10

Biodegradable Lignin-Based Plastics

Yi-ru Chen and Simo Sarkanen

University of Minnesota, Department of Bioproducts and Biosystems Engineering, 2004 Folwell Ave., Saint Paul, MN 55108, USA

10.1 Lignocellulose Biorefineries

Outlook. Over 2×10^{11} t of lignocellulose is biosynthesized annually in the form of plant biomass, ~80% of which is embodied in trees. From 2008 onward, huge investments were regularly allocated to converting a sizable share of these renewable materials to biofuels and chemicals. By the year 2020, however, these ventures had not achieved profitability because lignin valorization had failed to amass sufficient economic gain.

Biomass collectively represents the most abundant renewable source of materials from which liquid biofuels (such as bioethanol) and valuable chemicals can be produced. The total annual plant growth (namely, primary biomass production) has been estimated [1] to be 220 billion oven-dry tonnes, 80% of which is manifested in trees [2]. The prospect of partially exploiting this vast potential has attracted enduring investments in Europe, Asia, and the United States. In 2006, the European Union published a forecast declaring that, by 2030, a quarter of road transport fuel needs could be derived from biofuels [3]. Correspondingly, the United States projected that, by 2030, enough biomass could be sustainably harvested for producing a quantity of biofuels equivalent to 25% of the nation's 2015 energy consumption – without encroaching on demands for food, feed, and fiber [4].

The single most abundant renewable polymer is cellulose, which consists of (unbranched) 1-O-4' linked β -D-glucopyranose chains. Some of it occurs in a rather pure form, such as cotton plant seed hairs, for example, but most appears in combination with lignin and other polysaccharides (i.e. hemicelluloses) in the cell walls of vascular plants, including trees [5]. The lignins in these composite plant materials are aromatic; they represent the second most abundant group of biopolymers on the Earth. Annually, around 2×10^{10} t of new lignins have been independently estimated to form among the metabolic products of photosynthesis [6].

It is clearly understood that the high cost of converting the polysaccharides in plant cell walls to biofuels arises from the recalcitrance of lignocellulosic biomass

330 10 Biodegradable Lignin-Based Plastics

toward chemical and/or enzymatic deconstruction [7]. Indeed, a 2013 technoeconomic analysis of cellulosic diesel range fatty acid blend stock production from corn stover uncovered an alarming situation. The report concluded that the corn stover lignin fraction must acquire an economic value of equal importance to the fermentable carbohydrates if the 2022 target selling price of US\$0.80 per gasoline equivalent liter was going to be attained for the renewable fuel component [8]. In 2017, the prospect of profitable cellulosic ethanol sales had been weakened by comparable fears. The unsubsidized production cost of this liquid biofuel was not expected to fall below US\$1.20 per gasoline equivalent liter, even by 2025 [9].

Various means have been contemplated as plausible routes for valorizing cellulose and hemicelluloses more profitably than converting them to biofuels. These have been succinctly organized [10] by way of consecutive acid-catalyzed transformations to successive platforms based on monosaccharides (from polysaccharide cleavage), furan derivatives (formed through monosaccharide dehydration), and finally levulinic acid, followed by a reductive step to γ -valerolactone (GVL). This appealing blueprint has fostered the further expectation that profitable lignin valorization will ultimately depend on efficient depolymerization to non-macromolecular compounds [10].

Lignin depolymerization may be achieved either pyrolytically, enzymatically, or catalytically. Both pyrolysis and biological depolymerization require, for intrinsically different reasons, extensive purification schemes to obtain products in profitable yields, while the costs of catalysts for the third alternative must be kept down to achieve economic viability [10]. Thus, formulations for plastics with very high (~90 wt%) lignin contents should also be evaluated thoroughly: success could provide inexpensive solutions to the formidable task of biorefining lignocellulose profitably, if adequate performance indices for such new materials can be secured.

Lignocellulose composition varies quite substantially between the cell walls of different vascular plants [11a]. Among (monocotyledonous) grasses and other non-woods, (eudicotyledonous) hardwoods, and (gymnospermous) softwoods or conifers, cellulose contents extend from 30 to 50 wt%, while hemicelluloses (lower molecular weight polysaccharides composed of pentoses and hexoses) encompass a 15–35 wt% range, and lignins contribute 15–35 wt% to the dry plant matter [11a, 12].

It has been generally believed that covalent bonds between lignin and hemicelluloses are responsible for the difficulties encountered in separating carbohydrates completely from lignin, when fractionating milled wood or other plant materials by physicochemical means [13]. However, solid-state NMR analyses of ¹³C-labeled maize stems have revealed that the cell wall lignin and polysaccharide domains are dynamically distinct. Lignin exhibited the shortest ¹H-T_{1ρ} and longest ¹³C-T₁ relaxation times, whereas the reverse was observed in regard to the polysaccharides. Numerous electrostatic interactions were envisaged to occur between hydrophobic lignin nanodomains and the hemicellulose, xylan, but any effects from covalent linkages between the separate phases fell below the detection limits of the solid-state NMR techniques employed [14].

10.2 Macromolecular Lignin Configuration

Debated revision smoldering for almost 60 years. Between four and six linkages interconnect the hydroxyphenylpropanoid units that form lignin chains. In 1960, lignin macromolecules were considered to be cross-linked biopolymers. By 2019, branching and cross-linking had tended to fade from native macromolecular lignin structures. This drastic revision could reinforce prospects for lignin valorization, but strong disagreement persisted in the lignin field.

Lignins are assembled by the dehydrogenative polymerization of one, two, or (occasionally) three monolignols that are usually derived from phenylalanine biosynthesized in the plastid, where the aromatic amino acid precursor is formed by means of the shikimate pathway from phosphoenol pyruvate and erythrose 4-phosphate [15]. After being shuttled to the cytosol, phenylalanine is deaminated by phenylalanine ammonia lyase to cinnamate, which is converted through the phenylpropanoid pathway to *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol (Figure 10.1). Following enzyme-catalyzed single-electron oxidation to the corresponding radicals, these traditional monolignols undergo coupling to form *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units, respectively, in lignin macromolecules [16]. It is worth mentioning that commelinid monocotyledonous plants such as maize [17] or *Brachypodium distachyon* [18] may biosynthesize significant portions of their lignins through deamination of tyrosine directly to *p*-coumarate by the action of a bifunctional Phe-and-Tyr ammonia lyase.

The proportions of *p*-coumaryl, coniferyl, and sinapyl alcohols that are incorporated into lignins vary characteristically between gymnospermous softwoods, angiosperm eudicotyledonous hardwoods, and monocotyledonous grasses. Softwood lignins are composed almost exclusively of guaiacyl (G) units interconnected by six distinctive linkages [19]. Interestingly, spruce lignin has been separated (by Gellerstedt and coworkers) into two readily distinguishable fractions that preferentially interact (covalently or non-covalently) with the two pre-eminent cell wall hemicelluloses (Figure 10.2). The lignin chains forming complexes with xylans contain only β -O-4' ether structural linkages between guaiacyl units, while those participating in complexes with glucomannans embody all six linkages in appropriately adjusted proportions [19].



332 10 Biodegradable Lignin-Based Plastics



Figure 10.2 Structures suggested for softwood lignin–carbohydrate complexes isolated by successive fractionation of endoglucanase-treated spruce wood with aqueous 8 M urea, alkaline borate, and/or barium hydroxide. Source: Adapted from Göran Gellerstedt (2007) cited in Chen and Sarkanen [19] / with permission of Elsevier.

On the other hand, hardwood lignins are composed of syringyl (S) and guaiacyl (G) units in similar proportions interconnected primarily through four different linkages (Figure 10.3), among which β -O-4' ethers are the most frequent [20]. In contrast, a representative 20-unit chain segment in a monocotyledonous lignin [16] may be composed of 13 syringyl (S) and 5 guaiacyl (G) residues with a *p*-hydroxyphenyl (H) unit at the phenolic end and a 5-linked ferulate ester (F) at the non-phenolic terminus (Figure 10.4). Macromolecular chain assembly involves formation of four



Figure 10.3 Twenty-unit model section of a hardwood (poplar) lignin chain. Source: Ralph et al. [20] / with permission of Springer Nature.

inter-unit linkages, among which β -O-4' ethers are again predominant. A coumarate ester group is attached to the γ -carbon atom in four of the monomer residues, while an acetate ester occupies the γ -position in two other units (Figure 10.4).

A particularly noticeable aspect of this monocotyledonous lignin chain is the absence of branching. It has been claimed that, as of 2019, no structural evidence for branching in lignins had come to light [16]. Consequently, the schematic representations of softwood and hardwood lignin chains [19, 20] that were previously published (Figures 10.2 and 10.3, respectively) could be thought of in their revised forms [16], but the matter remains unresolved. A high degree of branching and/or cross-linking in lignin macromolecules has been a widely held belief since

334 10 Biodegradable Lignin-Based Plastics



Figure 10.4 Twenty-unit model section of a monocotyledonous lignin chain. Source: Ralph et al. [16] / with permission of Elsevier.

1960 [21]; it will require further analyses to establish unanimous agreement about this crucial question [22]. The answer profoundly affects the perceived likelihood of creating functional thermoplastics with high lignin contents. The inevitable rigidity of highly branched [22] or cross-linked [21] lignin chains would lessen the possibility of overcoming the adverse impact of interstices between neighboring molecular entities in such materials.

Regardless of the case, there is a strong correlation between the configuration of a softwood lignin macromolecule and the adjoining hemicellulose chains (Figure 10.2) in a plant cell wall domain. Moreover, the non-covalent forces between



Fiaure 10.5 (a) Molecular weight distributions of dehydropolymerizates successively formed from coniferyl alcohol in the presence (upper profiles) and absence (lower profiles) of unmethylated macromolecular lignin template (weight-average molecular weight $\overline{M}_{w} = 206\,000, 1.0 \times 10^{-8}$ M initial concentration). Monolignol and H₂O₂ (1:1.05 ratio) were added gradually to aqueous 20% dioxane solution (pH 7.3) containing peroxidase (2.6 unit/l); total concentration of monomer units: 3.08×10^{-5} M (1) after 20 hours, 6.29×10^{-5} M (2) after 50 hours, 8.18×10^{-5} M (3) after 75 hours, 8.34×10^{-5} M (4) after 77.5 hours, and 8.50×10^{-5} M (5) after 80 hours. (b) Molecular weight distributions of dehydropolymerizates successively formed from coniferyl alcohol in the presence (upper profiles) and absence (lower profiles) of methylated macromolecular lignin template (weight-average molecular weight $\overline{M}_{y} = 15400$, 2.7×10^{-8} M initial concentration). Monolignol and H₂O₂ (1:1.05 ratio) were added gradually to aqueous 20% dioxane solution (pH 7.3) containing peroxidase (2.6 unit/l); total concentration of monomer units: 3.1×10^{-5} M (1) after 20 hours, 6.3×10^{-5} M (2) after 50 hours, 7.9×10^{-5} M (3) after 70 hours, 8.2×10^{-5} M (4) after 75 hours, and 8.5×10^{-5} M (5) after 80 hours. Source: Guan et al. [23] / with permission of Elsevier.

cofacially disposed aromatic rings in macromolecular lignin structures are thought to be stronger than those governing GC/CG base pair interactions in DNA double helices [19]. Thus, pre-existing lignin macromolecules in lignifying plant cell walls are also poised to influence the configurations of new lignin chains as they are formed during biosynthesis.

