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Chunbao Xu
Fatemeh Ferdosian

Conversion of Lignin into Bio-Based Chemicals and Materials

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Preface

Lignin is the second most abundant natural renewable polymer after cellulose. Natural lignin is a phenolic polymer formed by radical coupling polymerization of three monolignols, and it has amorphous macromolecular structure. Lignin is currently produced as waste or by-product streams from paper pulping and lignocellulosic ethanol processes, with limited applications for heat and power generation. Many studies have been conducted on value-added utilization of lignin. The availability, the presence of various functional groups (aromatic and hydroxyl) on lignin, lypohydrophilic structure, biodegradability, antioxidant and reinforcing capability make it a potential candidate for the production of bioaromatic chemicals (such as vanillin and phenols), bio-based polymeric materials (resins and polymers), and carbon fibers or for consumption as reinforcement fillers in thermoplastic polymers or dispersants. The reactivity of lignin could be enhanced through some chemical modifications and thermochemical depolymerization processes. Thus, lignin has great promise for production of biochemicals and biopolymers.

Although there are some books on the lignin chemistry and properties, the unique feature of this book is that it focuses on utilization of modified (e.g., via depolymerization and liquefaction) or non-modified lignins for high-value bio-based chemicals and materials.

This book consists of eight chapters, as detailed below. Chapter 1 introduces the fundamentals of chemical structure and properties of lignin and various delignification processes to extract lignin from lignocellulosic biomasses. Chapter 2 describes fast pyrolysis of lignin, the lignin pyrolysis mechanism, and the composition of lignin-derived pyrolytic products, as well as the influence of operation parameters and reactor design on the yields and composition of the pyrolytic products from lignin. Chapter 3 overviews depolymerization of lignin through various thermochemical processes including hydrolytic, reductive, and oxidative depolymerization to reduce the molecular weight of lignin with improved reactivity. Chapter 4 focuses on the performance of lignin (modified or non-modified lignin) as a reinforcement filler for thermoplastic polymers as well as its potential as a precursor or a starting material for production of carbon fibers. Chapter 5 describes the application of lignosulfonate as effective surfactants and dispersants in various industries. Chapter 6 presents a comprehensive overview on the production of lignin-based phenol formaldehyde resins, and analyzes the effects of lignin type, synthesis conditions and pre-treatment of lignin on the substitution ratio of lignin and its performance as a wood adhesive for different engineering wood composites. Chapter 7 provides an overview on chemistry, properties and applications of epoxy resin, as well as the production, curing kinetics and physiochemical properties of lignin-based epoxy resins. Chapter 8 presents the potential of lignin as a bioreplacement for polyol in the production of lignin-based PU for various applications including elastomers, coatings/adhesives/sealants, flexible foams, and semirigid or rigid foams.

This book covers a wide range of scientific and technical aspects on utilization of modified (e.g., via depolymerization and liquefaction) or non-modified lignins for high-value bio-based chemicals and materials. It is expected that the text would be of interest to students, researchers, academicians, and industrialists in the areas of valorization of lignin for the production of high-value bio-based chemicals and materials with industrial applications.

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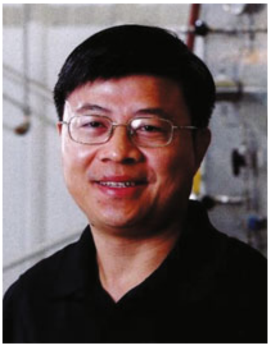
About the Authors



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He has co-edited two Springer books on biorefineries and published 12 book chapters and 130+ papers in peer-reviewed journals. His research has also resulted in three international patents (PCT) and five US provisional US/Canadian patents filed, as well as nearly 20 reported inventions. He received the Syncrude Canada Innovation Award in 2011 from CSChE, the 2014 Outstanding Profile Award in Professionals Sector from Fairchild Television, and more recently the 2015 VELUX Visiting Professorship at Aalborg University, Denmark, and the 2016 Visiting Erskine Fellowship at the University of Canterbury, New Zealand. He currently serves as the co-editor-in-chief for the *International Journal of Chemical Reactor Engineering* (IJCRE). Email: cxu6@uwo.ca

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Chapter 1
Structure and Properties of Lignin

Abstract Lignin is a phenolic natural polymer, second only to cellulose. It can be extracted from lignocellulosic biomass through various chemical, physical, mechanical, and enzymatic treatments. The chemical structure and properties of the extracted lignin are mainly depended on the extraction method, vegetal species, location, season, etc. Based on the separation method, several types of lignin, also called technical lignin, could be obtained, including alkali lignin/kraft lignin, lignosulfonate, organosolv lignin, milled wood lignin (MWL), klason lignin, and hydrolytic lignin. The separation conditions can influence the cross-linked structure and molecular weight distributions of the technical lignin products. By far, lignin is mainly regarded waste or by-product streams from paper pulping mills and cellulosic ethanol plants with a limited application for heat and power generation. However, the abundant availability and unique structure of lignin make it a potential feedstock for the synthesis of biochemicals and biopolymers such as surfactants/dispersants, carbon fibers, phenolic resins, epoxy resins, and polyurethane resins, etc.

Keywords Lignin · Phenolic natural polymer · Technical lignin · Alkali lignin · Kraft lignin · Lignosulfonate · Organosolv lignin · Milled wood lignin (MWL) · Klason lignin · Hydrolytic lignin

1.1 Lignin

Wood, a heterogeneous, hygroscopic, cellular and anisotropic material, consists of cells, and the cell walls consist mainly of three organic components including cellulose (40–60 wt%), hemicelluloses (25–35 wt%), and lignin (15–30 wt%) (Fig. 1.1) [1]. Lignin can be extracted from lignocellulosic biomass (such as woody biomass and other plants) by various treatments such as chemical, biochemical, and physical processes. The properties of extracted lignin (so called technical lignin), and its chemical structure and purity are strongly dependent on the treatment

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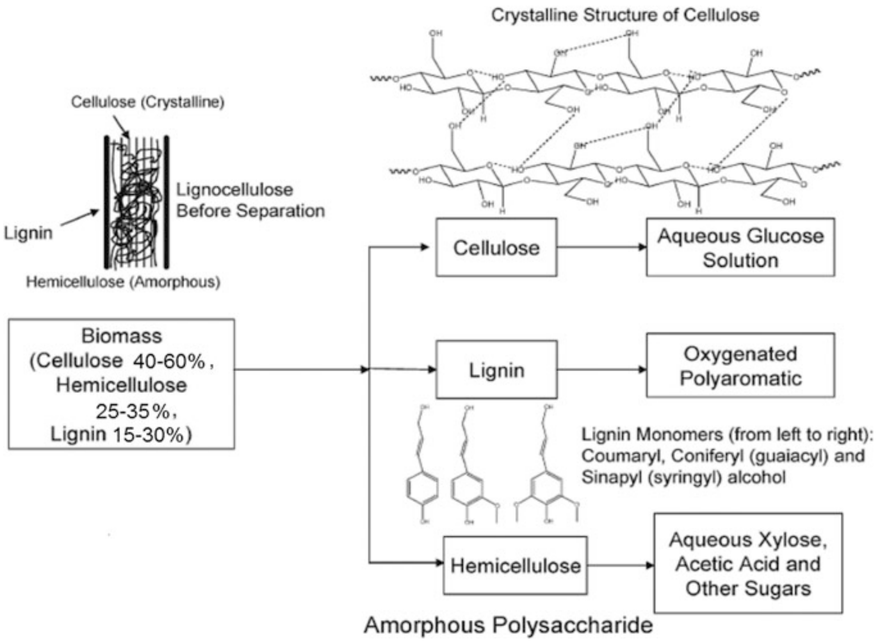

Fig. 1.1 Schematic structure of wood cells, reprinted with permission from Ref. [6] with modifications. Copyright (2006) American Chemical Society

method [2–4]. The industrial processes for lignin extraction can be classified into two different categories: sulfur processes and sulfur-free processes. Figure 1.2 shows various extraction processes and their corresponding products [2, 5]. Currently, the majority of technical lignin is generated in kraft pulping processes, and the annual kraft lignin (KL) generation is estimated to be 50 million tons, present in the form of "black liquor" that is used mainly in the recovery boilers for heat and power generation in the kraft pulping mills.

Lignin is the second most abundant natural renewable polymer after cellulose [7, 8] and accounts for between 15 and 30 wt% of lignocellulosic biomass as mentioned previously, contributing to the rigidity and strength of plant cell walls. Table 1.1 shows the contents of cellulose, hemicellulose, and lignin in common lignocellulosic biomass [9]. Unlike cellulose that has unique well-defined structure, lignin has a three-dimensional network structure and the structure depends on the vegetal species, location, season, etc. [3]. Elucidation of lignin structure plays an important role in its utilization for chemicals and materials. Different analytical methods such as FTIR [10], NMR [11–13] and GPC [14] have been widely used in exploring the structure of lignin.

Lignin is a phenolic polymer formed by radical coupling polymerization of three monolignols (Figs. 1.3 and 1.4) [14], and it has amorphous macromolecular structure comprising three types of phenyl-propanols, i.e., p-hydroxyl-phenyl propanol, guaiacyl-propanol and syringyl-propanol, linked mainly by ether linkages

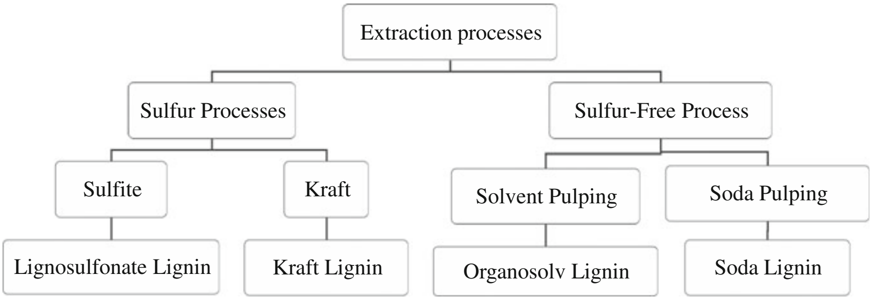

Fig. 1.2 Various lignin extraction processes and their dominant products (modified from Ref. [2])

Table 1.1 Contents of cellulose, hemicellulose, and lignin in common lignocellulosic biomass (reprinted with permission from Ref. [9])

Lignocellulosic materials	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Hardwoods stems	40–55	24–40	18–25
Softwood stems	45–50	25–35	25–35
Nut shells	25–30	25–30	30–40
Corn cobs	45	35	15
Grasses	25–40	35–50	10–30
Paper	85–99	0	0–15
Wheat straw	30	50	15
Sorted refuse	60	20	20
Leaves	15–20	80–85	0
Cotton seed hairs	80–95	5–20	0
Newspaper	40–55	25–40	18–30
Waste papers from chemical pulps	60–70	10–20	5–10
Primary wastewater solids	8–15	NA	24–29
Swine waste	6.0	28	NA[a]
Solid cattle manure	1.6–4.7	1.4–3.3	2.7–5.7
Coastal Bermuda grass	25	35.7	6.4
Switch grass	45	31.4	12.0

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[a] Not available

(e.g., α-*O*-4, 5-*O*-4 and β-*O*-4) and condensed linkages (e.g., 5-5, β-β, β-5 and β-1 linkages) [15–17] (Fig. 1.3). Around 40–60% of total intermolecular linkages in the structure of lignin are ether bonds and the β-O-4 bond is a predominant ether linkage [14, 18]. The dominant monomer in softwood lignins is Guaiacyl (G) monomer, while hardwood lignins consist of both Syringyl (S) and Guaiacyl (G) units [19]. The reactivity of lignin depends on the form and composition of reactive functional groups within monomer units, in particular, its three types of functional groups: p-hydroxy-phenyl, aliphatic hydroxyl, and carboxylic acid groups [19].

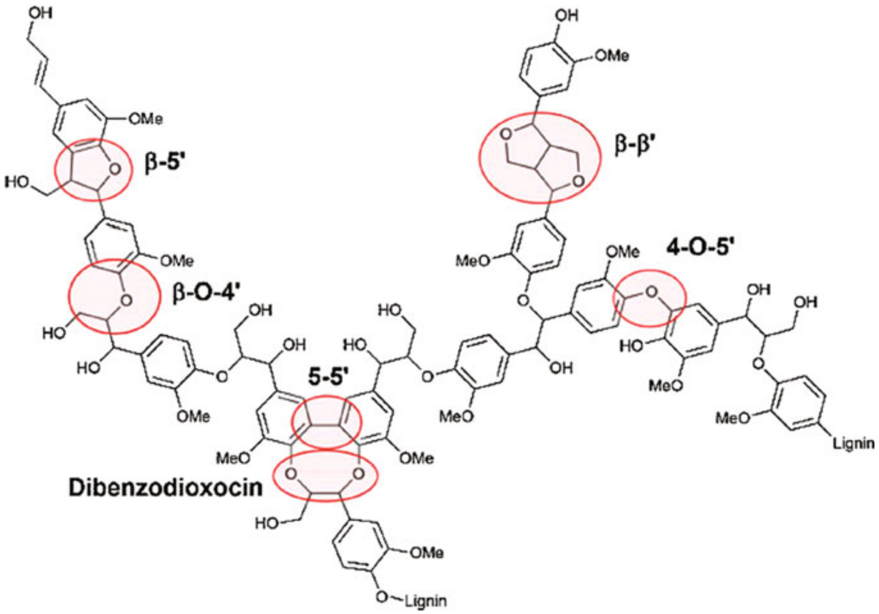

Fig. 1.3 A fraction of lignin model structure, reprinted with permission from Ref. [20]. Copyright (2013) Royal Society of Chemistry

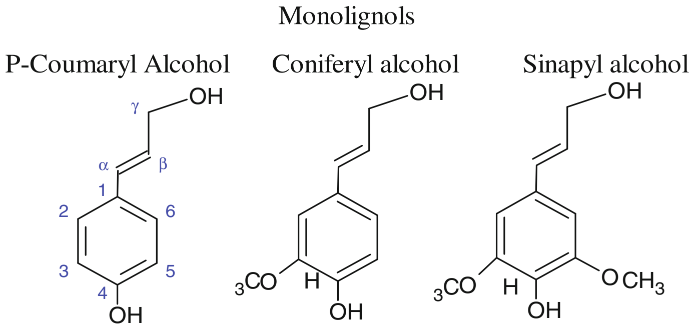

Fig. 1.4 Structure of three lignin monomers

1.2 Types of Lignin

Technical lignin is conventionally named after the separation (extraction) method, e.g., lignosulfonate lignin, kraft lignin, organosolv lignin, and soda lignin (Fig. 1.2). The lignin separation methods can also be categorized into two classes: (1) dissolving lignin into a solution, and (2) hydrolyzing cellulose and hemicellulose in acidic media and separating lignin as an insoluble residue [21, 22]. The soluble lignin has an amorphous structure, and the insoluble one has the virginal morphological structure of the raw material fibers [22]. The presence of some functional groups such as phenolic hydroxyl and carboxyl on the structure of lignin facilitates its solubility in alkaline solutions. Organosolv lignin is soluble in various solvents such as dioxane, DMSO, methanol, ethanol, acetone, and pyridine. The common solvents for alkali lignin and lignosulfonate are dilute alkali, water, and salt solution. Acidic/enzymatic hydrolyzed lignin cannot be dissolved in any solvents [22]. The molecular weight and polydispersity of lignin are affected by the separation methods too due to the partial degradation of lignin during the extraction process [22]. In addition, the separation conditions including mechanical action, enzymes, or chemical reagents can influence the crosslinked structure of lignin and formed lignin fragments with different molecular weight distributions.

Some important types of technical lignin are described as follows:

- *Alkali Lignin/Kraft Lignin*
  Alkali lignin is isolated from biomass in the presence of NaOH solution at high temperature and pressure. The linkages to polysaccharides are broken and lignin fragments are dissolved in the solvent, forming black liquor. The resulted lignin separated from black liquor with Na_2CO_3 is called soda lignin. The lignin separated in the presence of Na_2SO_4 is named kraft lignin [21, 23].
- *Lignosulfonate*
  Lignosulfonates or sulfonated lignins are water-soluble anionic polyelectrolyte polymers, recovered from the sulfite pulping of wood (brown liquor) [24]. In the pulping process, an aqueous solution containing sulfur dioxide and a sulfurous acid salt are used to break down the linkages to polysaccharides [21]. Depending on the type of bases in pulping process, various lignosulfonates such as calcium [25, 26], sodium [27, 28], magnesium [29], and ammonium lignosulfonates [30] can be formed. Finally, lignosulfonates can be isolated from spent pulping liquors by various methods including precipitation in alcohol, dialysis, electrodialysis, ion exclusion, ultrafiltration, supported liquid membrane (SLM), and extraction with amines [24, 31, 32].
- *Organosolv Lignin*
  Organosolv pulping is conducted in the presence of an aqueous organic solvent at the temperature ranging from 140 to 220 °C. In this process, the alpha aryl-ether linkages of lignin are broken down by hydrolytic cleavage and the obtained fragments dissolve in the solvent [21, 33]. One of the suitable catalysts for organosolv pulping is HCl in the presence of water with different solvents including acetone, methanol, ethanol, butanol, ethylene glycol, formic acid or acetic acid, or their mixtures etc. [34, 35]. The concentration of solvent in water varies in the range of 40–80%. Dozens of organosolv methods have been reported in the literature and the obtained lignin was commonly named as organosolv lignin [34], among which four main organosolv pulping processes are Organocell process [34, 36, 37], Alcell process [34, 38], alkaline sulfite-antraquinone-methanol (ASAM) process [34, 39–41], and acetosolv

process [34, 42–44]. It was reported that the organosolv process with ethanol-water mixed solvent produces a higher pulp yield than that of kraft process, and the tensile and tear strength of softwood organosolv pulps fall between the corresponding values of kraft pulp and sulphite pulp [45].

- *Milled Wood Lignin (MWL)*
  The milled wood lignin is obtained from milling wood in a ball-mill for tens of hours and the linkages to polysaccharides are broken mechanically. The fragmented lignin is dissolved in solvents such as 0.2 mol/L NaOH solution followed by extraction with dioxane-water mixture [21, 46, 47]. Crestini et al. [48] investigated the chemical structure of different softwood and hardwood milled wood lignins by combining quantitative data arising from ^{31}P NMR and QQ-HSQC analyses. It was suggested that the milled wood lignin is a linear oligomer rather than a network polymer. The yield of isolated lignin from MWL is often low and many studies have been conducted to improve this process. Lin and Dence [49] proposed a novel process called milled wood enzyme lignin

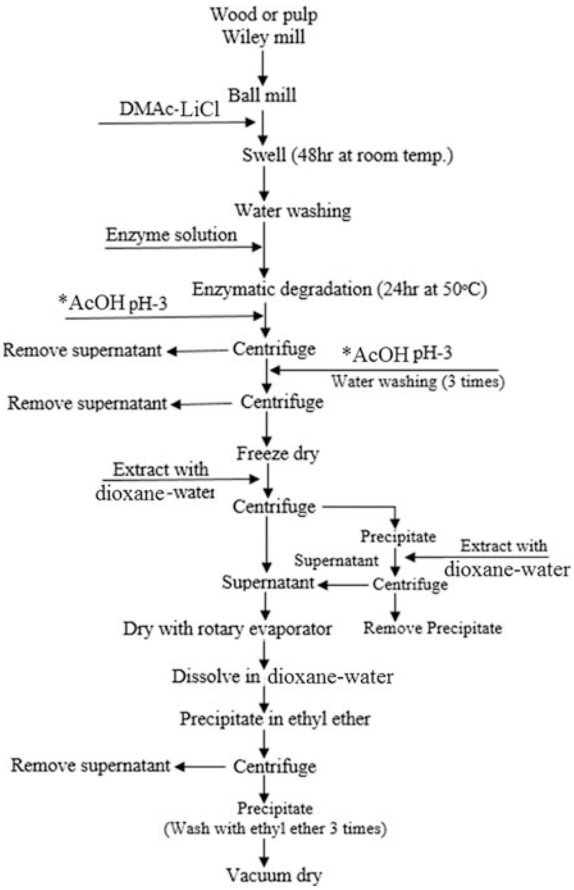

Fig. 1.5 SEL process for isolation of lignin, reprinted with permission from Ref. [50]. Copyright (1995) Springer

(MWEL) process with higher yield of lignin by treating the milled wood with enzymes to solubilize the carbohydrate components. However, this process requires ten or more days to accomplish due to the high crystalline structure of cellulose. To overcome this challenge, swelled enzyme lignin (SEL) was tested by Chen et al. [50]. The procedure of SEL is displayed in Fig. 1.5. Lignin yields were as high as 24–67% based on the total amount of lignin present.

Some typical types of lignin isolated by insoluble methods are listed below:

- *Klason Lignin*
  Klason method is a standard method for determination the lignin content in wood [51]. In this process, all polysaccharide linkages are hydrolyzed with 72% sulfuric acid and leaving the solid lignin residue [21, 52].
- *Hydrolytic Lignin*
  In a dilute acid, most of the polysaccharides linkages are hydrolyzed into fermentable sugar and the resulted residue is hydrolytic lignin [9, 21]. The hydrolytic lignin, extracted from the residues of the cellulosic ethanol production, is commonly known as "enzymatic hydrolysis lignin (EHL)". As enzymatic hydrolysis processes of biomass normally operates under relatively mild conditions, the most active functional groups such as phenolic hydroxyl and alcoholic hydroxyl can be preserved [53]. As a consequence, the resulting EHL is expected to be more reactive in comparison with lignosulfonate or kraft lignin [53, 54]. However, in practice, the hydrolytic lignin has a very large molecular structure with strong steric hindrance and normally contains sugar impurities, so it is not as reactive as organosolv or kraft lignin in chemical applications. As such, enzymatic hydrolysis lignin is usually used as a fuel in combustion or gasification processes to generate steam or electricity [53].

1.3 Utilization of Lignin

Until recently, lignin has been considered as a waste by-product of paper pulping mills and cellulosic ethanol plants. It is mainly consumed in the mills/plants in recovery boilers for heat and power generation [55], and a small quantity of lignin (<1%) is used as fillers such as ink varnishes, paints, and elastomeric matrices or surfactants/dispersants [3]. While in recent decades, there is a growing interest in utilization of lignin as a feedstock for the synthesis of bioaromatic chemicals (such as vanillin and phenols) and bio-based polymeric materials (resins and polymers) due to the following driving forces [56]:

(1) The material is sustainable and renewable,
(2) There is immense generation of lignin as a by-product in pulp/paper industry and cellulosic ethanol industry,

(3) There are various functional groups present in lignin structure which enable a variety range of chemical reactions,
(4) Lignin has intrinsic biodegradability and it is believed that the incorporated polymers with lignin would be more biodegradable than the petroleum based polymers.

Normally, lignin can be used as a filler or can substitute <20–30 wt% of some reactive components in polymers (such as phenols for phenolic resins and polyols for polyurethane, or bisphenol-A for epoxy resins, etc.) [3, 16, 57]. Limited by lignin's detrimental properties (large M_w with steric hindrance effects, poor solubility in organic solvent and low reactivity), a greater substation ratio of lignin in polymer materials is challenging, but can be achieved by modifications on its structure. Different lignin modification technologies have been explored, which include chemical [58, 59], biological [60], photochemical [61, 62], and electrochemical [61, 63] methods. Among these methods, chemical modification processes have attracted significant interest. It is well known that lignin is a polydisperse natural phenolic polymer, as shown in Figs. 1.3 and 1.4. Lignin contains both polar (hydroxyl) groups and nonpolar hydrocarbon and benzene rings, it is thus expected to act as a compatibilizer between hydrophilic natural fibers and a hydrophobic matrix polymer [7, 64–66]. The presence of the phenolic hydroxyl groups in lignin has also enabled its utilization in the synthesis of various polymers such as phenolic resins [67], epoxy resins [68, 69], polyurethanes [56, 57, 70], and polyesters [70, 71]. These lignin-based polymers will be introduced in details in the subsequent chapters.

1.4 Summary

Lignin is the second most abundant natural renewable polymer after cellulose. Natural lignin is a phenolic polymer formed by radical coupling polymerization of three monolignols, and it has amorphous macromolecular structure comprising three types of phenyl-propanols, i.e., p-hydroxyl-phenyl propanol, guaiacyl-propanol and syringyl-propanol, linked mainly by ether linkages (e.g., α-*O*-4, *5*-*O*-4 and β-*O*-4) and condensed linkages (e.g., 5-5, β-β, β-*5* and β-1 linkages). Technical lignin can be extracted from lignocellulosic biomass by various separation methods. The chemical structure and the properties of technical lignin are mainly affected by the delignification process. The typical types of technical lignin are kraft lignin, organosolv lignin, lignosulfonate, milled wood lignin, and hydrolysis lignin. Currently, the annual kraft lignin generation is estimated to be 50 million tons, present in the form of "black liquor" that is used mainly in the recovery boilers for heat and power generation in the kraft pulping mills. However, the availability and the presence of various functional groups (aromatic and hydroxyl) on lignin make it as a potential candidate for the synthesis of bioaromatic chemicals (such as vanillin and phenols) and bio-based polymeric materials (resins and polymers).

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Chapter 2
Degradation of Lignin by Pyrolysis

Abstract Fast pyrolysis is an efficient technique for thermal degradation of lignin to bio-oils containing bio-phenols for the synthesis of adhesives, resins, and polymers. Lignin has a complex structure, and hence a large number of pyrolytic components are generated during the pyrolysis process. The composition of the pyrolytic products depends on the type of lignin, temperature, types of catalyst, and the design of the pyrolysis reactor. It was suggested that the pyrolysis of lignin consists of two steps. In the first step, by thermal cracking of the lignin macromolecule, vapor of monomeric phenolic compounds is formed during the vapor condensation process, followed by re-oligomerization of the monomeric compounds, forming pyrolysis oils comprising remarkable amounts of dimeric and other oligomeric products. However, the precise mechanism of the pyrolysis of lignin is not clear due to the complexity of the process.

Keywords Fast pyrolysis of lignin · Degradation of lignin · Bio-oils · Bio-phenols · Adhesives · Resins · Polymers

2.1 Pyrolysis Technology

Pyrolysis is a thermochemical process operated in the absence of oxygen, which can be divided into three categories according to the process conditions (heating rate): slow pyrolysis, intermediate pyrolysis, and fast pyrolysis [1, 2]. The conditions of each process are shown in Table 2.1. Slow pyrolysis is conducted at a low temperature for a longer vapor residence time, leading to producing more charcoal and noncondensable gases. Intermediate pyrolysis operates at moderate temperatures and residence time. In contrast, fast pyrolysis is conducted at a high temperature and a short residence time, to produce more liquid fuels that can be used as fuels and chemicals [1, 3].

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Table 2.1 Typical modes of pyrolysis, modified from Refs. [1, 2]

Types of pyrolysis	Residence time	Temperature (°C)	Yield (%)		
			Liquid	Char	Gas
Slow	Hours/Days	400	30	35	35
Intermediate	10–30 s	500	50	25	25
Fast	~1 s	500	75	12	13

2.2 Fast Pyrolysis of Lignin

Fast pyrolysis of biomass is a promising technology for generation of liquid biofuels from lignocellulosic biomass. In general, the pyrolysis of biomass consists of two steps: production of free radical fragments by thermal cracking of the biomass components (cellulose, hemicellulose, and lignin) via the cleavage of covalent bonds, and combination of free radical compounds to form pyrolysis products [4]. The liquid (pyrolysis oil) yield depends on various parameters including biomass types, temperature, residence time, char separation, and ash content of biomass [1]. Among three main components of a lignocellulosic biomass, lignin has a significant effect on the pyrolysis behavior of biomass [5]. As described in Chap. 1, lignin is a natural aromatic polymers comprised of p-hydroxyphenyl, guaiacyl, and syringyl, which are linked by C–O–C ether bonds (β-O-4, α-O-4, 4-O-5) and C–C bonds (β-1, β-5, 5-5) (Fig. 1.3) [5, 6]. The β-O-4 ether bond is the most dominant bonds which made around 46–60% of the total linkages depending on the source of wood [7, 8] and approximate 6–8% of the total linkages occupies by α-O-4 linkages [8]. Due to the complex structure of lignin, the exact mechanism of its pyrolysis remains unknown. In pyrolysis of lignin, it is generally believed that first the cleavage of ether bonds occurs to depolymerize lignin. Subsequently, the side chains cleave from the monolignols via the hemolytic cleavages of O–CH_3 and radical-induced rearrangements [6]. Figure 2.1 shows the evolution of the compounds obtained from thermal pyrolysis of lignin [9].

