms

The primary structure of lignin is formed by radical polymerization of monolignols, the radical sites being initiated by the enzymes peroxidases and laccases (Figure 2) [13–15]. Radical coupling between lignin monomers leads to the formation of an important variety of inter-unit linkages. The most abundant one involves the β carbon of one unit and the phenolic

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hydroxyl of the other: the so called β—O—4 linkage accounts for almost 50% in softwood [12,16]. In addition, other types of ether bonds (α—O—4, 4—O—5) exist, together with C—C bonds (β—β, β—5, β—1) [12,16] and more complex structures involving 3 sub-units (dibenzodioxocin) [17].

Fig. 2. Enzymatic formation of phenoxy radical onto monolignols, leading to the resonance-stabilized forms, and their propensity to radical coupling (reproduced from Gellerstedt and Henriksson [12] with permission from Elsevier)

The proportions of the three monomer types in lignin dictate the type of inter-unit linkages present in the lignin molecule, which in turn determines the degree of branching [18], as well as the reactivity of lignin [19,20]. The lignin structure also differs depending on the biological tissue it originates. For instance, the middle lamella lignin has been shown to have a higher content of p-hydroxyphenyl structures in it than the cell wall lignin, and is more branched [21–23].Overall, the diversity in inter-unit linkages results in a molecule with a high degree of heterogeneity, as visualized in Figure 3.

Fig. 3. Structural Motif of Softwood Lignin (reproduced from Crestini et al. [24] with permission from Elsevier)

In contrast to other biopolymers like cellulose, the suggested heterogeneity in lignin structure, coupled with the lack of stereo-regularity imposes limitations in the transformation of lignin into functional materials and polymers. Notwithstanding, progress in analytical fractionation of lignin as lignin-carbohydrate complexes (LCC) and spectroscopic analysis by [31] P NMR suggests that the structure of individual lignin molecules within the same sample may differ significantly, with some of its molecules exhibiting high degree of linearity and others high degree of branching [23]. These new discoveries imply that progress in lignin applications will greatly depend on development of novel techniques to fractionate its molecules based on structural differences. It is worth noting that the exact structure of native lignin remains elusive attributable to the necessity to isolate it before analysis, which infers modification to its native structure (see paragraph 3.1).

2.2.Lignin structural characterization

As can be seen on Fig. 3, the lignin macromolecule carries multiple functional groups: hydroxyl groups, either phenolic or aliphatic, are clearly predominant, but technical lignins can also present relatively high contents in carboxyl or carbonyl groups. The use of lignins as

a substrate for chemical functionalization demands a precise knowledge of its content in functional groups, which are responsible for its reactivity. Historically, wet chemical methods have been used for hydroxyl content determination (periodate oxidation [25], aminolysis [26], potentiometric titration [27]…), but they have later been replaced by spectroscopic techniques. UV spectroscopy [28], ^{1}H NMR [29,30] and ^{13}C NMR [31,32] can be used to quantify hydroxyl groups in lignins, but the most convenient technique nowadays seems to be ^{31}P NMR. Developed by Argyropoulos and co-workers [33,34], it allows the quantification of hydroxyl and carboxyl groups, as well as the differentiation between aliphatic, condensed and non-condensed phenolic groups, within short analysis time.

The understanding of the inter-unit linkages in lignin has been greatly favored by the development of degradative methods, able to provide a controlled bond cleavage to liberate lignin fragments, which can later be characterized by *e.g.* GC-MS. Thioacidolysis, and derivatization followed by reductive cleavage (DFRC), respectively developed by Lapierre [35] and Ralph's teams [36,37], are the most common techniques. Their combination with ^{31}P NMR can further bring additional information on the branching degree in lignins [38,39]. More recently, strong developments in 2D NMR techniques applied to lignin, including quantitative HSQC NMR [40–42], provided a detailed picture of the inter-unit linkages diversity in lignins. It should be emphasized that most of the spectroscopic methods described above are complementary to each other and more accurate quantification of the inter-unit linkages can be derived when a combination of two or methods are applied together.

The knowledge of the lignin macromolecular structure requires reproducible and reliable data on its molecular weight distributions. Despite many studies devoted to the size exclusion chromatography (SEC) of lignins, including interesting inter-laboratory standardization efforts [43], some concerns remain effective. The large majority of the published SEC studies are based on standard calibration, using commonly polystyrene standards. However, structural differences between linear polymer standards and branched lignin macromolecules are a known source of error, leading to underestimation of the true molecular weight [44,45]. The use of molecular weight sensitive detectors, like viscosimetric [44] or laser light scattering detectors [45–49], can offer a much more precise picture of the lignin macromolecule, although they are also less common and more expensive than classical concentration detectors. In addition, to improve the solubility of lignins in SEC eluents, such as tetrahydrofuran (THF), derivatization is required. Some of them, like the widely used acetobromination [50], are susceptible to cleave some bonds within the lignin macromolecule

[36,37], inducing further bias in the molecular weight determination. In addition, lignin shows tendencies to self-aggregate in some solvents [51], leading to erroneous molecular weight determinations.

Earlier on, methods based on colligative properties have been used to determine average molecular weights of lignin. These include vapor pressure osmometry [52] or cryoscopy [53], and it was shown that associative forces between lignin and solvents were operative and led to erroneous molecular weight determinations.

Recently, MALDI-ToF MS techniques have been applied to determine molar mass of lignin and compared with SEC. Results have shown some inconsistencies, with MALDI data showing lower molecular weights than the SEC data [54]. Crestini et al. [55] also proposed a method based on end group titration, involving a combination of QQ-HSQC NMR, ^{31}P NMR and DFRC coupled with ^{31}P NMR. They were thus able to calculate a number average molecular weight M_n for spruce lignin, which was clearly inferior to the value obtained by SEC (1 800 g.mol^{-1} by end group titration against 14 200 g.mol^{-1} by SEC in THF after acetobromination).

Improved methods for determination of the accurate molecular weight of lignin are therefore of great value to research concerning lignin based materials.

3. Lignin extraction processes

Many processes have been developed throughout the years to separate wood components. They can be separated into two different kinds, depending on the scale of the extraction: those only applicable to an analytical scale and those used at an industrial level. The aim of this part isn't to give an exhaustive discussion of lignin extraction processes, but rather to focus on the structural and functional differences between the lignins depending on the separation process.

3.1. Analytical scale processes

As discussed above, despite important progresses toward its elucidation, the knowledge of the lignin structure remains challenging. Since pioneering work by Björkman in the 1950s [56], different processes have been developed to try to extract lignin in a form as close as possible to the native lignin, in order to gain insights into its *in vivo* structure. They aim at isolating lignin with solvents in neutral or mild acid conditions, and the extraction yields can further be improved by the use of enzymes able to digest part of the surrounding carbohydrates.

3.1.1. Milled wood lignin (MWL)

For the extraction of milled wood lignin (MWL), wood chips are first reduced into fine particles by ball milling. The fine wood powder is then extracted at room temperature by 1,4-dioxane, and the extracted lignin later precipitated in water. This process, first described by Björkman [56], only allows low recovery yields, generally from 20 to 40%.

Even if MWL is usually considered to be representative of the lignin present in wood, the milling process induces some structural changes. Some of the aryl ether linkages (β—O—4 bonds) are cleaved, liberating lignin fragments of low molecular weight and generating an increase in free phenolic OH groups [57]. Condensation and side chain oxidation reactions could also be induced by milling [58]. Increasing the milling time or intensity allows higher extracting yields, but always at the cost of more pronounced structural modifications of the lignin [59,60]. A recent evaluation of the MWL structure by 2D NMR depicted it as low molecular weight fragments with low branching, *i.e.* linear oligomers that were likely to form supramolecular aggregates, rather than branched polymer network [55].

3.1.2. Mild acidolysis lignin (MAL)

A slight modification of the MWL isolation process consists in the addition of low concentration of acid to the dioxane – water solution used to solubilize the lignin. The acid catalyzes the hydrolysis of some of the bonds linking lignin to the surrounding carbohydrates, and favors its extraction in greater yields than MWL.

3.1.3. Cellulolytic enzyme lignin (CEL)

Ball milled wood can also be treated with a cocktail of cellulolytic and hemicellulolytic enzymes, able to digest carbohydrates. The lignin thus "liberated" from the surrounding carbohydrates can then be extracted in a similar manner to MWL, but higher yields can be achieved [61]. Cellulolytic enzyme lignin (CEL) is structurally very close to MWL [57], even though subtle differences may originate from a higher content of MWL in middle lamella lignin [62].

3.1.4. Enzymatic mild acidolysis lignin (EMAL)

Finally, a combination of enzymatic and acid hydrolysis have been described by Wu and Argyropoulos [63]. The milled wood is first treated with cellulolytic enzymes and later with low concentration of acid to cleave the remaining lignin – carbohydrate bonds, thus liberating

a lignin of high purity in yields up to 5 times higher than MWL or CEL [58,64]. The enzymatic mild acidolysis lignin (EMAL) also present much higher molecular weight, suggesting that this protocol allows the isolation of lignin fractions that are not accessed by the other methods [58,64].

3.2. Industrial processes

Industrial processes to separate wood components are historically paper pulp processes, the most important one in terms of tonnage being the Kraft process, with about 120 Mt.yr^{-1} of pulp produced [65]. The basis of paper pulp processes is to solubilize the lignin and the hemicelluloses to obtain a cellulose pulp as pure as possible.

Technically available lignins have undergone significant structural modifications. Though they are structurally deemed to be more complicated and sophisticated for application than native lignin in terms of reactivity, they are very attractive in light of the abundant co-production with chemical pulps.

3.2.1. Kraft lignin (KL)

The Kraft process applies an aqueous solution containing NaOH and Na$_2$S to solubilize lignin and hemicelluloses into the so called black liquor. During Kraft cooking, lignin is depolymerized by cleavage of aryl ether bonds [16,66], yielding a soluble fraction, referred to as Kraft lignin (KL), which is rich in phenolic hydroxyl groups resulting mainly from the cleavage of aryl ether bonds in lignin. Condensation reactions are also contributing to modifications in the structure of both the dissolved and residual lignins. These condensations often result in the formation of carbon-carbon bonds. Due to the use of Na$_2$S, KL contains sulfur in small amounts, which can constitute a drawback for chemical functionalization, especially when catalysis is required.

Traditionally, Kraft lignins are burnt in a recovery boiler, providing the energy required to recover the pulping chemicals and to run the pulp mills. Thus, the amount of KL actually isolated and commercially available is ridiculously low: less than 100 000 t.yr^{-1} [67] out of approximately 70 Mt.yr^{-1} generated worldwide by the Kraft process [66]. However, more lignin is produced than that required for the energy production. With the emergence of potential value addition from technical lignins, new industrially feasible methods to isolate KL from the process stream have been developed. KL can be precipitated from the black liquor by applying acidic conditions, as in the Lignoboost process [68,69]. The availability of

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large amounts of technical KL obtained by such precipitations is an important step towards its transformation to a value-added polymer or material.

3.2.2. Lignosulfonates (LS)

The bisulfite process is minor in terms of pulp production (about 7 Mt.yr^{-1} [65]), but is the most important one in terms of commercially available lignin, with about 1 Mt.yr^{-1} of lignosulfonates (LS) produced (Table 1) [67].

During cooking, high amounts of sulfur are incorporated into the lignin structure, in the form of sulfonate groups SO_3^- bound to the benzylic carbon of the phenylpropane unit in lignin, in quantities ranging from 0.4 to 0.5 sulfonate groups per C_9 unit [45,46,66]. LS are thus anionic polyelectrolytes, highly soluble in water. The nature of the counter-ion depends on the cooking chemicals used (Mg^{2+}, Ca^{2+}, Na^+, NH_4^+). LS exhibit surfactant properties, and are commonly used in several industries, as dispersant, water reducer in concrete, additive in coal-water slurry or viscosity reducer [66].