Such an effect can be induced in an open solution by small quantities of macromolecular lignin components (Figure 10.5) during the peroxidase-catalyzed dehydrogenative polymerization of coniferyl alcohol (Figure 10.1) by H_2O_2 [23]. When the intermediate monolignol radical concentration remained low, dramatic increases occurred in the populations of the largest dehydropolymerizate species that were formed (Figure 10.5a). The result was not caused by preferential monolignol radical coupling with any unpaired electron that may have appeared in the pre-existing lignin macromolecules: prior methylation of the aromatic hydroxyl groups in the latter did not suppress this striking outcome (Figure 10.5b).

336 10 Biodegradable Lignin-Based Plastics

Thus, under these conditions, pre-existing lignin macromolecules may act, by non-covalent means, as templates for the chains of lignin substructures that are formed through the dehydrogenative polymerization of coniferyl alcohol. No information came to light about the replicative degeneracy of the process, but the matter is clearly worthy of further investigation.

10.3 Industrial Availability of Lignins

Reliable quantities of lignin derivatives. Traditional kraft pulping of wood chips has dominated production of cellulosic fibers from lignocellulose. Two industrial processes have been devised for purifying the co-product kraft lignins.

Recognition of plant biomass as a potential inventory of renewable starting materials for producing liquid biofuels and biodegradable plastics has prompted development of new approaches to fractionating lignocellulose. For example, compared to dilute aqueous acid alone, 25 minutes of pretreatment in 1:1 (v/v) THF/water with 0.5 wt% sulfuric acid at 150 °C engenders marked improvements in sugar yields resulting from enzyme-catalyzed saccharification of corn stover [24]. Alternatively, dissolution of corn stover, hardwood, or softwood in homogeneous mixtures of GVL and water at elevated temperatures enables fractionation of lignocellulose into cellulose along with sugars from hemicelluloses and lignin in which structures close to the native biopolymer are initially preserved [25]. Thus, mildly acidic 4:1 (v/v) GVL/water at 120 °C can thermocatalytically saccharify maple wood lignocellulose as the carbohydrates and lignins in the biomass dissolve completely within 30 minutes [26].

Interesting developments such as these could form the basis of "second-generation" lignocellulose biorefineries, but their unsubsidized profitability has not yet been demonstrated. Therefore, it may be premature to invest substantially in valorizing lignins formed as co-products of such fractionation procedures, promising although they may be. Rather, it would be more productive to focus on fully optimized "first-generation" processes such as kraft pulping, which has been used since 1890 to convert wood chips into cellulosic fibers for making paper. In 2015, the kraft process was generating about 80% of virgin pulp worldwide [27]. The annual production capacity of co-product kraft lignin was estimated to be 265 000 t in 2018 [28], but an optimistic forecast for the year 2025 predicted an almost 10-fold increase in commercial kraft lignin production [28].

Delignification during kraft pulping takes place in aqueous solution at pHs above 12 in the presence of ~0.5 M (bi)sulfide over one to three hours at a maximum temperature of 160–180 °C [29]. Two commercial processes have been developed for partially purifying the kraft lignin that can be isolated from the so-called "black liquor" into which it dissolves during pulping in the digester. The LignoBoost process (developed by Innventia and licensed to Valmet) uses CO_2 to bring the black liquor from the digester to pH ~10, whereupon the precipitated kraft lignin is washed with dilute aqueous sulfuric acid (pH 2.0–3.5) to remove impurities [30]. On the other hand, the LignoForce System (developed by FPInnovations and NORAM) uses O_2

to detoxify sulfur compounds in the digester black liquor at 80 °C before the kraft lignin is separated from solution by lowering the pH to 9.5 with CO_2 ; the resulting precipitate is then washed with dilute sulfuric acid and water [11b, 31].

The dissolution of wood cell wall lignin during kraft pulping is a complicated process involving macromolecular depolymerization (primarily through β -O-4' alkyl aryl ether cleavage), conversion of native structural features to styryl ethers and stilbenes, demethylation of methoxyl groups, and repolymerization through the formation of new inter-unit linkages involving aromatic ring C-atoms [32, 33]. Detailed analyses of acetone-soluble and acetone-insoluble softwood kraft lignin fractions led to the structural schemes depicted in Figure 10.6 [33]. These kraft lignin components have clearly undergone extensive chemical transformations in relation to the native biopolymer (Figure 10.2).

10.4 Compelling Traits in Physicochemical Behavior of Kraft Lignin Species

Governing structural features. Despite some pronounced chemical changes, kraft lignins preserve vestiges of native lignin structures that restore continuity within subsets of interacting molecular components in solution.

There are underlying traits among the physicochemical properties of kraft lignin components that do not emerge from the structural complexity portrayed in Figure 10.6. One distinctive feature has appeared in semilogarithmic absolute molecular weight calibration curves for the size exclusion chromatographic elution of softwood and hardwood kraft lignins in aqueous 0.10 M NaOH through Sephadex G100: these curves are parallel to the corresponding plot for poly(styrene sulfonate) fractions [34]. Thus, the hydrodynamic behavior of kraft lignin components is consistent with what would be expected for appreciably expanded unbranched random coil chain conformations. In agreement, as far as the ratio of z-average to weight-average molecular weight ($\overline{M}_z/\overline{M}_w$) is concerned, the polydispersity of paucidisperse softwood kraft lignin fractions in aqueous 0.10 M NaOH does not increase with their molecular weight [35].

The justification for choosing kraft lignins as a foundation for developing biodegradable plastics lies in the pronounced tendency of the individual molecular components to associate extensively with one another. The associative/dissociative processes are well defined under a broad range of solution conditions. Under aqueous alkaline conditions at pHs within a fairly narrow range above 11.5, the molecular components and complexes in >100 g/l kraft lignin solutions undergo reversible association. On the other hand, the associated complexes dissociate reversibly in aqueous 0.10 M NaOH solutions containing <1 g/l kraft lignin [36]. The apparent molecular weight distributions of kraft lignin preparations that have been thus modulated are illustrated in Figure 10.7 (after having been desalted). The elution profiles intersect through a common (isosbestic) point, indicating that the members of the set of kinetic rate processes are somehow coupled to the same rate-controlling step.



Figure 10.6 Structures proposed for acetone-insoluble higher molecular weight fragment and one of four acetone-soluble lower molecular weight components in softwood kraft lignin. Source: Crestini et al. [33] / with permission of the Royal Society of Chemistry.

Throughout the overall process, the number-average product of the molecular weights of interacting kraft lignin complexes and components, $\langle m_c m_l \rangle$, remains constant despite the marked change in overall degree of association. A plot of weight-average (\overline{M}_w) vs. reciprocal of number-average ($1/\overline{M}_n$) molecular weight [36] generates a curve with slope $-2\langle m_c m_l \rangle$, which, in this and other limiting cases, is invariant during the course of the associative/dissociative changes that result in kraft lignin preparations altered solely by incubation in aqueous alkaline solution (Figure 10.7). Evidently, associated kraft lignin complexes behave as well-defined entities that can only interact productively with individual kraft lignin components in a selective manner.

The highest degrees of association that can be attained in aqueous alkaline solutions are limited, inter alia, by the negative charge densities on the polyphenolic



kraft lignin complexes. Non-aqueous polar solvents, however, can tolerate a far greater upper limit to the size of soluble complexes that are formed through spontaneous self-assembly of individual kraft lignin components. For example, the formal weight-average molecular weight of an underivatized kraft lignin preparation can surge from approximately 7000 g/mol in aqueous 0.10 M NaOH to around 1.1×10^8 g/mol in DMF (Figure 10.8).

Such effects are quite dramatic; fortunately, the underlying non-covalent interactions are not restricted to hydrogen bonding alone. After acetylation (Ac₂O/pyridine) and methylation (CH₂N₂), the unimodal size exclusion chromatographic elution profiles of the underivatized kraft lignin preparations in DMF are replaced with multimodal distributions of supramacromolecular complexes [37] extending to very high molecular weights (again around 1.0×10^8 g/mol). In each acetylated methylated sample, the relative proportions of species with apparent molecular weight above 2×10^6 g/mol are related to the degree of association of the corresponding underivatized preparation in aqueous alkaline solution (Figure 10.8). These findings



Molecular weight distributions of kraft lignins in aqueous alkali

Polystyrene standard mol. wt.

Figure 10.8 Apparent molecular weight distributions during elution in aqueous 0.10 M NaOH through Sephadex G100 (blue) of kraft lignin samples subjected to Sephadex LH20/aqueous 35% dioxane fractionation after association for (1) 6740 hours, (2) 3910 hours, and (3) 1630 hours at 195 g/l in 1.0 M ionic strength aqueous 0.40 M NaOH, compared with the same samples, following their acetylation and methylation, during elution in DMF through a 10^7 Å pore size poly(styrene-divinylbenzene) column; relationship to apparent molecular weight distributions in DMF (red) of underivatized kraft lignin samples after Sephadex LH20/aqueous 35% dioxane fractionation following association for (1) 300 hours ($M_w = 7900$), (2) 144 hours ($M_w = 7100$), and (3) 0 hours ($M_w = 5900$) at 170 g/l in aqueous 0.40 M NaOH (made up to 1.0 M ionic strength with 0.6 M NaCl). Source: Adapted from Refs. [36, 37].

suggest that the process of association advances through discrete stages. At a particular point in its development, every assembly of associating kraft lignin components will interact preferentially with a matching complex rather than a nascent molecular entity. This would ultimately lead to the formation of continuous material domains devoid of prominent interstices that could initiate crack propagation in our targeted kraft lignin-based plastics, when under mechanical stress.

10.5 Kraft Lignin-Based Plastics

Molecular configuration. Plastics with high kraft lignin contents are composed of associated macromolecular complexes rather than individual kraft lignin components. Nevertheless, blends of kraft lignin with miscible eco-friendly components are fully biodegradable.

The operation of a traditional kraft pulp mill is organized in such a way that the rate-limiting step in the overall process is housed in the recovery boiler (where "black liquor," concentrated from the digester, is burned to maximize chemical and heat recovery). Consequently, an increase in cellulosic pulp production would require removal of some of the kraft lignin in the black-liquor stream. Ordinarily, 15–30% of the kraft lignin can be thus separated from a pulp mill without the need for other modifications [32, 38]. As a result, there are strong incentives to gain value from the surplus kraft lignin in black liquor.

The most obvious way of valorizing co-product lignins from biorefineries of any kind would be to create biodegradable plastics with high lignin contents. Since 1960, however, arguments in favor of this simple goal have been received with profound skepticism: descriptions of lignin macromolecules in terms of highly branched or cross-linked chains [21, 22] have raised concerns that a search for such formulations might not succeed.