Pyrolysis of lignin yields up to 40 wt% bio-oil (Tar, such as aromatic and phenolic compounds), 50 wt% biochar, and 10 wt% gaseous species (such as CO, CO_2, CH_4, and H_2) [10–12]. The biochar could be used in various applications such as fuel, soil improver, solid bitumen additive, and as a precursor for activated carbon [11, 13]. The bio-oil has a great potential to be used as a renewable resource of chemicals (such as phenol and polyol) in synthesis of adhesives, resins, and polymers [11, 14–16].

2.2.1 Lignin Pyrolysis Mechanism

A wide variety studies has been conducted on the pyrolysis of lignin to elucidate the pyrolysis mechanism by using advanced analytical techniques such as

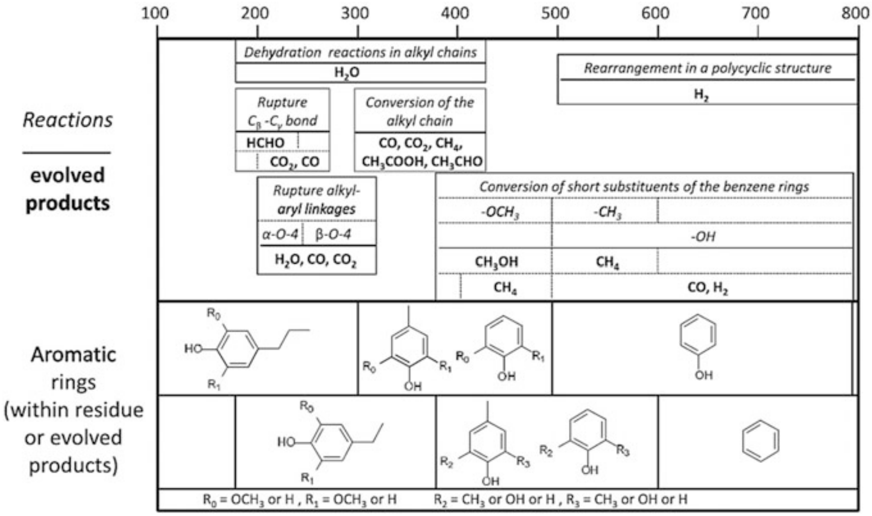

Fig. 2.1 Evolution of the compounds obtained from thermal pyrolysis of lignin, reprinted with permission from Ref. [9]. Copyright (2014) Elsevier

thermogravimetric analysis-Fourier transform infrared spectroscopy (TGA-FTIR) and Pyrolysis–Gas Chromatography/Mass Spectroscopy (Py-GC/MS) [17–21]. Guo et al. [4] modeled kraft lignin pyrolysis by using Boltzmann-Mont Carlo pyrolysis model and validated by the experimental results at temperatures of 400–600 °C. Patwardhan et al. [22] suggested that the pyrolysis of lignin consists of two steps. In the first step, by thermal cracking of the lignin macromolecule vapor of monomeric phenolic compounds are formed such as phenol, 4-vinyl phenol, 2-methoxy-4-vinyl phenol, and 2,6-dimethoxy-phenol, followed by re-oligomerization of the monomeric compounds to produce remarkable amounts of dimeric and other oligomeric products during the vapor condensation process. However, elucidation of detailed mechanism of lignin pyrolysis is very difficult due to the complexity of the lignin structure. Lignin model compounds were commonly used for better understanding the pyrolysis process due to their simple structures and formation similar pyrolysis products [8, 23–28]. Kotake et al. [23] conducted in-depth study on the formation of monomers and oligomers during the pyrolysis of a softwood lignin and coniferyl alcohol (CA) as a model compound in the presence of an aprotic solvent (diphenoxybenzene, DPB) or H-donor (1,2,3,10b-tetrahydrofluoranthene). DPB prevented the polymerization of CA via the inhibition of the proton-transfer, and H-donor promoted the production of the side-chain reduction products as a source of the hydrogen radical. Figure 2.2 presents the proposed mechanism of pyrolysis of CA. It was found that DPB and H-donor played important roles in the formation of monomers (such as dihydroconferyl alcohol and isoeugenol) and oligomers from lignin. At low operation temperature (250 °C), coniferyl aldehyde was the dominant product due to the H-donor/radical balance.

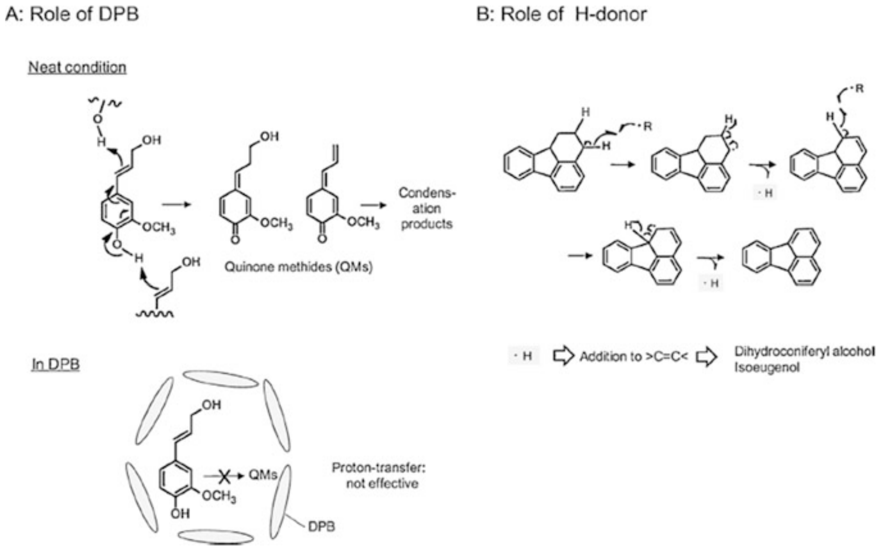

Fig. 2.2 Proposed mechanism of pyrolysis of coniferyl alcohol in the presence of an aprotic solvent (diphenoxybenzene, DPB) or H-donor (1,2,3,10b-tetrahydrofluoranthene), reprinted with permission from Ref. [23]. Copyright (2014) Elsevier

The following pathway was also proposed by Shin et al. [7, 29] for the pyrolysis of vanillin as a lignin model component to form aromatic hydrocarbons using mass spectroscopy and multivariate analysis (Fig. 2.3).

A β-O-4 type lignin model dimer (1-(4-methoxyphenyl)-2-(2-methoxyphenoxy) ethanol) was also pyrolyzed by Py-GC/MS to explore the mechanism of product formation with respect to temperature [30]. The pyrolysis of lignin model dimer involves three possible pathways: homolysis of the C_β–O bond, homolysis of the C_α–C_β bond, and C_β–O concerted decomposition, as illustrated in Fig. 2.4. At a low temperature (300 °C), the pyrolysis process is initiated by homolysis of C_β–O due to low dissociation energy (221.4 kJ/mol), producing 4-methoxystyrene and guaiacol. Homolysis of C_β–O and C_β–O concerted decomposition mainly control the degradation process at a moderate pyrolysis temperature (500 °C), producing 4-methoxystyrene, guaiacol, and carbonyl-containing substances. At a high temperature (800 °C), a wide variety of small molecular compounds are generated from the secondary thermal cracking of the products derived from C_β–O homolysis and C_β–O concerted decomposition.

A theoretical study was conducted on the mechanism of pyrolysis of lignin dimer model component with α-O-4 linkage by employing density functional theory (DFT) method at B3LYP/6-31G(d, p) level [8]. Figure 2.5 shows the hemolytic cleavages of the α-O-4 linkage lignin dimer and their corresponding bond dissociation energies. According to the calculated bond dissociation energies, there are three possible pathways for pyrolysis of the α-O-4 linkage lignin dimer: (i) the hemolytic cleavage of C_α–O bond, (ii) the hemolytic cleavage of O–CH_3, and (iii) the hemolytic

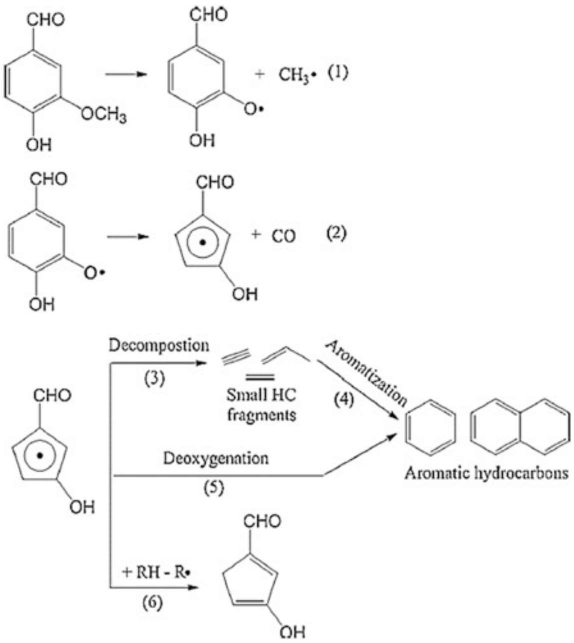

Fig. 2.3 Pyrolysis of vanillin as a lignin model component to form aromatic hydrocarbons, reprinted with permission from Ref. [7]. Copyright (2016) Elsevier

cleavage of C_α–C_β. The major reaction is the breakdown of C_α–O bond and the main products are phenolic compounds including guaiacol, p-hydroxyphenyl-ethanol, p-hydroxyphenyl-acetaldehyde, and 2-hydroxybenzaldehyde. Similarly, the mechanism of formation of CO, CO_2, and CH_4 during the pyrolysis of lignin was theoretically studied in detail by Huang et al. [31] using the DFT method, and it was proposed that CO, CO_2, and CH_4 could be formed through decarbonylation of phenol (p-hydroxyphenyl, guaiacyl, and syringyl) acetaldehyde, decarboxylation of phenyl (p-hydroxyphenyl, guaiacyl and syringyl) formic acid, and concerted reactions, respectively.

2.2.2 Effects of Types of Lignin

Different types of lignin have different structure, depending on the bioresources of lignin and the methods of isolation [9, 18, 32–39]. Thus, it is needed to investigate on pyrolysis behavior of various types of lignin. For example, Custodis et al. [33] studied the influence of lignin isolation processes on product yields from both catalytic [a commercial Zeolite (H-USY)] and non-catalytic pyrolysis processes. Various types of lignin were extracted from the same soft- and hardwoods by Organosolv-, Klason-, and Dioxane-methods, and they were pyrolyzed at different temperatures. The study revealed that the product yields noticeably depended on the lignin separation methods not on the source of lignin. The highest yield of pyrolysis

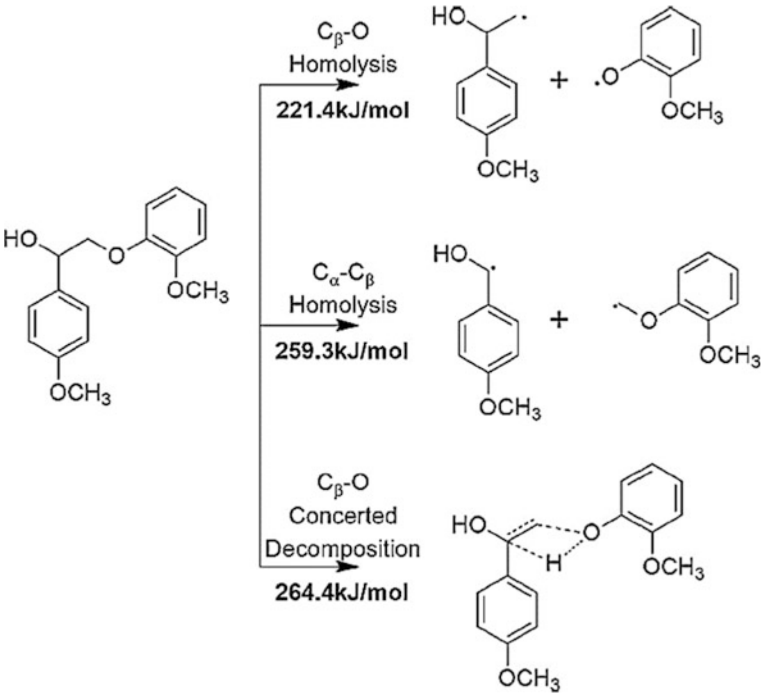

Fig. 2.4 Mechanism of pyrolysis of lignin dimer, reprinted with permission from Ref. [30]. Copyright (2015) Elsevier

oil (66 wt%) was produced from Dixance hardwood lignin at 650 °C. Increasing the temperature enhanced the yield of lignin monomers in the bio-oil, and operation at above 550 °C led to significantly higher gas formation. As discussed in the previous section, at a low temperature the pyrolysis of lignin started with depolymerization via radical formation by homolytic fission or hydrogen abstraction, followed by other reactions such as retro-ene, dehydration-, decarboxylation-, and condensation reactions. A high pyrolysis temperature enhanced the Maccoll reaction of the 2-phenethyl phenyl ether types of compounds, hence the main products changed from phenol alkoxyl ketone (rich in the low-temperature pyrolysis oil of lignin) products to phenols. It was also reported that pyrolysis of hardwood lignin produced more liquid products in comparison with softwood lignin, owing to more β-O-4 bonds on the hardwood lignin that are weaker than the C–C bonds in softwood lignin. Figure 2.6 depicts the main pyrolysis products from lignins at different temperatures.

Bahrle et al. [12] observed in situ radical formation from pyrolysis of a softwood and hardwood lignin, respectively by in situ high-temperature electron paramagnetic resonance spectroscopy. For both lignins, the highest radical concentration occurred between 350 and 400 °C, and again more radicals and volatile products were detected with the hardwood lignin than with the softwood lignin.

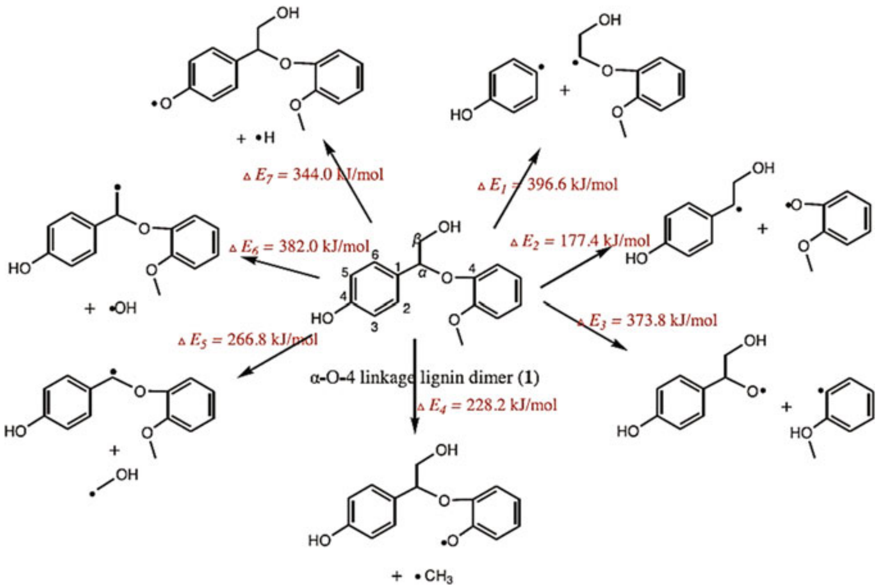

Fig. 2.5 Hemolytic cleavages of the α-O-4 linkage lignin dimer and their corresponding bond dissociation energies, reprinted with permission from Ref. [8]. Copyright (2015) Elsevier

In another study, pyrolysis behaviors of four types of lignin, alkali lignin (AL), klason lignin (KL), organosolv lignin (OL), and milled wood lignin (MWL), isolated from the same pine wood, were studied by TG-FTIR and Py-GC/MS as well as ^{13}C NMR spectroscopy [5]. The ^{13}C NMR results showed that the chemical structure of these isolated lignins is different and the distribution of functional groups is presented in Table 2.2. Ether bonds such as β-O-4 have lower thermal stability and decompose easily at low temperatures. Thus, lignins consisting of more ether bonds would show weaker thermal stability or exhibit a lower temperature at maximum weight loss rate upon heating. This was evidenced by the experimental observation: AL and MWL, due to the presence of more β-O-4 bonds in their structures, have a lower temperature at maximum weight loss rate (346 and 359 °C, respectively) that that of OL (396 °C) or KL (405 °C). Thus, pyrolysis of AL and MWL yielded more phenol compounds at lower temperatures. The dominate products in pyrolysis of these softwood lignins are guaiacyl-type compounds due to lack of syringyl-type unit in the structure of softwood and the maximum of phenol yield was obtained at 600 °C.

Pyrolysis behaviors of various lignins extracted from eight different agricultural wastes (e.g., walnut shell, wheat straw, cotton stalk, rice husk, bamboo, rape straw, corncob, and peanut shell) were studied by TG-FTIR and Py-GC/MS [34]. The composition of gaseous products depended on the biomass species. The formation of catechol type fragments (catechol, 3-methylcatechol, 4-methylcatechol, and ethylcatechol) was significant in two types of lignin from peanut shell and cotton

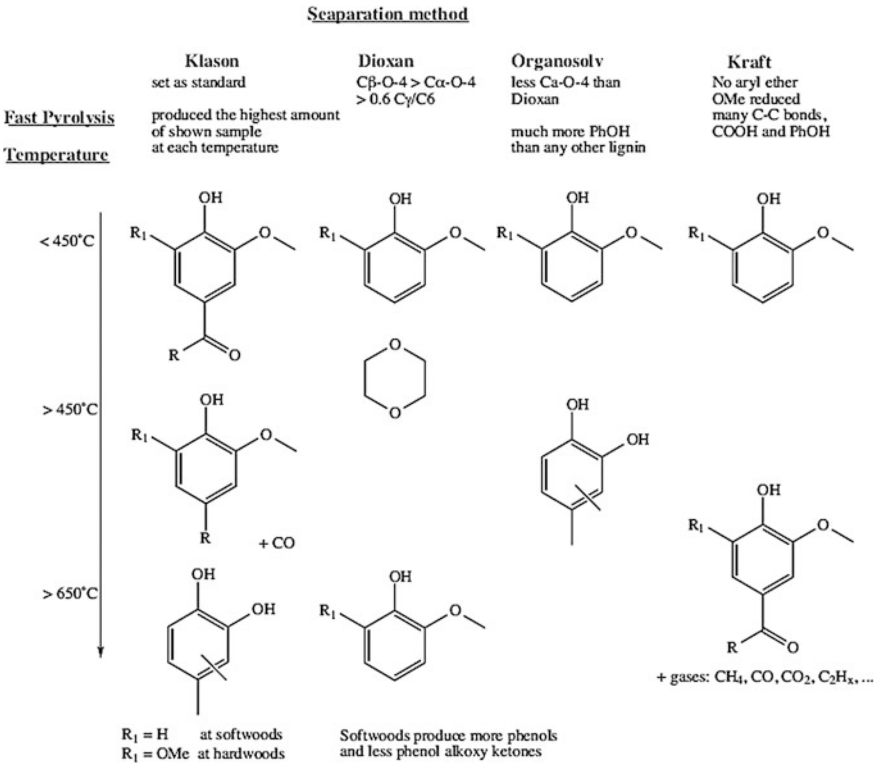

Fig. 2.6 Main pyrolysis products from lignin at different temperatures, reprinted with permission from Ref. [33]. Copyright (2015) Elsevier

stalk and the presence of hemicellulose in these crude lignin samples led to production of styrene and 4-hydroxy-3-methoxystyrene in the pyrolysis oil products. Bai et al. [38] investigated the formation of phenolic oligomers during fast pyrolysis of lignin in a micropyrolyzer. It was reported that more than 500 phenolic compounds with molecular weight less than 504 Da were generated and the most predominant products were monomers followed by dimers, trimers, and tetramers. De Wild et al. [11] pyrolyzed two wheat straw-derived organosolv lignins, Granit lignin (from a mixture of wheat straw and Sarkanda grass) and an Alcell organosolv lignin from hardwood in a bubbling fluidized bed reactor. It was observed that around 80 wt% of the dry lignin was converted into bio-oils and bio-chars. 25–40 wt% of the bio-oil produced was made of phenolic fragments (7–11 wt% monomeric compounds and 14–24 wt% oligomeric compounds). The straw-based lignins including the Granit lignin produced more guaiacol, alkylphenols and catechols and less syringols compared with Alcell lignin from hardwood.

On the other hand, it was also observed that the final residue weights depended on the methoxyl content in the lignin structure: lignins with a higher methoxyl content have lower condensed structural units, resulting in lower thermal stability

Table 2.2 Distribution of functional groups of four kinds of lignin, i.e., alkali lignin (AL), klason lignin (KL), organosolv lignin (OL), and milled wood lignin (MWL), isolated from the same pine wood, reprinted with permission from Ref. [5]

Chemical shift (ppm)	Assignment	Functional group distributions (mol/100 g)			
		AL[a]	KL[b]	OL[a]	MWL[a]
195–190	Carbonyl C=O	0.003	–	0.026	0.017
172	Ester COO-R	0.011	–	0.000	0.003
168	Carboxyl C=O	0.079	–	0.105	0.077
160–140	Aromatic C–O	0.844	1.178	0.753	0.770
140–123	Aromatic C–C	1.086	1.023	1.277	1.055
123–102	Aromatic C–H	0.784	0.899	1.245	1.027
89–57	Aliphatic C–O	0.841	0.960	0.573	0.858
89–78	C_β in β-O-4, C_α in β-5, β-β	0.281	–	0.153	0.271
73–71	C_α in β-O-4	0.112	–	0.046	0.106
64–61	C_γ–OR	0.205	–	0.190	0.273
57–54	$-OCH_3$	0.597	0.407	0.622	0.742
31–29	C_α and C_β in $-CH_2-$	0.069	–	0.075	0.043
15	C_γ in $-CH_3$	0.011	–	0.088	0.023

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[a] Data obtained by solution-state ^{13}C NMR spectrum

[b] Data obtained by solid-state ^{13}C CP/MAS NMR spectrum

and less char production [5]. Wang et al. [35] investigated pyrolysis behavior and product selectivity for two milled wood lignins from different tree species: Manchurian ash (MA—hardwood) and Mongolian Scots pine (MSP—softwood), respectively. Compared with the softwood lignin, the hardwood lignin (MA lignin) showed less thermal stability and a lower yield of charcoal residue (26 wt%) upon pyrolysis due to the fact that the hardwood lignin has a higher content of syringyl monomer (i.e., a higher methoxyl content).

Alkali lignin contains sodium salts that could be in two forms: organic bond Na salts [phenolic sodium ($-CH_2ONa$), and carboxylic sodium (–COONa)] or the dissolved salts (NaOH, and Na_2CO_3) [19, 40]. The effect of these dissolved salts on the pyrolysis process of alkali lignin was studied using TGA-FTIR analysis [19]. It was revealed that the production of alcohols and phenols required a higher pyrolysis temperature in the presence of sodium salts, while the formation of aldehydes and ketones was promoted due to the intensive cracking of $-CH_2ONa$ and –COONa bonds.

In order to investigate the role of β-O-4 linkages in the thermal stability of lignin, a milled wood lignin was first treated thermally in the temperature range of 150–300 °C prior to the pyrolysis, and the behaviors was characterized using a pyrolysis-GC/MS analyzer [41]. It was found that the low-temperature thermal treatment produced a thermally stabilized lignin as the β-O-4 linkages were deformed by condensation and charring reactions. As a result, the evolution of pyrolysis products from the thermally treated lignin was found to be delayed to a higher temperature. For example, the maximum evolution of pyrolytic products was obtained at a high temperature (600 °C) for the lignin sample thermally treated at 300 °C.

Moreover, the pyrolysis kinetics of nine lignins isolated by various methods was investigated by thermogravimetric analysis (TGA) [42]. The obtained activation energies of lignin thermal degradation varied in the range of 130–175 kJ/mol, with the types of lignin.

2.2.3 *Effects of Temperature*

Effects of temperature on distribution of the pyrolytic products of lignin have been studied by many researchers [6, 36, 43–46]. Commonly the maximum bio-oil yields from wood can be obtained at a pyrolysis temperature around 450–500 °C [43]. In pyrolysis of a kraft lignin, char yield decreased from approx. 50 to 47 wt% while increasing the pyrolysis temperature from 470 to 560 °C, accompanied by an increase in pyrolysis oil from ~30 to 38 wt% [43]. For example, an enzymatic/mild acidic hydrolysis lignin from bamboo was pyrolyzed in a tubular reactor at different temperatures, i.e., 400, 500, 600, 700, and 800 °C [6]. It was found that the reaction temperature played a significant role in the yields of pyrolysis products (gas, bio-oil, and char) and the products compositions. With rising the temperature from 400 to 800 °C, the gaseous yield increased from 6.2 to 20.3 wt%, the char formation decreased from 42 to 26.6 wt%, and bio-oil yield increased to a maximum value (57.1 wt%) at 500 °C and then decreased to 53.3 wt% at 800 °C (see Fig. 2.7). The maximum concentration of phenols (G-type and S-type phenols, phenol, p-methylguaiacol, vanillin, etc.) in bio-oil was as high as 79.3% obtained at 600 °C. At lower temperatures (<500 °C), the pyrolysis of lignin was incomplete but at higher temperatures (>700 °C), the secondary reactions such as dehydration, decarboxylation, and demethylation, and radical's rearrangement occurred, generating more gases including CO, CH_4, and H_2. The obtained phenolic bio-oils from lignin could be used as a potential feedstock for synthesis of biopolymers.

Shen et al. [47] reported that the predominant products in non-catalytic pyrolysis of lignin were phenolic compounds and the yield of maximum aromatic monomers (such as guaiacol, phenol, benzone, toluene, etc.) attained at 650 °C also, the portion of guaiacyl-type compounds decreased noticeably with elevating temperature due to the secondary cracking reactions such as demethoxylation reaction. A study was reported by Patwardhan et al. [22] on pyrolysis of cornstover lignin at various temperatures. By increasing the temperature, the char yield decreased from 60 wt% at 300 °C to 22 wt% at 700 °C, accompanied by an increase in the formation of low molecular weight compounds (such as acetic acid), gaseous products, and phenolic products including phenol, 2-methyl phenol, 4-methyl phenol, 2,5-dimethyl phenol, and ethyl phenol, as illustrated in Fig. 2.8.

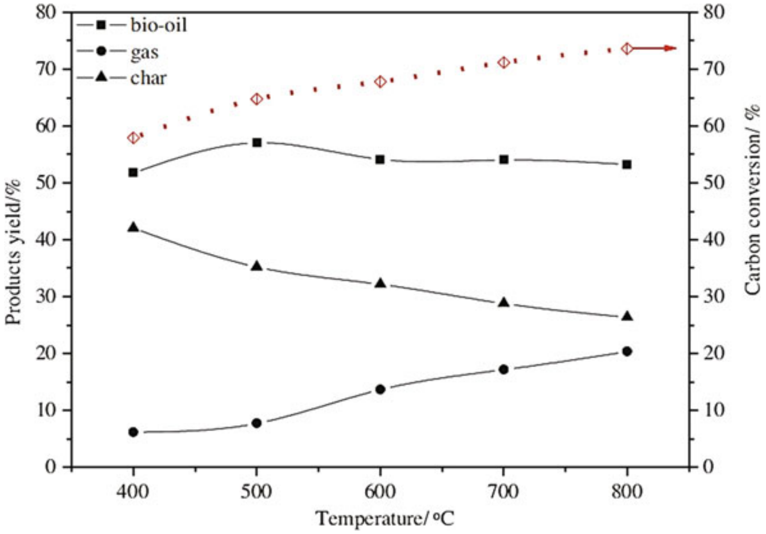

Fig. 2.7 Product yields and carbon conversion derived from pyrolysis of an enzymatic/mild acidic hydrolysis lignin derived from bamboo, reprinted with permission from Ref. [6]. Copyright (2015) Elsevier

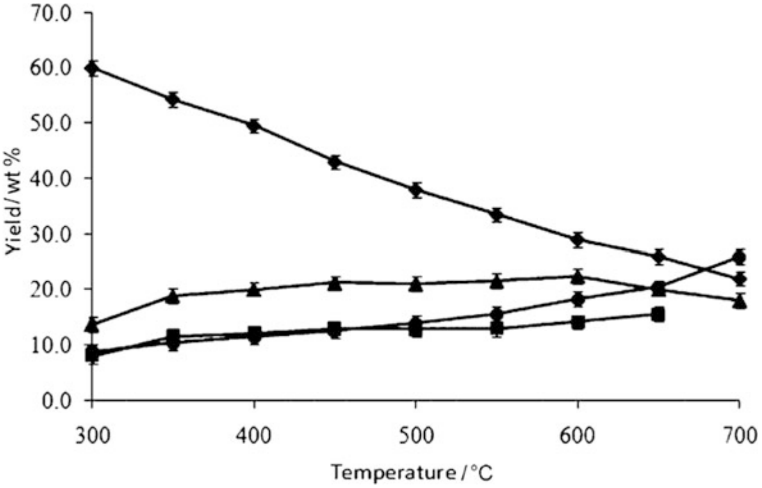

Fig. 2.8 Yields of pyrolytic products of lignin over temperature, Char (♦), Phenolic compounds (▲), low molecular weight compounds (■), and gaseous species (●), reprinted with permission from Ref. [22]. Copyright (2011) John Wiley and Sons

The dependency of pyrolytic products of lignin on temperature in the range of 400–800 °C was investigated on two types of lignin (Alcell lignin and Asian lignin) by Jiang et al. [46]. The maximum yield of phenolic compounds was obtained at

600 °C, being 15.5 and 17.2% for Asian lignin and Alcell lignin, respectively. The main pyrolytic products were 5-hydroxyvanillin at a yield of 4.3% for Alcell lignin, and 2-methoxy-4-vinylphenol at a yield of 4.2% for Asian lignin.