3.2.3. Soda lignin (SL)

In the Soda process, lignin is dissolved by the action of an alkaline solution, at conditions similar to Kraft pulping but without inclusion of hydrogen sulfide anions. Structurally, Soda lignin is therefore quite similar to kraft lignin, with the exception that it is sulfur free. The absence of sulfur makes it particularly attractive for polymer applications [70,71]. It is mostly applied to the pulping of non-wood material, such as bagasse, wheat straw, hemp, kenaf or sisal [72].

3.2.4. Organosolv lignins (OSL)

Organic solvents and acids have also been applied to produce pulps, by solubilizing the degraded lignin. The different processes are generally referred to as organosolv pulping and the lignins thus obtained as organosolv lignins (OSL). In the 1990s, a few organosolv processes were operational: Alcell technology applying ethanol as solvent [73], Organocell applying methanol [74–77], Alkaline Sulphite Anthraquinone Methanol (ASAM) process [78], Acetosolv applying acetic acid [79] and Milox using peroxyformic acid [80]. Structurally, Organosolv lignins have increased phenolic functionality resulting from the acidolytic or alkaline cleavage of aryl ether linkages. Condensation reactions are quite limited

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due to the presence of organic solvents. These lignins are therefore more structurally similar to native lignin than those produced by the other industrial processes

Apart from the ASAM, the lignins produced hereby are sulfur-free and present a good source for polymer applications. However, the high cost of the solvents and the lowest quality of the pulp as compared to Kraft or soda pulps precluded those processes to become industrially attractive for pulp production. Nevertheless, some of them have found a renewed interest in the last few years, mainly on the basis of second generation biorefineries, aiming at producing fuels and/or chemicals from lignocellulosic biomass. Since first generation biorefineries mainly focused on starch for the production of bioethanol, the competition with human feeding has led the research and industry to rather focus on non-food lignocellulosic residues (woody biomass, wheat straw, sugarcane bagasse…).

To be economically attractive, cellulose-to-ethanol processes need to adopt an integrated approach and to valorize as much material as possible. In addition to carbohydrates, they also aim at isolating lignin in good yields and purity, for high added-value applications. Some processes have already reached pilot plant scale, using ethanol [81] or formic acid [82] as pulping chemicals. The amount of commercially available lignin produced by those processes is still extremely low, but their development could contribute to bring large amounts of sulfur-free lignin to the market in the next few years.

Table 1. Commercial production of lignin [67]

3.3. Toward low polydispersity lignin fractions

One of the main issues regarding applications of technical lignins is their heterogeneity and high polydispersity. Polydispersity indexes (PDI) in the range of 5 – 10 are commonly reported [43]. High PDI values would obviously complicate the attempts to produce functional polymers and materials. It is therefore imperative to fractionate lignin molecules based on size in addition to the aforementioned fractionation based on structure (see 2.1).

Research on industrial application of nano- and ultrafiltration techniques [83–87] for fractionating KL based on molecular size is promising. Indeed, less polydisperse lignin fractions can be produced, potentially offering better control of reactivity in subsequent transformations. The possibility to fractionate lignin based on its solubility in different organic solvents have first been reported in the 1950s [88] and since then widely used on an academic research level to isolate low polydisperse fractions of KL [89] or other technical and

native lignins [90]. However, the scaling up of this technique seems compromised by the use of high quantities of organic solvents. To this end, fractionation of KL based on selective precipitation has recently been reported [91,92].

As will be discussed later in this review, the elaboration of lignin-based functional polymers requires a good control of its reactivity, which is closely related to a good knowledge of its macromolecular structure. The ability to isolate fractions of technical lignins of reduced polydispersity is probably one of the most important challenges to meet in the near future to favor the use of lignin in polymer applications.

4. Direct use of lignin in polymer applications

The direct use of the lignin polymer has received great attention, because unmodified lignins can appear as a relatively cheap raw material. Promising opportunities have for example been revealed in the field of adsorbing material. The high carbon content of lignin makes it an interesting precursor for all kind of carbon materials, such as carbon fibers or activated carbons. The use of unmodified lignins as polymer materials is more delicate, but different possibilities have been investigated, generally by blending it with other polymers.

4.1. Adsorbents from lignin

Lignin presents a good capacity to adsorb heavy metals ions and has thus been studied as a potential low cost adsorbent for wastewater purification. The adsorption capacity of lignin has been studied *e.g.* against chromium (trivalent Cr(III) or hexavalent Cr(VI)) [93–95], copper, cadmium [96,97], lead, zinc, nickel [97], cobalt or mercury [98].

Lignin possess two types of acidic sites (carboxyl and phenol groups) that participate in the sorption mechanism, but phenolic groups have been shown to have a higher affinity toward metal ions [97]. The adsorption is highly pH-dependent, because the adsorption of metal cations is favored by the deprotonation of acidic groups at high pH. Generally, the adsorption capacity reaches a plateau above pH 5 – 6 [95–97]. The adsorption kinetic has been shown to follow a pseudo-second order model, suggesting that the rate-limiting step is the chemical sorption between the adsorbate and the adsorbent [95–97].

The adsorption capacity of lignin depends strongly on the oxidation state of the metal ion. Lignin can remove high amounts of Cr(III) but rather fail to efficiently adsorb Cr(VI) (up to 24 mg.g^{-1} of lignin against only 8 mg.g^{-1}), probably because Cr(VI) can exist as oxo-anion

$(CrO_4)^{2-}$, $HCrO_4^-$ or $(Cr_2O_7)^{2-}$ [94]. For divalent metal cations, the affinity has been shown to decrease in the order Pb > Cu > Cd > Zn > Ni [97]. The chemical structure of the lignin, especially its content in phenolic hydroxyl groups, must play a major role in the adsorbing capacity, and could explain important discrepancies reported for the adsorption capacity of Cu(II) (from 22,9 to 87,1 mg.g^{-1} of lignin) or Cd(II) (from 25,4 to 137,1 mg.g^{-1} of lignin) [96,97].

Most of the studies focused on the adsorption ability of lignin in single component solutions. However, potential use as part of a wastewater treatment requires high adsorption capacity even in the presence of more complex multi-component solutions. Mohan et al. [96] thus studied the adsorption of Cu(II) and Cd(II) in binary and multi-component solutions and obtained values close to those of simple solutions. Wu et al. [95] successfully used lignin to remove Cr(III) from wastewater. Even though the removal efficiency decreased as compared to a simple solution, 90% of Cr(III) could be removed using a lignin to wastewater concentration of 20 mg.L^{-1}.

4.2. Lignin as precursors for carbon materials

An interesting approach for the direct use of lignin consists in the exploitation of its high carbon content (in the range of 55 – 65% [99]), to prepare precursors for carbon-based materials, such as activated carbons or carbon fibers.

Activated carbons are porous carbon materials, with very high specific surface area, generally in the range of 500 – 1500 m^2.g^{-1} for commercial products. They thus have extremely high adsorbing capacity for a wide range of organic or inorganic substances in liquid or gaseous phase. They can be produced from any kind of carbonaceous source, including coal or biomass. The high carbon content of lignin makes it a very promising raw material for activated carbons production [100]. Two kinds of techniques exist for the activation. When physical activation is used, the precursor is first carbonized by pyrolysis in an inert atmosphere at 600 – 900 °C, and then activated in an oxidizing atmosphere (CO_2 or steam) at 600 – 1200 °C, resulting in the porous structure. For chemical activation, the precursor is first impregnated with chemicals, such as phosphoric acid H_3PO_4, and then heated at slightly lower temperatures than for physical activation (450 – 900 °C). Activation and carbonization proceed simultaneously to yield the final porous material [100]. The characterization of activated carbons is generally conducted by measuring the total surface area and the size of

the pores, which can be divided into micro- (< 2 nm), meso- (2 – 50 nm) and macropores (> 50 nm).

The influence of carbonization and physical activation time and temperature on the properties of lignin-based activated carbons have been discussed by several authors [100–102], and surface area as high as 1853 $m^2.g^{-1}$ have been reported [102]. Chemical activation has been performed using different chemical, *e.g.* $ZnCl_2$, H_3PO_4, KOH, NaOH, K_2CO_3 or Na_2CO_3 [100,103–105]. An increase in the carbonization temperature generates an increase in the specific surface area, up to an optimum value in the range of 600 – 800 °C depending on the activating chemical. Further increase in temperature favors the formation of mesopores to the detriment of micropores, causing the total surface area to decrease [103–105]. Lignin-based chemically activated carbons generally present higher specific surface area than physically activated ones [100], and impressive values of 3000 $m^2.g^{-1}$ have been reported [105].

Lignin has also recently been used to produce carbon black substituent [106]. The lignin particles, obtained after carbonization and ball milling, were in the same order of magnitude in size as carbon black. They also presented superior thermal conductivity, but lower electric conductivity, and should then be limited to non-electrical applications of carbon black.

Many efforts have also been devoted to the use of lignin as precursor for carbon fibers. Carbon fibers present high stiffness and strength, which together with their low density make them extremely valuable reinforcements for the elaboration of composite materials. Carbon fibers are currently manufactured from polyacrylonitrile (PAN), an expensive polymer, thus limiting their use to specialty applications, such as aerospace, sporting goods or high-end automotive industries. The use of lignin as precursor could contribute to a twofold reduction of the final cost of carbon fibers, according to estimations from the US Department of Energy cited in a recent review by Baker and Rials [107].

The production of lignin-based carbon fibers requires at least three steps: first the production of a lignin fiber, generally by melt spinning, followed by an oxidative treatment able to thermally stabilize the fiber, and finally the carbonization, which yields the carbon fiber itself.

The melt spinning step of lignin requires particular care: lignin has to present a softening temperature T_s, at which melting flow is observed under shear, not too high and necessarily below the degradation temperature. The spinnability of lignin appears to be highly dependent on its structure. Organosolv lignins, such as the one from the Alcell process, present low

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softening point and easy spinnability [108], presumably because of their low molecular weights. Hardwood lignins, whose structure is rather linear, can also be melt spun without any additive [108,109], but softwood lignins, which can crosslink *via* the free position of the aromatic ring (Figure 1b), are infusible and cannot be processed into fibers as such [108–110]. The spinnability can be enhanced by various strategies. A thermal pretreatment to remove volatiles can limit the formation of bubbles during the extrusion and preserve the fiber integrity [109–111]. Blending lignin with low amounts of synthetic polymers, such as poly(ethylene oxide) [108,112,113], or organoclays [114] can allow to reduce the softening temperature and greatly enhance the quality of the fibers. The lignin molecular weight finally seems to be a key parameter for the melt spinning process: low molecular weight lignin fractions can be melt spun whereas the initial unfractionated lignin cannot. Treatments able to remove the high molecular weight fractions, such as solvent extraction [110,115] or membrane filtration [109], can be applied to obtain spinnable lignin fractions. The first 100% softwood KL fibers were thus recently reported, with a lignin extracted from black liquor ultrafiltered at 15 kDa [109]. The same authors also showed that hardwood lignin from ultrafiltered black liquor could be successfully used as melt spinning agent for other kinds of unfractionated lignins, in proportion as low as 3%.

After melt spinning the lignin fiber and prior to its carbonization, a stabilization step is required. Indeed, the lignin T_g is far below the temperatures required for carbonization, and to avoid melting of the fibers during this step, it is mandatory to treat the lignin fibers [116]. The stabilization consists in air oxidation of the fiber while heating it up to temperatures above 200 °C, causing both crosslinking and oxidation reactions, and making the fiber infusible. As a consequence, the fiber T_g gradually increases during this step. If the heating rate is sufficiently low, it is possible to maintain $T_g > T$ during all processing, which means that the lignin fiber remains in the glassy state. This prevents the fibers to reach the liquid-rubbery state and to fuse together [108,116]. Optimal heating rates have been reported for hardwood fibers to range from 0,06 °C.min^{-1} [116] to 0,2 °C.min^{-1} [117]. Recently, Norberg et al. [118] managed to stabilize softwood KL fibers with heating rates as high as 15 °C.min^{-1}, reducing drastically the total stabilization time to 45 min.