Nevertheless, the first polymeric materials with industrial softwood kraft lignin contents of 85 wt% revealed that, as expected from their size exclusion chromatographic behavior [37], the constituent species were associated macromolecular complexes rather than individual kraft lignin components (Figure 10.8). These plastics were produced by solution casting so as to take the form of heterogeneous blends with 12.6% poly(vinyl acetate), 1.6% diethyleneglycol dibenzoate, and 0.8% indene [39]. The formulations were based on a series of kraft lignin preparations in which the degree of association between individual components had been altered by incubation at different concentrations in aqueous alkaline solution (Figure 10.9). Although none of these materials surpassed polyethylene in their mechanical properties, their tensile strengths and Young's moduli depended linearly on the weight-average molecular weight (\overline{M}_w) of the kraft lignin preparation used. Thus, the individuality of the associated complexes was preserved as material continuity in the kraft lignin domains gradually developed during the solution casting process.

Homogeneous kraft lignin blends can be far more effective for developing plastics formulations than biphasic blends. This is exemplified (Figure 10.10) in the tensile behavior of 95–98 wt% industrial softwood kraft lignin-based plastics containing small quantities of anthraquinone, phenanthrenequinone, *p*-nitrophenol, melamine, poly(vinyl alcohol), and poly(vinyl acetate). After solution-casting from dimethyl sulfoxide (DMSO), the tensile strengths of these plastics may approach values 1.5-fold greater than polystyrene as elongations at break become almost 7-fold



Figure 10.9 (a) Tensile behavior of thermoplastics containing biphasic blends of 85 wt% kraft lignin preparations that differ only in the degree of intermolecular association, with 12.6% poly(vinyl acetate), 1.6% diethyleneglycol dibenzoate, and 0.8% indene. (b) Dependence of (•) tensile strength (σ_{max}) and (\odot) Young's modulus (*E*, determined from the initial slope of stress-strain curve) upon weight-average molecular weight of kraft lignin preparations incorporated at 85 wt% levels in thermoplastics with the same blend composition. (c) Apparent molecular weight distributions (during elution in aqueous 0.10 M NaOH through Sephadex G100) of kraft lignin samples after dissociation for (1) 1220 hours, (2) 626 hours, and (3) 93 hours at 0.10 g/l in 0.10 M aqueous NaOH solution, (4) parent preparation, and after association for (5) 92.5 hours, (6) 618 hours, and (7) 1220 hours at 160 g/l in 1.0 M ionic strength aqueous 0.40 NaOH (Sephadex G100/aqueous 0.10 M NaOH elution profiles). Source: Li et al. [39] / with permission of John Wiley & Sons.

larger. The molecular weight distribution of the kraft lignin preparation can have a strong effect on the mechanical behavior of the formulations produced from it. The tensile strength of the plastic containing kraft lignin on its own (Figure 10.10) is reduced threefold when the DMSO solution is filtered through a $4.0-5.5 \,\mu\text{m}$ pore size fritted disc before casting [34].

The biodegradation of lignins is brought about by white-rot fungi through a process that requires some extraneous carbohydrate. The cleavage of native lignin macromolecules under these circumstances is thought, albeit implausibly, to be catalyzed primarily by extracellular fungal peroxidases and/or laccases [40]. Coincidentally, the final step in lignin biosynthesis involves catalysis by comparable (although not identical) plant peroxidases and laccases. Reliance on the same kinds



of enzyme activities, even if modulated, for constructing and deconstructing lignin macromolecules *in vivo* has been called "the lignin enigma" [41]. Nevertheless, the relevant catalytic activities, regardless of their fungal enzyme origins, do extend to softwood kraft lignins in neutral homogeneous culture solutions inoculated, for example, with *Trametes cingulata* mycelium. The primary vegetative white-rot fungal growth is accompanied by marked polymerization of the kraft lignin, as solution conditions become moderately acidic, but then a subsequent metabolic phase witnesses complete degradation of the dissolved high molecular weight kraft lignin species [42]. On the other hand, undissolved softwood kraft lignin may also undergo extensive degradation when immersed in (pH ~4.5) solutions containing *Phanerochaete chrysosporium* mycelial culture [43]. A later section (Section 10.11) more fully describes the biodegradation of all blend components in the kraft lignin-based plastics of Figure 10.10.

10.6 Tuning Strength and Production Cost of Plastics with High Kraft Lignin Contents

Adequacy of miscible blend components in small quantities. Plastics with high kraft lignin contents are primarily composed of associated macromolecular complexes that interact with one another through their peripheral domains. Miscible monomeric

344 10 Biodegradable Lignin-Based Plastics

or polymeric components blend preferentially with these peripheral regions, and thus quite small proportions may have dramatic effects on mechanical behavior.

The mechanical properties of plastics with kraft lignin contents near 95 wt% (Figure 10.10) are exquisitely sensitive to blend composition. Just 5 wt% of a miscible blend component such as melamine can increase the tensile strength by \sim 100–150%. Moreover, even though the non-lignin blend component is present in very low concentration, its configuration strongly affects its impact on mechanical behavior. This does not usually happen in homogeneous polymer blends. For example, the tensile strength of polystyrene increases by only 7% when blended with 5% poly(phenylene oxide) [44] with which it is miscible, while it decreases by 20% or 25% when blended with eco-friendly plasticizers such as dicinnamyl succinate or sebacate at 5% levels [45].

The 95 wt% kraft lignin-based plastics could be regarded as exhibiting antiplasticization characteristics in their behavior (Figure 10.10) because of the simultaneous increase in tensile strength and elongation at break [46]. Conceptually, however, such a description does not recognize the underlying mechanism responsible for the effect. It should be borne in mind that plastics containing very high proportions of kraft lignin [37, 39] and other lignin preparations generally [47] are composed primarily of associated complexes rather than individual components. The integrity of each complex resides in its inner domain where the aromatic rings interact with one another in cofacially offset arrangements [47]. On the other hand, the peripheral domain of this macromolecular entity embodies a higher frequency of edge-on aromatic ring arrangements [47]. The interactions between the neighboring associated complexes take place through interdigitation between the aromatic rings in these peripheral domains as material continuity develops during casting [34]. Non-lignin blend components interact preferentially with the peripheral domains [47]. In the process, they extend the motions of interacting aromatic rings in neighboring associated complexes in such a way as to enable more complete material continuity to be achieved in the biodegradable plastic being cast.

Even though the 95–98 wt% kraft lignin-based plastics illustrated in Figure 10.10 have been produced by solution casting, it is possible to estimate what an upper limit would have been in the year 2020 to the production cost (in US\$) of compounding such biodegradable materials. Thus, ~1.4 kg of industrial kraft lignin (US\$0.83 cost of commercial kraft lignin [48] that yields 0.95 kg purified starting material) is thoroughly washed with water (US\$0.55/kg [30]), air-dried, and blended with 5 wt% miscible blend component (US\$0.05 for 50 g melamine per kg blend [49]). The resulting mixture is then compounded (US\$0.21/kg [50]) to create a plastic blend with an expected production cost of about US\$1.64/kg. Even though this estimate does not take economies of scale into account, it compares favorably with the 2021 polystyrene trading price (~US\$2.10/kg) [51] which was expected to rise.

In the quest to improve formulations for plastics with high kraft lignin contents, it is important to bear in mind that both hydrogen bonding and other non-bonded orbital interactions between aromatic rings contribute to the irrepressible inclination of lignin components to associate extensively with one another. Alkylation can eliminate the impact of hydrogen bonding, but it will not annul the predisposition for intermolecular association [37].



Figure 10.11 Tensile behavior of ethylated and/or methylated kraft lignin-based polymeric materials in blends with poly(ethylene glycol) and aliphatic polyesters (test pieces filed to dog bone shape). Source: Data from Refs. [52, 53].

As might be expected, then, the tensile strength of a methylated softwood kraft lignin-based plastic on its own (20 MPa, 1.2% elongation at break) is appreciably lower (Figure 10.11) than that (Figure 10.10) of its unmethylated counterpart (28 MPa, 4.0% elongation at break). Nevertheless, plastics formed from miscible blends composed of methylated and unmethylated kraft lignin preparations (separately) at high levels both exhibit better mechanical behavior than the unblended materials. Thus, methylated kraft lignin blends with 20 wt% poly(butylene adipate) and 20 wt% poly(ethylene glycol) (PEG) possess (Figure 10.11) tensile strengths of 52 MPa (4.3% elongation at break) and 49 MPa (6.7% elongation at break), respectively. These surpass the tensile strength of polystyrene (46 MPa, 2% elongation at break) and are not very far below the corresponding parameter (Figure 10.10) for the unmethylated kraft lignin blend with 5 wt% poly(vinyl alcohol) (58 MPa, 6.4% elongation at break). Moreover, methylated kraft lignin blends with 30 wt% poly(butylene adipate) and 25 wt% PEG exhibit (Figure 10.11) the tensile strengths of 42 MPa (~9% elongation at break) and 43 MPa (~10% elongation at break), respectively. These exceed the tensile strength of polyethylene (30 MPa, 9% elongation at break) by a substantial margin.

The findings in Figures 10.10 and 10.11 are not sufficiently detailed in scope to identify immediate improvements for plastic formulations with very high kraft lignin contents, but they strongly suggest that a broad range of novel compositions could be profitably examined. Apparently though, blends of hardwood kraft lignin with poly(ethylene oxide) do not follow the same pattern as those involving the softwood kraft lignin (Figure 10.10) and methylated softwood kraft lignin (Figure 10.11). Hardwood kraft lignin on its own and when blended with 5 wt% poly(ethylene oxide) forms brittle plastics with tensile strengths around 24 MPa (0.6% elongation at break), and blends with poly(ethylene oxide) levels of 25–50 wt% suffer from pronounced reductions in that modest initial strength [54].

10.7 Ligninsulfonates (Lignosulfonates)

Sulfite pulping processes, in various versions, are less frequently used; they produce polyanionic lignin derivatives that are harder to incorporate at high levels into functional plastic formulations.

Less than 10% of virgin pulp is now produced by sulfite pulping, which treats wood chips with aqueous sulfurous acid ($pK_a \approx 2$) and bisulfite ($pK_a \approx 7$) under a variety of conditions between pH 1.5 and 4.5 [29]. Acid sulfite pulping is performed at pH ~1.5–2.0 in the presence of calcium counterions at 125–145 °C. Bisulfite pulping is carried out in a pH range of ~3.0–4.5 at 160–180 °C with either sodium, ammonium, (sometimes) potassium, or magnesium counterions depending on the process conditions employed [29].

Lignin macromolecules are sulfonated [55] extensively during sulfite pulping (Figure 10.12), but cleavage and other chemical transformations (such as stilbene formation) occur to a much smaller extent than the analogous changes that occur under kraft pulping conditions (Figure 10.6). For example, absolute molecular weight determinations for an industrial spruce ligninsulfonate (LS) sample revealed a weight-average molecular weight of 64 000 with a very high polydispersity index $(\overline{M}_w/\overline{M}_n)$ of 8.8 [56]. Paucidisperse fractions from this parent preparation were isolated by progressively dissolving the corresponding precipitated barium ligninsulfonate from a cellulose column into ethanol–water in steps facilitated by successive reductions in the proportion of ethanol. Six fractions were isolated spanning a 4.6–400 kg/mol range in molecular weight.