2.2.4 Effects of Catalyst

Various kinds of catalyst such as inorganic metal, transition metal, noble metal, spent FCC, alumina and zeolite have been applied for pyrolysis of lignin [10, 44, 48, 49]. Among these catalyst zeolite is an effective deoxygenation catalyst to produce bio-oil with reduced oxygen content but enriched aromatic hydrocarbons. Beside the type of catalyst, other factors such as catalyst amount, catalyst framework, acidity, and pore size distribution could affect the composition of the pyrolytic products of lignin. Kim et al. [44] investigated the effects of catalyst loading of Zeolite (HZSM-5) (catalyst/lignin ratio from 0.6 to 2 w/w) and catalyst composition (mole ratio of Si/Al from 30 to 280) on the products distribution in pyrolysis of a milled wood lignin. The mole ratio of Si/Al had an inverse effect on the acidity of HZSM-5 catalyst but less effect on the surface areas of the catalysts. A higher acidity of the catalyst increased the production of aromatic hydrocarbons (AH) such as benzene, toluene, xylene, and naphthalene, and the highest yield of AH products was obtained with HZSM-5(30) (2.62 wt%) despite its lowest surface area. It confirmed that the catalyst acidity plays an important role in the yield of AH than the surface area does. The catalyst amount could control the production of pyrolytic products. Additionally, it was observed that the AH production gradually increased with temperature up to 700 °C ($\sim$3 wt% of lignin) which could be ascribed to the enhanced thermal degradation of lignin, owing to the improvement of the pore size of HZSM-5, and the decreased energy barrier of the diffusion of large molecules into the catalyst pores at a high temperature [44, 50, 51]. As the coke formation increased above 600 °C, the optimum temperature for lignin pyrolysis was determined to be 600 °C. The effects of acidity, pore size, and structure of the zeolite catalysts on the bio-oil yield and selectivity of the desired products from lignin were investigated by Ma et al. [50]. It was found that a high content of catalyst provides more actives sites and could limit repolymerization reactions and minimize the char formation, a low Si/Al ratio for the HZSM-5 catalyst increases its acid sites and promotes the formation of AH products, and large pore size of the HZSM-5 catalyst would facilitate the penetration of large molecules of the lignin degradation products/intermediates and stabilizes the degraded products. Figure 2.9 presents the role of porosity in stabilization of intermediates compounds in fast pyrolysis of lignin.

Two pathways were proposed by Mullen and Boatenge for formation of aromatic hydrocarbons in pyrolysis of lignin in the presence of H-ZSM5 catalyst [18]. These pathways consists of: (i) the scission of the aliphatic linkages of the lignin network to form small olefins, (ii) depolymerization of lignin into alkoxy phenolic monomers. Figure 2.10 shows the proposed pathways of degradation of lignin over H-ZSM5.

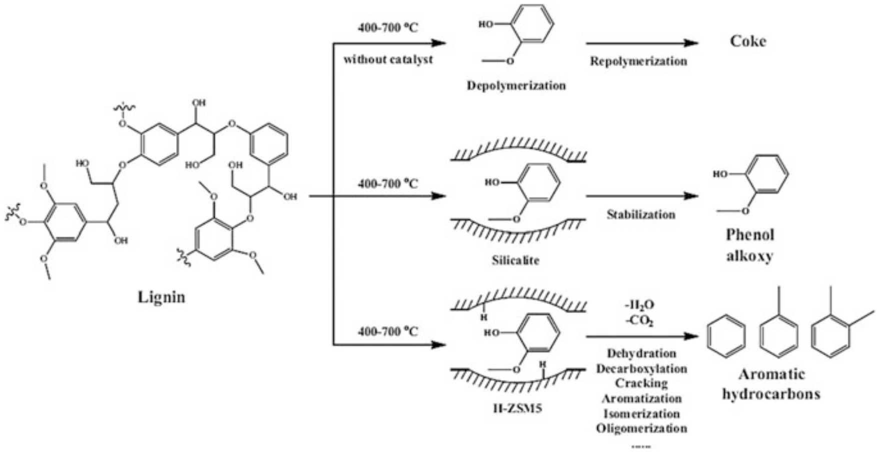

Fig. 2.9 Non-catalytic and catalytic fast pyrolysis of lignin, reprinted with permission from Ref. [50]. Copyright (2012) Elsevier

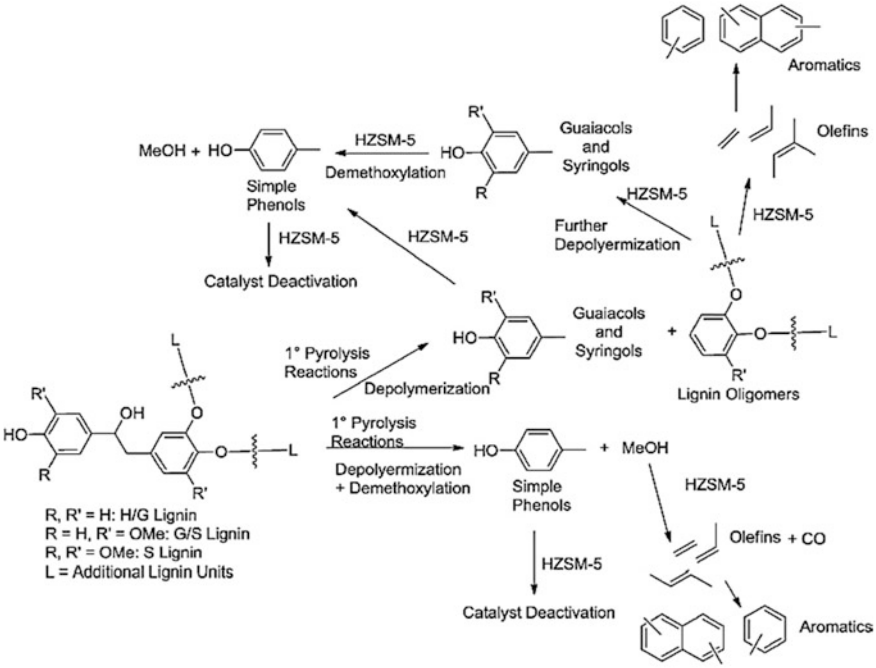

Fig. 2.10 The proposed pathways for depolymerization of lignin in the presence of HZSM-5, reprinted with permission from Ref. [18]. Copyright (2010) Elsevier

Three kinds of catalyst, i.e., HZSM-5, Y-Zeolite, and Pd/C were tested for the catalytic pyrolysis of softwood kraft lignin [52]. HZSM-5 and Y-Zeolite are acidic catalysts which enhanced the production of aromatic hydrocarbons with one to three rings and deoxygenated phenolic structures compared with non-catalytic pyrolysis. Pd/C is a nonacidic catalyst which increased the content of the reduced guaiacyl units. The effects of five different zeolite catalysts (HZSM-5(25), HZSM-5 (50), HZSM-S(210), H-β, and H-USY) on the composition of the bio-oil from the lignin pyrolysis was also examined by Shen et al. [47]. The maximum production of aromatic monomers, with different product compositions though, was achieved at 650 °C for both catalytic and non-catalytic pyrolysis of lignin. The zeolite catalysts promoted the deoxygenation reactions to generate more aromatic hydrocarbons. HZSM-5 (25) was found to be the most effective catalyst for producing aromatic monomers due to its strongest acidity (zeolite with a lower Si/Al ratio has a stronger acidity). HZSM zeolites are more effective than other types of zeolites in catalytic pyrolysis of lignin for production of aromatic monomers as HZSM zeolites have MFI orthorhombic structure and a unique three-dimensional pore system, while H-USY showed better deoxygenation performance, forming more aromatic hydrocarbons (benzene, toluene, and xylene) in the bio-oil from lignin pyrolysis. Li et al. [53] pyrolyzed sodium lignosulfonate with and without catalyst (HZSM-5, an aluminosilicate zeolite) from 30 to 650 °C and analyzed the resulting gases by TGA-FTIR to examine the degradation kinetics and product distributions. It was observed that the use of catalysts promoted the cracking of oxygenated products, decreased the molecular weight of pyrolyzed products, and reduced the char yield. The most abundant compounds in the vapor were water, CO, CO_2, aromatics, alkenes, and alkyls. The pyrolysis process could be divided into three stages with the corresponding activation energy of 104, 129, and 169 kJ/mol, respectively. Mullen and Boateng [18] pyrolyzed lignin from four different sources over an acidic zeolite (HZSM-5) and a mixed metal oxide catalyst (CoO/MoO_3). Although both catalysts demonstrated to be effective deoxygenation catalysts, promoting the production of aromatic hydrocarbons from lignin, the acidic HZSM-5 was found to be more active than the CoO/MoO_3.

A recent study by Wang et al. [10] described catalytic pyrolysis of alkali lignin with metal chlorides such as KCl, $CaCl_2$, and $FeCl_3$. The addition of $CaCl_2$ and $FeCl_3$ noticeably increased the yield of bio-oil with high phenol content. In contrast, the impregnation KCl inhibited the yield of bio-oil and promoted bio-char formation, implying the catalytic effect of KCl on repolymerization of low-molecule fragments derived from lignin pyrolysis. In another study, effects of Na_2CO_3, $Na_2CO_3/\gamma\text{-}Al_2O_3$, $\gamma\text{-}Al_2O_3$ on pyrolysis of lignin were studied using vanillyl alcohol as a lignin model component [7]. Vanillyl alcohol contains three functional groups typical on the structure of lignin derivatives: alkyl group, alkoxy group, and hydroxyl group. Pyrolysis of the model compound over the alkaline Na_2CO_3 catalyst produced a high yield of methoxyphenols. In the pyrolysis over $\gamma\text{-}Al_2O_3$ catalyst with both Lewis and Bronsted acid sites, however, the condensable phase only contained aromatic hydrocarbons due to the high deoxygenation effects of the acidic catalyst, while the yields of coke and gaseous products were also maximized.

In contrast, with $Na_2CO_3/\gamma\text{-}Al_2O_3$ catalyst, no methoxyphenol was detected and the 67 wt% of the condensable product was phenols. Such results may be explained by the fact that loading Na_2CO_3 onto $\gamma\text{-}Al_2O_3$ decreased the acidity of $\gamma\text{-}Al_2O_3$ and basicity of Na_2CO_3, hence restricting the formation of both aromatic hydrocarbons and methoxyphenols. Aspen lignin was pyrolyzed over two different zeolite catalysts, i.e., HZSM-5 and HY [54]. Similarly, the HY catalyst (with less acidity) produced more phenolic compounds, and HZSM-5 (a more acidic zeolite catalyst) yielded more aromatic hydrocarbons due to the high deoxygenation effects of the HZSM-5 catalyst.

$AlCl_3$ and $ZnCl_2$ (both Lewis acids) were used as catalysts by Maldhure and Ekhe [55] for pyrolysis of kraft lignin, it was observed that in the presence of either catalyst the residue (or char) yield decreased, accompanied by increased yields of both liquid (bio-oil) and gaseous products. With respect to bio-oil production from lignin, $AlCl_3$ demonstrated to be a more active catalyst than $ZnCl_2$. Characterization of the lignin pyrolysis products showed that the liquid products mainly contained substituted phenols, cyclic esters, mono- and dicarboxylic acids.

Again the study of Peng et al. [56] confirmed that the presence of alkaline catalysts (NaOH, KOH, Na_2CO_3, and K_2CO_3) at 10–20 wt% in lignin pyrolysis generated bio-oils composed mainly of 2-methoxy-phenol, 2, 6-dimethoxy-phenol, alkylphenols, and 2-ethoxy-4-alkylphenols, although these alkaline catalysts had negligible effects on the products yields. The hydroxide alkalis (NaOH and KOH) produced more alkylphenols, while the carbonate catalysts (Na_2CO_3 and K_2CO_3) promoted formation of methoxyphenols.

As commonly demonstrated in a number of studies, lignin pyrolysis with an acidic catalyst led to a higher yield of bio-oil rich in aromatic hydrocarbons due to the high deoxygenation effects of the acidic catalyst. Performance and optimum conditions of various acidic catalysts in lignin pyrolysis are compared in Table 2.3.

2.2.5 Pyrolysis Reactors

Pyrolysis technology is the only industrially realized technology for liquefaction of lignocellulosic biomass. Some representative industrial pyrolysis processes include Ensyn's patented RTP® technology and BTG (Biomass Technology Group)'s fast pyrolysis technology, both based on fluidized bed reactors, as well as the ABRI-Tech's patented pyrolysis based on augers reactor. It is estimated that 10–15% of the total capital cost of an industrial pyrolysis process allocated to the reactor.

Various types of reactor have been used for lignin pyrolysis, such as bubbling fluidized beds [1, 2, 45, 48, 59] (as schematically shown Fig. 2.11), rotating cone reactors [1], fixed bed reactor [10, 56], centrifuge reactors [60], and circulating fluid beds [1, 2], etc.

Table 2.3 Performance and optimum conditions of various acidic catalysts in lignin pyrolysis

Type of lignin	Catalyst	Catalyst loading (catalyst: lignin w/w)	Optimum temp. (°C)	Performance	Refs.
Mill wood lignin	Zeolite (ZSM-5 (Si/Al = 30)	2:1	600	3.6 wt% yield of aromatic hydrocarbon	[44]
Alkaline lignin	W_2C/MCM-41 (Si/W = 50)	10:1	750	20.8 wt% yield of arenes (aromatic hydrocarbons)	[57]
Kraft lignin	HZSM-5, Y-zeolite, Pd/C	1:1	600	High yield of aromatic hydrocarbons	[52]
Black liquor lignin	HZSM-5 (Si/Al = 25) or H-USY	2:1	650	Enhance aromatic monomers yields	[47]
Kraft lignin	$AlCl_3$, $ZnCl_2$	1:10	500	Lower char yield, and higher bio-oil production	[55]
Aspen lignin	HZSM-5	3:1	600	23 wt% yield of aromatic hydrocarbons (AH), and 28 wt% yield of aggregate sum of AH and phenolic compounds	[54]
Alkaline lignin	$Mo_2N/\gamma\text{-}Al_2O_3$	4:1	700	17.5% yield of aromatic hydrocarbon	[58]

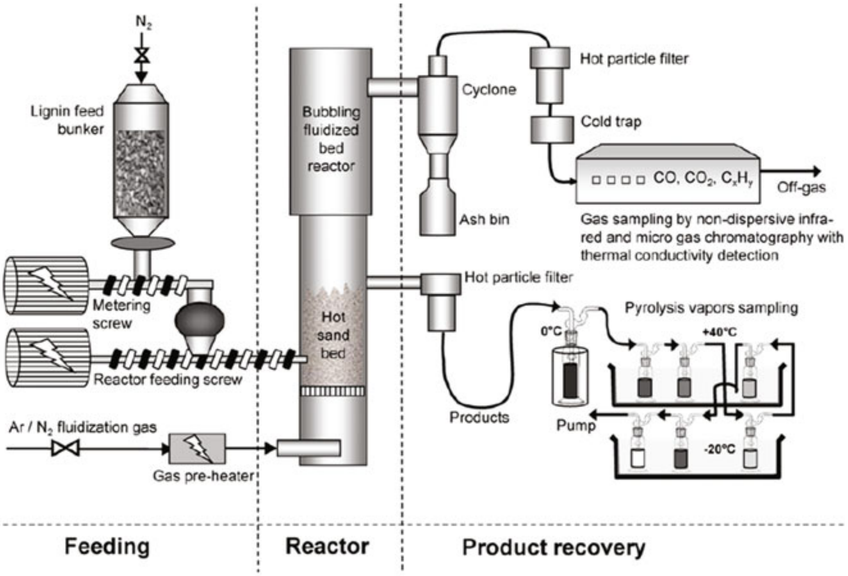

Fig. 2.11 Bubbling fluidized bed reactor for pyrolysis of lignin, reprinted with permission from Ref. [11]. Copyright (2012) Elsevier

Table 2.4 Product yields of the pyrolyzed Kraft lignin in different bed materials in a fluidized reactor (modified from Ref. [59])

Bed material	Gas yield (wt%)	Bio-char yield (wt%)	Bio-oil yield (wt%)			Yield of organic chemical (wt%)
			Dry bio-oil	Aqueous condensate	Total bio-oil	
Silica sand	30.1	32.6	21.3	16.0	37.3	23.1
Lignin char	26.8	36.0	24.5	12.8	37.3	25.9
Activated lignin char	21.5	35.5	30.4	12.5	43.0	31.3
Birch bark char	31.8	36.0	19.8	12.5	32.3	21.2

In bubbling fluidized-bed pyrolysis reactors, the bed materials, normally silica, olivine sand or other catalyst particles, serve as the heat transfer medium and (if catalyst is used) catalyze the pyrolysis process to alter the products distribution and in situ upgrade the bio-oil products. For example, effect of various bed materials in a bubbling bed reactor (silica sand, lignin char, activated lignin char, birch bark char, and foamed glass beads) were investigated on the yield and quality of bio-oil from the pyrolysis of kraft lignin at 550 °C [59]. The bed materials were found to not only facilitate the heat transfer during the pyrolysis process but also can have a catalytic effect to change the products yields and enhance the quality of the generated bio-oils, as displayed in Table 2.4. Among these bed materials, the activated lignin char provided the higher total bio-oil yield of 43% with a lower molecular weight, a higher phenolic concentration, and similar heating value as compared to standard lignin pyrolysis with a sand bed.

Two major challenges of pyrolyzing lignin in fluidized bed reactors were commonly identified in the feeding (due to the low melting points of lignin, in particular organosolv and kraft lignins) and the formation of lignin-foams and agglomeration of bed materials (which could cause de-fluidization of the bed) [61]. To address these challenges, colleagues of the authors at the Institute for Chemicals and Fuels from Alternative Resources (ICFAR) at Western University have developed a novel bubbling bed reactor system for pyrolysis of kraft lignin as illustrated in Fig. 2.12 [59]. In this reactor system, lignin powders are fed into the reactor using a patented feeder using compressed nitrogen and a pinch valve avoids melting of the lignin feedstock. The reactor is equipped with an internal stirrer with blades of Inconel, to prevent and break the lignin-foams/agglomerates of sand and char during the pyrolysis process. The obtained bio-oil vapor passes through a train of three condensers in series to achieve a dry bio-oil product. The condensing system made of two cyclonic condensers kept at a warm and cold temperature, respectively, and an electrostatic precipitator-cum-condenser (C-ESP). The obtained dry bio-oils contain less than 1 wt% water but are rich in phenolic compounds and of improved heating values.

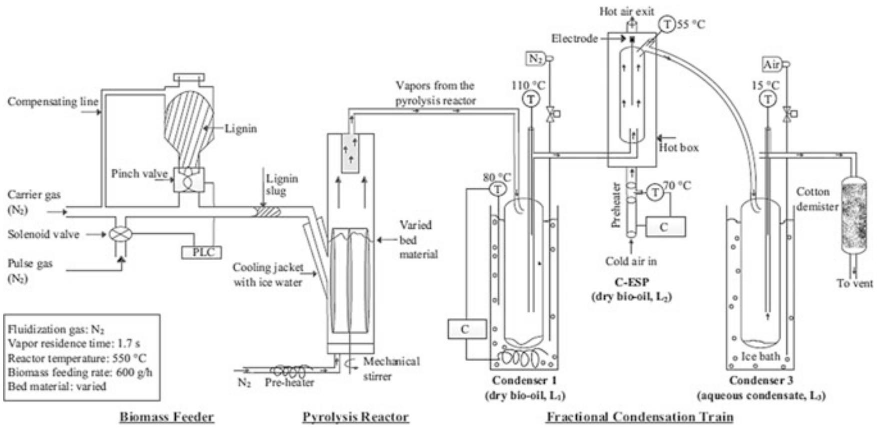

Fig. 2.12 Schematic of a modified bubbling fluidized reactor with an internal stirrer and a three-condenser train, reprinted with permission from Ref. [59]. Copyright (2015) Elsevier

2.3 Summary

Fast pyrolysis of lignin is a promising technology for production of phenolic bio-oil as a potential feedstock to be used as a renewable energy resource and biore-placement of phenol in synthesis of adhesives, resins, and polymers. The exact mechanism of pyrolysis of lignin is remained unknown due to its complexity in structure. However, the general pathway of lignin pyrolysis contains two-step process: first, the ether bonds cleave to depolymerized lignin, followed by the cracking of side chains on monolignols through the hemolysis of O–CH_3 and radical-induced rearrangements. The pyrolytic products of lignin consist of phenolic bio-oil, bio-char, and gaseous fragments. The content and combination of the pyrolytic products depend on the type of technical lignin, pyrolysis temperature, type of catalyst, and the reactor design.

Various types of reactor have been used for lignin pyrolysis, such as bubbling fluidized beds, rotating cone reactors, fixed bed reactor, centrifuge reactors, and circulating fluid beds, etc. Fluidized bed reactors are the most common reactor type in the pyrolysis technologies commercially developed by far. Two major challenges of pyrolyzing lignin in fluidized bed reactors were commonly identified in the feeding (due to the low melting points of lignin, in particular, organosolv and kraft lignins) and the formation of lignin-foams and agglomeration of bed materials (which could cause de-fluidization of the bed). Worldwide research is going on to address these challenges.

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Chapter 3
Degradation of Lignin by Depolymerization

Abstract This chapter mainly presents depolymerization of lignin to generate depolymerized lignin or oligomers with smaller molecules and higher reactivity as a potential feedstock for the synthesis of biopolymers. Depolymerization of lignin can be realized with various thermochemical methods including hydrolytic, reductive, and oxidative depolymerization. Possible mechanisms of thermal depolymerization of lignin for the generation of predominant products, and effects of operation factors such as the type of lignin, residence time, reaction temperature, concentration of catalyst, and composition of the reaction media (solvents) on the composition of the resultant products were discussed.

Keywords Depolymerization of lignin · Hydrolytic depolymerization · Reductive depolymerization · Oxidative depolymerization · Depolymerized lignin · Smaller molecules · Higher reactivity

3.1 General Introduction on Lignin Depolymerization

As discussed in the previous chapters, lignin is a macromolecule comprised of three phenyl-propanols i.e., p-hydroxyl-phenyl propanol, guaiacyl-propanol and syringyl-propanol, via primarily ether linkages (e.g., α-O-4, 5-O-4 and β-O-4) as well as some condensed linkage (e.g., 5-5, β-β, β-5 and β-1 linkages) [1, 2]. Lignin thus has great potential as precursors for aromatic (phenolic) chemicals for sustainable production of various bio-based chemicals and materials such as adhesives, polyurethane foams, flocculants and epoxy coating [3].

However, lignin has lower reactivity and high steric hindrance effect due to its large molecular weight and branched structure, which limits the direct use of lignin as chemicals. Several approaches have been taken to enhance reactivity of lignin [4]. One approach is through chemical modification of the chemical structure of lignin, e.g., phenolation or methylolation of lignin could improve the reactivity of lignin in the synthesis of lignin-based phenol formaldehyde resins [4]. The other more effective approach is through depolymerization to generate depolymerized

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lignin (DL) or oligomers with smaller molecules [5]. Using DL, biophenol–formaldehyde (BPF) resins of a phenol substitution ratio up to 75–90% was successfully produced in the authors' lab [5, 6].

Lignin de-polymerization methods mainly include biological method using enzyme and thermal method using heat (such as pyrolysis) and thermochemical methods using heat and chemicals [7–9]. Thermochemical depolymerization of lignin includes hydrolytic depolymerization using water and alkaline catalyst, reductive depolymerization using hydrogen, and oxidative depolymerization of lignin using in the presence of oxygen to produce aromatic aldehydes or carboxylic acids. Among those methods, biological process is a very slow process [1], while pyrolysis operated at 400–800 °C is fast, but lignin pyrolysis resulted in a low oil product yield (20–40 wt%) with high energy consumption in particular for wet feedstocks [2]. Thermochemical depolymerization of lignin operates under milder conditions requiring moderate temperatures (<400 °C) although under elevated pressure (up to 200 bar) commonly employing a catalyst [10].

This chapter focuses on lignin depolymerization via various thermochemical methods, i.e., hydrolytic, reductive and oxidative methods.

3.2 Hydrolytic Depolymerization of Lignin

Hydrolytic depolymerization process is performed in sub- or supercritical water to cleave the ether bonds of lignin in the presence of an acid or an alkaline catalyst, resulting in lower molecular weight oligomers or mono-phenolic compounds. The common operating conditions of lignin hydrolytic depolymerization processes are: in subcritical or supercritical water at 280–400 °C, 20–25 MPa, for a few minutes to few hours, at a water/lignin mass ratio of 2–50 with or without a base or acid catalyst [2, 7, 10]. Hydrothermal degradation of lignin produces various phenols, catechol, guaiacol, and other methoxy phenols through the hydrolysis of ether bonds. Further degradation of methoxy groups can take place, while the benzene ring is stable in this condition, as illustrated in Fig. 3.1 [10]. Additionally, heavier products, i.e., solid residue or char can be produced via the repolymerization/condensation of reaction intermediates at high temperatures and long reaction time during the hydrothermal treatment of lignin. The addition of catalysts such as K_2CO_3, $Ca(OH)_2$, and NaOH in water medium could reduce char formation and catalyze the lignin depolymerization [10]. Another effective way to improve lignin or DL solubility and prevent char formation is using a mixture of water with an organic solvent, e.g., water–ethanol [11, 12], water–methanol [13], water–butanol [14], water–phenol [15–17], water–isopropanol [18], water–acetone [19], and water–formic acid [20], etc. Severe formation of undesired biochar was observed in hydrothermal depolymerization of lignin in water at above 180 °C, and increased dramatically while further increasing temperature [21].

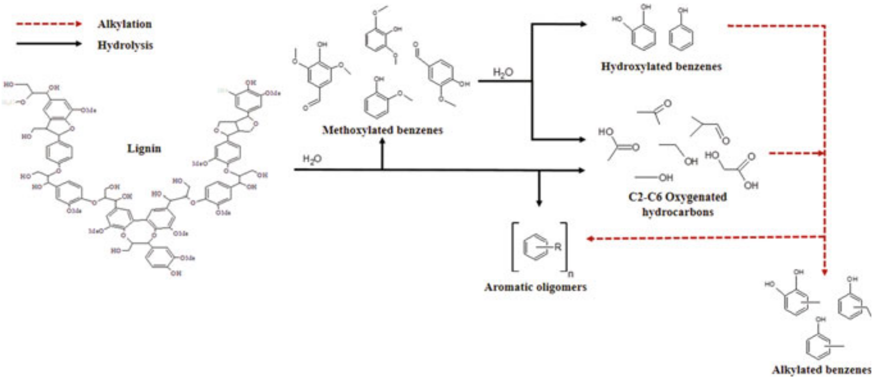

Fig. 3.1 Hydrothermal treatment of lignin, modified from Ref. [10]

To elucidate the mechanism of lignin hydrolytic depolymerization, lignin model compounds such as guaiacol have been investigated. For instance, in a study by Wahyudiono et al. [22], influences of reaction temperature and time were investigated on the product composition in hydrothermal treatment of guaiacol. The degraded products were mainly composed of catechol, phenol, and o-cresol at a maximum yield of 40.73, 14.18, and 4.45 wt%, respectively. With a longer reaction time, the compositions of both guaiacol oligomers (formed by repolymerization/condensation of reaction intermediates) and low molecular weight compound were found to both increase. From the kinetic analysis of the process at varying temperatures, the activation energy of the guaiacol decomposition and the formation of catechol, phenol, and o-cresol was reported to be approx. 39, 21, 65, and 180 kJ/mol, respectively. In a subsequent study by the same authors, catechol as another lignin model compound was hydrothermally treated in near- and supercritical water without any catalyst at temperatures of 643–693 K at various pressures [23]. Formation of phenol from catechol was found to proportionally increase with an increase in the water density. In addition, it was found that the decomposition of catechol followed a first order kinetics. The global rate constant in the range of $(3.0 \sim 11.0) \times 10^{-4}$ min^{-1} and the activation energy was determined to be 50.72 and 38.91 J mol^{-1} in near-critial water and supercritical water, respectively.