Carbonization of the stabilized fibers is typically conducted at 1 000 °C. Total yields after carbonization are generally in the range of 40 – 50 %. The reported mechanical properties (Young's modulus from about 30 to 60 GPa and tensile strength from 300 to 600 MPa [108,111,112,115,119,120]) are still low compared to commercial carbon fibers based on

PAN. However, the great cost reduction associated to the use of lignin, the argument for a renewable raw material, together with potential improvements coming from higher quality lignin sources (see paragraph 3.3), still encourage further developments.

4.3. Unmodified lignin – polymer blends

As discussed above, the poor thermal stability and difficult melt processing of the lignin polymer make its direct use as material not competitive. For this reason, many studies have focused on the incorporation of lignins in polymer materials, by blending it with synthetic or other bio-based polymers, and several comprehensive reviews have been dedicated to this field [72,121].

Lignin phenol groups are well known for their antioxidant properties, because they are able to scavenge free radicals [122]. When it is incorporated into different polymer matrices, like polyethylene (PE), polypropylene (PP), polystyrene (PS) or natural rubber (NR), lignin can act as a stabilizer against UV degradation or thermo-oxidation [122–127].

The functional properties of polymer blends are largely dependent on the phase structure of the material, *i.e.* on the compatibility between both polymers, which can either form miscible blends or display a phase separation. Because of its numerous OH groups, the lignin molecule is relatively polar, and will generally present better affinity toward polar polymer matrices [128].

Lignin has been shown to form miscible blends with poly(ethylene oxide) [129–131], polyethylene terephthalate (PET) [132], poly(N-vinyl pyrrolidone) (PVP) [133] and natural or synthetic rubber [70,126]. It is on the other hand immiscible over the whole composition range with PP [132], poly(vinyl acetate) (PVAc) [133], poly(vinyl chloride) (PVC) [134] or poly(vinyl alcohol) (PVA) [135].

In phase separated systems, the mechanical properties are generally lowered as compared to the neat polymer, because of poor stress transfer between the phases. However, the adhesion between the phases can be improved in the presence of a compatibilizer, to yield materials with maintained mechanical properties [136–138]. The reduction of lignin OH content [139], as well as the use of low MW lignins can also increase the compatibility [134,140,141].

Many efforts have been dedicated to the incorporation of lignin into other natural polymers, to form 100% bio-based materials. The addition of KL to starch [142], soy proteins [143], fish

proteins [144] or wheat gluten [145–147] generally helps to reduce the water sensitivity, while improving the rigidity. The role of LS seems quite different, because a plasticizing ability has been described when they are incorporated into starch [148], gluten [146], polycaprolactone (PCL) [149] or poly(hydroxybutyrate-*co*-hydroxyvalerate) (PHBV) [150].

In most of the studies however, the lignin content cannot be increased over 20 – 30 % wt. In one case blends of poly(vinyl acetate) (PVAc) with up to 85% KL have been successfully prepared [151], but only by the solvent casting technique. To increase the potential applications of lignins in polymeric materials, some chemical modifications have thus been developed.

5. Chemical modifications of lignins to enhance their use in polymer materials

As mentioned earlier, the use of unmodified lignins in polymer materials is somehow limited. To overcome these limitations and enhance their potential, different strategies have been set up. They are based on chemical modifications of the lignin macromolecule, whose reactivity is essentially based on 2 distinct structural features:

- the presence of free ortho position on the phenolic ring. Guaiacyl-type lignins from softwood can indeed have reactive sites on unsubstituted C5 position of the phenolic ring. Lignins containing coumaryl type units (H units), such as some lignins from annual plants, can also present additional reactive sites on C3 positions (Figure 1).
- the presence of multiple OH groups, and their ability for various chemical modifications. Depending on the chemistry envisaged for the functionalization of OH groups, it can be necessary to differentiate between the aliphatic (primary or secondary) and the phenolic hydroxyls (condensed or non-condensed).

A wide range of chemistries have thus been applied to lignin, either to compatibilize lignin-polymer blends, produce lignin graft copolymers, or to use the lignin macromolecule as a monomer for thermoplastics or thermoset production.

5.1. Compatibilization of polymer blends

Lignin compatibility with non-polar polymer matrices can be enhanced by derivatizing some or all of the OH groups, to expose non-polar groups at the chain end. The most common reactions employed are alkylation (methylation or ethylation) and acetylation.

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Methylated and ethylated lignins can form miscible blends with various aliphatic polyesters. The supramolecular lignin complexes are disrupted by the polyesters, resulting in plasticization as the polyester content increases, and blends of interesting mechanical properties have been prepared [152,153]. Lignin methylation is generally achieved by reacting with diazomethane or dimethyl sulfate. However, both reagents are highly toxic, which constitute a major drawback when considering the use of lignin in a more global green chemistry effort. Their replacement by methyl iodide for lignin methylation has recently been studied, but failed to achieve quantitative functionalization of phenolic OH groups [154].

To enhance lignin solubility in non-polar solvents, Thielemans and Wool prepared lignin esters with several anhydrides, in a solvent-free reaction using 1-methylimidazole as catalyst [155]. They found that increasing the carbon chain length on the ester group improved the lignin solubility, and that saturated groups favored solubility to a higher extent than unsaturated ones. For lignin esterified with butyric anhydride, complete solubility in styrene could be achieved.

Esterification of OSL with anhydrides of various chain length, from 2 to 5 carbon atoms, also greatly enhanced the miscibility in polycaprolactone (PCL) [156]. The best results were obtained for chains of 4 and 5 atoms, because the grafted acyl chains present great similarity with the PCL repeating unit. The esterification of lignin also prevents the deterioration of the mechanical properties when it is blended with PP, to a higher extent than alkylated lignin [157]. The same trend has been observed for blends with LDPE, because of an enhanced interfacial adhesion between esterified lignin and LDPE [158]. Finally, other examples further report the use of esterification to favor the compatibility of lignin with PHB [159] or cellulose triacetate [160].

5.2. Elaboration of lignin graft copolymers

Many studies focused on the elaboration of lignin graft copolymers. This aims at attaching polymer chains to the lignin hydroxyl groups, thus resulting in a star-like branched copolymer, with a lignin core. Two distinct routes can be used for the elaboration of graft copolymers, and both have been applied to the elaboration of lignin graft copolymers, as depicted on Fig. 4:

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- "grafting from" (Fig. 4a): lignin plays the role a macro-initiator for the polymerization. A monomer first reacts with the lignin hydroxyls, and then the polymerization starts. The polymer chain is built on the lignin core.
- "grafting onto" (Fig. 4b): the polymer chain is first synthesized, and functionalized at one end, to be able to react with the lignin OH functions. The polymer chains are then grafted to the lignin core.

Fig. 4. Schematic synthesis of lignin graft copolymers by "grafting from" (a) or "grafting onto" (b) techniques

5.2.1. *"Grafting from"*

Two types of polymerization reactions have been carried out to produce lignin-graft copolymers by the "grafting from" route. The first one involves the ring opening polymerization (ROP) of different monomers, initiated by lignin hydroxyl groups, whereas the second one involves the radical polymerization of vinylic monomers onto the lignin macromolecule.

Scheme 1. Ring Opening Polymerization (ROP) of propylene oxide (a), ε-caprolactone (b) and lactide (c) initiated by lignin hydroxyls to synthesize lignin graft copolymers

The reaction of lignin with cyclic ethers, most commonly propylene oxide (PO), has probably been one of the most studied [154,161–167]. The reaction of PO with lignin OH groups leads to the formation of a liquid lignin polyol, called oxypropylated lignin (Scheme 1a). As a side reaction, PO homopolymer is also formed, but can be separated from oxypropylated lignin by solvent extraction [161]. The length of the grafted PO chains depends mostly on the stoichiometry and the amount of catalyst used [163–165], and average DP from 1 to 7 have been reported [162–164,166,167]. Increasing the grafted chain length leads to a strong decrease of the T_g of the copolymer [163], as well as to a reduced viscosity [165].

By conducting the reaction in an aqueous NaOH solution of appropriate concentration, oxypropylation can be fully specific to phenolic hydroxyls. This specificity stems from the lower pK_a of phenolic hydroxyls as compare to the aliphatic ones. With an excess of PO (2,5 mol per mol of phenolic OH), a quantitative functionalization could be achieved [154].

Fully oxypropylated lignin presents the advantage of bearing only aliphatic hydroxyls, because lignin phenolic OH have been replaced by secondary aliphatic hydroxyls at the end of

the PO chains, making its reactivity toward further derivatization much more homogeneous. Oxypropylated lignin has thus widely been used as a "macro"-monomer for *e.g.* polyurethane synthesis (see 5.3).

Lignin hydroxyl groups can also initiate the ROP of ε-caprolactone (CL), to yield lignin-*g*-polycaprolactone (PCL) copolymers (Scheme 1b). The reaction can be conducted either in a toluene solution [71] or directly in bulk, because CL can solubilize the lignin [71,168–170]. The number of OH groups per lignin molecule, *i.e.* its functionality, will determine the number of PCL arms that will be grafted, whereas the CL/OH ratio will control the length of the PCL grafted chains [169]. All the lignin OH groups are not activated during the reaction, but an increase in the amount of catalyst can enhance their conversion, leading to an increased grafting density [71]. CL/OH ratios from 1 to 100 have been reported [71,168], resulting in different PCL chain lengths, but for high CL/OH ratios, PCL homopolymer is detected together with the copolymer, limiting the maximum grafted chain length to a DP of about 60 [71].

The thermal properties of the copolymers are highly dependent on the length of the grafted PCL chains. For CL/OH ratios below 5, an amorphous structure is obtained, whereas for higher values, the grafted PCL chains can crystallize [71,168,169]. The melting temperature of the crystallites T_m increases with the PCL chain length, and levels off at about 50 – 60 °C. The degree of crystallinity, X_c, follows the same trend, with maximum values around 60 % [168,169].

Recently, ROP has also been used to synthesize lignin-*g*-polylactic acid (PLA) copolymers (Scheme 1c) [171]. Lignin was reacted in bulk with lactide (LA) in the presence of an organocatalyst. End group titration by ^{1}H NMR allowed the determination of the number average MW of the grafted PLA chains, which increased from 200 to 11 000 Da when the LA/lignin ratio was increased. Lignin phenolic OH groups were found to be slower initiator than their aliphatic counterpart, but are still taking part in the reaction, even though their conversion is incomplete. The reduction of lignin functionality, by a partial acetylation of OH groups, led to an increase in the grafted PLA chain length.

Thermal properties of the lignin-*g*-PLA copolymers are dependent on the weight fraction of lignin, and on the resulting PLA chain length. T_g varies between 45 and 85 °C, and below a critical MW corresponding to a DP of 14, the PLA chains cannot crystallize. These copolymers can further be blended with PLA, resulting in homogeneous materials with

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increased mechanical properties and UV blocking capability, thus improving their potential use as packaging.

Many lignin-graft copolymers have also been prepared by free radical polymerization of vinylic monomers onto the lignin macromolecule. This technique has first been described by Koshijima and Muraki [172], and later mostly developed by Meister and co-workers [173–178]. It requires the creation of a radical on the lignin macromolecule, which is then able to initiate the polymerization of a vinylic monomer, as described on Scheme 2.
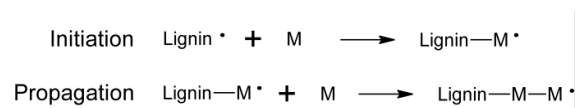
Initiation   Lignin $\cdot$ +   M   ⟶   Lignin—M$\cdot$

Propagation   Lignin—M$\cdot$ +   M   ⟶   Lignin—M—M$\cdot$

Scheme 2. Scheme of the free radical polymerization of vinylic monomers to synthesize lignin-graft copolymers. Lignin "macro"-radicals, which can be produced by several methods, are able to initiate the radical polymerization of the monomer.