Multi-angle light scattering analyses of the components in these ligninsulfonate fractions during their serial elution through a suitable size exclusion chromatographic column enabled the respective z-average (\overline{M}_z) , weight-average (\overline{M}_w) , and number-average (\overline{M}_n) molecular weights to be reliably determined. The contiguous semilogarithmic column–calibration curve was linear between 2 and 700 kg/mol. The two polydispersity indices, $\overline{M}_z/\overline{M}_w$ and $\overline{M}_w/\overline{M}_n$, for each fraction were, within experimental error, equal to one another; their ratio (0.93 ± 0.07) displayed no systematic trend within the overall molecular weight range. Thus, all six fractions [56] possessed a distinct logarithmic normal distribution [57] of ligninsulfonate components characterized by the same column–calibration curve. These results imply that long-chain branching and cross-linking are absent from ligninsulfonate components. Such a conclusion is reminiscent of a previous finding that $\overline{M}_z/\overline{M}_w$ for a series of paucidisperse softwood kraft lignin fractions in aqueous 0.10 M NaOH remains constant throughout the span of their molecular weights [35].

The value of pursuing functional polymeric materials with a high polyanionic lignin derivative content has been investigated using a ligninsulfonate formed by calcium bisulfite pulping of softwood [58]. This ligninsulfonate preparation possessed an uncommonly low $\overline{M}_{\rm w}$ of 7100 g/mol with polydispersity index $\overline{M}_{\rm w}/\overline{M}_{\rm n} = 3.8$. Phenolic hydroxyl-group methylation was carried out with dimethyl sulfate in aqueous dioxane. As shown in Figure 10.13, both the underivatized and methylated ligninsulfonate exhibited quite modest tensile behavior, reaching ~21 MPa in strength with ~3% elongation at break [58]. Nevertheless, simply as



Figure 10.12 Model of 28 units for softwood ligninsulfonate fragment. Source: Adapted from Lund [55]. (LS denotes ligninsulfonate.)

a result of blending with 15 wt% levels of various miscible aliphatic polyesters, a cluster of stress-strain curves manifested themselves, attaining tensile strengths between 30 and 47 MPa with elongations at break from 4% to 7% in the mechanical testing of an entirely new series of 85 wt% ligninsulfonate-based materials (Figure 10.13). When blended with 15 wt% poly(trimethylene glutarate) (PTMG), on the other hand, the resulting 85 wt% methylated ligninsulfonate-based material exhibited a tensile strength of 46 MPa (equal to that of polystyrene) with ~11% elongation at break (Figure 10.13).



Figure 10.13 Tensile behavior of plastics composed of unmethylated and methylated ligninsulfonates (LS and sMLS) blended with aliphatic polyesters. Source: Data from Sarkanen et al. [58] and from S. Sarkanen & Y.-Y. Wang, unpublished results (2015).

Despite their polyanionic characteristic, immersion of ligninsulfonate- and methylated ligninsulfonate-based test pieces in distilled water for 120 hours under ambient conditions did not engender any component dissolution or reduction in tensile strength. However, the molecular weight distribution of the softwood ligninsulfonate can have a substantial impact on the mechanical properties of plastics formed from it alone, from its simple derivatives, or nearby blends [58, 59].

Ligninsulfonate biodegradability. The white-rot fungus *P. chrysosporium* is quite capable of depolymerizing ligninsulfonate preparations in aqueous solution through a two-phase process where polymerization precedes macromolecular cleavage. However, dissolved SO₂ in industrial calcium bisulfite liquors tends to inhibit the enzyme-catalyzed degradation of polymerized ligninsulfonate [60]. The intervention of ligninsulfonate polymerization before the onset of depolymerization exemplifies the inevitability of "the lignin enigma" [41] that would arise if the activities of peroxidases and/or laccases were actually responsible for white-rot fungal cleavage of lignin macromolecules during lignin biodegradation [40]. Almost identical kinds of enzyme activity engender mono- and oligolignol dehydropolymerization during lignin biosynthesis in plant cell walls; their catalytic effects assuredly contribute to the dehydrogenative polymerization of any phenolic lignin components that may be present in fungal culture solutions.

10.8 Laboratory Ball-Milled Lignins

Native structural characteristics endow underivatized and methylated ball-milled lignin-based plastics with promising mechanical properties in a range of formulations with monomeric and polymeric blend components.





Ball-milled lignin (or milled-wood lignin) is thought to be structurally close to the native biopolymer, except that some homolytic cleavage would have occurred during the first step in its isolation. The procedure is straightforward: according to the currently accepted protocol, ball-milling of wood or other plant material is followed by 24-hour extraction with aqueous 96% dioxane [61]. Plastics solution-cast from softwood ball-milled lignin alone (Figure 10.14) in their tensile strength (34 MPa, 6% elongation at break) surpass polyethylene [34]. Small quantities of non-lignin blend components such as 5 wt% PTMG, 5 wt% 3,3',5,5'-tetrabromobisphenol A, and 2 wt% poly(ethylene oxide-*b*-1,2-butadiene-*b*-ethylene oxide) can result [34] in increasing tensile strengths of 40, 54, and 58 MPa with 7%, 7.5%, and 9% elongations at break, respectively (Figure 10.14). Although the two sets of blend compositions differ, such examples of tensile behavior are comparable (but not identical) to those of plastics with 95–98 wt% proportions of softwood industrial kraft lignin (Figure 10.10). It is conceivable that the underlying skeletal structures of these two dissimilar lignin derivatives (Figures 10.2 and 10.6) may be quite similar.

The tendency of ball-milled lignin components to form, when solution-cast, reasonably strong solid domains (by associating with one another) of course is not governed by hydrogen bonding alone. Methylation of softwood ball-milled lignin can result, through solution-casting, in a material that on its own (Figure 10.15a) surpasses polystyrene in its tensile behavior (~50 MPa strength with 7–8% elongation at break) [47]. Interestingly, the tensile strength of 100% methylated ball-milled lignin-based plastics can be adversely affected during casting by the loss of methylated lignin oligomers (Figure 10.15a). Removal of lower molecular weight lignin components by ultrafiltering the parent ball-milled lignin before methylation brings about analogous effects in plastics formed from blends with poly(ethylene oxide-*b*-1,2-butadiene-*b*-ethylene oxide), as shown in Figure 10.15c [47].





Figure 10.15 Tensile behavior of methylated ball-milled lignin (MBML)-based polymeric materials. (a) 100% MBML-based plastics prepared by solution casting at 140 °C. (b) Blends of 80–90 wt% MBML with bromo-substituted aromatic compounds cast at 140 or 150 °C. (c) Progressive plasticization of parent and higher molecular weight MBML-based materials with triblock poly(ethylene oxide-*b*-1,2-butadiene-*b*-ethylene oxide) (EBE). (d) Plasticization effects of 5–15 wt% of poly(ethylene glycol)s (PEGs) with different molecular weight distributions on MBML-based blends: 100% MBML; (1) 5% PEG, M_n 400 Da; (2) 5% PEG, M_n 400 Da and 5% PEG, M_n 10 kDa; (3) 15% PEG, M_n 4.6 kDa; (4) 5% PEG, M_n 400 Da and 5% PEG, M_n 400 Da; (6) 15% PEG, M_n 2 kDa; (7) 15% PEG, M_n 10 kDa; and (8) 15% poly(ethylene glycol) methyl ether, M_n 5 kDa. Source: From Wang et al. [47].

Sizable electron-withdrawing atomic substituents in miscible non-lignin blend components had been expected to improve the tensile strength and/or ductility of methylated ball-milled lignin-based plastics. Thus, 10 wt% proportions of 3,3',5,5'-tetrabromobisphenol A (a flame retardant) can engender a ~50% increase in tensile strength (Figure 10.15b), but a similar result was not obtained with compounds such as 3',5'-dibromoacetophenone or 4,4'-dibromobenzophenone [47].

The triblock copolymer, poly(ethylene oxide-*b*-1,2-butadiene-*b*-ethylene oxide), brought about a tensile strength of almost 70 MPa with 7% elongation at break at 15 wt% levels when blended in a miscible way with solution-cast methylated ball-milled lignin (Figure 10.15c), but larger (20, 25, and 30 wt%) proportions of the block copolymer resulted in progressive reductions in tensile strength with accompanying increases in elongation at break [47]. Curiously, blends of a higher molecular weight ($\overline{M}_w 4800$, $\overline{M}_w/\overline{M}_n$ 1.4) polydisperse methylated ball-milled lignin fraction with 15 and 20 wt% poly(ethylene oxide-*b*-1,2-butadiene-*b*-ethylene oxide) manifested considerably worse tensile behavior than the corresponding plastics based on the parent lignin preparation (Figure 10.15c). Low molecular weight methylated ball-milled lignin components evidently possess significant plasticizing capacity in these miscible blends [47].

Small proportions (5–15 wt%) of PEG in miscible blends with the parent methylated ball-milled lignin have unevenly dramatic effects. The tensile behavior is affected by both the quantity and the molecular weight distribution of PEG. For example, 5 wt% $\overline{M}_n = 400$ PEG creates a material exhibiting a tensile strength of 65 MPa with ~9% elongation at break (Figure 10.15d). Otherwise, 5 wt% each of $\overline{M}_n = 400$ PEG and $\overline{M}_n = 4600$ PEG together result in a blend with 53 MPa tensile strength and ~13% elongation at break. However, a methylated ball-milled lignin-based blend containing 15 wt% $\overline{M}_n = 5000$ PEG methyl ether possesses a tensile strength of only 37 MPa with an elongation at break below 9% [47].

10.9 Blend Configuration in Ball-Milled Lignin-Based Plastics Exemplifies the General Case

Thematic Preface. X-ray powder diffraction patterns reveal how the **peripheral and inner domains of associated complexes** in methylated ball-milled lignin-based plastics vary with the proportion of blended PEG. Non-covalent rearrangements of aromatic rings at elevated temperatures in ball-milled lignin-based plastics affect glass transition temperature.