As mentioned above, the addition of catalysts such as K_2CO_3, $Ca(OH)_2$, and NaOH in water medium could reduce char formation and catalyze the lignin depolymerization [10]. An alkaline lignin was hydrolytically degraded in hot-compressed water–ethanol mixed solvent system with NaOH as a catalyst and phenol as a capping agent at 220–300 °C by the authors' group [11]. With increasing the reaction time and temperature, the phenol combination rate and the solid residue yield increased due to the repolymerization and crosslinking between the reactive sties of the combined phenol and the side chains of the degraded lignin. The optimum degradation conditions were determined to be: 1 h at 260 °C with the lignin/phenol ratio of 1:1 (w/w), obtaining almost 100% yield of degraded lignin and negligible formation of solid residue (<1 wt%) and gaseous products. The molecular weight of alkaline lignin decreased significantly from M_w ~ 60,000 g/mol (M_n ~ 10,000 g/mol) to M_w ~ 1000 g/mol (M_n ~ 450 g/mol) under the optimum conditions. The base-catalyzed lignin degradation mechanism was proposed for this process. Initially, the phenol-OH groups of lignin were converted into phenolate anions under alkaline condition, followed by several electron migration steps, and a phenolate side chain was eliminated through hydrolytic cleavage of an ether bond to form a quinone intermediate. Then, the quinone intermediate reacted with a sodium phenolate forming a phenol capped product. Simultaneously, OH^- could react with another ether bond to hydrolyze phenol-alkyl ether causing the formation a phenol and alkyl alcohol. The capping reaction between phenol and lignin side chain was limited due to the presence of abundance of water in the reaction media. Mahmood et al. [12] investigated the hydrolytic depolymerization of hydrolysis lignin (HL) in water and water–ethanol mixed solvent at 250 °C for 1 h with 20% (w/v) HL concentration in the presence and absence of catalyst (H_2SO_4 or NaOH). The non-catalyzed process of HL in water–ethanol mixture seemed to be the best condition for depolymerization of lignin with high yield of 70 wt% and low molecular weight of M_w ~1000 g/mol. Acid catalyzed depolymerization of HL in both media increased the molecular weight of the depolymerized HL, suggesting acid catalyzed repolymerization reactions. Alkaline hydrolysis process of the KL led to a reduction in M_w in water media and an increase in M_w in water–ethanol mixture.

Erdocia et al. [24] investigated on the hydrolytic depolymerization process with three different organosolv lignins (acetosolv, formosolv and acetosolv/formosolv) under alkaline hydrolysis conditions, and the composition of the resultant bio-oil and residual lignin were analyzed by GC-MS, MALDI-TOF and GPC. The highest oil production was obtained from the acetosolv lignin, while depolymerization of formosolv lignin produced bio-oil with the highest content (~30%) of monomeric phenolic compounds such as catechol owing to the lowest M_w of this lignin.

Water–alcohol mixed solvents were commonly used for hydrolytic depolymerization of lignin due to its better performance than the water-alone medium. The role of the presence of an alcohol in the mixed solvent was investigated by Yoshikawa et al. [14], where an organosolv lignin and kraft lignin was subjected to hydrolytic depolymerization using water/butanol (BuOH) mixture (4:1 molar ratio) over silica-alumina at 537–623 K for 2–4 h. Depolymerization of lignin in the water phase over the Lewis acid sites of silica-alumina forms lower molecular weight liquid products such as monomers, dimers, and oligomers. Water/butanol mixture then played an important role in extraction of the depolymerized fragments such as phenolic compounds and carboxylic acids from the water phase into BuOH phase (as illustrated in Fig. 3.2), which prevented the occurring of the repolymerization/condensation reactions of the DL intermediates and hence reduced solid residue (char) formation in the process.

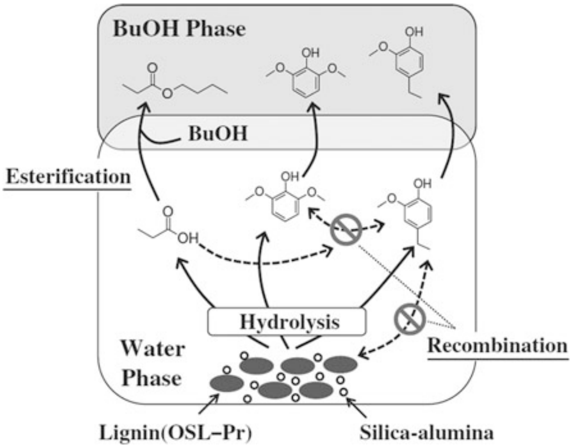

Fig. 3.2 Proposed reaction routes in the depolymerization of lignin using H_2O/BuOH mixed solvent over silica-alumina catalyst, reprinted with permission from Ref. [14]. Copyright (2013) Elsevier

In another similar study [25], hydrolytic depolymerization of various types of lignin was investigated in a novel water–butanol–hexane emulsion using an ionic liquid catalyst ($BSbimHSO_4$). This novel emulsion system was found to intensify the lignin depolymerization, under optimum conditions (0.5 g lignin, 20 mL of n-butanol, 20 mL of H_2O, 2 mL of n-hexane, 3 mmol of $BSbimHSO_4$, 523 K, and 30 min), approx. 90% of bagasse lignin was converted and the yield of desired phenolic compounds was about 30 mg/g, more than three times higher than that without the emulsion (mixed solvents). Hydrolytic depolymerization of other lignins (from rice straw, corn stalk and corncob) at the above optimum conditions led to >90% conversion of lignin, and a total yield of phenolic monomers >40 mg/g for the corn stalk or corncob lignin.

Base-catalyzed hydrolytic depolymerization of kraft lignin was performed in near-critical water (350 °C, 25 MPa) with K_2CO_3 (0.4–2.2 wt%) and water–phenol mixed solvent (approximately 4.1 wt% phenol), where 17% yield of phenolic monomers were obtained [26]. A rapid depolymerization of lignin was also conducted in water–phenol mixture at 400 °C without char formation [16]. After 0.1 h reaction, the molecular weight of lignin reduced from 2100 to 660 g/mol. With further increasing the reaction time to 1 h, the content of low molecular weight fragment increased and the DL showed 99% solubility in THF. The conversion of organosolv lignin was studied in supercritical water with or without phenol at 400 °C and various water densities in the range of 0–0.5 g/cm^3 [15]. Figure 3.3 shows the effects of phenol content in the water–phenol mixed solvents, reaction time and water density on the yield of tetrahydrofuran-insoluble products (TIS products or char). As shown in the Figure, the yield of TIS or char increased with increasing reaction time due to the repolymerization reactions of the reaction intermediates, but the TIS or char yield reduced by increasing the content of phenol in the water–phenol mixture solvent or by raising the water density.

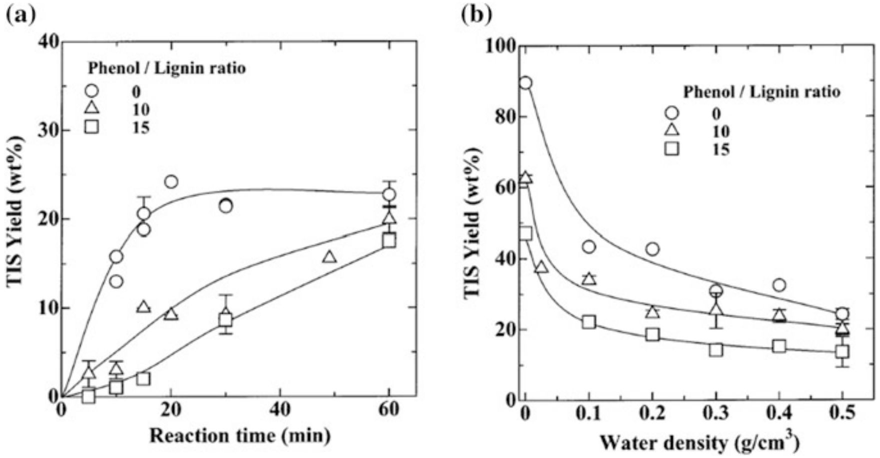

Fig. 3.3 Effects of phenol content (water density of 0.5 g/cm^3) (**a**) and water density (reaction time of 60 min) (**b**) on the TIS or char yield at 400 °C, reprinted with permission from Ref. [15]. Copyright (2003) American Chemical Society

3.3 Reductive Depolymerization of Lignin

Reductive depolymerization of lignin is realized by hydrogenolysis or hydrocracking in the presence of hydrogen and a supported catalyst, such as expensive carbon-supported Pt or Ru catalyst, at temperatures ranging from 300 to 600 °C to rupture the ether bonds of lignin by the addition of hydrogen [7]. The liquid products are mainly composed of volatile hydrocarbons together with phenol and methyl-, ethyl-, and propyl substituted phenol, catechols, and guaiacols [27]. At low temperatures, guaiacols are the dominant product with small amounts of aldehydes. While at high temperatures, the phenols are the more stable compounds with benzene, toluene, and xylene and the formation of char increases as well [27]. In reductive lignin depolymerization processes, hydrogen can be supplied externally in gaseous form [28, 29] or in situ via an active hydrogen donating solvents, such as formic acid [7, 20], 9,10-dihydroanthracene [30], sodium formate [20], and tetralin (1,2,3,4-tetrahydronaphtalene) [31].

3.3.1 *Reductive Lignin Depolymerization in Hydrogen Donating Solvents or Reductive Agents*

Many studies have demonstrated effective depolymerization of lignin using hydrogen donating solvents as in situ hydrogen source rather than external hydrogen source. Formic acid is an active hydrogen source as it decomposes at elevated temperature to produce hydrogen [32]. For instance, reductive depolymerization of kraft lignin (KL) was performed in an ethanol–water medium with formic acid as an in situ hydrogen donor by Huang et al. [7]. In this study, effects of various parameters such as reaction temperature, reaction time, concentration of formic acid, and ethanol concentration in ethanol–water reaction media were investigated to obtain the optimum reaction conditions. Formic acid decomposes to hydrogen and carbon dioxide at elevated temperature ($HCOOH \rightarrow H_2 + CO_2$). With increasing the concentration of formic acid, the molecular weight and polydispersity index (PDI) and solid residue (SR) reduced, accompanied by an increase in the yield of depolymerization (DL). The experimental results demonstrated that kraft lignin ($M_w \sim 10{,}000$ g/mol) was effectively converted into DL products of $M_w \sim 1270$ g/mol at a high yield of ~90 wt% (solid yield <1 wt%) at the optimum conditions (300 °C, 1 h, ethanol–water (50/50 v/v) and formic acid to lignin mass ratio of 0.7–2.4). The process also had a positive effect in reduction of the sulfur content from 1.5 wt% in the KL to 0.6 wt% in the DL product obtained under the optimum conditions.

Rahimi et al. [20] developed a novel process for depolymerization of oxidized lignin (aspen lignin) under mild conditions in aqueous formic acid with 60 wt% yield of aromatics of a low molecular mass. Oxidation of the C_α alcohol of lignin to a ketone was performed using stochiometric Mn or Cr oxide reagents to promote cleavage of the β-O-4 linkage (Fig. 3.4). While, the depolymerization of unoxidized lignin led to only 7.2 wt% yield of low molecular mass aromatics, depolymerization of oxidized aspen lignin under the formic acid/sodium formate reaction conditions at 110 °C for 24 h led to 52% lignin depolymerization efficiency, producing 19.8 wt% yield of well-known aromatic compounds, mainly syringlyl and guaiacyl-derived diketones, and 4 wt% yield p-hydroxybenzoic acid. The mechanism of cleavage of C–O linkages of the oxidized model compound is illustrated in Fig. 3.5 based on a redox-natural process without net consumption of formic acid.

Feghali et al. [33] reported reductive depolymerization of lignins using hydrosilanes and $B(C_6F_5)_3$ as a reductant and a Lewis acid catalyst, respectively, at ambient pressure and temperature. Hydrosilane contains slightly polar Si–H bonds which can be activated at low temperature to reduce C–O linkages. The Lewis acid catalyst enhances the reduction of a diverse carbonyl derivatives such as ketones, esters, amides, and carbonates. Lignin was converted into a liquid bio-oil with a low oxygen content for motor fuel application via one-step pyrolysis/solvolysis process

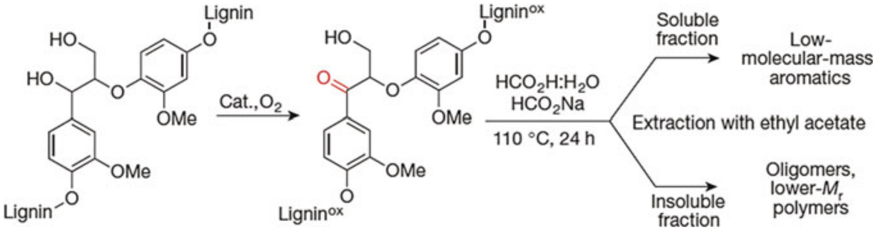

Fig. 3.4 Depolymerization of oxidized aspen lignin using formic acid, reprinted with permission from Ref. [20]. Copyright (2014) Nature Publishing Group

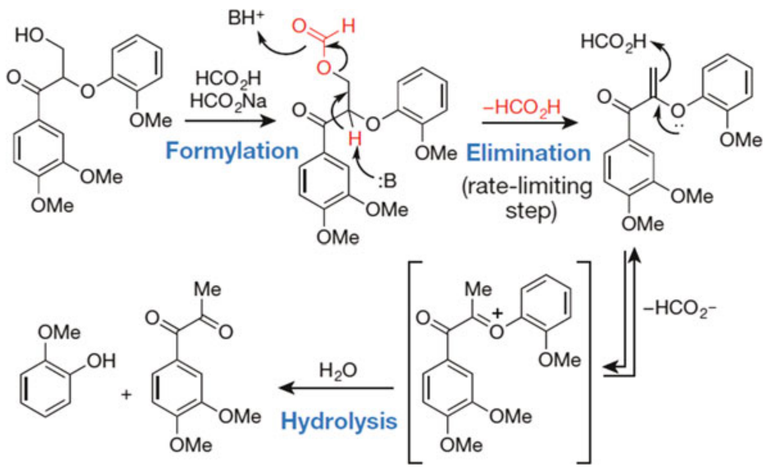

Fig. 3.5 Possible mechanism of cleavage of C–O linkages on the oxidized lignin model compound, reprinted with permission from Ref. [20]. Copyright (2014) Nature Publishing Group

in formic acid/alcohol mixture [34]. In this process, both depolymerization and deoxygenation occurred at the same time. Formic acid was used as a hydrogen source and alcohol acted as a solvent to improve the yield of bio-oil and the H/C (hydrogen to carbon) ratio with small amount of coke formation (5%).

A switchgrass lignin was depolymerized into phenolic monomers using formic acid as hydrogen source, ethanol as a solvent over 20 wt% Pt/C catalyst [35]. It was observed that the reaction time was predominant factor controlling the yield and composition of the DL products. After 4 h reaction, 21 wt% of lignin was converted into phenolic monomers including phenol, p-cresol, guaiacol, p-methylguaiacol, p-ethylguaiacol, p-propylguaiacol, and homovanillyl alcohol. With a longer reaction time (20 h), the yield of liquid-phase reached 76 wt% and the obtained liquid DL products had better quality with reduced O/C molar ratio by 50% and increased H/C molar ratio by 10%. Another similar work was reported by Huang et al. [36] in which supercritical ethanol was used as a hydrogen-donor solvent as well as a capping agent, stabilizing the highly reactive phenolic intermediates by O-alkylating the hydroxyl groups and by C-alkylating the aromatic rings. $CuMgAlO_x$ acted as an inexpensive catalyst. Ethanol was found to be more effective than methanol in depolymerization of lignin.

Organosolv lignins from hardwood and wheat straw were effectively depolymerized in supercritical carbon dioxide/acetone/water mixed solvent medium in the presence of low content of formic acid as hydrogen donor at 300 °C and 100 bar into monomeric aromatic compounds (10–12 wt% yield) [19]. The process is similar to other base-catalyzed lignin depolymerization processes, producing phenolic monomers rich in syringic acid and syringol (at a yield of ∼4 wt%) with wheat straw lignin and organosolv hardwood lignin, respectively.

The so-called Lignin-to-Liquid (LtL) process was reported by Kleinert and Barth [30], where lignin was depolymerized/liquefied to produce monomeric phenolic compounds at 350–400 °C in the presence of formic acid–isopropanol/ethanol mixed solvents. The liquid products were exclusively composed of monoaromatic phenols with several alkylations varying from C_1–C_2 side chains. The yield of the isolated phenolic fraction was as high as 25–35 wt% of the original lignin. Additionally, it was observed that the effects of temperature and residence time on the product yield were negligible.

Tetralin with capability of reversible hydrogenation/dehydrogenation can also be used as a hydrogen donation solvent for the liquefaction of lignin [10]. For instance, Thring et al. [37, 38] investigated conversion of an organosolv (ethylene glycol) hardwood lignin in the presence of tetralin over nickel–tungsten catalyst at temperature of 370–410 °C. Up to 60% of lignin was converted into various phenolic monomers, depending on reaction conditions. At harsh reaction conditions, lignin was mainly degraded into phenol, catechol, and their methyl and ethyl derivatives, while at mild reaction conditions, the dominant products were syringols, guaiacols, aromatic aldehydes, and ketones. The addition of nickel–tungsten heterogeneous catalyst could slightly improve the yield of monomeric phenolic compounds. The effects of tetralin were also studied on liquefaction of kraft lignin with molten $ZnCl_2$-KCl catalyst at 400–700 °C [39]. The results revealed that the addition of tetralin would produce hydrogen radical that can participate in the depolymerization of lignin, forming phenolic monomers (such as p-cresol, m-cresol, o-cresol, phenol, 2,5-xylenol, and 2,6-xylenol). Compared with the neat pyrolysis process, the introducing of 4 mol% tetralin improved the yield of phenolic monomers attained the maximum at 600–650 °C.

3.3.2 *Reductive Lignin Depolymerization in Gaseous Hydrogen*

External hydrogen sources or gaseous hydrogen has been commonly utilized for reductive depolymerization of lignin [10], and the presence of hydrogen contributed to significantly suppress the char formation and alter the yield and composition of the DL products [27]. Heterogeneous metal catalysts (commonly expensive noble metals such as Ru, Pd, Rh, and Pt) have been widely used for promoting hydrogenation/hydrogenolysis reactions in lignin depolymerization with hydrogen through activating hydrogen [10].

A novel two-step process was proposed by Yan et al. [40] for degradation of lignin over noble metal catalyst such as Ru/C, Pd/C, Rh/C, and Pt/C. In the first step, catalytic cleavage of C–O–C linkages in lignin takes place in water or dioxane/water (v/v = 1:1), to produce lignin monomer,dimer and oligomer fragments. In a second step, the formed fragments are undergone hydrogenolysis reactions to transform into C_9 and C_{14}–C_{18} alkanes and methanol byproduct, as illustrated in Fig. 3.6. Over Pt/C catalyst at 200–250 °C with 4 MPa H_2 for 2 h, the

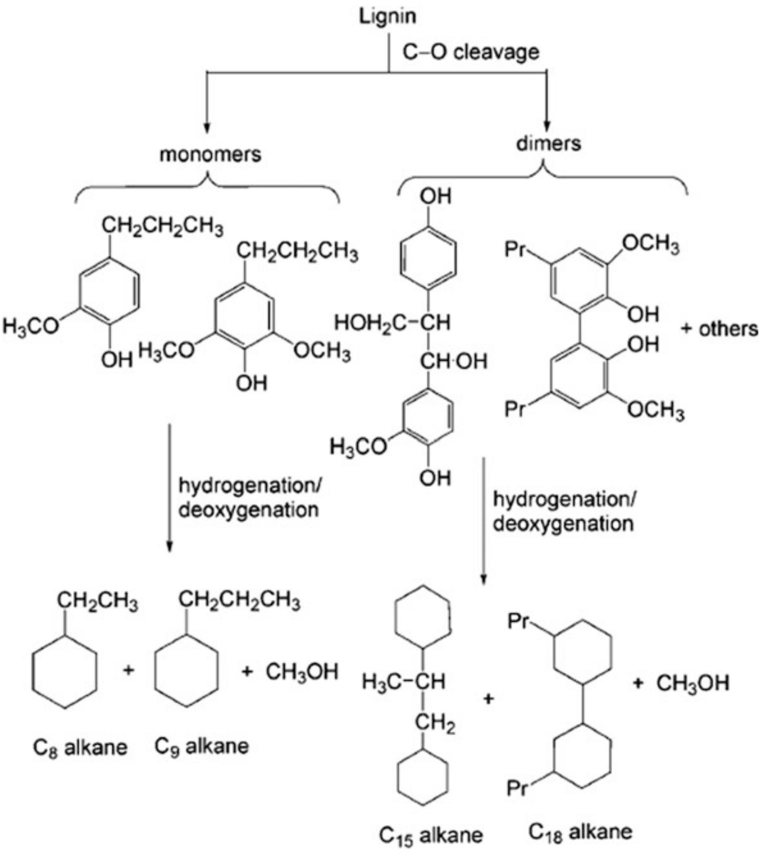

Fig. 3.6 Conversion of lignin into alkanes and methanol by hydrotreatment, reprinted with permission from Ref. [40]. Copyright (2008) John Wiley and Sons

highest yield of monomers and dimers attained 33.6 and 8.7 wt%, respectively, with a total yield of over 42 wt%. Incorporation of H_3PO_4 (0.2 wt%) into the reaction system further enhanced the yields of monomers to 37.9 wt% and dimers to 9.9 wt%. Addition of a co-solvent such as dioxane or ethylene glycol mono ethyl ether could also improve the yields of monomers and dimers.

Reductive depolymerization of organosolv lignin (OL) with gaseous hydrogen was performed by the authors [41]. In this process, OL was dissolved in acetone in the presence of Ru/C as a catalyst and reacted for 1 h at 350 °C at the initial pressure of 100 bar H_2. The resulting viscous liquid product was designated as depolymerized organosolv lignin (DOL) rich in phenolic monomers, and the yield of DOL in this reductive depolymerization process was as high as 85 (±2) wt%. In a similar study, a pyrolytic lignin was undergone hydrotreatment in dodecane solvent for 1 h at 350 °C with 100 bar hydrogen pressure with Ru/C catalyst [31], producing cyclohexanol, alkyl-substituted cyclohexanols, cyclohexanol and linear alkanes that can be used as a fuel additive. The effects of other catalysts such as Ru/ZrO_2/SBA-15 and Ru/SO_4^{2-}/ZrO_2/SBA-15 were examined on the hydrocracking of pyrolytic lignin at 260 °C in supercritical ethanol [42]. A small amount of pyrolytic lignin was converted to coke or tar and the liquid fuel was the predominant product with a high heating value of 34.94 MJ/kg. The liquid product consisted mainly of phenols, guaiacols, anisoles, esters, light ketones, alcohols, and long-chain alkanes, among others.

In addition to the supported noble metal catalysts, molybdenum proved to be an inexpensive but effective catalyst for reductive degradation and hydrotreatment of lignin [43]. In a study by Cheng et al. [44], reductive depolymerization of alkali lignin (AL, $M_w \sim 60{,}000$ g/mol) was investigated in sub/supercritical conditions of water–ethanol (50/50 v/v) and pure ethanol at 200–450 °C under 5 MPa H_2 with or without a catalyst. Various catalysts such as Ni10/Al_2O_3, Ru10/Al_2O_3, Pt10/AC, Ru10/AC, and Ni10/AC, prepared by the incipient wetness impregnation method, were used. Although the addition of the catalyst in either solvent systems had less significant effect on the yield of DLs, the DLs exhibited improved solubility in tetrahydrofuran likely owing to its lower molecular weight. Degradation of AL at 300 °C for 2 h without catalyst in 50/50 v/v water–ethanol mixture produced DL with M_w of $\sim$1000 g/mol at 89 wt% yield. Meier et al. [45] reported a study on catalytic hydropyrolysis of organocell lignin in a semi-continuous reactor, where it was found that oil yield was significantly affected by hydrogen pressure and the total oil yield (middle and light oils) attained over 80 wt% at 400 °C, 14 MPa H_2, for 360 min using inexpensive catalysts, i.e., nickel or chromium oxide supported on alumina/silicate. Nickle-based catalysts demonstrated to be very effective for production of phenolic monomers (such as propylguaiacol and propylsyringol) by reductive depolymerization of a birch wood lignin in an alcohol such as methanol, ethanol, and ethylene glycol under H_2 [46]. The mechanism of lignin degradation in an alcohol solvent was proposed to be through a two-step process. Firstly, lignin thermally decomposes into smaller lignin fragments, and the second step involves the hydrogenolysis cleavage of the fragments into monomer phenols. In addition, NiAu catalyst was found to be an efficient catalyst for hydrogenolysis of organosolv lignin in pure water at a low temperature (170 °C), yielding 14 wt% aromatic monomers [47].

One strategy for reducing the cost of noble metal catalysts may be addition of an inexpensive homogenous catalyst (such as H_2SO_4) as a co-catalyst together with a noble metal catalyst for lignin depolymerization. For instance, Pt/Al_2O_3 and H_2SO_4 as a co-catalyst demonstrated to be effective in reductive depolymerization of lignin in water/ethanol solvent, yielding 17 wt% of monomeric guaiacol-type products, compared to less than 6 wt% yield with the Pt/Al_2O_3 catalyst only. Another strategy for reducing the cost of noble metal catalysts can be addition of an inexpensive metal to a noble metal, to form bimetallic catalysts. For instance, Zhang et al. [48] developed a series of bimetallic catalysts such as NiRu, NiRh, and NiPd and tested them in the hydrogenolysis of lignin in water medium. It was found that NiRu catalyst, composing of 85% Ni and 15% Ru, had a synergistic effect on depolymerization of β-O-4 ether bonds under low temperature (100 °C) and low H_2

pressure (1 bar) owing to the increased concentration of surface metallic atoms, enhancing H_2 and substrate activation. Similarly, other bimetallic catalysts: NiRu and NiPd also exhibited better reactivity and selectivity for the hydrogenolysis of lignin, compared to their single-component counterparts. Tungsten phosphate (WP) based-catalyst was found to be active for hydrogenolysis of alkaline lignin in water–ethanol solvents [49], where doping Fe and Ni into WP/C catalyst, resulted in increased selectivity of phenols formation while the overall yield of phenol reduced.

Other novel inexpensive supported metal catalysts, such as Cu-doped porous metal oxide derived from an easily prepared hydrotalcite precursor [50], activated carbon-supported α-molybdenum Carbide catalyst (α-MoC_{1-x}/AC) [51], and Ni-supported double layered hydrotalcite [52], were reported in the literature for reductive depolymerization of lignin for the production of aromatic monomers at 250–300 °C.

3.4 Oxidative Depolymerization of Lignin

Oxidative depolymerization of lignin is realized by oxidation or oxidative cracking of the lignin macromolecule due to the presence of hydroxyl groups [2, 27]. Various linkages of lignin such as aromatic rings, aryl ether bonds could be cleaved to form phenols, aromatic aldehydes or carboxylic acids, depending on the reaction conditions [2, 53]. Nitrobenzene, hydrogen peroxide, and metal oxides such as CuO, Fe_2O_3 are the most common oxidants for lignin depolymerization [2, 8, 27]. Figure 3.7 shows a proposed mechanism for the oxidative depolymerization of lignin by molecular oxygen as the oxidizing reagent [27].