Lignin radicals can be created by irradiation [172,179–181], or through the use of a chemical initiator, generally a peroxide [173–178]. The dissociation of the peroxide will generate a radical, which can further react with the lignin to form the lignin "macro"-radical.

Through this technique, lignin-g-polystyrene (PS) [172,177–181], lignin-g-polyacrylamide (PA) [173–175], lignin-g-poly(acrylic acid) (PAA) [182,183] or lignin-g-poly(vinyl acetate) (PVAc) [184] have been synthesized. Lignin-g-PA have a good water solubility, which can further be improved by the grafting of cationic monomers together with acrylamide [176]. Lignin-g-PS are on the other hand hydrophobic, and are for example able to reduce the water sensitivity of wood when coated on the surface [178].

As compared to the ROP, free radical polymerization initiated by lignin seems to provide less control of the grafting reaction. In addition to the creation of the lignin "macro"-radical, the presence of free radicals from the initiator can also initiate the homopolymerization of the vinylic monomers, thus limiting the grafting efficiency [182,184]. Besides, it is not clear where on the lignin macromolecule does the grafting take place, because radicals are resonance-stabilized on different positions on the aromatic ring: on the oxygen atom (phenoxy radicals) [179,182], on carbon C5 in softwood lignins [174] or on carbon C_β, especially if the lignins are methylated [179] (Figure 2). Finally, radical coupling reactions between lignin "macro"-radicals could also occur and compete with the grafting.

An efficient way to control the radical grafting of vinylic monomers onto lignin is to use atom transfer radical polymerization (ATRP). ATRP is a form of controlled living radical polymerization, which allows the formation of long polymer chains of very low polydispersity and controlled macromolecular architecture [185,186].

Its application to the formation of lignin-graft copolymers first requires the preparation of a lignin "macro"-initiator, which can be obtained by the grafting of common ATRP initiators on lignin phenolic OH [187,188]. Depending on the stoichiometry, lignin "macro"-initiators with different functionalities can be prepared, thus resulting in different numbers of grafted chains per lignin molecule. Subsequently, the polymerization of different monomers onto the lignin "macro"-initiator can be achieved in the presence of an appropriate catalyst.

Kadla and coworkers thus prepared lignin-*g*-poly(N-isopropylacrylamide) (PNIPAM) copolymers, with average DP of the PNIPAM chains ranging from 5 to 43, and PDI as low as 1,09 [187]. Depending on the amount of PNIPAM chains grafted, the copolymers were either water soluble or able to form stable suspensions. When heated above its lower critical solution temperature LCST (32 °C), PNIPAM undergoes a transition from a hydrophilic to a hydrophobic structure, leading to the precipitation of the copolymer. They later used the same technique to graft PNIPAM brushes on the surface of lignin fiber mats prepared by electrospinning, to obtain surfaces exhibiting both temperature and ionic-responsive capacities [189].

ATRP has further been used by several authors to synthesize lignin-*g*-PS and lignin-*g*-PMMA, with very long grafted chain length of up to DP 450 [188]. The graft copolymers could then be used to prepare nanocomposites of well-defined structure and increased toughness as compared to those obtained by blending. Bio-based monomers coming from rosin, the main component of pine resin, were also successfully polymerized onto lignin by this technique, resulting in polymers showing excellent water resistance, because of the hydrophobicity of the rosin chains [190].

5.2.2. *"Grafting onto"*

There are only a few publications on the elaboration of lignin graft copolymers by the "grafting onto" method. Unlike "grafting from", which can be performed in a single reaction step, this technique requires successive steps: first the synthesis of the polymer chain that will be grafted, then its functionalization at one end with a chemical function able to react with

lignin OH groups, and finally the attachment of the polymer chains onto to the lignin macromolecule, to provide the final graft copolymer, as depicted in Fig. 4. The characterization of the grafted chain (MW, chemical structure…) can be much easier, because it can be carried out prior to its attachment to the lignin. However, steric constraints associated with coupling of high MW polymers can contribute to limit the grafting density.

De Oliveira and Glasser thus prepared lignin-g-PCL [169] and lignin-g-PS [191]. They reacted PCL or PS polymers terminated at one end by OH groups with a diisocyanate, to obtain polymer chains bearing free isocyanate groups at one end. The isocyanate-terminated chains were then reacted with lignin OH groups to form the graft copolymers. Korich et al. used PCL functionalized by a boronic acid function $B(OH)_2$, able to form cyclic arylboronate esters with lignin aliphatic hydroxyls located at C_α and C_γ positions (Scheme 3) [192,193].

Scheme 3. Grafting of boronic acid-terminated polymers onto lignin [193]

Similarly to the "grafting from" strategy, the copolymer properties will depend on both the amount of grafted chain and their length. As the length of the grafted polymer chains is here constant and well characterized prior to the attachment, the only parameter to assess is the amount of chains grafted per lignin molecule, which can be modulated either by the control of lignin functionality [169] or by the stoichiometry [193].

5.3. Use of lignin as a "macro"-monomer

Lignin is a macromolecule with a molecular weight generally in the range of several thousands $g.mol^{-1}$, bearing multiple reactive sites per molecule. It is thus well suitable for a use as "macro"-monomer, for the elaboration of lignin-based copolymers.

Considering the lignin macromolecule as a multifunctional monomer (a "macro"-monomer), its reaction with a bifunctional monomer can lead to the formation of a copolymer, as depicted in Fig. 5. Depending on the ratio of lignin reactive sites to monomer, the reaction can lead to the formation of a linear or most likely branched copolymer (path a on Fig. 5), or to a cross-linked polymer network (path b on Fig. 5), this latter option being the most investigated one.

As expressed before, both free phenolic positions and hydroxyl groups can be involved. Many researchers have focused on the replacement of phenol by lignin in phenol-formaldehyde type

resin, whereas the exploitation of lignin hydroxyl reactivity have been mostly studied for the elaboration of polyesters and polyurethanes.

Fig. 5. Reaction of lignin with bifunctional monomer. Depending on the ratio of lignin reactive sites to monomer, the reaction can lead to either branched or linear copolymer (a), or to the formation of a network (b)

5.3.1. *Lignin as source of phenol in thermoset resins*

Being the most abundant source of renewable phenolic groups, lignin has long been seen as a potential replacement of phenol in different types of thermoset resins, such as phenol – formaldehyde (PF) resins.

PF resins are formed by the reaction of formaldehyde on ortho and para positions of phenol, resulting in a crosslinked, three-dimensional network, often used as adhesive. For that purpose, lignin can act as a source of phenol, as already addressed in different reviews [72,194–196]. However, as seen in part 2.1, lignin phenolic groups are always substituted in the para position by the aliphatic chain. In G-type units, one ortho position is also occupied by a methoxyl group, whereas they both are in S-type units. This higher degree of substitution results in an obviously lower reactivity of lignin as compared to phenol, that is further reduced by the steric hindrance imposed by the bulky methoxy groups [196].

Several strategies can be adopted to increase the reactivity of lignin toward formaldehyde [197]. Methyl groups can be removed from the methoxyl substituents of the aromatic rings, in the presence of sulfur, to produce DMSO and a demethylated lignin of higher reactivity. Another common way to enhance the reactivity is to previously react lignin with formaldehyde, to introduce a methylol group ―CH_2OH on the C5 position [72,196–199]. The methylolated lignin can then be reacted with phenol, and PF resins with up to 50% lignin have been formulated. The lignin can also be sequentially derivatized with formaldehyde and phenol, to prepare prepolymers [200], which can later be crosslinked with phenol to prepare lignin-based PF resins [201].

Finally, additional phenol groups can be attached to benzylic carbons of lignin [197,202]. This so-called phenolation reaction proceeds in acidic medium, and yields a lignin with additional ortho and para reactive sites on the grafted phenol groups. Side chain reactions generally cause lignin fragmentation, resulting in a decrease in the molecular weight [202], which favors the incorporation of the phenolated lignin in the resin network. Funaoka

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developed a process which allows in one or two steps the separation of lignin from the carbohydrates, and its functionalization with phenol derivatives, attached to the Cα [203]. Many kinds of substituted phenols have thus been attached to lignin, providing it new properties which have been extensively studied [204–206].

5.3.2. Lignin-based polyurethanes (PU)

Polyurethanes (PU) are a class of polymers where the monomeric units are linked together by urethane linkages, produced by the reaction of an isocyanate NCO with a hydroxyl OH, as depicted in Scheme 4. Depending on the structure and functionalities of the monomers used (polyisocyanates and polyols), a wide variety of PU materials can be produced, from thermoplastics to elastomers and thermosets, covering a great range of mechanical properties. PU are thus very versatile polymers, with a wide range of applications, the main one being the production of insulating foams.

Scheme 4. Formation of the urethane linkage by the reaction of a hydroxyl with an isocyanate

The lignin macromolecule can then be used as a source of OH groups, able to react with diisocyanates to yield polyurethanes. As each lignin macromolecule possesses multiple OH groups, an insoluble polymer network tends to be formed if sufficient amount of diisocyanate is added (Fig. 5b). Nevertheless, the reactivity of lignin OH groups is somehow limited, and decreases from primary aliphatic, to secondary aliphatic and finally phenolic hydroxyls, whose reactivity is supposed to be almost nonexistent [207]. Steric hindrance may also limit the reactivity, as it seems that during the network formation, some unreacted OH can be entrapped in the network, and become inaccessible to react [208]. A common way to overcome these limitations and enhance the lignin reactivity toward urethanization is to use oxypropylated lignin, because it only possesses aliphatic OH groups of higher reactivity.

Lignin acts as a polyfunctional monomer of high rigidity, which favors the formation of a network, and can even lead to very brittle materials. To facilitate the material processing and enhance its ductility, many studies used together with lignin another polyol as comonomer. This is generally a long chain aliphatic polymer, terminated on both sides by OH groups, which will play the role of chain extender, thus reducing the crosslinking density, and act as soft segment in the material, such as polyethylene glycol (PEG) [209–212], polybutadiene glycol (PBG) [213] or polycaprolactone (PCL) [208]. A way to avoid the use of another polyol as comonomer is to use a long chain polymeric diisocyanate, which will be able to play

both the roles of crosslinker and soft segment, *e.g.* oligoethylene oxide diisocyanate (ODI) [207] or polybutylene diisocyanate (PBDI) [214].

Table 2 summarizes the different types of lignin modifications, polyol comonomer and polyisocyanate which have been used for lignin-based polyurethane formulation. The polyisocyanates can either be bifunctional monomers (HDI, TDI or MDI), polymers with functionality higher than 2 (PMDI) or telechelic oligo- or polymers (ODI, PBDI).

The material properties are directly dependent on the network crosslink density, which is inversely proportional to the average molecular weight between crosslinks, M_c. This value can be determined by swelling tests, using the Flory-Rehner equation [215]. A key parameter to control the crosslinking density is the ratio of monomer isocyanate functions to the lignin hydroxyl functions, *i.e.* the NCO/OH ratio. Theoretically, a NCO/OH ratio of 1 is sufficient to form a network, but due to the limited reactivity of lignin and the possible loss of volatile diisocyanate during processing, many studies emphasize on the need for higher ratios. Working with KL, Glasser and coworkers found a maximum in the crosslinking density, corresponding to a minimum in swelling, for NCO/OH between 3 and 3,5 [216,217]. With OSL, optimum values of NCO/OH between 1,5 and 2 have been reported [207,209].

At constant NCO/OH ratios, different parameters can influence the crosslinking density. The main important one is the lignin functionality, *i.e.* the average number of OH groups per lignin macromolecule: a higher lignin functionality favors the formation of networks with higher crosslinking density. This implies that high MW lignin fractions, bearing higher number of OH groups per molecule than low MW ones, yield PU with higher crosslinking density [210,218,219]. The choice of technical lignin is therefore a critical factor: for instance partly acetylated lignins from acetic acid pulping are less prone to network formation [207]. Consequently, reducing the OH content of lignin, by a selective masking, will also reduce the crosslinking density [220]. When another polyol than lignin is used as comonomer, a relative increase in the lignin content leads to higher crosslinking density, because the lignin functionality is generally much higher than the one of the polyol [209,212,221].