Methylated ball-milled lignin-based plastics composed of blends with 0–15 wt% PEG exhibit X-ray powder diffraction patterns consisting of two overlapping Lorentzian peaks [47] with maxima at equivalent Bragg spacings (d) of 4.0–4.1 and 5.3–5.6 Å (Figure 10.16b–d). For semicrystalline polymers, chain segment packing in amorphous domains may follow a pattern that is characteristic of the corresponding crystal structure [62]. The approximately parallel aromatic rings in the crystal structures of dimeric [63, 64] and trimeric [65] lignin model compounds are separated by an average d-spacing of ~4.0 Å, while edge-on aromatic rings in the crystal structure of a (non-phenolic) β -O-4' lignin-model dimer present d-spacings of ~5.3 Å [66]. These values are quite close to the two Lorentzian component peak maxima (4.1 and 5.5 Å) in the X-ray powder diffraction patterns of the methylated ball-milled lignin-based plastics (Figure 10.16b–d). Accordingly, the two Lorentzian



Figure 10.16 X-ray powder diffraction patterns of MBML-based materials. X-ray powder diffraction patterns of (a) uncast 100% MBML, (b) cast 100% MBML, and (c) MBML blend with 15 wt% poly(ethylene glycol) (PEG). The X-ray diffraction patterns of the amorphous polymer blends were analyzed by using two Lorentzian functions $I(x) = I(0)/(1 + x^2/hwhm^2)$, $x = 2\theta - 2\theta_k$, where I(x) is the scattered intensity at *x* from the Bragg angle $2\theta_k$ for the peak, 2θ is the scattering angle, and hwhm is the half-width at the half-maximum of the peak. (d) Relative areas of lower- θ Lorentzian component peaks in X-ray powder diffraction patterns of methylated ball-milled lignin-based material blends with increasing PEG content (each point depicting the average area and equivalent d-spacing for blends with the same amount of PEG). Source: From Wang et al. [47].

peaks have been assigned [47], in part, to random distributions [67] of inner cofacially offset arrangements of aromatic rings within the associated lignin complexes (centered at $2\theta \approx 21.8^{\circ}$, $d \approx 4.1$ Å) and corresponding edge-on orientations of aromatic rings in the peripheral components of these macromolecular entities (centered at $2\theta \approx 16.2^{\circ}$, $d \approx 5.5$ Å).

The maximum of the Lorentzian peak circumscribing (in part) the edge-on aromatic rings shifts from $d \approx 6.1$ Å to a smaller d-spacing (~5.6 Å) when the methylated ball-milled lignin powder is cast to form a plastic material (Figure 10.16a,b). The shift is accompanied by a significant increase in edge-on peak area because material continuity is achieved during casting through interdigitation between aromatic rings in the peripheral domains of adjacent associated lignin complexes [34]. When the methylated ball-milled lignin is blended with progressively greater proportions (5, 10, and 15 wt%) of PEG, the edge-on Lorentzian peak area undergoes further increases as the d-spacing at the peak maximum shifts to appreciably smaller values (Figure 10.16c). Thus, the PEG interacts preferentially with the aromatic rings in the peripheral domains of the macromolecular complexes. Indeed, there is less of a change in the d-spacing of the maximum in the Lorentzian peak encompassing the inner cofacially offset aromatic rings in these associated complexes.

Plastics composed of unmethylated ball-milled lignin are also characterized by X-ray powder diffraction patterns that similarly consist of two overlapping Lorentzian peaks [58], as are those composed of methylated ligninsulfonates [59]. In marked contrast, however, materials composed of unmethylated ligninsulfonate components alone present X-ray powder diffraction patterns consisting of only one prominent Lorentzian peak ostensibly representing cofacially offset aromatic rings [59]. The evident absence of a distinct peripheral domain may afford some insight into the reasons for the lower tensile strengths encountered with some of these unblended lignin-based materials (Figure 10.13).

The integrity of the associated complexes, of which plastics with high lignin contents are primarily composed, resides in their inner domains through cofacially offset arrangements of aromatic rings. The development of mechanical strength during casting occurs by establishing continuity between the peripheral domains of adjoining associated complexes. This is illustrated in reference to the contours on a methylated ball-milled lignin-based plastic surface, where the interacting associated complexes are clearly visible (Figure 10.17). Concomitant changes in the distributions of aromatic ring arrangements are reflected in the extent to which new contributions to the two Lorentzian peaks alter the overall X-ray powder diffraction



Figure 10.17 AFM height image of the associated lignin complexes on 100 wt% methylated ball-milled lignin-based plastic surface. Material continuity between adjoining complexes is established by inter-digitation between aromatic rings in interacting peripheral domains. Source: Chen et al. [34] / MDPI / CC BY 4.0.

354 10 Biodegradable Lignin-Based Plastics

pattern. The resulting populations of aromatic ring arrangements are determined by how readily cofacially offset orientations can be organized by inter-digitation between "edge-on" and "on-edge" aromatic rings on the interacting peripheral domain surfaces of neighboring lignin complexes (Figure 10.17). Thus, the manifest characteristic of the peripheral domains may be augmented or diminished within the bounds of the lignin-based plastic that is formed through casting [34].

Differential scanning calorimetric (DSC) thermograms of ball-milled softwood lignin, its methylated derivative, and higher molecular weight fractions thereof provide critically important insight into the physicochemical behavior of lignin preparations as they are cast into plastic test pieces. Thermograms of the uncast solvent-free parent methylated ball-milled lignin are systematically displaced toward higher temperatures during successive thermal cycles (Figure 10.18a). In the process, the apparent glass transition temperature (T_g) rises in gradually decreasing increments. A comparable change occurs in the glass transition temperature of an uncast higher molecular weight methylated ball-milled lignin fraction as it similarly responds to successive thermal cycles, but the temperature range over which T_g increases is about 40 °C above that found for the parent methylated preparation (Figure 10.18b). On the other hand, thermal cycling of the unmethylated parent ball-milled lignin resulted in a greater change in $T_{\rm g}$ over a temperature range, only part of which overlapped with that of the higher molecular weight methylated fraction (Figure 10.18c). Accordingly, the three related but contrasting lignin preparations exhibited comparable changes in T_{g} over different ranges of temperature [47].

A persistent rise in T_g resulting from thermal cycling of a lignin preparation past the glass transition region may occur for more than one reason. A reduction in the enthalpy change during traversal of the transition could be caused by increasing covalent cross-link density [67, 68]. Alternatively, the greater stability conferred by more favorable arrangements of non-covalently interacting lignin components would result in a much smaller reduction in the enthalpy change accompanying the glass transition to the rubbery plateau. This enthalpy change was calculated from the area under the thermogram between the glass transition onset and end with respect to the tangent extending from the heat flow-temperature curve segment approaching the T_g region from the lower temperature direction [47].

The enthalpy change characterizing the traversal across the T_g transition region in the 10 °C/min thermograms (Figure 10.18d) shows little dependence on the extent to which the T_g rises, whether for the parent ball-milled lignin (Figure 10.18c), or for its methylated derivative (Figure 10.18a), or for the higher molecular weight methylated fraction (Figure 10.18b). These observations indicate that covalent cross-linking is not occurring to a significant extent during DSC thermal cycling. Presumably, the same conclusion can be drawn about the configurations of the macromolecular species in corresponding plastics produced by solution casting from DMSO. Thus, the rise in T_g during thermal cycling may be ascribed to the increasing occurrence of more stable aromatic ring arrangements between interacting lignin components that are facilitated by the heightened thermal motions at temperatures above the glass transition.



Figure 10.18 DSC thermograms characterizing T_g variations of methylated and unmethylated ball-milled lignin-based polymeric materials. Successive thermal cycles of (a) uncast methylated parent ball-milled lignin (MBML), (b) uncast higher molecular weight M_w 4800 MBML, and (c) uncast unmethylated parent ball-milled lignin (BML). (d) Enthalpy changes (beyond requirement for heat capacity $[C_p]$ increase) accompanying passage through T_g region in 10 °C/min thermograms that reflect DSC thermal cycling of uncast methylated parent ball-milled lignin (MBML), uncast higher molecular weight MBML, and uncast unmethylated parent ball-milled lignin (BML). Source: Wang et al. [47].

10.10 Lignin–Lignin Blends

Extrinsic lignin preparations can impart functionality to incipient ligninbased plastics composed of interacting associated complexes with peripheral domains *that, on their own, are insufficient for thorough interpenetration.*

It is important to bear in mind that the apparent T_g values of plastics with very high lignin contents are determined largely by thermal motions in the peripheral domains of the associated complexes of which these materials are made. For example, for a representative plastic composed solely of a softwood (Douglas fir) ligninsulfonate $(\overline{M}_w = 9700, \overline{M}_w/\overline{M}_n = 5.0)$, the X-ray powder diffraction pattern consisted of just a single Lorentzian peak reflecting the cofacially offset





Figure 10.19 Enhancement of tensile behavior in lignin–lignin blends: ball-milled softwood lignin (BML) and ball-milled corn stover lignin (BMCSL); industrial softwood kraft lignin (KL) and maple γ -valerolactone (GVL) lignin. Source: Chen et al. [34] / MDPI / CC BY 4.0.

aromatic ring arrangements in the inner domains of the constituent associated complexes [59], while the corresponding DSC thermograms manifested no discernible $T_{\rm g}$. Thus, it would be expected that small proportions of extrinsic lignin preparations could improve the performance of lignin-based polymeric materials with inadequate mechanical properties. It is actually possible to achieve such an outcome with lignin–lignin blends.

Potentially restorative lignin-lignin blends [34] have been found for lignin preparations as diverse as industrial softwood kraft lignin and laboratory ball-milled softwood lignin (Figure 10.19). In regard to creating the kraft lignin-based plastics in these studies, a DMSO solution of the industrial sample was filtered through a 4.0–5.5 μ M pore size fritted disc before casting. This intervening step led to a plastic (Figure 10.19) with an approximately threefold lower tensile strength (9 MPa) than obtained without filtration (cf. Figure 10.10). However, the plastic formed from a blend of the kraft lignin with just 10 wt% maple GVL lignin [26] exhibited a tensile strength (35 MPa) very similar to that of the GVL lignin on its own (Figure 10.19). A comparable effect has been observed with a ball-milled softwood lignin (Figure 10.14) that had a tensile strength of 34 MPa on its own. The plastic produced from a blend of this ball-milled lignin with just 10 wt% ball-milled corn stover lignin possessed a tensile strength of 52 MPa with 9% elongation at break, well beyond the corresponding parameters for polystyrene (Figure 10.19). Indeed, the stress-strain curve exhibited very little sign of plastic deformation [34]. Thus, lignin–lignin blends with small (as yet unexplored) quantities of non-lignin components may uncover new pathways to enhanced performance for lignin-based plastic formulations.

10.11 Biodegradation of Kraft Lignin-Based Plastics

Among the plastics with very high lignin contents described in this chapter, those based on industrial softwood kraft lignins are likely to be commercialized first. The pulp and paper industry has begun to deploy processes [30, 31] through which kraft lignins from pulp mills can be partially purified in routine ways. Moreover, the production cost of functional >90 wt% kraft lignin-based plastics (Figure 10.10) should not be prohibitive (vide supra).

As far as the overall life cycle assessment of kraft lignin-based plastics is concerned, controlled biodegradability will be a significant advantage. White-rot fungi are the pre-eminent microorganisms responsible for macromolecular lignin cleavage *in vivo* [40]; their biodegradative activity can be controlled by the requirement for some extraneous carbohydrate. However, a complete understanding of the relevant extracellular white-rot fungal enzymology has been hampered by "the lignin enigma" [41], a dilemma that seeks to address a potential conflict in assigning enzymes with comparable mechanistic capabilities (peroxidases and laccases) to both lignin biosynthesis and lignin biodegradation.

The extracellular white-rot fungal enzymes [40] generally assumed to be responsible for lignin depolymerization – laccase, manganese-dependent peroxidase, and lignin peroxidase – can all function as single-electron oxidants. Consequently, from phenolic or non-phenolic units in lignin macromolecules, all three can generate, directly or indirectly, phenoxy radicals that will undergo bimolecular coupling unless pre-empted from doing so by a competing transformation. To investigate the situation in regard to kraft lignin biodegradation, *T. cingulata* was selected because it does not express lignin peroxidase activity [42]; indeed, when Mn^{II} is absent from the culture solution, this white-rot fungus does not exhibit manganese-dependent peroxidase activity either.