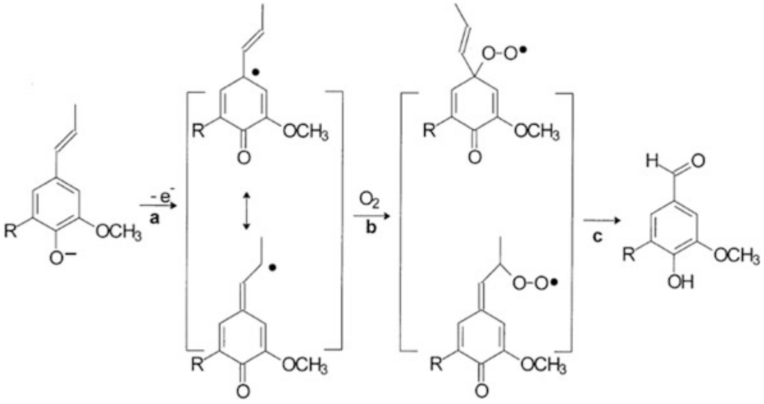

Fig. 3.7 A proposed mechanism for the oxidation of lignin, reprinted with permission from Ref. [27]. Copyright (2000) Elsevier

Oxidative degradation of five types of lignin including pyrolytic lignin, hydrolytic lignin, alkali lignin, sodium lignosulfonate, and calcium lignosulfonate was examined over $H_5PMo_{10}V_2O_{40}$ catalyst using molecular oxygen [54]. Effects of the property of lignin, reaction temperature, reaction time, concentration of catalyst, solvent, and initial O_2 pressure were evaluated. The oxidative depolymerization of pyrolytic lignin produced the best yield of aromatic DL product (over 65 wt% at the optimal conditions). The applied catalyst was recyclable and reused for five times without obvious deactivation.

In another study by Hasegawa et al. [55], hydrothermal oxidation of various types of lignin was performed to produce organic acids in the presence of diluted hydrogen peroxide as an oxidant at 150–200 °C. The mechanism of production of organic acids by hydrothermal oxidation of lignin was proposed and illustrated in Fig. 3.8. The treatment of alkali lignin at 200 °C for 2 min led to production of organic acids, namely formic, acetic and succinic acids, at an overall yield of 0.45 g/g, and the remaining was DL product with M_w >1000 g/mol. While the oxidative depolymerization of organosolv lignin gave the total yield of organic acids of 0.2 g/g and DL product with a smaller M_w ~300 g/mol. Thus, the molecular structure of original lignin played a considerable role in the distribution of the DL products.

Lignin was oxidatively depolymerized by polyoxometalates in the presence of ethanol or methanol as a solvent, and polyoxometalates (POM) such as $H_3PMo_{12}O_{40}$ acted as reversible oxidants and radical scavenger to prevent repolymerization

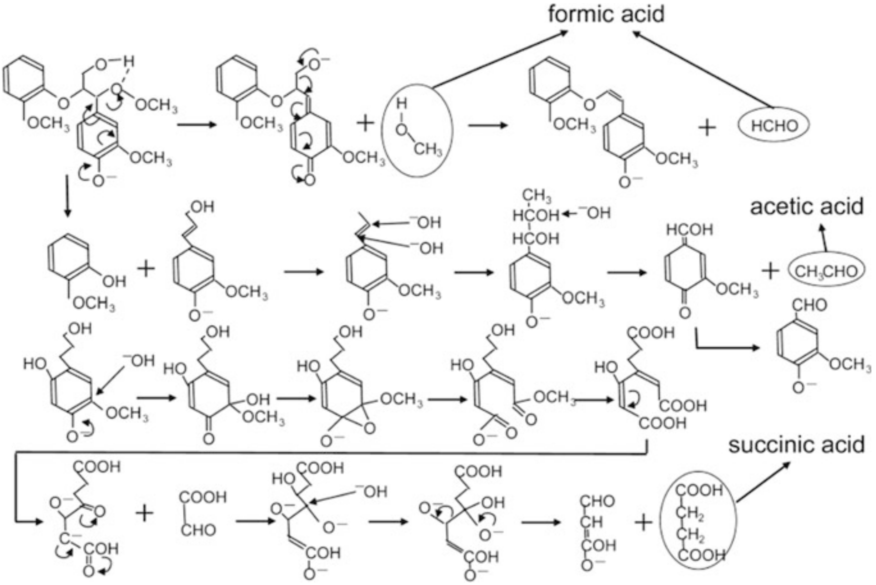

Fig. 3.8 Proposed mechanism for formation of organic acids, reprinted with permission from Ref. [55]. Copyright (2011) American Chemical Society

reactions [56]. The addition of ethanol or methanol into aqueous $H_3PMo_{12}O_{40}$ media greatly improved the production of monomeric compounds by a factor of up to 15. The main species in the obtained products were in vanillin and methyl vanillate (in methanol/water mixed solvent) as well as ethyl vanillate (in ethanol/water mixture). The yields and distribution of vanillin and methyl vanillate products from kraft lignin at 170 °C for 20 min in the presence of methanol–water versus water, POM ($H_3PMo_{12}O_{40}$) versus H_2SO_4, and N_2 versus O_2 atmosphere are comparatively shown in Table 3.1. The results in the Table clearly show that the presence of alcohol, $H_3PMo_{12}O_{40}$ or O_2 atmosphere remarkably enhanced the yields of vanillin and its derivatives. The oxidative depolymerization of kraft lignin at 170 °C for 20 min in the presence of methanol–water (16/4, v/v), $H_3PMo_{12}O_{40}$ and O_2 atmosphere produced a combined yield of vanillin and methyl vanillate at 5.18 wt% in relation to the weight of dry lignin employed.

Various transition metal catalysts in ionic liquids were applied in oxidative depolymerization of beech lignin [57]. $Mn(NO_3)_2$ in 1-ethyl-3-methylimidazolim trifluoromethanesulfonate [EMIMI][CF_3SO_3] was found to be the most effective reaction medium for the lignin oxidation process. Beech lignin was converted into phenol, unsaturated propylaromatics, and aromatic aldehydes at the maximum yield of 66.3% after 24 h reaction at 100 °C in 84×10^5 Pa air. Zakzeski et al. [58] reported the catalytic oxidation of Alcell lignin, soda lignin, and lignin model compounds over several transition metal catalysts in the ionic liquid 1-ethyl-3-methylimidazolium diethylphosphate (EMIM DEP). Under mild conditions, $CoCl_2 \cdot 6H_2O$ in EMIM DEP showed the best performance for the lignin oxidation. The 5-5′, β-O-4, and phenylcoumaran linkages remained unchanged during the oxidation reaction, while benzyl and alcohol functional groups were severely decomposed. A comprehensive study was conducted to elucidate the reactions involved in oxidative conversion of several lignin model compounds:

Table 3.1 Production of vanillin and methyl vanillate from kraft lignin at 170 °C for 20 min, reprinted with permission from Ref. [56]

Acid	Solvent (mL)		pH		Gas	Products (mg)		Yield[a] (%)
	H_2O	MeOH	Start	End		Vanillin	Methyl vanillate	
H_2SO_4	20	0	1.13	0.98	N_2	0.47	0	0.26
POM	20	0	1.13	0.91	N_2	3.35	0	1.84
H_2SO_4	4	16	1.00	1.17	N_2	1.06	0.80	1.01
POM	4	16	1.15	1.27	N_2	1.06	1.3	1.29
H_2SO_4	20	0	1.11	0.95	O_2	2.17	0	1.18
POM	20	0	1.13	0.92	O_2	4.49	0	2.45
H_2SO_4	4	16	1.13	1.28	O_2	2.94	2.12	2.76
POM	4	16	1.13	1.24	O_2	4.99	4.51	5.18

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[a] Combined amount of vanillin and methyl vanillate divided by the weight of dry lignin employed

veratryl alcohol, cinnamyl alcohol, and a model compound with a β-O-4 linkage in the presence of cobalt catalyst and ionic liquids by in situ ATR-IR, Raman, and UV–Vis spectroscopy [59]. Figure 3.9 displays the possible reactions and products from oxidation of each lignin models.

Compared to the above mentioned heterogeneous and homogenous catalytic processes, electrochemical catalysis processes could be efficient for depolymerization of lignin without using any complex organometallic catalysts, hence it could be a cheaper and more environmentally friendly method. For instance, electro-catalytic oxidative depolymerization of an alkali lignin was performed in triethylammonium methansulfonate as a protic ionic liquid (PIL) using anodes coated with oxidation-stable ruthenium–vanadium–titanium a potential ranging from 1.0 to 1.5 V [60]. Lignin was successfully cleaved into a wide range of aromatic fragments including 3-methylfuran, 3-furaldehyde, benzaldehyde, acetovanillone, m-tolualdehyde, guaiacol, 2,6-di-tert-butyl-4-methyl-phenol, diphenylether, 2-methoxy-4-vinylphenil, syringol, and vanillin. The product composition are strongly affected by the applied potential, and with increasing the potential, low molecular weight aromatic compounds became the predominant products in the electro-catalyst process. Figure 3.10 illustrated a possible mechanism of the electro-catalytic oxidative cleavage of the lignin C_α–C_β bond, involving the formation of H^+ and a proton conducting ionic liquid.

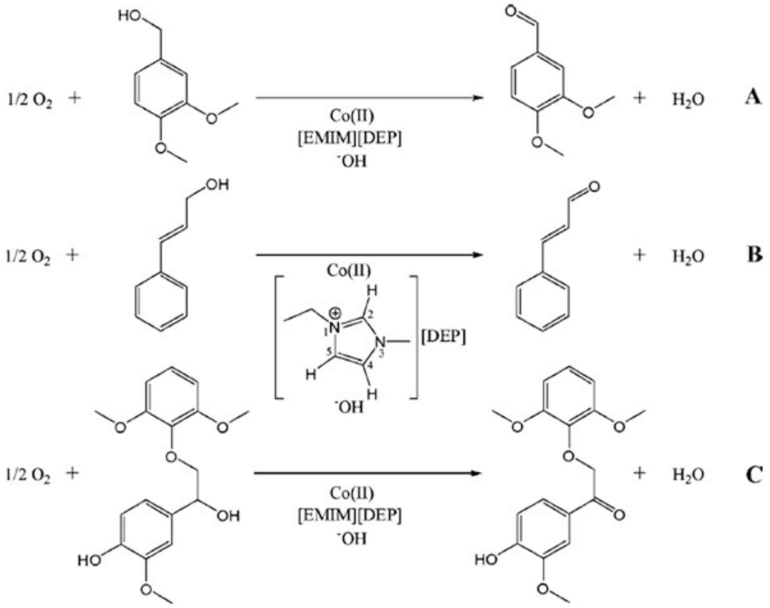

Fig. 3.9 Oxidative conversion of **A** veratryl alcohol to veratraldehyde, **B** cinnamyl alcohol to cinnamaldehyde, and **C** β-O-4 model compound to the corresponding ketone, reprinted with permission from Ref. [59]. Copyright (2011) Royal Society of Chemistry

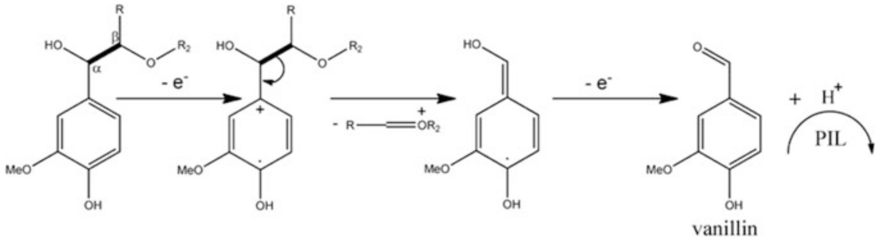

Fig. 3.10 Possible mechanism of the electro-catalytic oxidative cleavage of the lignin C_α–C_β bond, reprinted with permission from Ref. [60]. Copyright (2012) Royal Society of Chemistry

3.5 Summary

Lignin has lower reactivity and high steric hindrance effect due to its large molecular weight and branched structure, which limits the direct use of lignin as chemicals. One approach to enhance reactivity of lignin is through chemical modification of the chemical structure of lignin, e.g., phenolation or methylolation of lignin could improve the reactivity of lignin in the synthesis of lignin-based phenol formaldehyde resins. The other more effective approach is through depolymerization to generate depolymerized lignin (DL) or oligomers with smaller molecules. DL products, with lower molecular weights and less steric hindrance effects and hence higher reactivity, can be used as bioreplacements for phenol, polyols and bisphenol A in the synthesis of phenol–formaldehyde (PF), polyurethane (PU) and epoxy resins.

This chapter focuses on degradation/depolymerization of lignin into value-added chemicals and fuels through thermochemical methods including hydrolytic, reductive, and oxidative depolymerization processes. Hydrolytic depolymerization cleaves the ether linkages of lignin to produce low molecular weight phenolic compounds in sub- or supercritical water under acidic or alkaline condition. Using the mixture of water and organic solvent (such as alcohol, acetone or phenol) could prevent the repolymerization of lignin fragments and improve the stability of phenolic oligomers in hydrolytic treatment. The reductive depolymerization is another thermal treatment of lignin to generate biophenols in the presence of gaseous hydrogen or hydrogen donating solvents (such as formic acid, ethanol, propanol, and tetralin). The char formation could be reduced with increasing the hydrogen content in the reductive depolymerization of lignin. Oxidative depolymerization of lignin is realized by oxidation or oxidative cracking of the lignin macromolecule due to the presence of hydroxyl groups. Various linkages of lignin such as aromatic rings, aryl ether bonds could be cleaved to form phenols, aromatic aldehydes or carboxylic acids, depending on the reaction conditions. Nitrobenzene, hydrogen peroxide, and metal oxides such as CuO and Fe_2O_3 are the most common oxidants for lignin depolymerization. In general, the yield and the product composition of these lignin depolymerization processes are predominantly affected by type of lignin, residence time, reaction temperature, concentration of catalyst, and composition of the solvent as the reaction media.

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Chapter 4
Utilizations of Lignin for Polymer Reinforcement and Carbon Fibers

Abstract This chapter describes the performance of lignin as a reinforcement filler for thermoplastic polymers as well as its potential as a precursor for production of carbon fibers. Literature studies show that lignin could improve the antioxidant, thermal stability, mechanical performance, UV stability, and biodegradability of various thermoplastic polymers such as natural rubber, PE, PP, SBR, PVC, and polystyrene. However, the polarity and relatively large particle size of lignin could limit its miscibility with the polymeric matrix. To overcome this challenge, it is required to modify lignin to reduce its polarity before compounding with thermoplastic polymers. In addition, lignin is a renewable source of carbon and can be utilized into carbon fibers. There are three categories of carbon fibers that incorporate lignin in the manufacturing processes: (1) carbon fibers from raw lignin without any further modification, (2) carbon fibers from physical lignin/polymer blends, and (3) carbon fibers from modified lignin.

Keywords Lignin · Reinforcement filler · Precursor · Carbon fibers · Thermoplastic polymers · Polarity · Miscibility · Modified lignin

4.1 Lignin for Polymer Reinforcement

Lignin, as a major component of lignocellulosic plants, is a polar hydrophilic macromolecule with on average one or two hydroxyl groups per building block with surface energies of 53–56 mJ/m^2. It provides rigidity to the cell walls in plants, contributing to the resistance of the plants to impact, bending, and compressive deformation [1, 2]. Some unique properties of lignin, such as immense availability, environmental friendliness, biodegradability, low price, antioxidant, and reinforcing capability, make it as a promising candidate for applications as a reinforcing filler to modify various polymers (plastics or rubbers) [3]. Lignin has been incorporated in wide varieties of thermoplastics such as polyethylene [4], polypropylene [2, 5], natural rubber (NR, cis-1,4-polyisoprene) [6–9], styrene-butadiene rubber (SBR)

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[1], neoprene rubber [8], polyvinyl acetate [10], polyethylene terephthalate (PET) [11], poly(vinyl chloride) (PVC) [12], rosin [13] and nitrile rubber [8], etc. It was observed that the incorporation of lignin into various polymers could enhance the properties of the final products such as crosslink density, thermal stability, mechanical performance, processability, and biodegradability [2, 6, 14, 15]. On the other hand, there are two main obstacles that could limit the application of lignin as a filler in polymers are: its large particle size and the polarity of lignin that would decrease its compatibility and miscibility with polymers [1, 2, 16].

There are several methods to investigate the miscibility of polymer blends such as microscopy, thermal analysis, mechanical analysis, and solid-state NMR spectroscopy. The compatibility of kraft lignin in various polymeric matrices such as low density polyethylene, polypropylene, poly(methylene oxide), polyethylene oxide, polystyrene, polyacrylonitrile, polyvinyl chloride, plasticized polyvinyl chloride, polyvinyl acetate, poly(hydroxybutyrate-co-hydroxyvalerate), polyester amide, poly (butylene succinate-adipate)(bionolle), and starch was examined by Pouteau et al. [17] using image analysis. The polarity of the polymers played a significant role on the production of a compatible blend with lignin. When the solubility parameter of the polymer is low ($\Delta\delta = 1$ cal·cm^{-3}), both homogeneous and heterogeneous systems were obtained. It was observed that lignins were lower molecular weights and are more compatible with nonpolar or very polar polymer matrixes. In some research, the surface of lignin has been modified by grafting to improve its miscibility into polymeric matrix [18–20]. For instance, poly(lactic acid) (PLA) was grafted onto lignin by ring-opening polymerization in a presence of triazabicyclodecene to produce lignin-g-PLA copolymers [21]. The lignin-g-PLA copolymers were then used as dispersion modifiers in PLA-based polymers to improve the polymers' UV absorption property and to reduce their brittleness.

Extensive studies have been conducted on reinforcement of polymers by introduction of lignin [1, 4, 22]. In the following sections, the applications of lignin in various thermoplastic/lignin composites and their properties and performance are reviewed.

4.1.1 Natural Rubber (NR)/Lignin Composites

Effects of lignin on the thermo-oxidative performance of a carbon black-filled natural rubber (NR) were investigated by Gregorova et al. [6] and compared with a commercial rubber antioxidant, N-phenyl-N-isopropyl-p-phenylene diamine (IPPD). It was revealed that the presence of lignin in the rubber formulation at concentration of 1–8 phr (parts per hundred parts of rubber) increased the crosslink density during the accelerated due to the presence of sulfur in the lignin which took part in further crosslinking. As a result, the tensile properties of the NR/lignin composites increased after aging process, comparable with the IPPD stabilized samples. In addition, the performance of the commercial antioxidant IPPD was improved by the addition of 1 phr lignin. A sulfur-free lignin was utilized as a stabilizer in vulcanizates that contain NR to inhibit the thermal degradation of vulcanizates [7]. The addition of lignin changed the curing characteristics of NR, increasing the minimum torque and cure rate while decreasing the maximum torque, scorch time, and optimum cure time. It could be explained by the hydroxyl groups on the structure of lignin, which accelerated the vulcanization process. In addition, the presence of lignin in the NR vulcanizates greatly enhances most of the physicomechanical properties such as 100% modulus, tensile strength at break and elongation at break for the composites with lignin at all concentration, although it has negligible effect on hardness, as shown in Table 4.1. Moreover, the thermal stability of the NR vulcanizates was promoted by the addition of lignin due to radical scavenging of lignin and, the best performance was observed with the NR vulcanizate containing 20 phr lignin.

Jiang et al. [23] reported a novel method to prepare nano-lignin/NR composites. First, colloidal lignin-poly (diallydimethylammonium chloride) (PDADMAC) complexes (LPCs) were formed via self-assembly technology. The LPCs have an average particle size <100 nm owing to extensive interactions between lignin and PDADMAC via cation-π and π-π linkages. Then, the nano-lignin/NR composites were produced by addition of LPCs into NR to form LPCs/NR composites. It was observed that thermal stability, thermos-oxidative stability, and mechanical properties of the obtained LPCs/NR composites were all enhanced substantially, attributed to the homogeneous dispersion of nano-LPCs in the natural rubber matrix.

The mechanical and dielectric properties of composites of NR-soda lignin or NR-thiolignin were evaluated by Botros et al. [24]. Incorporation of both lignins into the natural rubber reduced curing time, tensile strengths, and elongations at break, but it increased maximum torque and thermal stability. NR-thiolignin composite at 20 phr of lignin loading exhibited the best thermal stability. On the other hand, the permittivity (ε′) of composites was measured over frequency range from 100 Hz to 100 kHz at 20–80 °C. It was noticed that ε′ of the composites increased by increasing the loading content of thiolignin into NR, attributed to an increase in the orientation polarization owing to the presence of C=S dipoles on the thiolignin structure.

Table 4.1 Mechanical properties of lignin-filled NR vulcanizates, reprinted with permission from Ref. [7]. Copyright (2006) John Wiley and Sons

Lignin content (phr)	Modulus 100% (MPa)	Tensile strength (MPa)	Elongation at break (%)	Hardness (Shore A)
0	–	1.87 ± 0.33	89 ± 9	48 ± 1
10	2.29 ± 0.31	3.99 ± 0.25	187 ± 21	48 ± 1
20	2.46 ± 0.020	10.61 ± 2.31	267 ± 19	50 ± 1
30	2.48 ± 0.25	16.83 ± 4.21	357 ± 83	51 ± 1

4.1.2 Polyethylene (PE)/Lignin Composites

Kraft lignin and NovaFiber lignin (a sulfur-free lignin derived from a novel alkaline-pulping process) were used as UV stabilizers (owing to lignin's better UV absorption property) in polyethylene, compared with HALS (Hindered Amine Light Stabilizer) [4]. The mechanical properties (stiffness, strength, and elongation properties) of both lignin stabilized polyethylene composites remained approximately unchanged after exposing to UV radiation up to 42 days. Both types of lignin showed good performance as a UV stabilizer for PE, comparable to the relatively expensive HALS, hence lignin has a great potential as UV stabilizers for thermoplastics for its superb cost performance index. Lignin can also be used in wood/polymer composites (WPC) as effects of lignin addition on photodegradation of wood/high-density polyethylene (HDPE) composite were investigated using UV–Vis spectrophotometry, FTIR, SEM, and DSC [25]. Lignin at various amounts 0–29 wt% (with respect to the total mass of lignin and wood flour) was blended with wood flour and then compounded with HDPE in a twin-screw extruder. In each composite, the total content of lignin and wood flour remained at 20 wt% over the entire composite. It was found that the presence of lignin facilitated the photodegradation of HDPE matrix in WPCs under UV weathering, due to the strong UV absorption property of lignin originated from the chromophoric groups of lignin.

High-density polyethylene (HDPE) composites with high lignin content (up to 73 vol.%) were fabricated by the catalytic grafting technique of polyethylene on lignin particles [26]. Such catalytic grafting technique enhances the wetting, adhesion, and dispersion of lignin particles into the HDPE matrix, resulting in composites with improved morphology and tensile/impact properties. Sailaja and Deepthi [19] investigated the mechanical and thermal properties of low density polyethylene (LDPE)/lignin composites. Maleic anhydride was used as a compatibilizer as it can graft lignin to form esterified lignin, improving compatibility of lignin with LDPE. The results revealed that LDPE/lignin composites with up to 40% lignin content provided comparable mechanical performance with the neat LDPE, and addition of the compatibilizer improved the mechanical properties. Moreover, the char content increased with increasing the lignin content in LDPE composites, suggesting improved thermal stability of LDPE by addition of lignin (or esterified lignin).

4.1.3 Polypropylene (PP)/Lignin Composites

The annual global consumption of polypropylene was reported to be approximately 30 million tons and the properties of the final product could be adjusted using a variety of additives [5]. Many studies have reported oxidative degradation of polypropylene and performance of a number of antioxidants. The acceptable properties of antioxidants are their good solubility, mobility, low volatility, and stabilizing efficiency [2, 5]. Quite a few studies have demonstrated that lignin can be a promising antioxidative agent with potential in application for polypropylene (PP) composites. Photooxidation of PP composites containing up to 10 wt% beech pre-hydrolysis lignin (hardwood) or spruce organosolv lignin (softwood) was examined by Kosikova et al. [27]. The results indicated that the type and content of lignin could change its role as a stabilizer or initiator for polymer degradation. For instance, the PP film containing 2 wt% pre-hydrolysis lignin showed similar photostability compared to the PP film stabilized with 0.15 wt% 2,6-di-tert-butyl-4-meyhylphenol. Antioxidative effect of lignin on PP and recycled PP was examined by non-isothermal differential scanning calorimetry (DSC) [5]. Both PP samples were blended with 0.5–10wt% lignin and compared with a synthetic antioxidant Irganox 1010 (pentaerythrityl terakis [3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate]). The onset oxidation temperature (T_i) of the lignin stabilized polypropylene was increased compared with the neat PP, while the effects were strongly affected by the lignin content (Fig. 4.1). A similar trend was observed for the recycled polypropylene. These results evidenced that lignin has a thermally stabilizing effect on the PP polymer. The results of this work also exhibited that the optimum concentration of lignin is between 2 and 5 wt% with the lignin of a low molecular weight (M_w 2000) and low polydispersity (1.2). The addition of lignin also increased the Vicat softening temperature of both PP blends. It could be concluded that lignin has a positive effect on oxidative stability of polypropylene, as well as its rigidity.

15 lignin samples were extracted from different botanical origins by using various delignification processes, then were incorporated at 1 wt% blending ratio into polypropylene to investigate the antioxidant behavior [2]. In this study, the solubility of lignin in PP matrix was assessed by optical microscopy to observe the distribution (size and number) of the lignin aggregates in the composites.

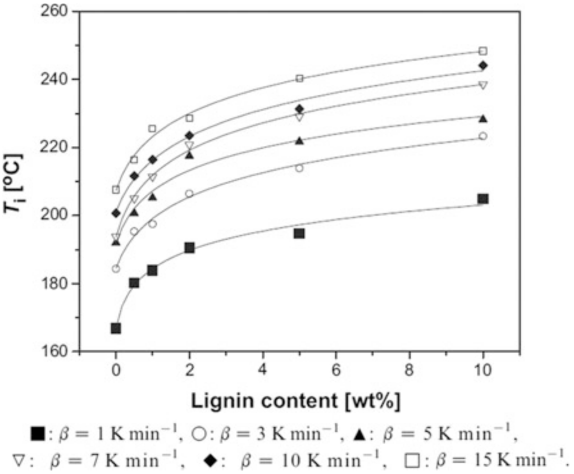

Fig. 4.1 Concentration dependences of the onset oxidation temperatures, reprinted with permission from Ref. [5]. Copyright (2005) Elsevier

The average molecular weights of the extracted lignins varied from 480 to 8300 g/mol with polydispersity of 2.0–7.0. The results demonstrated that lignins of a lower molecular weight and lower total hydroxyl content (aliphatic and phenolic) could improve its compatibility and consequently enhance the antioxidant activity. Moreover, it was demonstrated that the polydispersity of lignins have a negative effect on the solubility of lignin in PP—nonpolar matrix.

Kraft lignin and PP were undergone plasma treatment with acryloyl chloride, also known as 2-propenoyl chloride, in a rotating electrode-less plasma reactor to enhance the strength properties of the prepared composites [28]. In this modification, the surface of lignin particles and PP flakes was efficiently treated for a short reaction time. The compatibility of PP and lignin was improved by the copolymerization of acryloyl chloride on polypropylene and lignin induced by plasma-state graft co-polymerization.

Yu et al. [29, 30] succeeded to enhance the thermal and flammability properties of PP by introducing functionalized lignin grafted by phosphorous–nitrogen elements (PN-lignin). To further improve the thermal stability, 2 wt% nickel (cobalt or zinc) acetates were incorporated into the PP/PN-lignin composites. The TGA profiles of the PP-based composites with PN-lignin and the salt acetates additives are illustrated in Fig. 4.2, which evidences positive effects of PN-lignin and the salt acetates on the thermal stability of PP in a nitrogen condition. The presence of PN-lignin and $Ni(Ac)_2$ dramatically increased the char residue by 44% and improved the limited oxygen index (LOI) from 17.5 (pure PP) to 22 (PP/PN-lignin) and to 26 (PP/Ni $(Ac)_2$/PN-lignin), suggesting enhancement in flame retardancy of the PP-based composites. However, the addition of cobalt or zinc acetate did not show obvious effect on thermal properties and flame retardancy of the composite.