For oxypropylated lignins, an increase in the grafted chain length will naturally increase the average molecular weight between crosslinks, *i.e.* reduce the crosslinking density [222]. When it is used, an increase in the comonomer molecular weight will obviously have the same effect [212].

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The material mechanical properties are mainly controlled by the network crosslinking density, and thus influenced by all the parameters addressed above: Young's modulus and tensile strength increase with the crosslinking density [209,210,212,216,218,219,221,222]. The evolution of the elongation at break is somehow more complicated: it generally presents a maximum corresponding to the full network formation, followed by a decrease for further increase in crosslinking density.

The nature of the diisocyanate also influences the material mechanical properties: aromatic diisocyanates such as TDI generate materials with higher modulus and strength, but lower elongation at break, than those prepared with aliphatic ones, *e.g.* HDI [216,217]. The incorporation of a soft segment, such as PEG, enhances the ductility of the materials at the expense of their rigidity [211], providing that no macro phase separation occurs, because this would cause a severe loss in mechanical properties [213].

The thermal properties of lignin-based PU, especially their glass transition temperature T_g, have also been largely studied. Just like the mechanical properties, the T_g is directly dependent on the crosslinking density: an increase in the crosslinking density causes a decrease in molecular mobility, and thus an increase in T_g [211,212,217,219,220,222]. Consequently, the incorporation of a soft segment leads to reduced T_g [211,213].

The T_g of the PU will also depend on the T_g of its monomers. The use of rigid aromatic diisocyanates will increase the T_g compared to aliphatic diisocyanates [216,217], and a good correlation exists between the lignin T_g and the PU T_g [218,223]. An increase in the grafted chain length in oxypropylated lignins causes a decrease in the T_g of both the lignins and the ensuing PU [222].

Table 2. Summary of the different monomers used for lignin-based PU elaboration. PEG = polyethylene glycol, PBG = polybutadiene glycol, PCL = polycaprolactone

5.3.3. *Lignin-based polyesters*

Polyesters are polymers containing an ester function in the repeat unit. Esters are formed by condensation reaction of a hydroxyl group with either a carboxylic acid, releasing water (Scheme 5a), an acyl chloride, releasing hydrochloric acid (Scheme 5b) or an anhydride, releasing a carboxylic acid (Scheme 5c). The lignin macromolecule containing multiple OH groups, polycondensation reactions with diacids or diacyl chlorides can lead to the formation

of lignin-based polyesters. Because of the high lignin functionality, insoluble networks tend to be formed rather than thermoplastic polyesters (Figure 5b).

Scheme 5. Formation of the ester linkage via reaction of a hydroxyl with a carboxylic acid (a), an acyl chloride (b) or an anhydride (c)

The esterification between a hydroxyl and a carboxylic acid corresponds to an equilibrium, and specific experimental conditions are required to favor the formation of the ester. When acyl chlorides are used instead, complete reaction can quickly be achieved, making this route more convenient for the polymer synthesis.

The synthesis of lignin-based polyesters has been extensively studied by Gandini and coworkers. Esterification has been performed on KL and OSL with either an aliphatic (sebacoyl chloride, SC) or an aromatic (terephtaloyl chloride, TC) acyl chloride (Table 3) [224–226]. IR spectroscopy reveals the formation of both aromatic and aliphatic ester bonds, but unreacted OH groups still remain after the reaction [224,226]. The reactivity of phenolic OH can be favored by the use of triethylamine as catalyst, whereas the use of pyridine promotes the reactivity of aliphatic OH groups [224]. Because the lignin functionality is high, an insoluble network is formed in the presence of an excess of acyl chloride, with a maximum yield for COCl/OH ratios between 1,5 and 2 [224,226]. However, even in these conditions, structural characterization by ^{13}C NMR revealed that almost none of the lignin phenolic OH had reacted, whereas aliphatic primary and secondary hydroxyls had been esterified to about 85 and 50 % respectively [226]. Steric hindrance and strong hydrogen bonding are likely to be responsible for the lack of reactivity of lignin phenolic OH groups, limiting the network formation.

Similarly to lignin-based PU, PEG can also be used as comonomer. In addition to its role of chain extender, the use of PEG allows to perform the reaction in a solvent-free environment, because PEG can actually dissolve lignin [225,226].

The polyesters thus produced are thermally stable up to at least 200 °C [224–226]. No T_g can be detected by DSC for pure lignin-based polyesters, most likely because it is spread over a wide temperature range because of structural heterogeneity of the network. However, lignin-based polyesters produced using PEG as comonomer have a T_g between -45 and -60 °C with SC or -5 and -40 °C, depending on the lignin type and content, and the PEG chain length [225,226].

By pursuing polyesterification within similar conditions, some authors claimed to have prepared thermoplastic lignin copolyesters, even though the high lignin functionality and COCl/OH ratios used (from 1 to 3) would likely lead to the formation of a network [227,228]. Indeed, no actual proofs of thermoplastic behavior are presented.

Saito et al. also designate their polyesters prepared using KL and a long chain polybutadiene dicarboxylic acid (PBDA, Table 3) as thermoplastics [229]. Using a lignin pretreated with formaldehyde to increase its molecular weight, they obtained a solid at room temperature, which could be compression molded into films at 120 °C. These films exhibit two distinct thermal transitions as measured by DMA, the first one corresponding to the T_g of the soft rubber segments around -70 °C, and the second one at about 20 °C being qualified as the flow or softening temperature. Even though some MW increments are shown by SEC, a structural description of the ensuing polyester is missing (branched thermoplastic or crosslinked network).

The preparation of lignin-based polyesters thus appears to be still challenging. To the best of our knowledge, mechanical properties of lignin-based polyesters have never been reported. The nature of the obtained polyesters is also sometimes controversial, with some claims of thermoplasticity being not clearly verified.

Table 3. Summary of the different monomers used for lignin-based polyesters elaboration. PEG = polyethylene glycol, PBG = polybutadiene glycol, PCL = polycaprolactone

5.3.4. *Other lignin-based copolymers*

Some other types of polymerization reactions have been carried out in order to produce lignin-based polymers. They first require the grafting of polymerizable groups on lignin hydroxyls, such as activated double [230] or triple bonds [231], and their further polymerization or copolymerization.

Deffieux and co-workers managed to graft allylic, vinylether and styrenic groups onto lignin model compounds, showing a reactivity of both phenolic and aliphatic hydroxyls [230]. Those groups can further be polymerized through free radical polymerization or copolymerization with ethylenic monomers. However, free phenolic hydroxyls inhibit the polymerization because they are able to scavenge the radicals formed on the initiator [232]. An excess of initiator or the acetylation of the remaining phenolic OH groups is then required. They further prepared lignin "macro"-monomers by grafting methacrylic or styrenic groups (Fig. 6), and

proceeded to radical copolymerization with MMA, yielding lignin-PMMA random copolymers [233]. By modulating the ratio of grafting reagent to lignin, they prepared lignin "macro"-monomers with different functionalities, *i.e.* different amounts of polymerizable groups per molecule, and could obtain either soluble linear or branched copolymers, or insoluble polymer networks. The same approach has recently been applied to a lignin from agricultural wastes, which was copolymerized with butyl methacrylate, after functionalization with an acrylic group [234].

Fig 6. Lignin "macro"-monomers functionalized by methacrylic (a) and styrenic (b) groups [233]

Argyropoulos and co-workers used propargyl bromide to introduce alkyne groups onto the lignin macromolecule [231]. This reaction presents the advantage of being specific to phenolic hydroxyl groups, and depending on the stoichiometry of reagent used, the amount of alkyne groups introduced can be controlled, up to a quantitative functionalization. Homopolymerization has then been conducted, either via oxidative coupling or Claisen rearrangements (Scheme 6), leading to polymers of enhanced thermal stability. The presence of alkyne groups also offers the possibility to envisage "click chemistry" reactions, whose interest in polymer science is continuously growing [235,236].

Scheme 6. Lignin propargylation to introduce alkyne groups, followed by oxidative coupling or Claisen rearrangement (adapted with permission from Sen et al. [231]. Copyright 2013, American Chemical Society)

The same group also reported the synthesis of poly(arylene ether sulfone) copolymers, based on the reaction of KL phenolic OH groups with 4,4'-difluorodiphenyl sulfone (DFDPS, Scheme 7) [237]. The control of the amount of KL phenolic OH groups by selective masking with methylation allowed them to produce different copolymers of varying MW, with very high thermal stability (up to 300 °C) and T_g between 150 and 170 °C.

Scheme 7. Copolymerization of lignin with DFDPS to form poly(arylene ether sulfone) (adapted with permission from Argyropoulos et al. [237]. Copyright 2014, American Chemical Society)

6. Toward micro- and nanostructured lignin-based materials

In the previous paragraph chemical reactions that can be employed to modify the lignin macromolecule and produce polymer materials were discussed. The current chapter discusses how some of these techniques have been exploited to develop materials with a controlled structure down to the micro or nano scale. This field is still largely underexploited for lignin-based materials, but recent years have seen promising achievements, with the development of *e.g.* lignin-based micro- and nanoporous structures, micro- and nanoparticles or nanocapsules.

6.1. Lignin-based micro- and nanoporous materials

Aerogels are a class of porous materials, with a very important potential for various applications, such as insulating material, adsorbent, catalyst… They are commonly prepared by sol-gel polymerization of a resin, followed by solvent exchange and drying to recover the final porous product. Phenolic resins, such as resorcinol-formaldehyde, are common for this purpose. As already described in part 5.3.1, lignin has long been thought to be a potential source of phenols for this kind of resins. Recently, several authors tried to use lignin-based resins to produce aerogels.

Chen et al. thus replaced part of resorcinol by lignin to produce resorcinol-lignin-formaldehyde resins in aqueous solutions of NaOH [238]. Grishechko et al. similarly formulated phenol-lignin-formaldehyde [239] and tannin-lignin-formaldehyde resins [240]. To obtain gels, they noticed that lignin can't be the sole source of phenolics, because of its relatively low reactivity as a result of its high degree of substitution. Nevertheless, 50 % lignin could be incorporated in resorcinol-based resins [238], and up to 75 % in tannin- or phenol-based ones [239,240].

Subsequent drying of the product yielded the target aerogels. The drying step is critical for the properties of the final product. Particularly, shrinkage has to be as low as possible to maintain the porous structure. An efficient way to limit shrinkage, mainly driven by capillary forces, is to dry the gel using supercritical fluids. Supercritical CO_2 (scCO_2) is commonly used, even if an additional step of solvent exchange from water to an appropriate solvent (ethanol or acetone) is mandatory before the drying, because water isn't soluble in scCO_2 [239–241]. Drying can also be performed by freeze-drying, after solvent exchange in *tert*-butanol, but the shrinkage becomes more significant than in the case of supercritical drying [239].

The replacement of simple phenols by lignin generates an increase in the pore size, with the formation of macropores (> 50 nm) to the detriment of mesopores (2 – 50 nm). Even if this

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causes an increase in the overall porosity and consequently a decrease in the bulk density, the total surface area is reduced, thus limiting the final material properties, such as the adsorption capacity or the insulating performances [238–240].

Recently, lignin-based aerogels were produced without the use of formaldehyde and in the absence of any other phenol [241]. Lignin was crosslinked using oligo(ethylene glycol) or (propylene glycol) carrying epoxy groups at both chain end, and the obtained hydrogel dried with scCO$_2$. Long-chain crosslinkers appear to favor the gel formation, probably because they can more easily react with two different lignin molecules, thus favoring the network formation.

Lignin-based aerogels can present an overall porosity higher than 80 % and exhibit thermal conductivity in the range of 40 – 45 mW.K^{-1}.m^{-1}, close to those of commercial insulating materials like polystyrene foams [239–241].