In homogeneous culture solution, the kraft lignin substrate experienced conspicuous polymerization [42] during the vegetative growth of *T. cingulata* as the pH fell from 7.0 to ~4.0 (Figure 10.20a). Moreover, polymerization persisted (Figure 10.21a) after the removal of *T. cingulata* cells from the culture solution, in which laccase activity clearly remained [69]. Following a brief delay, the (still soluble) polymerized kraft lignin in the (original) *T. cingulata* culture solution underwent marked depolymerization [42] through a process that engendered complete preferential degradation of the high molecular weight species (Figure 10.20b). Upon adding FAD (flavin adenine dinucleotide) to the cell-free culture solution isolated during this secondary metabolic phase, the previously polymerized kraft lignin substrate was still degraded quite decisively (Figure 10.21b), *providing* that the solution had been treated with pepstatin A and phenylmethanesulfonyl fluoride [69].

These findings strongly suggested that the initial polymerization of the kraft lignin and its subsequent degradation were controlled by quite different enzymes. The most obvious candidates in white-rot fungal secretomes for the biochemical agents that could act as lignin depolymerases are flavin-dependent monooxygenases [70]. A fitting example would be salicylate hydroxylase, which exhibits broad substrate



Figure 10.20 (a) Initial polymerization of softwood kraft lignin in *Trametes cingulata* liquid culture. Molecular weight distributions for species in extracellular solution (1) 24 hours, (2) 96 hours, (3) 154 hours, (4) 178 hours, (5) 202 hours, (6) 226 hours, (7) 274 hours, and (8) 322 hours after inoculation. (b) Subsequent degradation of polymerized kraft lignin in *T. cingulata* liquid culture. Molecular weight distributions for species in extracellular solution (1) 5 hours, (2) 149 hours, (3) 329 hours, (4) 353 hours, and (5) 509 hours beyond 39 days after inoculation (Sephadex G100/aqueous 0.10 M NaOH elution profiles). Source: Nutsubidze et al. [42] / with permission of Elsevier.

versatility [71] through a mechanism that can bring about lignin depolymerization without (re)polymerization.

In homogeneous aqueous solution at a pH below neutrality where a native polymeric (milled-wood) lignin preparation remains soluble, salicylate hydroxylase reduces the radius of gyration of the substrate rapidly [70] while the molecular weight increases more slowly due to non-productive enzyme-mediated association between the cleaved components. However, certain proteins (xylanase, for example) acting in an auxiliary capacity are capable of competing effectively with the interactions between the degraded lignin components and salicylate hydroxylase. Typically, the flavin-dependent monooxygenase requires NADH for its activity toward its substrate [71], but the native lignin itself can furnish the necessary reductive capacity when the natural cofactor is absent [70]. These considerations are important for the productive deployment of lignin depolymerases in future biorefineries.

As far as the non-lignin blend components in the (unalkylated) industrial kraft lignin-based plastics (Figure 10.10) are concerned, none will accumulate in the environment. Several soil bacteria and white-rot fungi are capable of degrading anthraquinone [72] and phenanthrenequinone [73, 74], and *p*-nitrophenol biodegradation may be carried out by a number of bacterial genera including *Pseudomonas* spp. [75]. Moreover, melamine is degraded by various soil bacteria

Figure 10.21 Polymerization and subsequent depolymerization of kraft lignin substrates by (unconcentrated) cell-free *Trametes cingulata* culture solutions: molecular weight distributions for species in extracellular solutions (a) alone (1) 5 hours, (2) 215 hours, (3) 385 hours, (4) 550 hours, and (5) 1220 hours beyond isolation nine days after inoculation and with (b) 1.6×10^{-4} M FAD (1) 25 hours, (2) 95 hours, and (3) 240 hours beyond isolation 22 days (530 hours) after inoculation. Molecular weight distributions are depicted in terms of Sephadex G100/aqueous 0.10 M NaOH elution profiles. Source: Adapted from Mlynár et al. [69].

such as *Arthrobacter* spp. [76], *Nocardioides* sp. [77], and *Rhodococcus* sp. [78]. In regard to bacterial strains that can degrade poly(vinyl alcohol), many species are found in the genera *Pseudomonas*, *Sphingomonas*, *Alcaligenes*, and *Bacillus* [79]. On the other hand, poly(vinyl acetate) is not itself water soluble, but it can swell when exposed to water; further abiotic hydrolysis of the acetate groups may facilitate entry into an oxidative pathway that leads to chain cleavage [79].

10.12 Alternative Formulations for Polymeric Materials Containing More than 50 wt% Lignin

In shedding light on the circumstances under which the foregoing biodegradable lignin-based plastics were developed, other approaches describing how polymeric materials with >50 wt% lignin contents have been formulated recently (after the year 2010) are germane. Whether or not these alternative polymeric materials would be biodegradable, they should be functional. A reasonable demarcation line for their tensile strengths should not lie far below 30 MPa, the value characteristic of polyethylene.

A series of polyurethanes formed from reactions of three underivatized kraft lignin (KL) fractions with 4,4'-methylenebis(phenyl isocyanate) (4,4'-MDI) in the

Figure 10.22 Tensile behavior of polyurethanes produced by the reactions of underivatized softwood kraft lignin fractions and MDI with or without 4.0 kg/mol PEG or 4.0 kg/mol PTMG as secondary polyols. Source: Wang et al. [80] / with permission of American Chemical Society.

absence or presence of ~13% PEG or PTMG were compared according to their tensile behavior [80]. The strengths of the polyurethanes produced by the reactions of MDI with 60 wt% 14.5 kg/mol KL alone (30 MPa) and 57 wt% 3.8 kg/mol KL alone (25 MPa) were within 20% of one another despite an approximately fourfold difference in KL molecular weight (Figure 10.22). This similarity was ascribed to the survival, in these two-component polyurethanes, of associated kraft lignin complexes that would interact differently with the PEG and PTMG used in corresponding three-part formulations. Thus, H-bonding of PEG at ~13% levels with the KL fractions improved polyurethane tensile strength approximately 1.5-fold, while less effective interactions involving ~13% PTMG resulted in a roughly 1.5-fold reduction in tensile strength (Figure 10.22). The polyurethane produced from 52 wt% of a polydisperse 53.6 kg/mol KL fraction, MDI, and 13 wt% PEG exhibited a tensile strength of 49 MPa, appreciably above that of polystyrene (Figure 10.22). However, the corresponding polyurethane formed in the absence of PEG did not furnish a point of comparison because it was not homogeneous [80].

On the other hand, epoxidized ethyl-acetate-soluble low molecular weight KL fractions, when cross-linked with a poly(propylene oxide) diamine ("Jeffamine D400"), have generated thermoset materials containing 66 wt% eucalyptus and spruce KL that exhibit tensile strengths between 56 and 66 MPa, respectively, with elongations at break of 10.5% and 8% [81]. These mechanical properties follow fairly closely the tensile behavior of 95 wt% unfractionated Southern pine KL-based plastic blends containing 5 wt% melamine or 2 wt% anthraquinone together with 3 wt% phenanthrenequinone (Figure 10.10). The 95 wt% unfractionated KL-based blends reach tensile strengths of 64 and 69 MPa, respectively, with 10% and 13.5% elongations at break (Figure 10.10). These blends contain greater proportions of the original kraft lignin and are cheaper to produce. Nevertheless, the similarities

between the mechanical properties of the 95 wt% unfractionated KL-based blends (Figure 10.10) and the 66 wt% fractionated KL-based epoxy thermoset resins [81] have established reasonable expectations about what the tensile strengths should be of materials in which KL plays the more active role in determining the mechanical behavior.

Only in rare cases is an increasing proportion of polyanionic ligninsulfonate (LS) in a polymer blend accompanied by improvement in mechanical behavior. The more common outcome is exemplified by the results of mixing 10-70 vol% quantities of a ~1.9 kg/mol LS at elevated temperatures (180-220 °C) to create blends with polypropylene, polystyrene, polycarbonate, poly(methyl methacrylate), poly(lactic acid), and an ionomer composed of partially neutralized poly(ethylene-*co*-methacrylic acid) [82]. The LS was an industrial product with calcium counterions containing inorganic salts and sugars. Materials with 50 vol% LS spanned a range of tensile strengths between 10 and 35 MPa that, except for those of the ionomer-containing blends, fell on a downward slope as LS proportions were increasing.

Although all the blends were heterogeneous, none exhibited a $T_{\rm g}$ ascribable to the ligninsulfonate [82]. Moreover, none of these heterogeneous blends embodied LS contents that approached the 85 wt% levels in the homogeneous materials of Figure 10.13. Their tensile strengths would have fallen substantially below those of the homogeneous 85 wt% LS-based blends, had their formulations been able to preserve functionality with equivalent compositions. Actually, immersing 50–100 µm slices of the 10–70 vol% ~1.9 kg/mol LS-containing blends in water resulted in complete LS dissolution within 24 hours at ambient temperatures [82]. In contrast, immersion of the 85% 7.1 kg/mol LS-based test pieces (Figure 10.13) for 120 hours in water brought about no component dissolution nor reduction in tensile strength. The results with the heterogeneous LS blends [82] would have improved, had the industrial LS preparation been pre-purified.

A different approach to formulating polymeric materials with very high LS contents emerged from the laccase-catalyzed polymerization of a sulfonated lignin derivative produced in a magnesium bisulfite pulp mill [83]. Oxidative polymerization of the industrial LS hereby resulted in a ~ 15-fold increase in apparent molecular weight (from an initial value of 40 kg/mol) as brittle water-insoluble products were formed. Blending with 2.5–10 wt% levels of components such as sorbitol, glycerol, and xylitol or 0.6–20 kg/mol PEGs engendered striking improvements in tensile behavior (Figure 10.23).

The most promising formulations were those with 5 and 10 wt% contents of 0.6 and 1.0 kg/mol PEG [83]; the tensile strengths of these blends attained values as high as 74 MPa with elongations at break reaching 72% (Figure 10.23). Such results indicate that the skeletal structure in the polymerized LS chains allows preservation of material continuity as substantial material deformation takes place. It is unlikely that covalent cross-linking plays a central role in supporting the tensile behavior of the polymerized LS blends. Nevertheless, these findings are very encouraging, although a 20% average weight loss in the 90–97.5 wt% LS-based plastics occurred as a result of immersion in water. Thus, fundamental changes must be made if formulations like these [83] are going to produce useful materials.

Figure 10.23 Tensile strengths (σ_{max}) and elongations at break ($\Delta \epsilon \%$) of partially water-soluble laccase-polymerized ligninsulfonate-based blends with 2.5–10 wt% sorbitol, glycerol, xylitol, and poly(ethylene glycol)s (PEGs). Source: Bartolome et al. [83] / with permission of Elsevier.