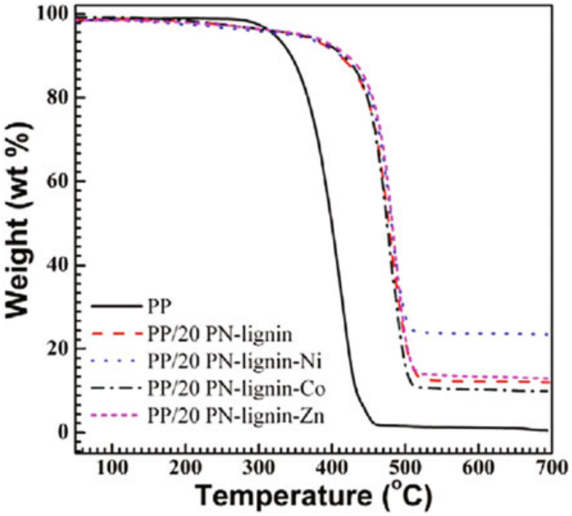

Fig. 4.2 TGA profiles of the PP-based composites with PN-lignin and the salt acetates additives, reprinted with permission from Ref. [29]. Copyright (2012) American Chemical Society

A series of lignin/PP composites were fabricated and their mechanical performances were evaluated by Toriz et al. [31]. The content of lignin varied from 10 to 60 wt%. The presence of unmodified lignin decreased the tensile and flexural strengths and unnotched Izod impact strength of PP, although improvement was observed on Young's and flexural moduli. The combination of unmodified lignin and mineral fillers including mica and talc, however, enhanced the mechanical properties of PP and improved the dispersion of lignin in the PP matrix. In addition, it was noted that treatment of lignin using a coupling agent such as maleic anhydride (MA) to form MA grafted PP (PP-g-MA) could improve the strength properties of the PP/lignin composites with the moderate content of lignin.

The influence of the incorporation of a organosolv lignin in PP/coir composites with/without a compatibilizer (maleic anhydride grafted polypropylene, PP-g-MA) on mechanical and thermal properties was studied [32]. Since lignin is less polar than lignocellulosic fibers, the incorporation of lignin increased the adhesion towards PP matrix. The introduction of lignin into PP/Coir composites (at 30% lignin and coir) did not alter the tensile strength significantly, but led to an abrupt increase in the initial thermal decomposition and oxidation induction times, attributed to the role of lignin as antioxidant agent. Rozman et al. studied the effects of lignin on mechanical properties of PP/coconut fiber composites [33]. Higher flexural properties were obtained by incorporation of lignin into the composites, whereas the tensile properties remained unchanged and the water absorption and thickness swelling reduced. In another published work by Rozman et al. [34], it was demonstrated that the addition of lignin improved the bonding strength between polar wood filler and nonpolar PP matrix and could increase the flexural and tensile properties of the composites.

An Alcell lignin chemically treated by glycidyl methacrylate (GMA) or allyl glycidyl ether (AGE) was used as a compatibilizer in the PP-oil palm empty fruit bunch (PP-EFB) [35, 36]. The compatibility of the systems could be enhanced by a series of linkages: (1) hydrogen bonding of hydroxyl and carbonyl groups of GMA and AGE with the hydroxyl groups of EFB, (2) van der waals bonding between the hydrocarbon groups of lignin with hydrophobic PP matrix, and (3) bonding between the unsaturated groups of GMA and AGE with PP polymer. The incorporation of the chemically treated lignin improved the mechanical properties (flexural modulus, flexural strength, tensile modulus, tensile strength, impact strength, and elongation at break) and increased the hydrophobicity of the PP-EFB composites. The GMA-modified lignin provided better mechanical performance than the AGE-treated lignin owing to its higher unsaturated groups (i.e., carbonyl groups).

The biodegradability of lignin-PP composites containing 4% organocell lignin was evaluated and the kinetics of *P. chrysosporium* culture was investigated [37]. A reduction in the elongation at break was observed after cultivation step and a correlation was determined between the decrease of mechanical property and the amount of the lignin fragments into the extracellular fluid. In another study, Milkulasova et al. [14] tested the biodegradability of lignin in polyolefin plastics using *phanerochaete chrysosporium* to reduce the environmental impact of the waste plastics. Lignin was blended with polyethylene (PE) or polypropylene (PP) in various concentrations 10, 20, and 30%. The growth of fungus was confirmed in the presence of lignin-PE and lignin-PP blends and the intensive amount of ligninolytic enzymes was detected during the cultivation process. The biodegradation of lignin produced oxidative species such as hydroxyl radicals which attacked the lignin component and cleaved the covalent bonds of the lignin. Also, the presence of lignin facilitated the biodegradation of PE and PP matrices and their tensile properties reduced after exposure to *P. chrysosporium*. The biodegradation efficiency of polyolefins increased with increasing the content of lignin in the composites.

4.1.4 Styrene-Butadiene Rubber (SBR)/Lignin Composites

Bahl and Jana [1] attempted to utilize lignosulfonate (LS) for reinforcement of nonpolar styrene-butadiene rubber (SBR). LS was first modified by cyclohexylamine (CA, a weak base) via acid–base reactions to reduce the polarity of LS and enhance its compatibility with SBR compounds via proton transfer and hydrogen bonding interactions. The modified rubber (100 wt. SBR with 30 wt. modified LS particles) showed a shorter curing time, and both the tensile strength at break and storage modulus were improved by 45 and 13%, respectively. Kramarova et al. [22] investigated the influence of various types of lignin as fillers in rubbers (natural rubber and SBR) on the vulcanization process. With lignin of a concentration above 20 phr, the crosslink density of SBR increased via the formation of cross bonds during the vulcanization process. SEM results demonstrated that the lignin added was dissolved in the elastomeric matrix and homogenous morphologies were obtained. Kosikova and Gregorova [38] investigated the reinforcement effects of a sulfur-free lignin derived from beech wood pre-hydrolysis on SBR. The average molecular mass and polydispersity of the lignin used were 2000 g/mol and 1.2, respectively. When the lignin was loaded at 20–50 phr into the SBR in the sulfur vulcanization process, a significant enhancement in physicomechanical properties was obtained. FTIR results indicated that the lignin added can interact with sulfur compounds during the vulcanization process, and the cure speed increased with increasing the addition amount of lignin, confirming the reinforcing effect of lignin. A novel hybrid filler of kraft lignin and carbon black was prepared by precipitating lignin from a solution onto carbon black particles via exploiting π-π stacking (non-covalent interactions) [16] and was then used in SBR, aiming to lower its viscoelastic loss. The formation of lignin coating layers on carbon black was characterized by electron microscopies (SEM and TEM), Raman spectroscopy, and zeta potential measurement. TEM images showed that nonspherical carbon black particles were coated by layers of kraft lignin. The hybrid fillers formed much less networking in comparison to carbon black, and the viscoelastic dissipation of the rubber with the hybrid fillers decreased by as much as 10%, compared to that of the rubber with only carbon black filler.

Xiao et al. [39] used lignin to improve the dispersion of layered double hydroxide (LDH) into SBR. Lignin-LDH complex was synthesized at various lignin contents by *in situ* method and then blended with SBR by the melt compounding method. X-ray diffraction and TEM confirmed well dispersion of lignin-LDH in SBR. The mechanical properties including tensile strength, elongation at break, 300% modulus, and hardness were all improved by the incorporation of lignin in the LDH/SBR composites. In addition, the thermal degradation temperature of lignin-LDH/SBR at 50% weight loss (T_{50}) shifted to a higher temperature compare to that of the LDH/SBR composite, suggesting the barrier effect of well-dispersed lignin-LDH in the rubber matrix.

4.1.5 Poly (Vinyl Chloride) (PVC)/Lignin Composites

Lignin can also be used for poly (vinyl chloride) (PVC)-based composites. For instance, a low M_w lignin was modified with methyl methacrylate (MMA) and used for interfacial modification in PVC/wood flour composites [40]. The MMA modified lignin could reduce the hydrophilicity of wood flour and improve the interfacial interaction between the wood flour and the PVC matrix. The treated PVC/wood flour composite containing 2 wt% of the modified lignin (MMA:lignin = 2:1 w/w) achieved the best mechanical performance, enhancing tensile strength and impact strength by 18.6 and 25.9%, respectively. Similarly, interfacial bonding of PVC/wood flour was improved by incorporation of a lignin-amine modifier [41].

The influence of poly(ethyl acrylate-co-acrylic acid), i.e., a polyacrylate, on the compatibility of lignin in PVC matrix was investigated by Liu et al. [12]. The carboxylic groups of the polyacrylate molecules were found to link into the surface of lignin by hydrogen bonds or ester linkages, which resulted in improved compatibility of the polyacrylate chains and lignin in PVC matrix. It was further found that the tensile and impact strengths of the lignin-PVC composites promoted even with a low loading amount of the polyacrylate.

4.1.6 Polystyrene/Lignin Composites

Lignin at a high content up to 80 wt% was introduced into polystyrene (PS) matrix and the mechanical, rheological and morphological properties of the prepared composites were studied [42]. SEM analysis showed that the poor wetting and poor interaction between lignin and PS and the fractured surface was very rough. Addition of a triblock copolymer, based on styrene and ethylene/butylene (SEBS) as a compatibilizer at 1 and 2 wt% improved the dispersion of lignin particles and the interfacial adhesion in the PS/lignin composites. With increasing the content of lignin, flexural and shear moduli of the composite enhanced, while the tensile strength, tensile modulus, and elongation at break reduced. Also, it was noticed that shear viscosity, storage (G′) and loss (G″) moduli increased by introducing the lignin particles due to the limited mobility of PS chains. El-Zawawy et al. [43] reported the use of lignin and lignin complex particles (modified with transition metal cations, cobalt (II)) as fillers at 5 wt% in PS composites for polymer packaging applications. The presence of lignin complex particles in PS decreased the glass transition temperature from 90.1 °C for pure PS to 86.7 °C for PS-Co(II)-lignin (5 wt%) composite and improved the tensile strength from 0.708 to 0.963 MPa.

4.1.7 Others Polymers/Lignin Composites

A series of poly(vinyl acetate) thermoplastic composites with kraft lignin at a high concentration of (85 wt%) and two plasticizers (diethyleneglycol dibenzoate, and indene) were fabricated [10]. The mechanical properties (tensile strengths and moduli) of the prepared thermoplastic composites were promising. The glass transition temperatures of these thermoplastics are near room temperature and the melt-flew index illustrates that these lignin-based polymeric materials can be processed by extrusion molding. Stibianu et al. [44] used lignin as a bulking filler (10–30 phr) in polydimethylsiloxane-α,ω-diol (PDMS). It was indicated that the introduction of lignin could reduce the cost of the materials and improve slightly the mechanical properties of the polysiloxane rubber, without altering the thermal properties.

Poly(ethylene terephthalate) (PET) was compounded with lignin with different percentages (2.5, 5, 10, and 20 wt%) with a single-screw extruder [11], where the dependency of thermal stability of PET on the content of lignin in the polymer bulk was studied. In general, at low temperatures (300–460 °C) the thermal degradation temperature shifted to a lower temperature, while at the higher temperature a reverse trend was observed. The addition of the lignin showed an antioxidant effect or a barrier effect on diffusion of gaseous products into the gas phase and diffusion of oxygen into the polymeric matrix during the thermal decomposition in air atmosphere. The addition of lignin influenced strongly on the melting behavior of the annealed samples. In another study, Canetti and Bertini [45] investigated the effects of lignin on the crystalline structure of PET. The morphology and particle size distribution of the lignin particles in the PET matrix were characterized with a polarizing optical microscopy (POM), a small-angle X-ray scattering (SAXS), and a wide-angle X-ray diffraction (WAXD). The lignin particles were found to disperse homogenously in the PET matrix with particles of a size from some tens of nm to some μm (70% of particles have a size from 0.15 to 0.5 μm). It was found that the crystallization rate of the PET/lignin composites was accelerated due to the nucleating effect of lignin. The Avrami analysis indicated that the crystallization process consists of primary and secondary stages, and the primary stages proceeded toward a higher percentage of the crystallizable PET fraction while increasing the content of lignin in the composites. Kadla and Kubo [46] investigated the miscibility of the blends of kraft lignin or methylated kraft lignin with poly(ethylene oxide) (PEO) by thermal analysis. The entire blends showed a single glass transition temperature (T_g), which confirmed the fully miscible blends. At low blending ratios of PEO (5–10%w/w) in lignin, the physical properties of lignin enhanced. However, increasing the PEO incorporation could disrupt the macromolecular structure of lignin, influencing the physical properties of lignin. The FTIR results indicated a strong hydrogen interaction between the aromatic hydroxyl proton in lignin and the ether oxygen in PEO. A novel absorbent was prepared by compounding poly(vinyl alcohol) (PVA) and a quaternized lignin for nitrate pollution treatment [47], where lignin was modified via phenolation reaction followed by quaternization reaction to produce the quaternized lignin. FTIR analysis confirmed the interaction of lignin and PVA via grafting quarternary ammonium groups or linkage of hydroxyl groups of PVA onto lignin.

Conventional fillers such as phenolic resin and carbon black have been widely used for reinforcement of nitrile rubber (NBR) elastomers. In a study conducted by Setua et al. [48], a crude kraft lignin and a modified one by benzyl peroxide were employed as reinforcing agents into NBR. It was observed that incorporation of the modified lignin into NBR enhanced the elongation, hardness and compression properties, compared with the composites with phenolic resin filler, although the properties were inferior to those with carbon black filler. Lignin-polybutylene succinate (PBS) composites were prepared by melt mixing method [49]. The results demonstrated that lignin had a reinforcing effect on tensile, flexural and some thermal properties of PBS composites. While the impact strength and the initial decomposition temperature slightly reduced with increasing the content of lignin. Introducing 1 wt% of polymeric methylene diphenyl diisocyanate (PMDI) into 50% lignin-PBS composite enhanced all mechanical properties attributed to the improved interfacial adhesion between lignin and PBS. Further addition of PMDI (2 wt%) improved the tensile strength of the composites, but led to an adverse effect on the flexural and impact strengths. Similarly, it was reported that 1 wt% PMDI improved the physicomechanical and thermal properties of the hybrid lignin/switchgrass/PBS composites [50]. The flexural strength, flexural modulus, and heat deflection temperature (HDT) of the hybrid filler reinforced composite improved by nearly 165, 375% and 24 °C, respectively, compared with those of the neat PBS.

4.2 Lignin for Carbon Fibers

Carbon fibers (CFs) are promising materials for the reinforcement of polymers due to its specific characteristics including its strength, stiffness, low weight, fatigue characteristics, resistance to corrosion, and heat insulation [51]. Accordingly carbon fiber polymer composites find wide applications in marine products, sport equipment, construction, aircraft and automotive industries [52, 53]. The global consumption of carbon fibers in various industries is summarized in Table 4.2. Carbon nanofiber (CNF) is an advanced category of carbon fibers manufactured via electrospinning of carbon precursors. Applications of CNF include lightweight

Table 4.2 Global consumption of carbon fibers, reprinted with permission from Ref. [60]. Copyright (2012) John Wiley and Sons

Industry	Carbon fiber consumption (tonne)				
	1999	2004	2006	2008	2010
Aerospace	4000	5600	6500	7500	9800
Industrial	8100	11,400	12,800	15,600	17,500
Sporting goods	4500	4900	5900	6700	6900
Total	16,600	21,900	25,200	29,800	34,200

composites, electromagnetic shielding, biomedical materials, Li^+-ion batteries, electrochemical double-layer capacitors, catalyst supports, fuel cells, and dye-sensitized solar cells [54–59].

Manufacture processes of carbon fibers generally consist of three main steps: fiber spinning, stabilization at 200–300 °C and carbonization under an inert atmosphere at 1000–2000 °C and sometimes graphitization at 2000–3000 °C [53, 61–63]. Lignin can be used as a carbon precursor in carbon fiber manufacture. For instance, in stabilization step, a thermoplastic spun lignin can be transferred a polymer matrix via crosslinking, oxidation, and cyclization reactions to prevent the fusion during further thermal treatment [63]. The stabilization step can proceed under various oxidative atmosphere including oxygen, nitrogen oxide, sulfur dioxide, sulfur trioxide, nitric acid, sulfuric acid, potassium permanganate, and hydrogen peroxide [63]. Oxidative stabilization under air atmosphere is the most common condition for fiber stabilization in the production of carbon fibers.

Currently, three most commonly used carbon precursors for commercial production of carbon fibers are: polyacrylonitrile (PAN, a synthetic petroleum-based polymer), petroleum-derived pitch or coal tar, and rayon (regenerated cellulose) [51, 63, 64]. The reaction pathway for production of carbon fibers from PAN is illustrated in Fig. 4.3.

Lignin is one of bio-macromolecules which can be a promising precursor for the production of carbon fibers (CFs). Several studies have been conducted on the manufacture of CFs from different technical lignins including kraft lignin [52, 61, 65], lignosulfonates [65, 66], steam explosion lignin [67, 68], and organosolv lignin [52, 65]. The nature and properties of lignin were found to play an important role in manufacturing of carbon fibers: hardwood lignin demonstrates to have acceptable spin-ability, while softwood lignin is insufficient for fiber spinning due to its highly branched and crosslinked structure with a high melting point [63, 64]. Nevertheless, structure of softwood lignin can be chemically modified to improve its processibility. The utilization of lignin in production of CFs has attracted significant interest, and many studies have been reported on producing lignin-based carbon fibers [60, 69, 70], and the recent progress on the manufacturing of low-cost carbon fiber from lignin was reviewed by Baker and Rials [62]. In literature, the production of CFs from lignin can be divided into three categories: (1) carbon fibers from raw lignin without any further modification, (2) carbon fibers from physical lignin/polymer blends, and (3) carbon fiber from modified lignin.

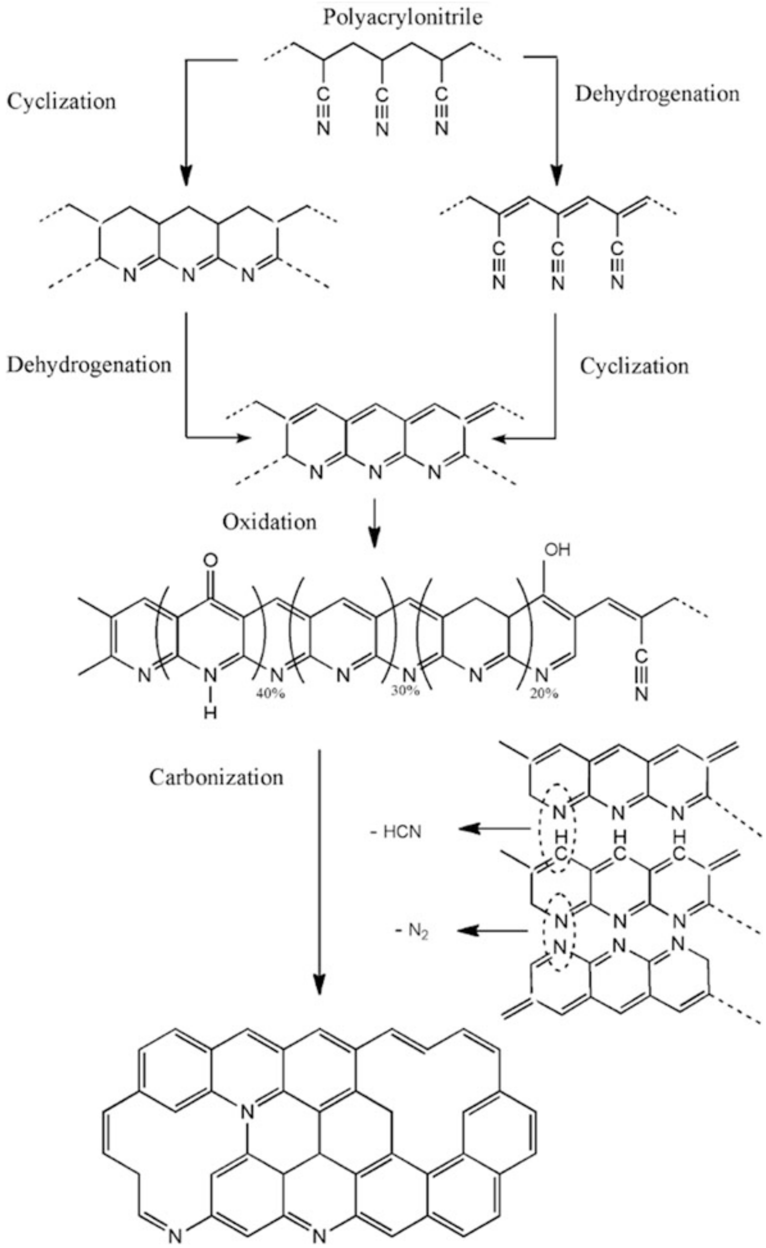

Fig. 4.3 Reaction pathway for production of carbon fibers from PAN, reprinted with permission from Ref. [60]. Copyright (2012) John Wiley and Sons

4.2.1 Carbon Fiber from Raw Lignin

In general, the glass transition temperature of a raw lignin is much lower than the temperature needed for the carbonization process, so it is required to modify lignin by air oxidative thermo-stabilization to increase T_g and convert fusible fibers into infusible ones. The oxidation reactions taking place during the thermo-stabilization process enhance the T_g of lignin by increasing crosslinking of lignin. Selecting an appropriate heating rate in the thermo-stabilization process plays an important role on the fiber formation process [52, 71]: by increasing the temperature slowly, the T_g rises faster than the thermo-stabilization temperature and the material maintains in non-tacky glassy state (owing to a $T_g > T$), while at higher heating rates, the T_g is lower than the thermo-stabilization temperature and the material would enter the tacky liquid-rubbery state.

The mechanism of carbon fibers production from hardwood Alcell lignin was investigated in details by solid-state and solution NMR techniques [72]. It was revealed that the main reactions during the oxidative thermos-stabilization consisted of three steps: (1) degradation of the most typical linkages of lignin or aliphatic side-chain groups on the structure of lignin, (2) demethoxylation reaction, and (3) formation of carboxyl and carbonyl functionality due to the crosslinking of the oxidized lignin macromolecules. In addition, the following reactions were proposed for the lignin-derived fiber carbonization process: (1) further reduction of methoxy groups, (2) reduction in the contents of carbonyl and carboxyl structures, (3) large increase in the content of aryl and condensed aryl carbons. The oxidative thermo-stabilization of kraft lignin for carbon fibers was investigated at temperature up to 340 °C to determine the optimum conditions based on a continuous heating transformation [71]. The results showed a decrease in hydrogen and carbon contents during air oxidation at 0.11–1.0 °C/min of heating rate. A sigmodial reduction of hydrogen proved autocatalytic processes, whereas the oxygen content increased at temperatures up to 250 °C due to carbonyl incorporation and then decreased by the formation of CO_2 via auto-oxidation process. In oxidation process, the dominant reactions varied based on the range of temperatures. At low temperatures, the process was controlled by the formation of carbonyl and carboxyl structures. With increasing the temperature, the formed groups converted into ester and anhydride bonds that enhance the crosslink density followed by the generation of carbon–carbon linkages. The DSC and elemental analyses revealed that the hydrogen content had an inverse effect on the glass transition temperature. It was suggested that the heating rate of 0.06 °C/min or lower would maintain $T_g > T$ during the thermo-stabilization process.

Norberg et al. [63] investigated the oxidative and thermal stabilization of softwood kraft lignin (SKL) and hardwood kraft lignin (HKL) for the manufacturing of carbon fibers. The stabilization step was optimized with respect to temperature, heating rate, holding time, and the presence of oxygen. It was found that the stabilization of SKL fibers was accomplished at a shorter time compared with the HKL fibers, although hardwood lignin has commonly better spin-ability than softwood lignin due to its highly branched and crosslinked structure of softwood lignin with a high melting point [63, 64]. Moreover, hardwood lignin could not be thermally stabilized at higher heating rate above 0.2 °C/min and in the absence of oxygen. In contrast, the softwood kraft lignin permeate was thermally stabilized at 4 °C/min, slower than the heating rate (15 °C/min) for its oxidative stabilization, to prevent the inter-fusion of fibers. The oxidative stabilization of SKL was achieved after 45 min, while it was reported 105 min needed for the blend of SKL- hardwood kraft lignin permeate (90:10, w/w), which confirmed the effect of HKLP as a softening agent. In addition, it was suggested in this research that the stabilization and carbonization of SKL fibers could be operated in a one-step process, which would be more cost and time effective for the production of carbon fibers.

A novel method was investigated to use softwood lignin obtained from atmospheric acetic acid pulping, namely softwood acetic acid lignin (SAL), as a precursor for preparation of carbon fibers. It was realized by removing the infusible high-molecular mass fraction with various concentrations of aqueous AcOH [73], and the separated low molecular mass fraction was converted into carbon fibers by direct carbonization without thermo-stabilization. The omission of the thermo-stabilization process lowered the total production cost and the mechanical properties of SAL-based carbon fibers were comparable with those from the phenolated exploded lignin. In addition, the potential of SAL after removing the high-molecular mass fraction, as a feedstock for production of activated carbon fibers (ACF) was investigated and compared with a hardwood acetic acid lignin (HAL)-based ACF [74]. The SAL was spun at 220 °C (higher than the thermal flow-starting temperature) and then thermo-stabilized at a faster heating rate compared with the HAL fibers. The activated carbon fibers were obtained by carbonization in nitrogen at 1000 °C, followed by steam activation at 900 °C for 40–80 min. The SAL-based ACF prepared with 40 min activation time had a greater specific surface area and lower yield compared with those of the corresponding HAL-based ACF. Moreover, the absorption properties and tensile strength of SAL-based ACF were comparable to those of commercial pitch-based ACF.

Nordstrom et al. [75] studied the strength distribution of CFs derived from softwood kraft lignin by employing Weibull model for single fibers with different diameters and lengths to optimize the manufacturing parameters such as die size and winding speed. It was noted that the tensile strength of lignin-based CFs was around 300 MPa which is lower than that of the commercial CFs, while its stiffness was approximately 30 GPa higher than that of the commercial isotropic CFs, and with strain at failure in range of 0.7–1.2% comparable to that of typical CFs.

4.2.2 *Carbon Fibers from Lignin/Polymer Blends*

Kuba and Kadla [61] reported the production of carbon fibers from hardwood lignin/synthetic polymers (poly(ethyleneterphthalate) (PET) and various polypropylene (PP)). The DSC results revealed that lignin/PP blends were immiscible while the mixtures of lignin/PET were miscible. Also, it was observed that both systems were easily converted into fibers and heating rate had a significant effect on the thermo-stabilization of the blend fibers. The incorporation of PET enhanced the thermal stability of the prepared polyblend fibers and could operate up to 120 °C/h heating rates. The overall carbon fiber yield was strongly dependent on the blend composition and the overall yield of carbon fibers from the lignin—25% plastic blends was even higher than that from petroleum pitch. Whereas, the morphology of the carbon fibers was influenced by the type of plastics, and immiscible blends leaded to a hollow or porous surfaces, and miscible blends provided a smooth surface for fibers. The mechanical properties of lignin/PET-based CFs were much higher than those of lignin/PP-based CFs, and were comparable with the performance of commercial pitch-based CFs. The maximum single fiber strengths of CFs were 0.605 GPa with a modulus of 61 GPa with 100% lignin, and 0.703 GPa with a modulus of 94 GPa with the 75/25 lignin/PET blend.

Carbon fibers were developed with two commercial kraft lignins (softwood and hardwood lignins) and organosolv lignin (Alcell) without any chemical modifications by Dallmeyer et al. [65]. It was indicated that hardwood kraft lignin and Alecell could form fibers at temperatures above 140 and 200 °C, respectively, while the softwood kraft lignin could not soften at this range of temperature and just charring due to high crosslink density of softwood lignin in compared with hardwood lignin. The lignins were thermally treated (devolatilized) before spinning process to remove the volatile compounds which negatively affected the fiber integrity and reduce the hydroxyl content of lignin by condensation reactions. Then, the devolatilized lignin blended with poly(ethylene oxide) (PEO) to facilitate the fabrication of fiber spinning. It was suggested that with PEO-kraft lignin blends containing PEO at greater than 5 wt%, and with PEO-Alcell lignin at all compositions, the prepared samples were thermally unstable with interfiber fusing during the carbonization process. The overall yields of carbon fibers were approximately 45% for hardwood kraft lignin and 40% for Alcell lignin. The mechanical properties of kraft lignin-based CFs and Alcell lignin-based CFs could meet the acceptable values for general performance grades CFs, for instance the tensile strength and modulus of kraft lignin-based CFs varied in the range of 400–550 MPa and 30–60 GPa, respectively, and the mechanical properties increased with decreasing the fiber diameter. Compere et al. [76, 77] reported carbon fiber preparation from lignin-polyester blends for transportation application. A kraft lignin was desalted by slightly acidic distilled water to prevent the void formation during the fiber production. In these studies, effects of fiber surface modification were investigated, and it was noted that a combination of plasma treatment and silanation could improve the compatibility of lignin-based CFs and epoxy resin. In another study by Thunga et al. [78], the influence of chemical modification and physical blending of lignin with poly(lactic acid) (PLA) as a suitable precursor for carbon fibers were investigated. In this study, a softwood kraft lignin was chemically modified to butyrated lignin (B-lignin) according to the method proposed by Thielemans and Wool [79] in order to improve the miscibility of lignin and PLA via forming ester functional groups. The pretreatment of lignin reduced the hydroxyl groups in lignin, resulting in a reduction in crosslinking ability of lignin and enhancing the melt processability of softwood lignin. The morphology of B-lignin CFs was strongly dependent on the composition of lignin, varying from discontinuous B-lignin rich spherical phase (50 wt% lignin-PLA blends) to co-continuous (75 wt% lignin-PLA blends), and to discontinuous PLA rich phases (90 wt% lignin-PLA blends) as illustrated in Fig. 4.4. It appears that the optimum composition of lignin-PLA blends is 75 wt% lignin, with high compatibility, yield, and surface area (535 m^2/g), and thermal and mechanical properties comparable to commercial CFs.