Lignin-based porous materials have also been produced directly from black liquor using the High Internal Phase Emulsion (HIPE) technique [242,243]. To obtain porous monoliths, the authors first added to a black liquor containing approximately 40 % lignin (w/v) epichlorohydrin as crosslinker and a surfactant. Castor oil was then added thanks to a home-made emulsification device, to obtain a castor oil-in-black liquor emulsion with an oil content of 55 %. The emulsion is then heated to generate lignin crosslinking in the continuous phase via reaction with epichlorohydrin. The obtained monoliths are then extracted with ethanol to remove the castor oil and yield materials with an interconnected porous morphology. Depending on the nature and amount of surfactant, different void sizes can be obtained, ranging from about 5 to 20 µm in diameter [242,243].

6.2. Functionalized lignin beads

Emulsion-based techniques can also be exploited for the elaboration of lignin beads, when the lignin solution constitutes the dispersed phase. Chen & Liu prepared black liquor suspensions in a mixture of oil and chlorobenzene containing a surfactant [244]. They later polymerized lignin inside the dispersed phase using epichlorhydrin as crosslinker, and recovered spherical beads with an average diameter of 300 – 450 µm. They showed that these lignin beads could be used as adsorbent for the amino acid L-lysine.

Saidane et al. [245,246] prepared in a similar manner emulsions of highly concentrated lignin alkaline solutions in 1,2-dichloroethane. The lignin is then crosslinked inside the dispersed

phase, using either epichlorhydrin [245] or the radical polymerization of previously grafted acrylic groups [246]. This technique allows the recovery of solid lignin beads with diameters in the range of 100 – 800 µm. The lignin beads were later functionalized in two steps, to expose sulfonhydrazine groups ―SO_2NHNH_2 on their surface. In a first step, free aromatic positions were sulfonated using mild conditions, to preserve the network structure. The sulfonated lignin beads were then treated with thionyl chloride and hydrazine hydrate to obtain the final functionalized lignin beads, with a loading of 0,5 to 0,7 mmol.g^{-1} of sulfonhydrazine groups [245,246]. Functionalized lignin beads are intended to be used in the wine industry, to remove carbonyl-bearing compounds responsible for SO_2 binding in sweet wines [247].

6.3. Nanoparticles from lignin

Several recent publications reported the preparation of lignin-based nanoparticles. Starting from lignin solutions in ethylene glycol, Frangville et al. reported the formation of nanoparticles by gradually adding HCl to the solutions [248]. The particle size was found to decrease from the micrometer scale down to less than 100 nm when the total amount of HCl added, its concentration or its rate of addition were reduced. The nanoparticles could later be crosslinked using glutaraldehyde, and after redispersion in water were found to be stable over a wide pH range (from 1 to 9) for up to a month. Interestingly, the nanoparticles didn't show any cytotoxicity for yeast or microalgae, and could be an interesting candidate for environmentally benign nanoparticles.

The gradual addition of a non-solvent (water) to a solution of acetylated lignin in tetrahydrofuran (THF) resulted in the formation of nanosized colloidal spheres [249]. The obtained spheres, with a hydrodynamic radius R_h around 100 nm, were water-dispersible and stable up to pH 12. Further increase in pH led to the hydrolysis of the acetyl groups, thus releasing free phenolic groups which prevented the colloidization because of electrostatic repulsion.

The formation of lignin colloids was also exploited by Jiang et al. [250] to produce lignin nanoparticles used to reinforce natural rubber composites. Lignin alkaline solutions were added to cationic polyelectrolyte solutions of poly(diallyldimethylammonium chloride). As lignin aggregates are negatively charged at high pH, because of the deprotonation of phenolic and carboxyl groups, they could adsorb the cationic polymer, resulting in colloidal particles with R_h around 200 nm, exhibiting a positive surface charge. Natural rubber latex particles

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carry negative charge on their surface, and could then associate in solution with the lignin-polyelectrolyte complexes. After drying, natural rubber materials reinforced with finely dispersed nanosized lignin particles were obtained. They exhibit enhanced mechanical and thermal properties.

6.4. Lignin-based micro- and nanocapsules for encapsulation

The potential of certain polymers to self-organize in solutions at specific conditions is a very attractive phenomenon, which can be exploited to produce *e.g.* nanoparticles, micelles or capsules, with great potential in pharmaceutical applications [251–253]. Two recent studies reported the preparation of lignin-based capsules able to encapsulate either hydrophobic [254] or hydrophilic drugs [255].

Tortora et al. used oil-in-water emulsions to prepare lignin microcapsules [254]. The emulsions were prepared by adding olive oil to lignin aqueous solutions (5 or 15 wt %) and sonication. Because of its hydrophilic groups (carboxyls and hydroxyls) bound to a hydrophobic aromatic skeleton lignin can be seen as an amphiphilic molecule, which will thus preferentially locate at the oil – water interface. Upon crosslinking, it is possible to "lock" the structure and recover the lignin capsules. Different strategies have been successfully applied to crosslink lignin: radical coupling under ultrasound, promoted or not by hydrogen peroxide H_2O_2, or use of a poly(ethylene glycol) terminated by epoxy groups able to react with lignin hydroxyls.

The obtained capsules were between 300 nm and 1 µm in diameter. They were later used to encapsulate the hydrophobic fluorescent probe coumarin, previously added to the oil phase. The capsules proved to be stable over a month period in water suspension. The complete release of coumarin could be obtained within one hour by addition of a surfactant to the suspension. Those lignin microcapsules were finally found to be non-cytotoxic, unlocking potential applications in biomedical or cosmetic fields.

Yiamsawas et al. applied the opposite strategy for the preparation of their lignin-based nanocontainers [255]. The lignin aqueous solution was emulsified in an organic phase of cyclohexane containing TDI (see paragraph 5.3.2 and Table 2) and a surfactant. The polymerization of lignin polyurethane takes place at the water – cyclohexane interface to yield hollow nanocapsules of lignin-based polyurethane. Because of the reaction of TDI with water, urea linkages are formed together with the target urethane linkages.

The particle size was found to be in the range of 162 – 220 nm in cyclohexane suspension, and between 311 and 390 nm when redispersed in water, whereas the wall thickness appeared to be about 10 to 20 nm. The encapsulating capacity and stability of the capsules was evaluated using the hydrophilic fluorescent dye sulforhodamine. Long time stability was observed over several months in both aqueous and organic phases. The release of the dye could be obtained by an enzymatic degradation of the lignin shell.

7. Conclusion and perspectives

As a functional polymer of relatively low molecular weight, lignin presents large opportunities for a use in polymer materials. This review presented the different possibilities that have been addressed in the literature for such aim.

The direct use of the lignin polymer, without any chemical treatment, is obviously attractive from the view point of reducing the dependence on fossil resources. One of the most promising perspectives is the use of lignin as a source of carbon for activated carbons or carbon fibers. Because the whole material is carbonized, it seems that the variability among different lignin sources could be somehow overcame. However, the lack of structural homogeneity still limits the properties of lignin-based carbon fibers.

The direct use of lignin as material is limited by the difficult or even impossible melt processing, but its blending with other synthetic or bio-based polymers can present some interests, mainly based on the antioxidant properties of the phenolic groups, which provide better resistance to oxidative degradation processes. However, the compatibility is restricted to polar polymer matrices, and chemical modifications are required to broaden the application areas.

The chemical nature of the lignin macromolecule offers a great variety of possible chemical modifications. Simple esterification or alkylation of hydroxyl groups can favor the compatibility of lignin with non-polar polymer matrices. The reactivity of lignin hydroxyls can further be exploited to produce a wide range of polymers, such as polyurethane or polyesters, and the use of lignin as a "macro"-monomer has been widely studied.

Most of the published literature focused on the development of polymer networks, able to be used in resins or adhesives. More recent studies tend to also focus on the production of lignin-based thermoplastics. As each lignin macromolecule bears multiple functional groups, a reduction of the lignin functionality is required to avoid the formation of an insoluble network

and achieve thermoplastic behavior. The control of lignin functionality appears to be one of the most important challenges for the development of such kind of materials. Detailed and precise knowledge of the macromolecular structure and the initial functional groups content, as well as partial and selective blocking to reduce the functionality will be the key to modulation of reactivity.

Industrial lignins generally have high levels of polydispersity, adding more complexity to achieve a good control of the macromolecular architecture after chemical derivatization. Many efforts have been devoted in the recent years to separate fractions of lower polydispersity, including ultrafiltration, solvent fractionation and selective precipitation. The reproducibility of those processes, their ability to be scaled-up to industrial levels, as well as economic and environmental considerations should be key points to assess in the next few years, in order to bring to the market larger volumes of well-defined lignin fractions, which would be suitable for high added-value applications.

Finally, the recent years have seen several developments towards the production of lignin-based materials with controlled architecture, down to the nanoscale. This field, which is still largely underexploited for lignin-based materials, is of particular interest to bring lignin to high added-value applications.

Acknowledgments

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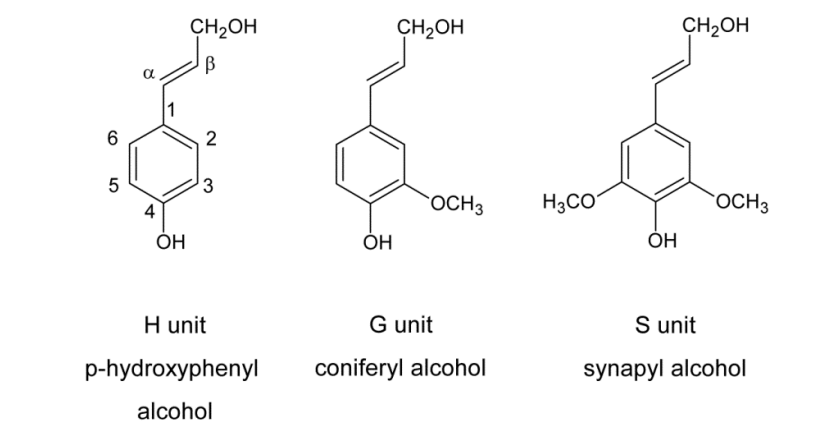
Figures & schemes captions

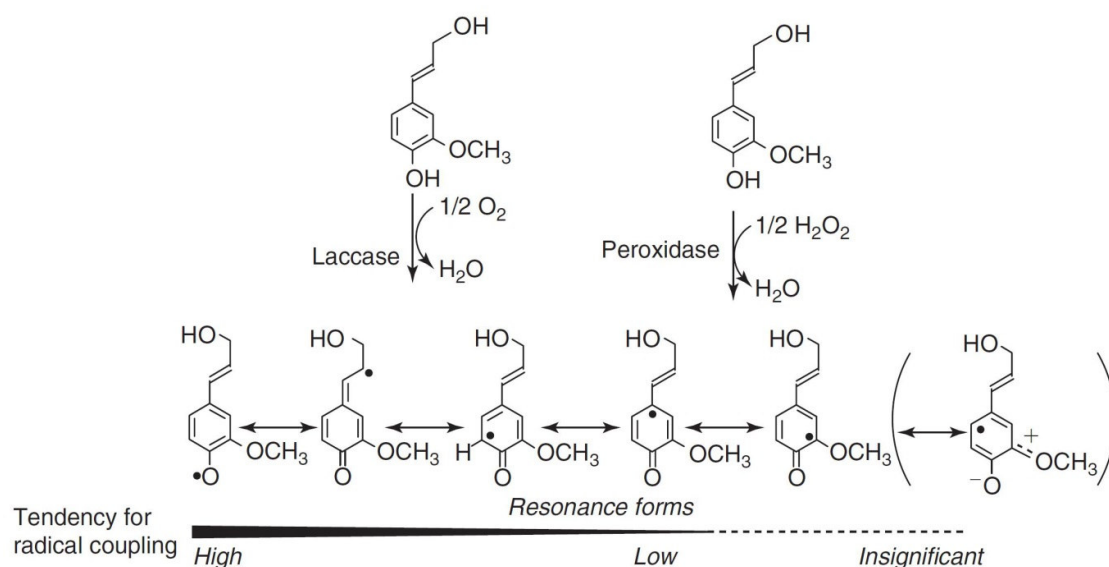Fig. 1. The three main monolignols, with the associated nomenclature for C atoms

