

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



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ARTICLE INFO

Article history:

Received 10 July 2014

Received in revised form 12 September 2014

Accepted 21 September 2014

Available online 28 September 2014

Keywords:

Lignin

Copolymer

Functionalization

Chemical modification

Materials

ABSTRACT

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.

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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

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-hydroxyvalerate; 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, sebacyl chloride; SL, soda lignin; TC, terephthaloyl chloride; TDI, 2,4-toluene diisocyanate.

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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 (Fig. 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].

The primary structure of lignin is formed by radical polymerization of monolignols, the radical sites being initiated by the enzymes peroxidases and laccases (Fig. 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 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].

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 Fig. 3.

In contrast to other biopolymers like cellulose, the suggested heterogeneity in lignin structure, coupled with the lack of stereoregularity 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 Section 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], ^1H 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

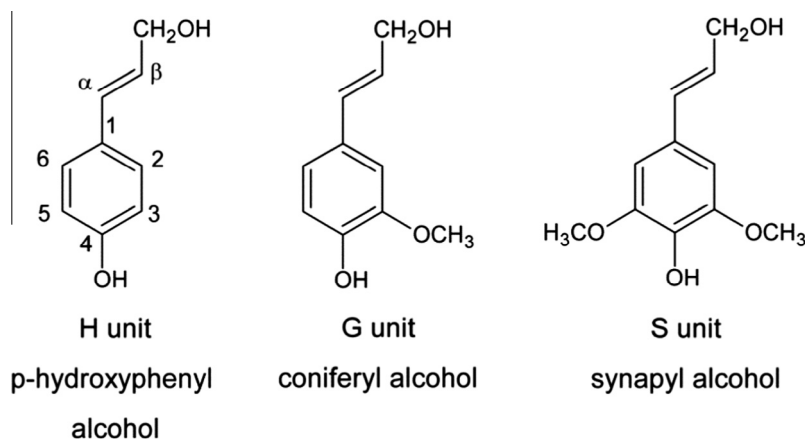


Fig. 1. The three main monolignols, with the associated nomenclature for C atoms.

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