Dallmeyer et al. [65] prepared micron or submicron diameter carbon fibers, using electrospinning technology, from seven different technical lignins, i.e., hardwood kraft lignin (HKL), softwood kraft lignin (SKL), sulfonated kraft lignin (SL), hardwood organosolv lignin (HOL), softwood organosolv lignin (SOL), pyrolytic lignin (PL), and lignosulfonate (LS). None of the lignins could be electrospun into uniform fibers. The addition of polyethylene oxide (PEO, 1–5 wt%) changed the electrospinning behavior dramatically, and uniform fibers were formed with an average diameter of 0.7–1.5 μm as shown in Table 4.3. With increasing the lignin concentration, the fiber diameter increased linearly. However, at the constant concentration of lignin, the diameters of fibers varied due to the differences in the viscosity and electrospinning behavior of lignin solutions. It revealed that the structure and intermolecular interactions of lignin affects the solution properties and elctrospinning behavior.

Ultrafine (100–500 nm) carbon fibers with high porosity were produced from alkali lignin (low sulfonate content) aqueous solutions by electrospinning followed carbonization and activation at 850 °C under N_2 [80]. The incorporation of PEO improved the spin-ability of lignin via chain entanglement as well as thermal stabilization. In addition, the activation in presence of NaOH or KOH at very low

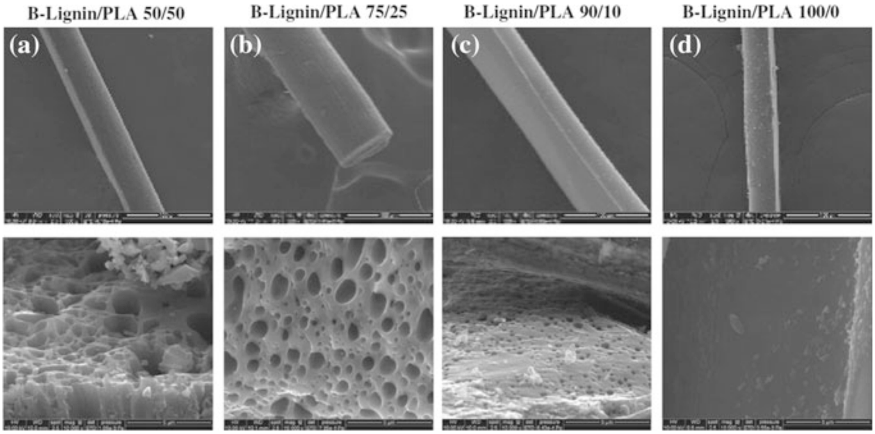

Fig. 4.4 SEM images of CFs from lignin-PLA blends with varying lignin contents, reprinted with permission from Ref. [78]. Copyright (2014) Elsevier

Table 4.3 Average diameters of CFs produced from lignin-PEO blend (99 wt:1 wt) by electrospinning (N = 200), reprinted with permission from Ref. [65]. Copyright (2010) Taylor and Francis

Lignin-PEO (99 wt:1 wt)	Concentration in DMF (%)	Diameter (nm)
SKL	40	1318 ± 251
HKL	40	1085 ± 188
SOL	50	1517 ± 415
HO	40	1135 ± 171
PL	40	912 ± 176
LS	30	1645 ± 371
SL	30	702 ± 186

impregnation ratios (≤ 0.5) could also convert the nonporous structure of lignin-PEO fibers into highly porous activated carbon fibers. It was reported that CFs with a specific surface area of >1400 m^2/g and porosity of >0.7 cm^3/g could be produced by varying the type and content of alkali hydroxides as the activation catalyst. Dallmeyer et al. [54] proposed an interesting strategy to improve the mechanical, electrical, and morphology of CFs. An inter-connected carbon submicron fibers was fabricated from kraft lignin-PEO solution in N, N-dimethylformamide (DMF) by electrospinning, followed by oxidative thermo-stabilization at 250 °C and carbonization at 600–1000 °C. The carbonization process induced interfiber bonding, resulting in an increase in tensile strength, electrical conductivity, and ductility of the kraft lignin-based carbon fibers. The electrical properties of the resulted CFs are comparable to PAN-based CFs, whereas its mechanical properties of the lignin-based CFs need to be improved by optimization of the thermal treatment conditions.

In addition, several studies have been reported on the co-extrusion of lignin-PAN blends for production of carbon fibers [81–84]. Seydibeyoğlu [83] investigated the replacement of PAN up to 30 wt% with lignin to reduce the total production cost of carbon fibers. The mechanical properties were studied by dynamic mechanical analysis (DMA). The storage modulus increased with the content of lignin from 9.2×10^8 for 100% PAN-based CFs to 1.7×10^9 for CFs from a 30%lignin-70%PAN blend.

4.2.3 *Carbon Fibers from Chemically Modified Lignin*

Lin et al. [85] isolated a thermally fusible softwood lignin from cedar wood chips through solvolysis process with a mixture of polyethylene glycol 400 and sulfuric acid. The extracted lignin (PEG-lignin) was converted to carbon fibers by melt-spinning at temperature from 145–172 °C without further modification and thermally stabilized under air or oxygen for 2 days. All the oxidative thermo-stabilized fibers were fused and adhered together at heating rate under 0.1 °C/min. It is indicated that the conventional oxidative thermo-stabilization method was not suitable for stabilization PEG-lignin. However, infusible fibers were achieved after chemical-thermo-stabilization of PEG-lignin with 6 M hydrochloric acid at 100 °C for 2 h via the cleavage of the PEG moiety from lignin. The prepared CFs showed slightly superior tensile strength (450 MPa). In another work, infusible polyethylene-lignin carbon fibers were fabricated from fusible softwood lignin isolated from solvolysis pulping of Japanese cedar in the presence of PEG by chemical-thermo-stabilization process [53]. In this process, PEG-lignin was cross-linked by hexamethylenetetramine (HMTA) in an aqueous HCl solution at 2 °C/min heating rate followed by thermo-stabilization under an air atmosphere for 3 h. The obtained carbon fibers were infusible and defect-free with high tensile strength (700 MPa). The preparation of carbon fibers from a lignin copolymer with acrylonitrile (AN) was reported also by Maradur et al. [86]. First, lignin was copolymerized with AN in the presence of dimethysulfoxide (DMSO) by the radical copolymerization. The FTIR results confirmed the formation of polyacrylonitrile (PAN)-lignin copolymer by the presence of C≡N, hydroxyl, ether, and aromatic groups. The synthesized PAN-lignin copolymer was successfully processed into carbon fibers by wet-spinning process (16 wt% PAN-lignin copolymer in a DMSO solution), followed by stabilization and carbonization processes with the overall yield of 56%. The SEM images of the prepared carbon fibers in each step of manufacture are presented in Fig. 4.5 at high magnification. Furthermore, the average tensile strength, tensile strain and modulus of PAN-lignin copolymer-CF were 2.41 gf/den, 11.04%, and 22.92 gf/den, respectively. It demonstrated that the introduction of lignin into PAN could be a cost-effective way for manufacturing of CFs.

A novel method was proposed by Ito [87] to extract a suitable lignin for carbon fiber production, from wood chips at high temperature and in the presence of water and cresols. The infusible lignin fibers were fabricated after thermal treatment at 3 °C/min to 200 °C. Shen et al. [88] described formation of several activated carbon fibers (ACFs) from lignin-based phenol formaldehyde (LPF) resins with various lignin contents from 8 to 20 wt%. The guaiacyl groups of lignin reacted with formaldehyde at 95 °C to produce LPF resins. The FTIR results confirmed the formation of LPF resins and their chemical structures were not affected by the

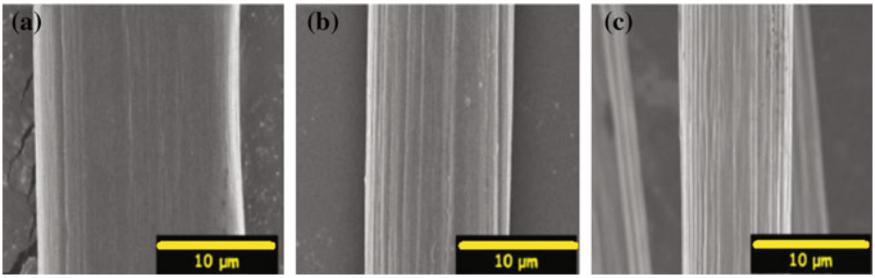

Fig. 4.5 SEM image of CFs prepared from PAN-lignin copolymer: as spun (**a**), stabilized (**b**) and carbonized (**c**), reprinted with permission from Ref. [86]. Copyright (2012) Elsevier

Table 4.4 Overall yield and mechanical properties of carbon fibers produced from various lignins and pitch, reprinted with permission from Ref. [89]. Copyright (2012) John Wiley and Sons

Precursor	Overall Yield (wt%)	Diameter (μm)	Modulus (GPa)	Strength (MPa)
Kraft lignin	46	49 ± 1	41 ± 3	412 ± 39
Alcell lignin	42	47 ± 2	37 ± 4	379 ± 34
Pyrolytic lignin	46	49 ± 2	36 ± 1	370 ± 38
Isotropic pitch	33	8–15	40–50	600–1000

content of lignin, while the thermal performance and the properties of the formed ACFs were controlled by the percentage of lignin. ACF containing 14% lignin showed better properties with reported porosity of 22.4%. Qin and Kadla [89] tested a pyrolytic lignin for carbon fibers manufacturing. The pyrolytic lignin was isolated from a bio-oil derived from hardwood sawdust and converted to CFs by thermal spinning followed by carbonization process. In compared with kraft and Alcell lignins, the pyrolytic lignin required a lower temperature for continuous fiber spinning due to its lower molecular weight and its higher free volume. The prepared pyrolytic lignin fibers had porous structure and fused together during thermo-stabilization. The hollow-fiber structure showed low mechanical performance but could be appropriate in some applications that require a high surface area. It was found that the thermal treatment of pyrolytic lignin at moderate temperature and time (160 °C and 1 h) before fiber spinning could improve the integrity of carbon fibers. The carbon fibers obtained from the pretreated pyrolytic lignin showed comparable mechanical properties and the overall yield to those produced from other technical lignins, as displayed in Table 4.4.

Zhang and Ogale [64] prepared carbon fibers derived from an acetylated softwood kraft lignin (Ace-SKL) by dry-spinning using acetone followed by thermo-oxidative stabilization. The SKL was acetylated with 0.66 ml acetic anhydride/lignin concentration at 85 °C for 0.25 h to produce the Ace-SKL with larger content of hydroxyl groups which could crosslink and stabilize fibers. The fabricated carbon fiber showed the highest tensile strength in compared with the values reported in literature on lignin-based carbon fibers. The mechanical properties of Ac-SKL-based carbon fibers with 7 μm diameter were measured as follows: 952 ± 2 GPa tensile modulus, 1.04 ± 0.1 GPa strength, and 2 ± 0.2% strain-to-failure. The Ace-SKL fibers obtained by dry-spinning displayed a crenulated surface due to the solvent diffusion and their surface area was 35% larger than those prepared by melt-spinning.

4.3 Summary

This chapter reviews the application of lignin as reinforcement fillers in thermoplastic polymers, and its potential as a starting material or precursor for manufacturing carbon fibers. Lignin is a polar hydrophilic biopolymer with biodegradability, antioxidant and reinforcing capability. These properties make lignin a potential candidate to improve the properties of thermoplastic polymers. However, the polarity of lignin limits the miscibility of lignin in nonpolar polymers. So, it is required to modify lignin before compounding it with a nonpolar polymer. The recent literatures showed that lignin could be blended with a wide range of polymers including natural rubber, PE, PP, SBR, PVC, and polystyrene, to improve their properties such as antioxidant, thermal stability, mechanical performance (impact, stiffness, strength, and elongation properties), UV stability, and biodegradability.

The promise of lignin to be used as inexpensive precursor materials for carbon fibers manufacture was also demonstrated in the literature, by using raw lignin without any further modification, physical lignin/polymer blends, or modified lignin. In order to produce infusible and better quality fibers from lignin, it is recommended to modify lignin before fabrication or to blend lignin with other polymers such as PP, PET, PEO, and PLA before the spinning process.

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Chapter 5
Utilization of Lignosulfonate as Dispersants or Surfactants

Abstract Lignosulfonate or sulfonated lignin is a water-soluble lignin extracted from the sulfite pulping process. Lignosulfonate is lypohydrophilic molecule due to the hydrophobic aromatic structure and the presence of the hydrophilic sulfonate groups on its structure. This unique structure of lignosulfonate makes it an effective dispersant or surfactant used in a wide range of industries, such as oil well dispersant, coal–water slurry dispersant, dye dispersion, ceramic colloidal processing, and polymer composites.

Keywords Lignosulfonate · Sulfonated lignin · Lypohydrophilic molecule · Hydrophobic aromatic structure · Hydrophilic sulfonate groups · Dispersant · Surfactant

5.1 Lignosulfonate and Structure

Lignosulfonates or sulfonated lignins are water-soluble anionic polyelectrolyte polymers which are recovered from the sulfite pulping of wood (brown liquor) [1]. Lignosulfonate can also been prepared by sulfonation of alkali lignin [2]. In the pulping process, an aqueous solution containing sulfur dioxide and a sulfurous acid salt is used to break down the linkages with polysaccharides [3]. Depending on the type of bases used in pulping process, various lignosulfonates such as calcium [4, 5], sodium [6, 7], magnesium [8], and ammonium lignosulfonates [9] can be produced. Lignosulfonates can be isolated from spent pulping liquors by various methods including precipitation in alcohol, dialysis, electrodialysis, ion exclusion, ultrafiltration, supported liquid membrane (SLM), and extraction with amines [1, 10, 11]. Figure 5.1 illustrates the chemical structure of sodium lignosulfonate (SL) [12], containing numerous aromatic structure and hydroxyl methyl–ether functional groups and sulfonate group ($-SO_3H^-$).

The presence of hydroxyl group and sulfonate group will enhance the hydrophilicity of lignosulfonates [13].

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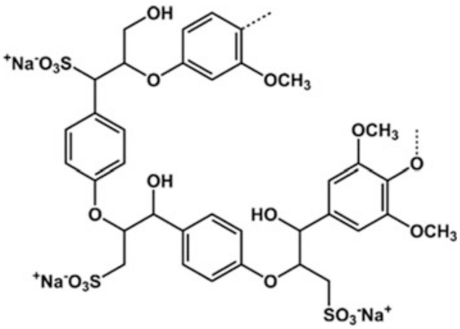

Fig. 5.1 Chemical structure of sodium lignosulfonate (SL), reprinted with permission from Ref. [12]. Copyright (2016) Elsevier

5.2 Lignosulfonate Applications

The world production of soaps, detergents, and other surfactants is more than 40 Mt, and lignosulfonates can be used as surfactants or dispersants in various applications such as chelating agents, water reducers of cement, dye dispersants, etc. [2]. As illustrated in Table 5.1, lignosulfonates account for a significant share in the market of surfactants in different industries [13].

Lignin calcium salts are water-insoluble and widely used as dispersant in non-aqueous media. Lignin alkaline (sodium, ammonium, potassium) salts are water-soluble and polyelectrolytes, used as heavy metal ions sequestrates or protein agglutinant for granulated food, and wastewater treatment [13]. Cationic surfactant can be used as softening and antistatic agent in fibers, corrosion inhibitor, emulsifier for asphalt, germicide, and flotation agent [14]. A novel water-soluble cationic surfactant was produced by Mannich reaction of phenolated sulfuric acid lignin (SAL) with dimethylamine in the presence of sulfuric acid catalyst as schematically

Table 5.1 Main types of surfactants and their applications and market shares, modified from Ref. [13]

Main types of surfactants	Applications	Market share (%)
Soaps (carboxylates) and lignosulfonates	Soaps for domestic use, other acids for industrial use	33
Synthetic detergents, mostly sulfonates or sulfates	Domestic use (powder, liquid), petroleum industry, concrete additives, agro and food processing, cosmetics and pharmaceuticals	22
Non-ionics (mostly ethoxylated) or ethoxysulfates	Ethoxylated alcohols, ethoxylated alkyphenols, fatty acid esters, amine or amide derivatives	40
Cationics, mostly quaternary ammoniums		4
Amphoterics, mostly betaines and amino acid derivatives		1

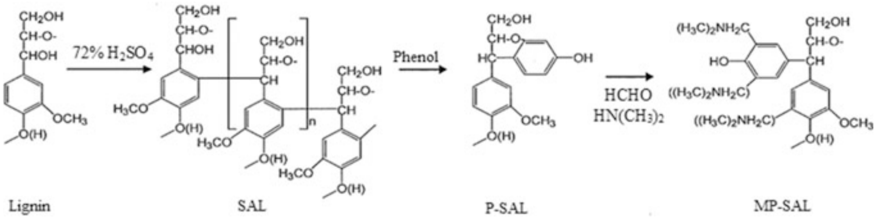

Fig. 5.2 Formation of water-soluble cationic surfactant (MP-SAL) via Mannich reaction, modified from Ref. [14]

shown in Fig. 5.2 [14]. The resulted surfactant (MP-SAL) has surface tension of 45 mN/m that is much lower than that of lignosulfonate.

Lignosulfonate (LS) is generally lypohydrophilic, but its surface activity and hydrophobicity of lignosulfonates (LS) could be improved by aluminum-containing organosilicon oligomer (olygoheterosiloxanolates) in the acidic media [15], or by treating LS and a cationic surfactant (S) through a concentrated gel phase at concentration ratio near charge equilibrium between LS and S [16]. Lignosulfonate is considered as a lypohydrophilic molecule due to the presence of hydrophilic sulfonic groups, despite the co-presence of hydrophobic aromatic structure [17]. The microscopic structure of lignosulfonate in solution has drawn attention by many researchers. For instance, Qiu et al. [17] investigated the aggregation behavior of sodium lignosulfonate in water solution using UV spectrophotometer and dynamic light scattering (DLS). The results revealed that the critical aggregation concentration (CAC) of lignosulfonate is 0.38 gL^{-1} in water solution. When the concentration of LS is below CAC, the LS molecules are dispersed individually in the solution. With increasing of LS concentration, the LS molecules started to agglomerate and micelles formed with further increasing the LS concentration.

5.2.1 *Oil Well Dispersants*

Oil drilling process could be enhanced by addition a small amount of surfactant through reducing the interfacial tension between the oil and water phase and improving the wettability of the reservoir rack [18]. A wide range of polymeric thinning agents could be used as oil well dispersants to decrease the viscosity of drilling mud. Lignosulfonate is a common thinner or surfactant in the oil drilling industry by reducing electrochemical attraction forces between bentonite clay particles and the deflocculated clay platelets [19]. In addition, lignosulfonate can improve the solubility of oil in water emulsions, hence reducing the required energy to rotate the drill stem and increasing the drill bit life. Several studies have demonstrated the combination of petroleum-based sulfonate and lignosulfonate as inexpensive but effective surfactants in oil recovery [18, 20–24]. For instance, the study of Novosad [18] showed effects of lignosulfonate on the enhancement of tertiary oil recovery by surfactant flooding, where lignosulfonate was used together with a co-surfactant, monoethanol amine salt of alkylorthoxylene. Consumption of lignosulfonate as a sacrificial agent in a surfactant flooding process was studied by Hong et al. [25]. The surfactant loss decreased markedly (more than 50% loss) in the presence of lignosulfonate preflush. The interfacial tension and phase behavior of petroleum sulfonate/lignosulfonate mixed surfactant were examined by Son et al. [26], and it was found that 50% of the petroleum sulfonate could be replaced by inexpensive lignosulfonate without compromising the surfactant performance, resulting in high economic implications in the recovery of oil from partially depleted oil fields. Ultralow interfacial tensions (<0.01 mN/m) could be achieved in an iso-octane system at a relatively wider range of NaCl concentration, comparable to crude oil system.

It was proposed by Kumar et al. [27] that the addition of divalent cations (Mg^{2+}, Ca^{2+}) into an admixture of sodium-based petroleum sulfonate–lignosulfonate could remarkably change the coalescence behavior of oil droplets. The phase behavior, along with interfacial tension (IFT), specific conductivity (SC), and pH values of a binary/ternary system of lignosulfonates (Na-based lignosulfonate and Ca-based lignosulfonate), and petroleum sulfonate were investigated [28]. The mixture consisting of the bivalent Ca^{+2} enhanced the interfacial activity of the surfactant system better than the univalent Na^{+} cation. The IFT increased with increasing the total concentration of ions, regardless of the type of lignosulfonate. The IFT and SC values revealed that liquid crystalline structure formed at a specific concentration of Ca-based lignosulfonate. It was also found that the IFT of various compositions of lignosulfonate surfactants remained constant after 8-day aging in iso-octane system (as a model oil system). Neale et al. [29] reported a study on performance of a co-surfactant consisting of lignosulfonate (0–4%) and petroleum sulfonate (0–5 wt %) with ultralow IFT in crude oil. Both the surface tension and IFT decreased with increasing the content of LS, reached to a minimum value at approx. 1–2 wt%, and afterward increased with increasing the LS content.

A Mixed-Surfactant-Enhanced Alkaline (MSEA) was developed for recovery of Saskatchewan heavy crude oil [30]. A commercial sulfonate surfactant (Petrostep B-100) and two lignosulfonate surfactants, Marasperse C-21 (Ca-based) and N-22 (Na-based), were mixed at various compositions. In the absence of NaOH, the addition of Ca-based LS (Marasperse C-21) into Petrostep B-100 solutions improved the interfacial activity by 90% and its performance was much better than its sodium-based LS (N-22). However, in the presence of NaOH solution, undesirable increasing trends were observed for IFT with time. At elevated temperatures, a very low IFT value of ternary MSEA solutions against the crude oil, ranging from 5×10^{-2} to 10^{-1}, could be obtained, suggesting its great potential for oil recovery process.

Ibrahim et al. [19] prepared tin–tannin–lignosulfonate (TTLS) by reacting lignosulfonate acid with tannin at 150 °C in the presence of formaldehyde, followed by chelating with stannous ions, and investigated the performance of TTLS as a thinning agent for oil drilling industry in comparison with lignosulfonate.

The TTLS exhibited better performance at various pH values and displayed more resistance to temperature and salt contamination, suggesting a great potential for commercialization. An environmentally friendly lignosulfonate, Fe–tannin–lignosulfonate (FTLS), was also developed as a polymeric thinner for aqueous bentonite and oilfields [31], where the FTLS was prepared by crosslinking of lignosulfonate acid with a tannin in the presence of formaldehyde, followed by chelating with ferrous ions. Compared to FeCr–LS thinning agent, the FTLS showed better thinning performance and more resistance to temperatures and salinity.

In another study, lignin was grafted with 2-propenamide (acrylamide) via a free radical reaction for preparation a drilling mud thinner used for high-temperature wells [32]. The prepared lignin–acrylamide graft copolymer was used as a thinning agent for aqueous bentonite mud. At the optimum concentration of 0.3 wt% of total mud volume, the grafted lignin-based thinning agent showed better thinner ability and more tolerance at high temperatures (190 °C) and in the presence of a high salt contamination compared with lignosulfonate. Yanhua et al. [33] developed a novel three-step process to produce modified LS with ultralow interfacial tension that can be used as a principal surfactant in enhanced oil recovery. The process included the following three steps: (i) Mannich reaction with aliphatic polyamine and aqueous 37% formaldehyde, (ii) acylation reaction with aliphatic acyl chloride at adjusted pH in the range of 8.5–9, and (iii) sulfomethylation reaction with sodium sulfite and aqueous 37% formaldehyde. The modified LS showed improved activity at the interface of crude oil and the solution over a wide range of surfactant concentration and alkali concentrations.

A novel surfactant for enhanced oil recovery was produced with two renewable chemicals including lignosulfonates and fatty amines [34], with better performance than a petroleum sulfonate surfactant, as shown in Fig. 5.3. Moreover, manufacture of the bio-based surfactant has largely reduced up-front cost by 40% in terms of raw materials.

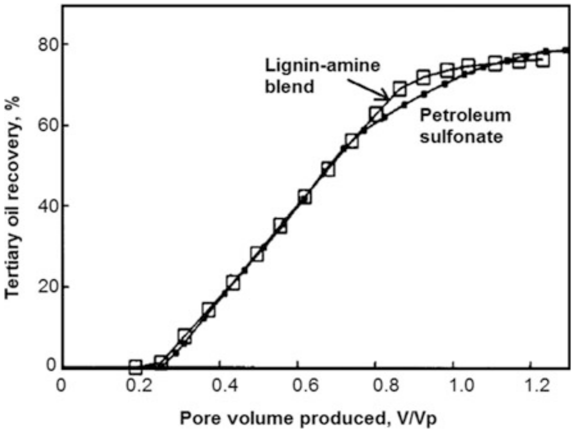

Fig. 5.3 Tertiary oil recovery with lignin/amine blend surfactant compared with petroleum sulfonate surfactant, reprinted with permission from Ref. [34]. Copyright (1992) Elsevier

5.2.2 Coal–Water Slurry (CWS) Dispersants

A typical coal–water slurry (CWS) contains 60–75% coal, 25–40% water, and around 1% chemical dispersants [35]. CWS is generally burned to generate energy, so it is more economical that a CWS has a high coal solid content and a low viscosity. Therefore, the presence of dispersant could be critical to control the viscosity, the flow, and sedimentation properties of CWS [35, 36]. The common CWS dispersants are humate and methylene naphthalene sulfonate–styrene sulfonate–maleate copolymer (NDF with M_w of 20,000 g/mol) [35]. Recently, the performance of lignosulfonate as a renewable CWS dispersant has been studied. For instance, Yang et al. [35] investigated the effects of sodium lignosulfonate (LS) with different molecular weights on the viscosity of a CWS. In this study, a commercial lignosulfonate was separated into five fractions with molecular weight ranges of <5000, 5000–10,000, 10,000–30,000, 30,000–50,000, and >50,000 g/mol, using ultrafiltration and dialysis methods. The results showed that the SL fraction with molecular weight of 10,000–30,000 g/mol consists of higher contents of sulfonic and carboxyl groups, leading to its highest zeta potential on the coal particles and more efficiency for reducing the viscosity of the CWS.

The mechanism of flotation of coal and mineral in deionized water and saline water in the presence of ionic dispersion (lignosulfonate D748) was investigated in detail by Liu and Peng [37]. With lignosulfonate at a low content, the flotation of coal in the presence of clay minerals was improved in deionized water, while no enhancement was observed in saline water. However, a high content of lignosulfonate resulted in the depression of coal flotation in both deionized water and saline water due to high adsorption of clay on coal surface.