Fig. 2. Enzymatic formation of phenoxy radical onto monolignols, leading to the resonance-stabilized forms, and their propensity to radical coupling (reproduced from Gellerstedt and Henriksson [12] with permission from Elsevier)
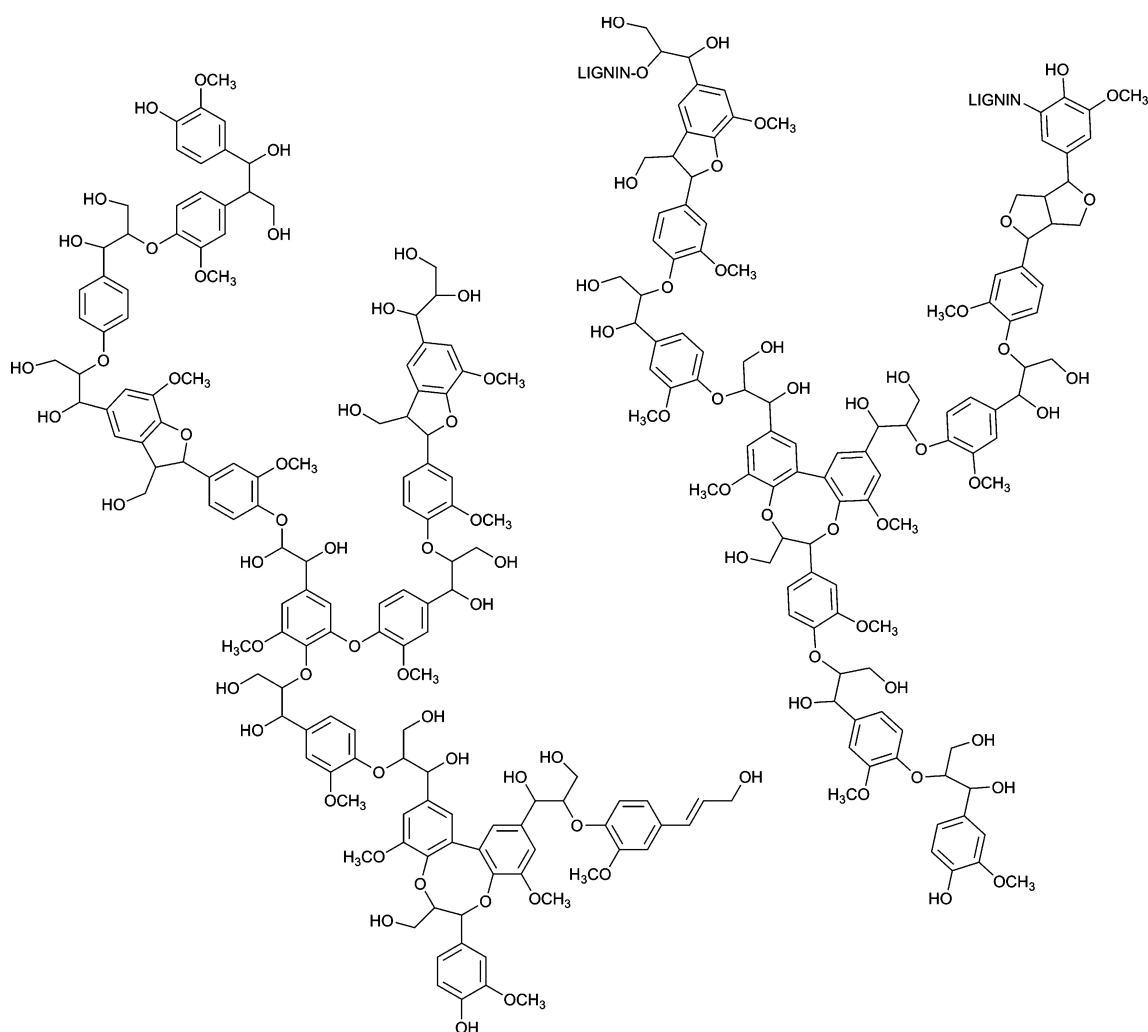
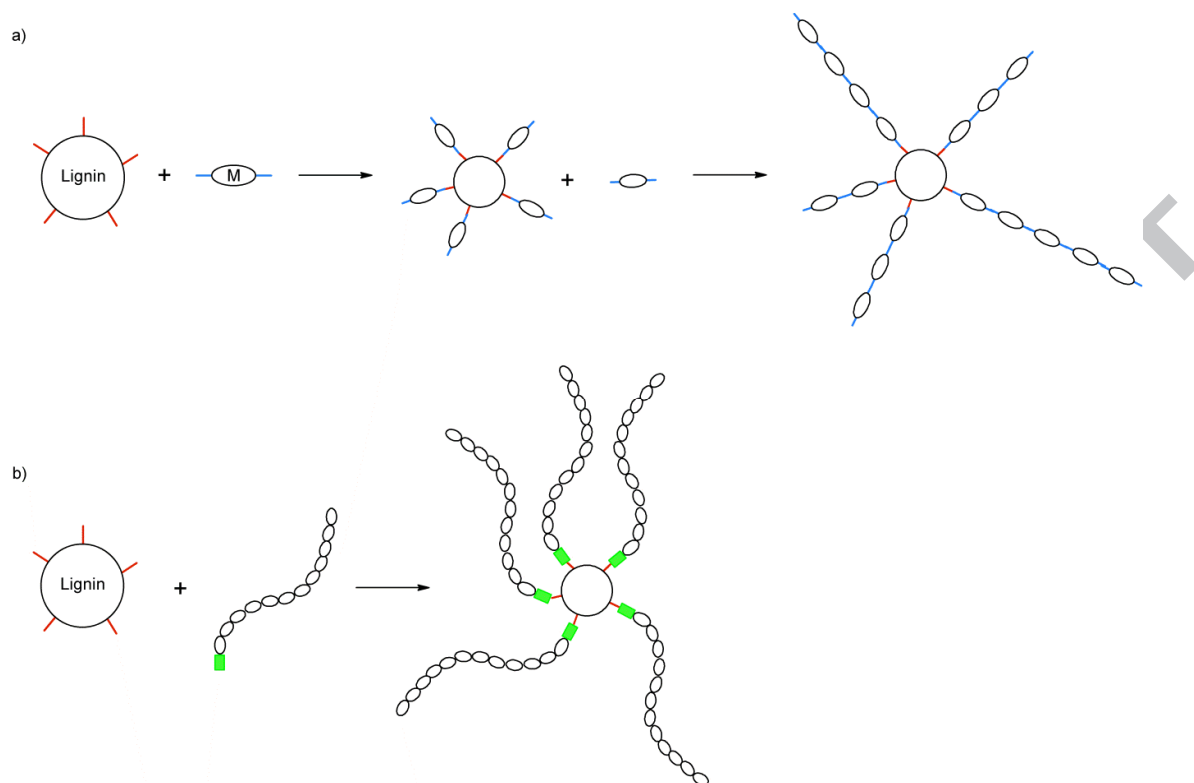Fig. 3. Structural Motif of Softwood Lignin (reproduced from Crestini et al. [24] with permission from Elsevier)

Fig. 4. Schematic synthesis of lignin graft copolymers by "grafting from" (a) or "grafting onto" (b) techniques
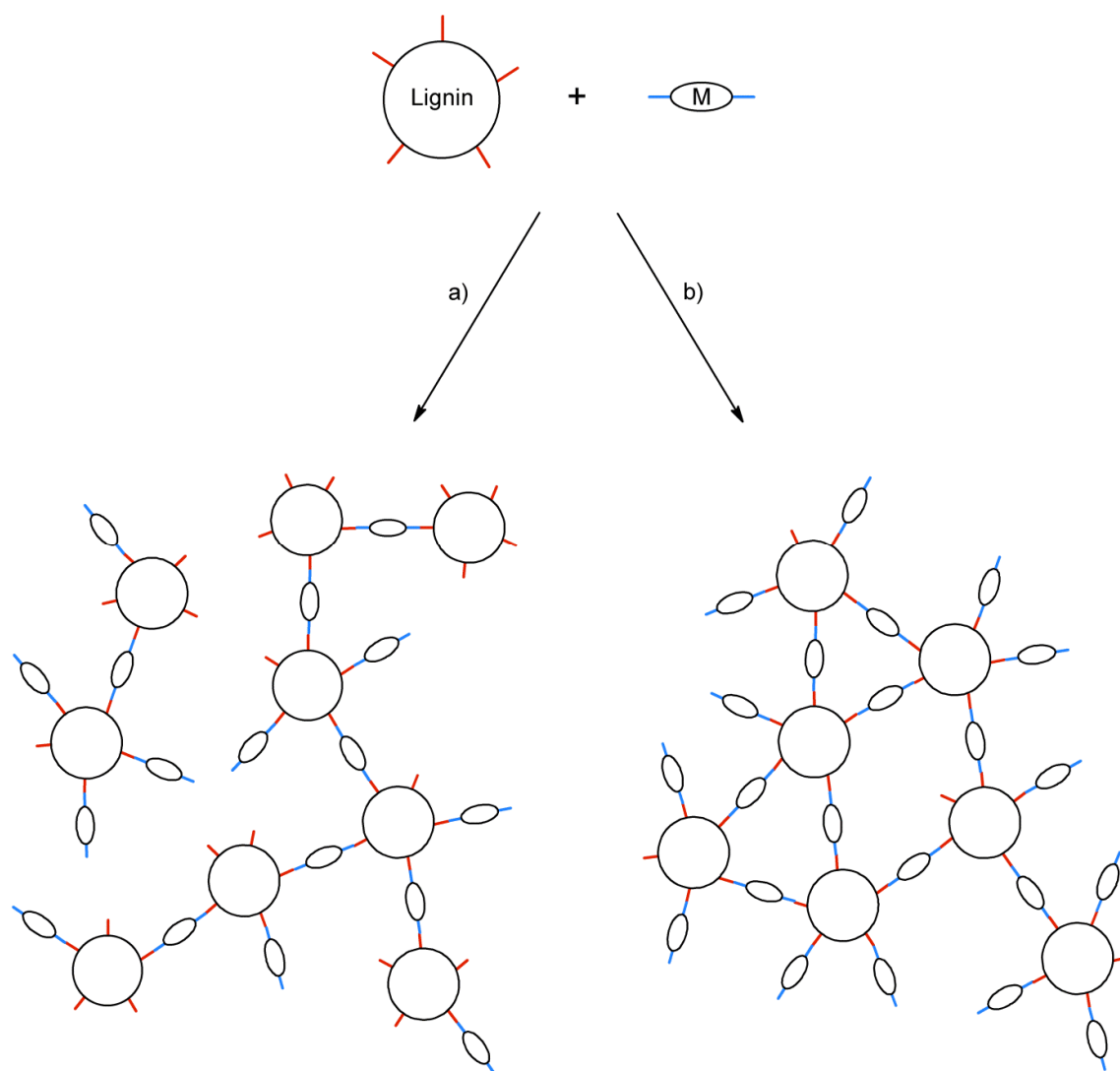
Fig. 5. Reaction of lignin with bifunctional monomer. Depending on the ratio of lignin reactive sites to monomer, the reaction can lead to either branched or linear copolymer (a), or to the formation of a network (b)
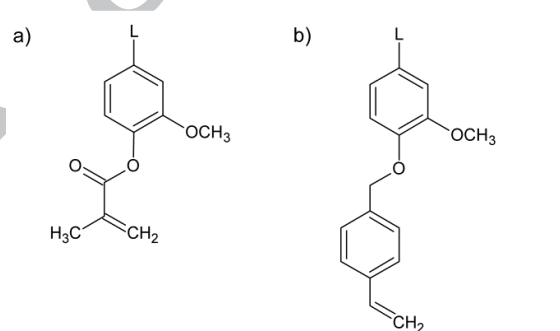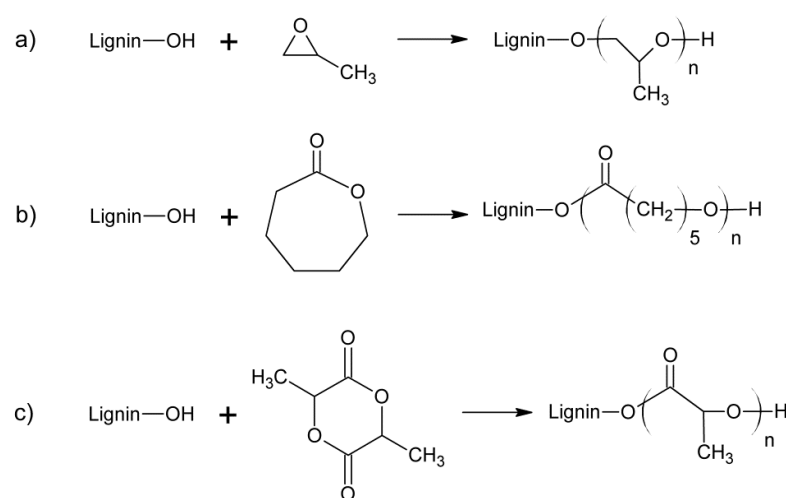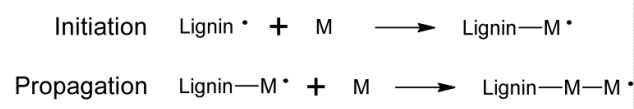
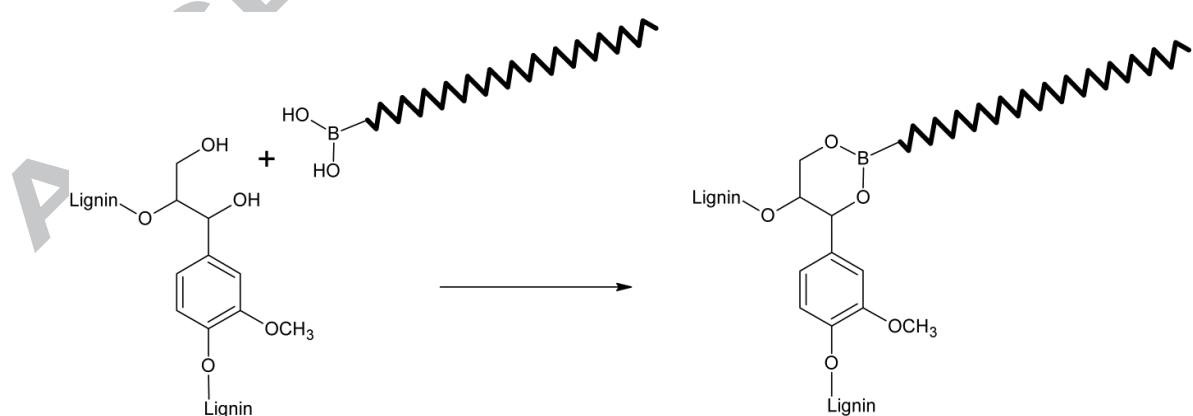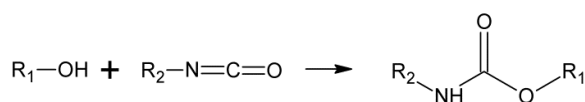Fig 6. Lignin "macro"-monomers functionalized by methacrylic (a) and styrenic (b) groups [233]