10.13 Concluding Remarks

The focus of this chapter has been confined to lignin-based plastics that are fully biodegradable. The limitation implies that the relevant thermoplastics or thermosets should embody lignin contents that are already above 50 wt% before blending or derivatization. Moreover, claims about overall biodegradability of these materials should be supported by reports about the susceptibility of all constituent components (whether covalently linked or not) to transformation by microorganisms under suitable conditions. Thus, numerous lignin-containing blends, composites, and copolymers that do not fit these criteria have been reviewed elsewhere [84], although "lessons from the past" [85] are unlikely to be productive because of entrenched views about macromolecular lignin cross-linking that were ultimately doubtful [16].

Blend alterations and transformations for compression and injection molding the industrial 95–98 wt% kraft lignin-based formulations (Figure 10.10) will enable materials to be manufactured that range from computer consoles and interior automobile components through doors and frames to manifold enclosures for which the dark color of these plastics would not be an issue. Later, identification and nullification of the dominant chromophores [86] will lead to many more applications for these renewable biodegradable plastics from lignins in plant materials and trees.

Acknowledgments

Work carried out at the University of Minnesota was supported by Agriculture and Food Research Initiative Grant no. 2011-67009-20062 from the U.S. Department of Agriculture (USDA) National Institute of Food and Agriculture (NIFA), a Subaward (115808 G002979) from the "Northwest Advanced Renewables Alliance" led by Washington State University and supported by USDA Agriculture and Food Research Initiative Competitive Grant no. 2011-68005-30416, a subcontract (XFT-8-88522-01) from the U.S. Department of Energy BioEnergy Science Center, and McIntire–Stennis Funds from USDA NIFA project MIN-12-085. The authors gratefully acknowledge receipt of the maple GVL lignin provided by A.H. Motagamwala and G.W. Huber at the University of Wisconsin, and the corn stover ball-milled lignin provided by R. Katahira and D.K. Johnson at the National Renewable Energy Laboratory.

References

- **1** Rosillo-Calle, F. and Woods, J. (2015). Overview of bioenergy. In: *The Biomass Assessment Handbook*, 2e (ed. F. Rosillo-Calle, P. de Groot, S.L. Hemstock and J. Woods), 7–33. New York: Routledge.
- **2** Hall, D.O. and Rao, K.K. (1999). *Photosynthesis*, 6e. New York: Cambridge University Press, 214 pp.
- **3** Biofuels Research Advisory Council (2006). Biofuels in the European Union: A Vision for 2030 and Beyond. EUR 22066. 39 pp.
- **4** U.S. Department of Energy (2016). 2016 Billion-Ton Report: Advancing Domestic Resources for a Thriving Bioeconomy, Volume 1 (BT16): Economic Availability of Feedstocks. Langholtz, M.H., Stokes, B.J. and Eaton, L.M. (Leads). Oak Ridge National Laboratory, Oak Ridge, TN; 10.2172/1271651. http://energy.gov/eere/bioenergy/2016-billion-ton-report (accessed 17 December 2021).
- **5** Klemm, D., Heublein, B., Fink, H.-P., and Bohn, A. (2005). Cellulose: fascinating biopolymer and sustainable raw material. *Angewandte Chemie, International Edition* 44: 3358–3393.
- **6** Sandermann, H. Jr., Scheel, D., and Van der Trenck, T. (1983). Metabolism of environmental chemicals by plants copolymerization into lignin. *Journal of Applied Polymer Science: Applied Polymer Symposium* 37: 407–420.
- **7** Himmel, M.E., Ding, S.-Y., Johnson, D.K. et al. (2007). Biomass recalcitrance: engineering plants and enzymes for biofuels production. *Science* 315: 804–807.
- 8 Davis, R., Tao, L., Tan, E.C.D. et al. (2013). Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbons. NREL/TP-5100-60223, National Renewable Energy Laboratory, Golden, CO. https://www.nrel.gov/docs/fy14osti/60223.pdf
- **9** Moriarty, K., Milbrandt, A., Lewis, J., and Schwab, A. (2020). 2017 Bioenergy Industry Status Report. NREL/TP-5400-75776, National Renewable Energy Laboratory, Golden, CO. https://www.nrel.gov/docs/fy20osti/75776.pdf, p. 17
- 10 O'Dea, R.M., Willie, J.A., and Epps, T.H. (2020). 100th Anniversary of macromolecular science viewpoint: polymers from lignocellulosic biomass. Current challenges and future opportunities. ACS Macro Letters 9: 476–493.
- **11** (a) Maki, K., Paleologou, M., Zhang, Y. et al. (2017). LignoForce kraft lignin extraction: process scale-up and product development. In: *Kraft Lignin Innovation Forum*. Iron Mountain, MI: Michigan Forest Biomaterials Institute,

visual 11. (b) Maki, K., Paleologou, M., Zhang, Y. et al. (2017). LignoForce kraft lignin extraction: process scale-up and product development. In: *Kraft Lignin Innovation Forum*. Iron Mountain, MI: Michigan Forest Biomaterials Institute, visual 14.

- **12** Galkin, M.V., Francesco, D.D., Edlund, U., and Samec, J.S.M. (2017). Sustainable sources need reliable standards. *Faraday Discussions* 202: 281–301.
- 13 Brunow, G. and Lundquist, K. (2010). Functional groups and bonding patterns in lignin (including the lignin-carbohydrate complexes). In: *Lignin and Lignans – Advances in Chemistry* (ed. C. Heitner, D. Dimmel and J.A. Schmidt), 267–299. Boca Raton, FL: CRC Press.
- 14 Kang, X., Kirui, A., Dickwella-Widanage, M.C. et al. (2019). Lignin-polysaccharide interactions in plant secondary cell walls revealed by solid-state NMR. *Nature Communications* 10: 347. https://doi.org/10.1038/s41467-018-08252-0.
- **15** Tohge, T., Watanabe, M., Hoefgen, R., and Fernie, A.R. (2013) Shikimate and phenylalanine biosynthesis in the green lineage. *Frontiers in Plant Science*, 4, 62. https://doi.org/10.3389/fpls.2013.00062.
- **16** Ralph, J., Lapierre, C., and Boerjan, W. (2019). Lignin structure and its engineering. *Current Opinion in Biotechnology* 56: 240–249.
- **17** Rosler, J., Krekel, F., Amrhein, N., and Schmid, J. (1997). Maize phenylalanine ammonia-lyase has tyrosine ammonia-lyase activity. *Plant Physiology* 113: 175–179.
- 18 Barros, J., Serrani-Yarce, J.C., Chen, F. et al. (2016). Role of bifunctional ammonia-lyase in grass cell wall biosynthesis. *Nature Plants* 2: 16050. https:// doi.org/10.1038/nplants.2016.50.
- **19** Chen, Y.-r. and Sarkanen, S. (2010). Macromolecular replication during lignin biosynthesis. *Phytochemistry* 71: 453–462.
- **20** Ralph, J., Lundquist, K., Brunow, G. et al. (2004). Lignins: natural polymers from oxidative coupling of 4-hydroxyphenylpropanoids. *Phytochemistry Reviews* 3: 29–60.
- **21** Gupta, P.R. and Goring, D.A.I. (1960). Physicochemical studies of alkali lignins. III. Size and shape of the macromolecule. *Canadian Journal of Chemistry* 38: 270–279.
- **22** Balakshin, M., Capanema, E.A., Zhu, X. et al. (2020). Spruce milled wood lignin: linear, branched or cross-linked? *Green Chemistry* 22: 3985–4001.
- 23 Guan, S.-Y., Mlynár, J., and Sarkanen, S. (1997). Dehydrogenative polymerization of coniferyl alcohol on macromolecular lignin templates. *Phytochemistry* 45: 911–918.
- **24** Nguyen, T.Y., Cai, C.M., Kumar, R., and Wyman, C.E. (2015). Co-solvent pretreatment reduces costly enzyme requirements for high sugar and ethanol yields from lignocellulosic biomass. *ChemSusChem* 8: 1716–1725.
- **25** Luterbacher, J.S., Rand, J.M., Alonso, D.M. et al. (2014). Nonenzymatic sugar production from biomass using biomass-derived γ-valerolactone. *Science* 343: 277–280.

- **26** McClelland, D.J., Galebach, P.H., Motagamwala, A.H. et al. (2019). Supercritical methanol depolymerization and hydrodeoxygenation of lignin and biomass over reduced copper porous metal oxides. *Green Chemistry* 21: 2988–3005.
- 27 Suhr, M., Klein, G., Kourti, I. et al. (2015). Best Available Techniques (BAT) Reference Document for the Production of Pulp, Paper and Board, Industrial Emissions Directive. 2010/75/EU, Integrated Pollution Prevention and Control. European IPPC Bureau, Joint Research Centre, Seville, Spain. https://doi.org/10 .2791/370629
- **28** Dessbesell, L., Paleologou, M., Leitch, M. et al. (2020). Global lignin supply overview and kraft lignin potential as an alternative for petroleum-based polymers. *Renewable and Sustainable Energy Reviews* 123: 109768.
- **29** Bajpai, P. (2018). *Biermann's Handbook of Pulp and Paper*, Raw Material and Pulp Making, 3e, vol. 1. Cambridge, MA: Elsevier.
- **30** Tomani, P. (2010). The LignoBoost process. *Cellulose Chemistry and Technology* 44 (1–3): 53–58.
- **31** Kouisni, L., Gagné, A., Maki, K. et al. (2016). LignoForce system for the recovery of lignin from black liquor: feedstock options, odor profile and product characterization. *ACS Sustainable Chemistry & Engineering* 4: 5152–5159.
- **32** Hu, Z., Du, X., Liu, J. et al. (2016). Structural characterization of pine kraft lignin: BioChoice lignin vs Indulin AT. *Journal of Wood Chemistry and Technology* 36: 432–436.
- **33** Crestini, C., Lange, H., Sette, M., and Argyropoulos, D.S. (2017). On the structure of softwood kraft lignin. *Green Chemistry* 19: 4104–4121.
- **34** Chen Y.-r., Sarkanen, S., and Wang, Y.-Y. (2019). Lignin-only polymeric materials based on unmethylated unfractionated kraft and ball-milled lignins surpass polyethylene and polystyrene in tensile strength. *Molecules* 24: 4611. https://doi.org/10.3390/molecules24244611.
- 35 Mlynár, J. and Sarkanen, S. (1996). Renaissance in ultracentrifugal sedimentation equilibrium calibrations of size-exclusion chromatographic elution profiles. In: *Strategies in Size Exclusion Chromatography*, ACS Symposium Series No. 635 (ed. M. Potschka and P.L. Dubin), 379–400. Washington, DC: American Chemical Society.
- 36 Dutta, S., Garver, T.M. Jr., and Sarkanen, S. (1989). Modes of association between kraft lignin components. In: *Lignin – Properties and Materials*, ACS Symposium Series No. 397 (ed. W.G. Glasser and S. Sarkanen), 155–176. Washington, DC: American Chemical Society.
- **37** Li, Y. (1995). Noncovalent interactions between kraft lignin components. M.S. thesis. University of Minnesota.
- Wallberg, O. and Jönsson, A.-S. (2006). Separation of lignin in kraft cooking liquor from a continuous digester by ultrafiltration at temperatures above 100 °C. *Desalination* 195: 187–200.
- **39** Li, Y., Mlynár, J., and Sarkanen, S. (1997). The first 85% kraft lignin-based thermoplastics. *Journal of Polymer Science Part B: Polymer Physics* 35: 1899–1910.
- **40** Chan, J.C., Paice, M., and Zhang, X. (2020). Enzymatic oxidation of lignin: challenges and barriers toward practical applications. *ChemCatChem* 12: 401–425.