Scheme 1. Ring Opening Polymerization (ROP) of propylene oxide (a), ε-caprolactone (b) and lactide (c) initiated by lignin hydroxyls to synthesize lignin graft copolymers

Scheme 2. Scheme of the free radical polymerization of vinylic monomers to synthesize lignin-graft copolymers. Lignin "macro"-radicals, which can be produced by several methods, are able to initiate the radical polymerization of the monomer.

Scheme 3. Grafting of boronic acid-terminated polymers onto lignin [193]

Scheme 4. Formation of the urethane linkage by the reaction of a hydroxyl with an isocyanate

Scheme 5. Formation of the ester linkage via reaction of a hydroxyl with a carboxylic acid (a), an acyl chloride (b) or an anhydride (c)

Scheme 6. Lignin propargylation to introduce alkyne groups, followed by oxidative coupling or Claisen rearrangement (adapted with permission from Sen et al. [231]. Copyright 2013, American Chemical Society)

Scheme 7. Copolymerization of lignin with DFDPS to form poly(arylene ether sulfone) (adapted with permission from Argyropoulos et al. [237]. Copyright 2014, American Chemical Society)

Figures

Fig. 1. The three main monolignols, with the associated nomenclature for C atoms

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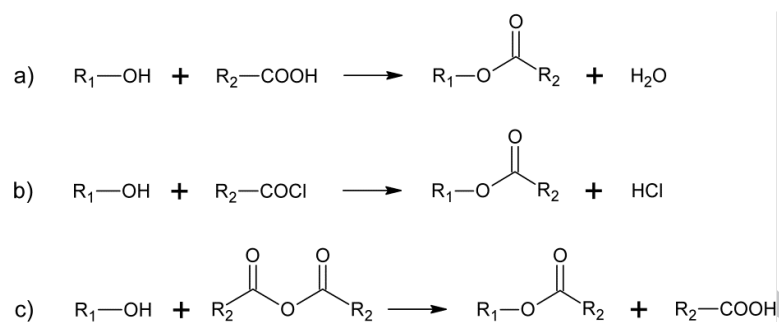
Scheme 5. Formation of the ester linkage via reaction of a hydroxyl with a carboxylic acid (a), an acyl chloride (b) or an anhydride (c). R_1, R_2 = alkyl or aryl chains
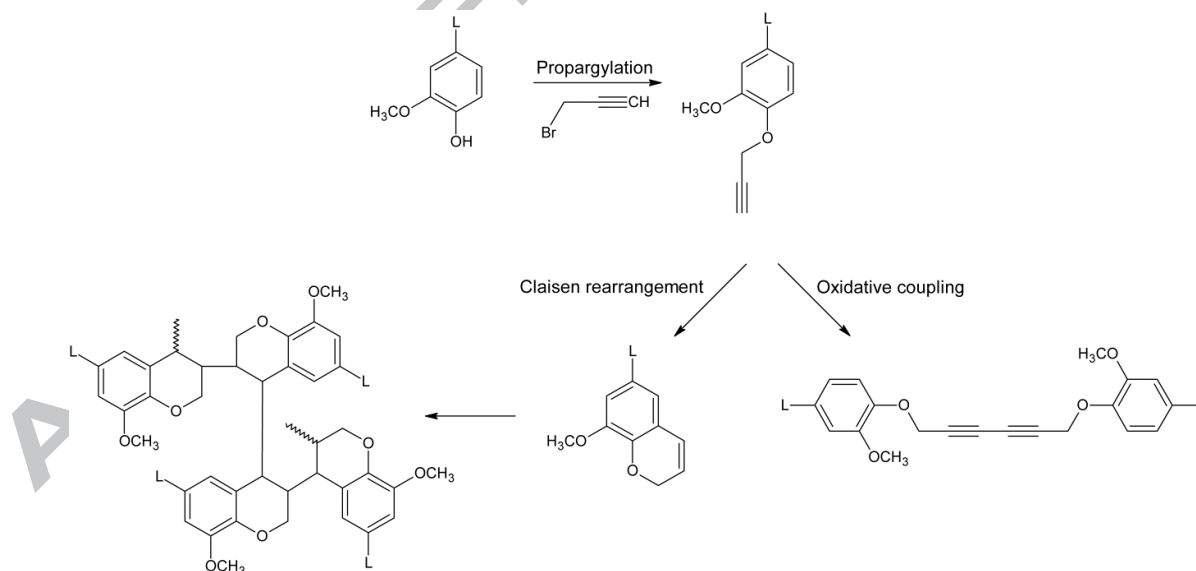
Scheme 6. Lignin propargylation to introduce alkyne groups, followed by oxidative coupling or Claisen rearrangement (adapted with permission from Sen et al. [231]. Copyright 2013, American Chemical Society)
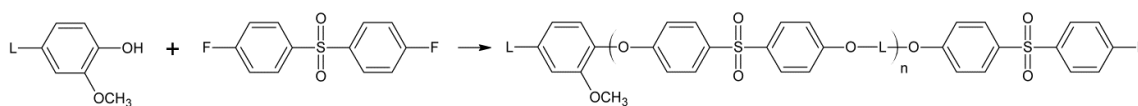
Scheme 7. Copolymerization of lignin with DFDPS to form poly(arylene ether sulfone) (adapted with permission from Argyropoulos et al. [237]. Copyright 2014, American Chemical Society)

Tables

Lignin type	Annual production (kt.yr^{-1})	Main producers
Lignosulfonates	≈ 1 000	Borregaard LignoTech Tembec Domjö Fabriker La Rochette Venizel Nippon Paper Chemicals
Kraft	≈ 90	MeadWestvaco Domtar (Lignoboost)
Soda	5 – 10	Greenvalue
Organosolv	≈ 3	CIMV Lignol Innovations DECHEMA/Fraunhofer Dedini

Table 1. Commercial production of lignin [67]
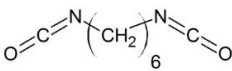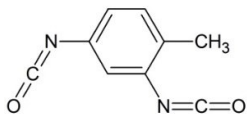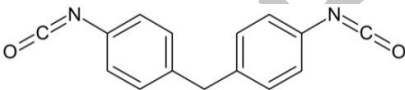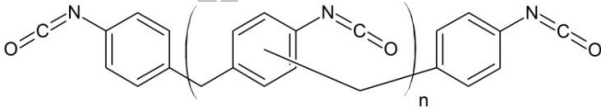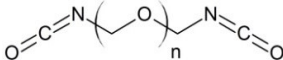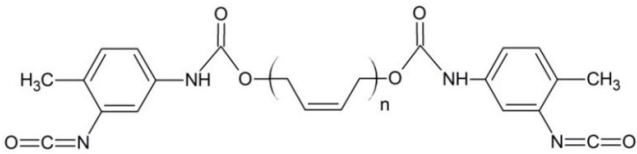
Lignin modification	Comonomer (polyol)	Diisocyanate	Ref
Oxy-propylation	-	Hexamethylene diisocyanate (HDI)	[216–218,220,222,223]
	PEG		[211]
	PBG		[213]
Oxy-propylation	-	2,4-toluene diisocyanate (TDI)	[216,217,222]
	PEG		[211]
	PBG		[213]
-	PEG	4,4' methylene diphenyl diisocyanate (MDI)	[209,210,212]
	PCL		[208]
Oxy-propylation	-	Polymethylene diphenyl diisocyanate (PMDI)	[166,167,256]
-	Polyethertriol		[219,221]
Oxy-propylation	Sucrose and/or glycerol polyol		[167]
-	-	Oligo(ethylene oxide) diisocyanate (ODI)	[207]
-	-	Polybutylene diisocyanate (PBDI)	[214]

Table 2. Summary of the different monomers used for lignin-based PU elaboration. PEG = polyethylene glycol, PBG = polybutadiene glycol, PCL = polycaprolactone
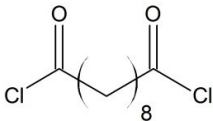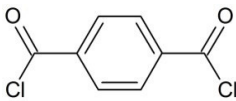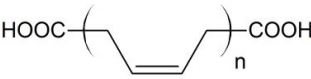
Lignin modification	Comonomer (polyol)	Diacyl chloride or diacid	Ref
-	PEG	Sebacoyl chloride (SC)	[225,226]
	-		[224,227,228]
-	PEG	Terephtaloyl chloride (TC)	[225,226]
	-		[224]
Formaldehyde crosslinking	-	Polybutadiene dicarboxylic acid (PBDA)	[229]

Table 3. Summary of the different monomers used for lignin-based polyesters elaboration.

PEG = polyethylene glycol, PBG = polybutadiene glycol, PCL = polycaprolactone