- 366 10 Biodegradable Lignin-Based Plastics
 - **41** Leisola, M., Pastinen, O., and Axe, D.D. (2012). Lignin designed randomness. *BIO-Complexity* 3: 1–11.
 - **42** Nutsubidze, N.N., Sarkanen, S., Schmidt, E.L., and Shashikanth, S. (1998). Consecutive polymerization and depolymerization of kraft lignin by *Trametes cingulata*. *Phytochemistry* **49**: 1203–1212.
 - **43** Ulmer, D.C., Leisola, M.S.A., Schmidt, B.H., and Fiechter, A. (1983). Rapid degradation of isolated lignins by *Phanerochaete chrysosporium*. *Applied and Environmental Microbiology* 45: 1795–1801.
 - 44 Fekete, E., Földes, E., Damsits, F., and Pukánszky, B. (2000). Interaction-structure-property relationships in amorphous polymer blends. *Polymer Bulletin* 44: 363–370.
 - **45** Worzakowska, M. (2015). Thermal and mechanical properties of polystyrene modified with esters derivatives of 3-phenylprop-2-en-1-ol. *Journal of Thermal Analysis and Calorimetry* 121: 235–243.
 - **46** Wypych, G. (2017). Plasticizer motion and diffusion (Chapter 7, pages 165–186), Effect of plasticizers on properties of plasticized materials (Chapter 10, pages 209–332). In: *Handbook of Plasticizers*, 3e (ed. G. Wypych). Toronto: ChemTec Publishing.
 - 47 Wang, Y.-Y., Chen Y.-r., and Sarkanen, S. (2017). Blend configuration in functional polymeric materials with a high lignin content. *Faraday Discussions* 202: 43–59.
 - **48** Lindgren, K., Samuelsson, Å., and Kulander, I. (2017). Techno economic evaluation of lignin extraction in a dissolving pulp biorefinery. Nordic Wood Biorefinery Conference. 118–123.
 - 49 www.alibaba.com/products/melamine_powder.html (accessed 28 October 2021).
 - **50** Rosen, M. and Kiani, A. (2016). The role of plastics compounding for injection molding. *Plastics Engineering* 72: 24–28.
 - **51** ChemAnalyst, Polystyrene Price Trend and Forecast, North America, December 2021. https://www.chemanalyst.com/Pricing-data/polystyrene-ps-11.
 - **52** Li, Y. and Sarkanen, S. (2002). Alkylated kraft lignin-based thermoplastic blends with aliphatic polyesters. *Macromolecules* 35: 9707–9715.
 - **53** Li, Y. and Sarkanen, S. (2005). Miscible blends of kraft lignin derivatives with low- T_{g} polymers. *Macromolecules* 38: 2296–2306.
 - **54** Kadla, J.F. and Kubo, S. (2003). Miscibility and hydrogen bonding in blends of poly(ethylene oxide) and kraft lignin. *Macromolecules* 36: 7803–7811.
 - 55 Lund, K. (2016). Industrial Binders from Borregaard Production and Applications. Sarpsborg: Borregaard ASA, 25 pp.
 - 56 Fredheim, G.E., Braaten, S.M., and Christensen, B.E. (2002). Molecular weight determination of lignosulfonates by size-exclusion chromatography and multi-angle laser light scattering. *Journal of Chromatography A* 942: 191–199.
 - 57 Sarkanen, S., Teller, D.C., Abramowski, E., and McCarthy, J.L. (1982). Kraft lignin component conformation and associated complex configuration in aqueous alkaline solution. *Macromolecules* 15: 1098–1104, and references therein.

- 58 Sarkanen, S., Chen Y.-r., and Wang, Y.-Y. (2016). Journey to polymeric materials composed exclusively of simple lignin derivatives. ACS Sustainable Chemistry & Engineering 4: 5223–5229.
- **59** Wang, Y.-Y., Chen Y.-r., and Sarkanen, S. (2015). Path to plastics composed of ligninsulphonates (lignosulfonates). *Green Chemistry* 17: 5069–5078.
- **60** Ritter, D., Jaklin-Farcher, S., Messner, K., and Stachelberger, H. (1990). Polymerization and depolymerization of lignosulfonate by *Phanerochaete chrysosporum* immobilized on foam. *Journal of Biotechnology* 13: 229–241.
- **61** Björkman, A. (1956). Studies on finely divided wood. Part I. *Svensk Papperstidning* 59: 477–485.
- **62** Murthy, N.S., Minor, H., Bednarczyk, C., and Krimm, S. (1993). Structure of the amorphous phase in oriented polymers. *Macromolecules* 26: 1712–1721.
- **63** Stomberg, R. and Lundquist, K. (1987). The crystal structure of *trans*-2,3dihydro-2-(4-hydroxy-3-methoxyphenyl)-3-hydroxymethyl-7-methoxybenzofuran. *Acta Chemica Scandinavica, Series B: Organic Chemistry and Biochemistry* 41: 304–309.
- 64 Lundquist, K. and Stomberg, R. (1988). On the occurrence of structural elements of the lignan type (β-β structures) in lignins. The crystal structures of (+)-pinoresinol and (±)-*trans*-3,4-divanillyltetrahydrofuran. *Holzforschung* 42: 375–384.
- **65** Roblin, J.-P., Duran, H., Duran, E. et al. (2000). X-ray structure of a trimeric 5,5'-biaryl/*erythro*-β-O-4-ether lignin model: evidence for through-space weak interactions. *Chemistry–A European Journal* 6: 1229–1235.
- 66 Stomberg, R. and Lundquist, K. (1986). Stereochemical assignment of the diastereomers of 1-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-1,3-propanediol from X-ray analysis. *Acta Chemica Scandinavica, Series A: Physical and Inorganic Chemistry* 40: 705–710.
- **67** Shan, L., Robertson, C.G., Verghese, K.N.E. et al. (2001). Influence of vinyl ester/styrene network structure on thermal and mechanical behavior. *Journal of Applied Polymer Science* 80: 917–927.
- **68** Rico, M., López, J., Bouza, R., and Bellas, R. (2011). Thermal behavior of blends based on a thermoplastic-modified epoxy resin with a crosslinking density variation. *Journal of Thermal Analysis and Calorimetry* 105: 599–606.
- 69 Mlynár, J., Nutsubidze, N., Sarkanen, S., and Shashikanth, S. (1995). Enzymatic macromolecular lignin depolymerization in vitro without peroxidases. *Proc. 8th International Symposium on Wood and Pulping Chemistry*, II, pp. 279–284.
- **70** Chen, Y.-r., Sarkanen, S., and Wang, Y.-Y. (2017). Lignin-degrading methods. US Patent 9, 796, 993, issued October 24.
- **71** Suzuki, K., Gomi, T., Kaidoh, T., and Itagaki, E. (1991). Hydroxylation of *o*-halogenophenol and *o*-nitrophenol by salicylate hydroxylase. *Journal of Biochemistry* 109: 348–353.
- **72** Rodgers-Vieira, E.A., Zhang, Z., Adrion, A.C. et al. (2015). Identification of anthraquinone-degrading bacteria in soil contaminated with polycyclic aromatic hydrocarbons. *Applied and Environmental Microbiology* 81: 3775–3781.

- 73 Kanaly, R.A. and Hamamura, N. (2013). 9,10-Phenanthrenedione biodegradation by a soil bacterium and identification of transformation products by LC/ESI-MS/MS. *Chemosphere* 92: 1442–1449.
- 74 Torres-Farradá, G., Manzano-León, A.M., Rineau, F. et al. (2019). Biodegradation of polycyclic aromatic hydrocarbons by native *Ganoderma* sp. strains: identification of metabolites and proposed degradation pathways. *Applied Microbiology and Biotechnology* 103: 7203–7215.
- **75** Kowalczyk, A., Eyice, Ö., Schäfer, H. et al. (2015). Characterization of *para*-nitrophenol-degrading bacterial communities in river water by using functional markers and stable isotope probing. *Applied and Environmental Microbiology* 81: 6890–6900.
- 76 Hatakeyama, T. and Takagi, K. (2016). Bacterial biodegradation of melamine-contaminated aged soil: influence of different pre-culture media or addition of activation material. *Environmental Science and Pollution Research* 23: 14997–15002.
- **77** Takagi, K., Fujii, K., Yamazaki K.-i. et al. (2012). Biodegradation of melamine and its hydroxy derivatives by a bacterial consortium containing a novel *Nocardiodes* species. *Applied Microbiology and Biotechnology* 94: 1647–1656.
- 78 Dodge, A.G., Wackett, L.P., and Sadowsky, M.J. (2012). Plasmid localization and organization of melamine degradation genes in *Rhodococcus* sp. strain Mel. *Applied and Environmental Microbiology* 78: 1397–1403.
- 79 Amann, M. and Minge, O. (2012). Biodegradability of poly(vinyl acetate) and related polymers. In: *Synthetic Biodegradable Polymers, Advances in Polymer Science*, vol. 245 (ed. B. Rieger, A. Künkel, G.W. Coates, et al.), 137–172. Heidelberg: Springer-Verlag.
- **80** Wang, Y.-Y., Wyman, C.E., Cai, C.M., and Ragauskas, A.J. (2019). Lignin-based polyurethanes from unmodified kraft lignin fractionated by sequential precipitation. *ACS Applied Polymer Materials* 1: 1672–1679.
- **81** Gioia, C., Colonna, M., Tagami, A. et al. (2020). Lignin-based epoxy resins: unravelling the relationship between structure and material properties. *Biomacromolecules* 21: 1920–1928.
- 82 Romhányi, V., Kun, D., and Pukánszky, B. (2018). Correlations among miscibility, structure, and properties in thermoplastic polymer/lignin blends. ACS Sustainable Chemistry & Engineering 6: 14323–14331.
- 83 Bartolome, M.J., Bischof, S., Pellis, A. et al. (2020). Enzymatic synthesis and tailoring lignin properties: a systematic study on the effects of plasticizers. *Polymer* 202: 122725. https://doi.org/10.1016/j.polymer.2020.122725.
- **84** Chung, H. and Washburn, N.R. (2012). Chemistry of lignin-based materials. *Green Materials* 1: 137–160.
- 85 Glasser, W.G. (2019). About making lignin great again some lessons from the past. Frontiers in Chemistry 7: 565. https://doi.org/10.3389/fchem.2019.00565.
- 86 Ajao, O., Jeaidi, J., Benali, M. et al. (2018). Quantification and variability analysis of lignin optical properties for colour-dependent industrial applications. *Molecules* 23: 377. https://doi.org/10.3390/molecules23020377.