5.2.3 Dispersants in Other Applications

Lignosulfonate has been widely used as a dye dispersant, but the dark color and the staining effect of lignosulfonate create some obstacles in this application. The dark brown color of lignin is attributed to the presence of quinonoid structures in lignin, derived from colorless catecholic structure of lignin via oxidizing reaction during the lignin isolation and pulping processes [38]. Nevertheless, several studies have been reported on usage of lignosulfonates as dye dispersing agents [38–40]. For instance, Yang et al. [38] studied the performance of sodium lignosulfonate with various molecular weights isolated by ultrafiltration (ranging from 2.5 to 50 kDa and above) in the dispersion of an azo dye, C.I. Disperse Blue 79. Although with increasing the molecular weight of LS, the contents of phenolic hydroxyl, carboxyl, and sulfonic acid groups reduced, the LS with a higher molecular weight showed better dispersion effects on the dye. In addition, the dye reduction degree and fiber staining (at LS concentration >6 g/L) reduced with increasing the molecular weight of LS. Similarly, lignosulfonate was used as a dispersing agent in preparation of monoazo disperse dyes [40], where LS as an ionic dispersant could stabilize the dilute dispersions by electrostatic repulsion. Moreover, the presence of LS improved the diffusion of dye into polyester owing to the presence of sulfonic groups on its structure.

The effects of lignosulfonates on the floatability of talc were studied by Ma and Pawlik in alkaline media with various pH values ranging from 7 to 11.2, adjusted using lime [41]. The calcium ions adsorbed on the surface of talc particles at high pH $\sim$ 11 activated the surface for LS adsorption. The study confirmed that there is a good correlation between the adsorption densities of LS and calcium hydroxyl species on the talc surface. Wei et al. [42] investigated the performance LS-based polymeric dispersant on the flotation of copper and gold from high and low clay ores with various grinding media. With stainless steel-made grinding media, LS mitigated the negative influence of clay minerals on copper–gold flotation, while with non-alloy steel media, the presence of a high amount of iron oxides depressed the flotation of copper–gold, and mitigated the positive effects of the LS dispersants.

In ceramic colloidal process, addition of macromolecular dispersants (e.g., polyelectrolytes) is essential to stabilize alumina suspension without any sedimentation. Commercially, polyacrylates are the commonly used polyelectrolytes that are costly and non-renewable-based materials. Therefore, finding an alternative is interesting to industries. Megiatto et al. [12] studied the performance of sodium lignosulfonate as a sustainable dispersing agent for aqueous alumina colloids. Effects of the LS concentrations on the viscosity of the suspension at various pH values were investigated. Figure 5.4 presents some typical results obtained in this work. A shown in the figure, with introducing 25 mg LS in 100 g total suspension of alumina (equivalent 250 ppm of LS in the suspension), the viscosity of the suspension significantly reduced by about 70%. Moreover, the presence of LS decreased the particle size of alumina, leading to a longer sedimentation time compared with the pristine alumina particles in the suspension.

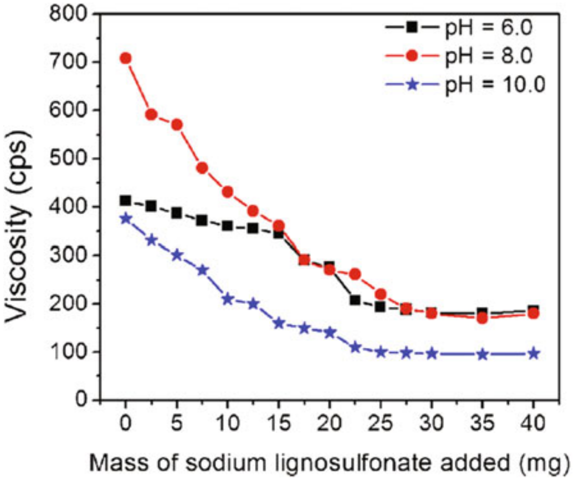

Fig. 5.4 Effects of LS concentration on the viscosity of alumina suspension (100 g total suspension consisting of 40 g alumina), reprinted with permission from Ref. [12]. Copyright (2016) Elsevier

Lignosulfonates have also been utilized dispersing agents in polymer composites. For instance, Xiao et al. [43] studied the effects of lignosulfonate on dispersion of layered double hydroxide (LDHs) in nitrile–butadiene rubber (NBR) through the melt-compounding method. Both X-ray diffraction and SEM analysis results proved better dispersion of LDH particles in NBR matrix in the presence of LS. The prepared SL–LDH–NBR composites also demonstrated improved thermal stability and mechanical properties, as well as an increased glass transition temperature compared to LDH–NBR composite, likely attributed to the improved interaction between LDH and NBR assisted by the LS dispersant.

5.3 Summary

Lignosulfonates or sulfonated lignins are water-soluble anionic polyelectrolyte polymers which are recovered from the sulfite pulping of wood (brown liquor), or prepared by sulfonation of alkali lignin. Lignosulfonates, consisting of both hydrophobic aromatic structure and hydrophilic sulfonic groups, have found applications as dispersant or surfactant in various industries. Lignosulfonates have been widely used as polymeric thinning agents in oil recovery process to reduce the viscosity of drilling mud and enhance the oil recovery. Lignosulfonates can also be utilized in preparation of coal water slurry as renewable dispersants, and other industrial applications, e.g., as chelating agents and water reducers in cement, and effective dispersing agents for dye dispersion, ceramic colloidal processing, and polymer composites.

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Chapter 6
Lignin-Based Phenol–Formaldehyde (LPF) Resins/Adhesives

Abstract This chapter presents a comprehensive overview on the synthesis of lignin-based phenol–formaldehyde (LPF) resin and its characteristics for using it as wood adhesives. Lignin has a phenolic structure with high hydrophobicity that makes it as a promising bioreplacement of phenol in the synthesis of PF resins. However, lignin has low reactivity toward formaldehyde compared with phenol due to its high molecular weight and steric hindering. To improve the reactivity of lignin, various chemical modifications such as methylolation, demethylation, phenolation, sulphonation, hydrolytic depolymerization, and reductive depolymerization were conducted on lignin before incorporation in the synthesis of lignin-based phenol–formaldehyde resins. Effects of some factors including the type of lignin, substitution ratio, and reaction conditions on the performance of the obtained LPF resins were discussed in detail.

Keywords Lignin-based phenol–formaldehyde (LPF) resins · Reactivity of lignin · Chemical modifications · Methylolation · Demethylation · Phenolation · Sulphonation · Hydrolytic depolymerization · Reductive depolymerization

6.1 Introduction

The global production and consumption of phenol–formaldehyde (PF) was approximately 3.0 Mt in 2009 with a market valued as much as \$2.3 billion, with an average annual growth of 3.9% from 2009 to 2013. A compounded average annual growth of 5.6% from 2015 to 2019 is predicted, and the global production of PF resins is expected to grow to 10 Mt valued at approx. \$13.36 billion in 2019 [1]. PF resins are the catalyzed polycondensation products from phenol and formaldehyde [2]. Depending on the synthesis conditions, two types of PF resins can be obtained, i.e., resoles and novolacs. Resoles are crosslinked resins produced with formaldehyde (F) and phenol (P) at a molar ratio of $F/P > 1$ under alkaline condition, while novolacs are linear polymers produced at a molar ratio of $F/P < 1$ under acidic condition.

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PF resins after curing provide great adhesive strength, high mechanical strength [3], excellent thermal stability [4], low initial viscosity, and great moisture resistance [2, 5, 6]. PF resins have been widely used as coating, molding materials, as well as wood adhesives for the production of engineered wood products, e.g., plywood, oriented strand board (OSB), and particleboard, waferboard, headboard, laminated veneer lumber, etc. [7–9]. PF resins can also be applicable for manufacture of closed cell foams for insulation applications where good fire resistance is required such as buildings insulation materials [10]. In addition, phenolic resins can be used for production gels (organic aerogels and cryogels) [11]. It was estimated that more than 50% of the entire production of PF resins is consumed as wood adhesives in the United State [12].

Currently, phenol is the main raw material for PF resins synthesis. Phenol is mainly derived from petroleum-based benzene through the cumene hydroperoxide process, which makes phenol the most expensive feedstock for PF resins manufacture. Substituting phenol with renewable and inexpensive biophenols would lead to great benefits with respect to the cost reduction. Exploration for phenol alternatives from renewable resources is of great significance to the sustainable development. In the past few decades, there are lots of literature reporting utilization of renewable phenol alternatives derived from lignocellulosic biomass materials (e.g., bark, wood and lignin) in PF resin production [13].

As discussed in Chap. 1, lignin has a phenolic structure that provides its potential replacement of phenol in the synthesis of PF resins. In addition, lignin has several properties attractive for being used as adhesives, e.g., high hydrophobicity, low glass transition temperature, low polydispersity in terms of molecular weight distribution, and high functionality, etc. [14]. Lignin is composed of three building blocks, i.e., guauacyl (G), synringyl (S), and p-hydeoxylphenol propane (p-H type) units, and the content of these three units in the structure of lignin depends on the original source of lignin and the delignification process [15–17].

The synthesis of lignin-based PF (LPF) resins occurs through electrophilic substitution of formaldehyde at a free ortho position of the phenolic hydroxyl group of lignin [18]. Thus, the G and p-H type units have reactive sites (ortho to the phenolic hydroxyl) towards formaldehyde. While in the S-type unit, both positions C3 and C5 are occupied by methoxy group and hence has least reactivity compared with G-type and p-H type units [16]. Softwood lignin normally contains more G units than lignins from hardwood and agricultural residues [15], which makes softwood lignin more desire for the synthesis of LPF resins.

Many studies have been published on incorporation of different types of lignin in synthesis of LPF resins, including enzymatic hydrolysis lignin, lignosulfonates, organosolv lignin, kraft lignin, and soda lignin, etc. [19–21]. Crude technical lignins have much less reactivity than phenol (with three available reactive sites: two ortho- and one para-positions) in reaction with formaldehyde due to the larger molecular structure and less reactive sites of lignin, and hence a higher reaction temperature and longer reaction time are normally needed in the LPF synthesis [3, 7, 22]. To improve the reactivity of lignin toward formaldehyde various modifications have been developed, such as methylolation [14, 17, 23], demethylation

[24], phenolation [7, 19, 22, 25], and sulphonation [7, 12]. In methylolation and phenolation of lignin, the lignin molecule is pretreated with formaldehyde or phenol, respectively, before the resin synthesis. These pretreatment methods increase the reactivity of technical lignin and enhance the degree of polycondensation during the synthesis of LPF resins. Besides chemical modifications of lignin, thermochemical processes, e.g., pyrolysis and depolymerization of lignin, as discussed previously in Chaps. 2 and 3, proved to be an effective way to enhance the reactivity of lignin, as the thermochemical processes produce degraded lignin with smaller molecular weights and more reactive sites. Lignin could be degraded into low molecular fragments via thermochemical processes, e.g., hydrocracking/ hydrogenolysis (or reductive depolymerization) [26], pyrolysis [27, 28], hydrolysis (or hydrolytic depolymerization) [29, 30], and oxidative depolymerization (in presence of various catalysts, e.g., Pd/Al_2O_3 [31], Cu^{2+}/Co^{2+} [32], and homogenous catalyst $H_3PMO_{12}O_{40}$ [33]). Among these processes, however, the oxidative degradation of lignin, generating significant amounts of ketones, benzoic acids, and benzaldehydes, is not appropriate for the synthesis of PF resins. In contrast, the hydrogenolysis (reductive depolymerization) and hydrolysis (or hydrolytic depolymerization) processes were found to be promising methods to produce biophenolic species from lignin for LPF resins synthesis [34].

The following sections of this chapter focus on the synthesis of lignin-based phenol–formaldehyde (LPF) resin.

6.2 LPF Resins from Lignosulfonates

Although lignosulfonates with a higher molecular weight have lower reactivity compared with kraft lignin and organosolv lignin, their wide availability and low price make them attractive phenol substitute in synthesis of LPF resins [35]. Ammonium-type lignosulfonates with better solubility in organic solvents were found to be more appropriate biophenol feedstock for the synthesis of LPF resins, compared to calcium, sodium and magnesium lignosulnotaes [35, 36].

Akhtar et al. [37] succeeded to replace phenol with lignosulfonate (LS) in synthesis of LPF resins at a bioreplacement ratio as high as 50%. At 20% bioreplacement ratio, the obtained LPF resins displayed the highest bond strength and wood failure, better than the commercial PF adhesives, and these properties remained constant in both wet and dry conditions, demonstrating good waterproof properties. Even the 50% LPF resin showed better bond strength properties than the commercial PF resin. Replacing phenol with LS at 50% bioreplacement ratio could achieve significant cost reduction for the production of PF resins. LS was liquefied in phenol and the resulted liquid products were used as a raw material to prepare a LPF resole by reacting with formaldehyde under alkaline condition [38]. The synthesized resole was used as a glue for manufacturing plywood, and the bonding strength was characterized in accordance to the CNS 1349 standard. The LPF resins from liquefied LS exhibited a dry bonding strength of 1.24 MPa, and a wet strength of 1.05 MPa, and 0.81 MPa, respectively, after warm water soaking and repetitive boiling water soaking. All strengths meet the minimum requirement (0.7 MPa) for plywood application. Matsushita et al. [18] reported synthesis of LPF resins from lignosulfonate at 15 and 30 wt% substitution ratios. As reported in this study, the presence of lignin in the resin formulation resulted in lower water resistance for the LPF resin than that of the petroleum-based PF resins. Turunen et al. [39] modified a PF resole using solid sodium lignosulfonate (at an amount of 4.9 wt% with respect to the amount of the LPF resin in liquid form) and liquid lignin-bearing lye (9.4 wt % with respect to the amount of the LPF resin in liquid form) during the synthesis process at the beginning stage of the condensation reaction. Addition of lignosulfonate increased dramatically the molecular weight of the resulted LPF sample that could not even be determined by GPC analysis. Whereas, the addition of lignin-bearing lye slightly increased the molar mass distribution (M_w and M_n) compared with those of the commercial PF resin. As commonly believed, the molar mass distribution of a PF resin has a significant effect on its bonding properties. PF resins with too small M_w would penetrate too much deeply into the porous structure of wood, leading to a low bonding strength. Similarly, PF resins with too large M_w cannot penetrate effectively into the wood structure, hence causing week adhesion properties either. The LPF resins were analyzed by DSC and demonstrated a lower curing peak temperature in comparison to the neat PF resin.

The chemical structure, thermal stability and rheological behavior of a neat PF resin and a LPF resin formulated with methylolated softwood ammonium lignosuldonate at 30 wt% substitution ratio were comparatively studied [40]. Although the LPF resin and the neat PF resin have similar chemical structure, the incorporation of lignin enhanced the thermal properties of the PF resin and change the flow behavior of the PF resin from Newtonian to pseudoplastic.

The curing process of PF resin is a complex process, generally consisting of two steps. First, the addition of hydroxymethyl groups into the free sites of phenol or lignin (ortho- or para-positions). The second step proceeds with the condensation reactions of methylol phenols with phenol/lignin and/or methylol phenols/lignins to form crosslinked structure [36]. Alonso et al. [35] studied the curing process of a LPF from a methylolated softwood ammonium lignosulfonate using dynamic DSC. The DSC thermographs of the LPF resin and a commercial PF resin exhibited two distinct exothermic peaks at a lower and higher temperature, corresponding to the reaction of free formaldehyde and the condensation/crosslinking reactions of methylol phenols with phenol/lignin and/or methylol phenols/lignins. In case of LPF resin, the total released heat is lower than that of the commercial PF resin, which could be explained by less reactivity and homogeneity of the LPF system in comparison with the PF resin. The cure kinetics of a LPF novolac resin at 30% substitution ratio and a methylolated LPF novolac resin were also investigated using hexamethylenetetramine (HMTA) by non-isothermal DSC and thermal mechanical analysis (TMA) [41]. It was observed that the gel point was remarkably reduced in the LPF resins with respect to that of a neat PF resin, due to the presence of more methylol groups in the structure of lignin that would promote the curing reactions.

LPF resins were prepared from methylolated lignin (softwood ammonium lignosulfonate), and the curing process of the resins was investigated using TMA and DSC [36]. TMA results revealed that the gelation point (α_{gel}) at various curing temperatures occurred at 47 and 65% for the FP resin and LPF resin, respectively. The activation energies for the curing process were calculated based on several isoconversional models including Ozawa, Kissinger–Akahari–Sunose, and Friedman. Based on these studied, it was concluded that lignin-based PF resin has lower activation energy throughout the curing process compared to the commercial PF resin.

6.3 LPF Resins from Kraft Lignin

As it is well known, chemical structure and properties of technical lignin varies with different isolation processes, e.g., kraft pulping, soda pulping, and organosolv pulping processes. Generally, kraft pine lignin is composed more by G-type units with the highest amount of hydroxyl groups, while the predominant structure of soda–anthraquinone flax lignin has limited hydroxyl groups, and the hardwood organosolv lignin consists of both G-type and S-type units in its structure. Among these types of lignin, kraft lignin has the highest average molecular weight due to the repolymerization reactions during the kraft pulping process. In addition, the thermal stability of kraft lignin and the ethanol–water organosolv lignin are generally better than the soda lignin. Accordingly, kraft lignin and organosolv lignin could be more suitable alternatives to phenol in synthesis of LPF resins [16].

A LPF resins with modified kraft lignin were synthesized at two phenol substitution ratios of 7 and 15 wt% and their surface characteristics were examined by contact angle measurement and inverse gas chromatography (IGC) [18]. With introducing a modified kraft lignin, the Lifshitz–van der Waals component of the work of adhesion between water and resin increased, while the acid–base component decreased. As a consequence, the LPF resin exhibited higher resistance to water compared to the commercial PF resins. In another study, mechanical properties of OSB manufactured using a kraft lignin-modified PF resin (KLPF, 50 wt%) were investigated and compared with a neat PF resin [42]. The modulus of elasticity (MOE) and modulus of rupture (MOR) of the OSB with KLPF sample were measured to be 2539 N/mm^2 and 20.33 N/mm^2, respectively, comparable to those of the sample with neat PF resin (2400 N/mm^2 and 22.03 N/mm^2, respectively), so were other properties such as internal bond strength, thickness swelling, and water absorption. It thus suggests that the KLPF resin could be a promising binder in manufacturing of OSB panels. Klasnja and Kopitovic [43] produced LPF resole resin for plywood adhesives, replacing up to 50 wt% of the phenol with kraft lignin, and the resulted liquid LPF resin (with viscosity of 500 mPa.s) demonstrated promise in plywood manufacture with acceptable strength properties. Danielson et al. [44] integrated an original kraft lignin (KL) into PF resin by blending with

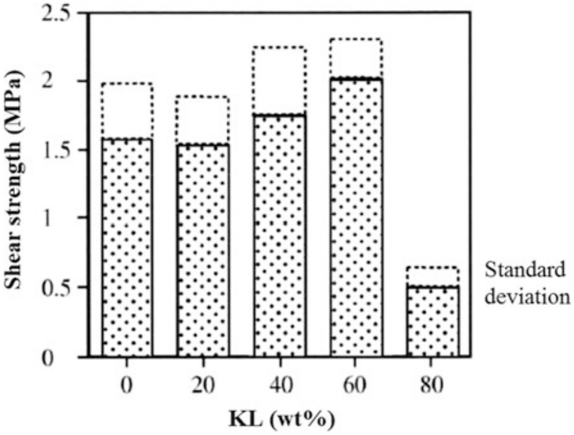

Fig. 6.1 Shear strength of plywood samples bonded with LPF resins from KL at various substitution ratios (20–80%), reprinted with permission from Ref. [44]. Copyright (1998) Taylor and Francis

different lignin contents (at 20–80 wt% phenol substitution ratios). The bonding ability of the LPF resins for plywood samples was measured, and the shear strength of plywood samples bonded with LPF adhesives with various contents of KL is illustrated in Fig. 6.1. As clearly shown in the Figure, the values of shear strength for LPF adhesives with a KL content in the range of 20–60 wt% are comparable or even better than that of the neat PF resin. However, at a higher phenol replacement level (80 wt%), the synthesized LPF resin was found to be brittle and of a much low shear strength.

A rice hull-derived acid-insoluble lignin was used as a biophenol for production of LPF resins through a novel process combining phenolation and three-step polymerization [22]. Initially, phenolation of lignin was carried out with phenol in sulfuric acid solution for 4 h at 80 °C. In the subsequent three-step polymerization process, firstly a low molecular weight PF resin was synthesized at 70 °C for 15 min, then a mixture of phenolated lignin (35% of phenol substitution ratio), formaldehyde, and sodium hydroxide was added and reacted for 15 min at 80 °C. Finally, a solution of formaldehyde, phenol, and sodium hydroxide was added and kept at 90 °C for 2 h resinification reaction. This LPF resin synthesis process improved the incorporation of phenolated lignin into the final resin products and avoided the competition of lignin and phenol in resinification reactions, leading to increased covalent interaction between the phenolated lignin and PF resin. The resulted LPF resins showed better temperature stability, morphology, water and ultraviolet resistance, compared with the LPF resins with phenolated lignin prepared via one-step resinification process.

Olivares et al. [24] conducted several chemical and physical modifications on kraft lignin and black liquor, in improving their reactivity toward formaldehyde in synthesis of LPF resins for production of particleboards. The effectiveness of following modifications has been demonstrated, including methylolation of lignin, demethylation of lignin, and ultrafiltration of black liquor to separate high molecular weight fraction. In general, the LPF resins from modified lignin exhibited better performance than those from unmodified lignin, particularly in mechanical performance. In another research, kraft lignin was utilized to substitute up to 50 wt % phenol in synthesis of LPF resole resins for production of plywood panels, and all LPF resins exhibited excellent dry and wet bonding strengths (with shear strength >2 MPa), better or comparable than those of a commercial PF resin [45].

A comprehensive study was conducted by Siddiqui [30] in the authors' group on the synthesis of LPF resins using depolymerized kraft lignin (DKL) at high phenol substitution levels up to 75%. The synthesis parameters including phenol substitution ratio (X_1: 25, 50, and 75 wt%), the average molecular weight (M_w) of DKL (X_2: 800, 1200, and 1700 g/mol), and formaldehyde/phenol (F:P) (including phenol and DKL) molar ratio (X_3: 1.2, 2.1, and 3) were optimized using Box–Behnken Design (BBD) to minimize curing temperature and maximize adhesive strength of the prepared LPF resins. The LPF resins were prepared using a two-step process: (1) DKL, phenol, NaOH solution, and methanol reacted at 60 °C for 2 h, and (2) formalin (37 vol.% formaldehyde water solution) was added drop-wise and reacted at 80 °C for 2 h. The results indicated that viscosity of the prepared LPF resins increased by increasing the M_w of DKL and the phenol substitution levels. The F:P molar ratio showed an inverse effect on the physical properties of the synthesized LPF resins, such as viscosity, pH, and nonvolatile contents (NOC), while a positive effect was attained for the F:P ratio on the curing reaction rate and crosslink density. Additionally, all LPF resins even with a high phenol substitution ratio (up to 75 wt%) met the minimum bonding strength 2.5 MPa for plywood applications, as illustrated in Fig. 6.2.

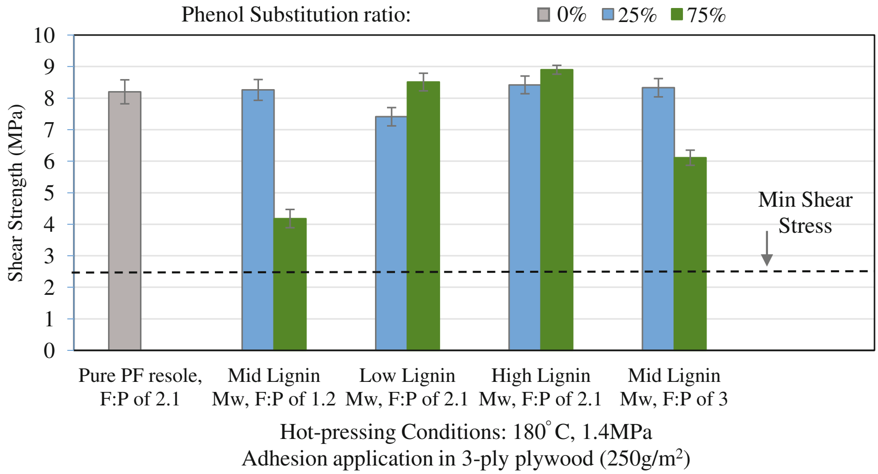

Fig. 6.2 Shear strength of plywood samples bonded with LPF adhesives from DKL at various phenol substitution ratios (25 and 75%), modified from Ref. [30]

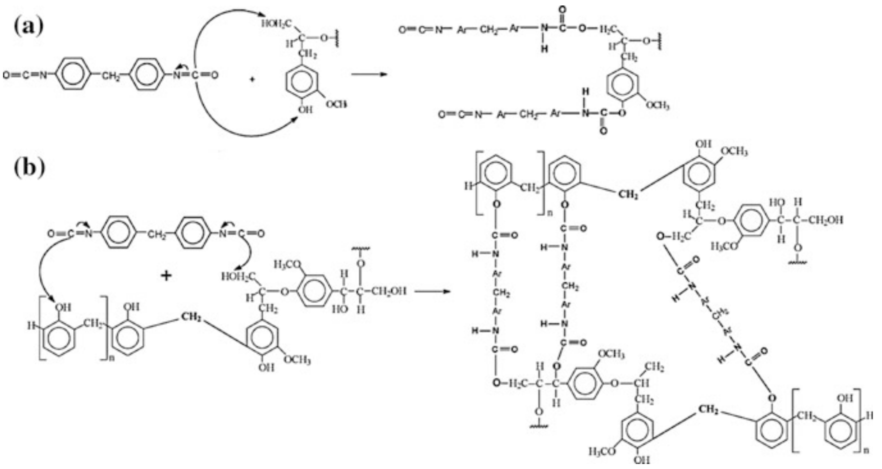

Fig. 6.3 Proposed mechanisms for the reaction between **a** MDI and lignin, and **b** MDI and LPF resin, with the formation of urethane groups/bridges, reprinted with permission from Ref. [47]. Copyright (2008) Elsevier

Compared with the LPF plywood adhesives prepared by Danielson et al. [44] using an original kraft lignin (KL) to substitute 20–80% of phenol, as shown previously in Fig. 6.1, the LPF resins from DKL have a much bonding strength (>2.5 MPa) for plywood applications. Thus, depolymerized kraft lignin with lower molecular weight appeared to be much more promising for substituting phenol for manufacture of LPF resins/adhesives. It was believed that the depolymerization process could effectively reduce steric hindrance, and sulfur content and increased reactive functional groups of lignin, accounting for the better performance of DKL products in the synthesis of LPF resins.

Four different types of technical lignin, including corn cob lignin (hydrolysis lignin), two poplar wood lignins (kraft lignins), and wheat straw lignin (Alkali lignin) were phenolated and used as partial replacement for phenol in production of LPF resins [6, 46]. The results showed that the phenolation treatment enhanced the reactivity of the technical lignins for LPF resin synthesis and the prepared LPF resins exhibited low emissions of formaldehyde and satisfactory performance as adhesives for plywood manufacture.

Moreover, novolac-type LPF resins (25–45 wt% phenol substitution ratios) were prepared from a sulphonated kraft lignin from mixed softwoods (Diwatex 40P) and successfully cured with methylene-diisocyanate (MDI) and hexamethylene-tetraamin (HMTA) [12, 47]. HMTA is a commonly used curing agent for novolacs. This study demonstrated that MDI can be an alternative curing agent for LPF curing, requiring a lower temperature than that of HMTA, and the MDI-LPF curing process takes place through a mechanism involving formation of urethane groups/bridges as shown in Fig. 6.3.

6.4 LPF Resins from Organosolv Lignin

Organosolv lignin was extracted from white pine sawdust by the authors' group employing an organosolv pulping process with 50 wt% ethanol–water solution [15]. It was observed that the optimal conditions for the 50 wt% ethanol–water organosolv pulping were at 180 °C for 4 h. Processing at above 180 °C led to thermal decomposition of cellulose, while processing at below 150 °C proved to be insufficient for extraction of lignin from pine sawdust. In the lignin extraction process, water played as a nucleophile agent to fascinate the cleavage of lignin, and ethanol acted as an impregnating agent to separate lignin from wood texture [15]. The obtained lignin was used as a feedstock to synthesize LPF resole resins at 25–75 wt% phenol substitution ratio at 80 °C for 4 h reaction with a fixed F:P molar ratio of 1.3 [15]. The molecular weights and polydispersity index (PDI) of the synthesized resol resins were found to increase with increasing phenol substitution ratio. The introduction of lignin in the resole resins influenced the curing process. For LPF resins at a low substitution level (<50 wt%), the curing process was controlled by phenol reactivity and catalyzed by lignin. However, at a higher substitution level, the low reactivity of lignin could govern the LPF curing process, significantly retarding the LPF curing. Moreover, the presence of lignin had a diverse effect on the thermal stability of the LPF resole resins, as commonly observed in the literature.

A methylolated organosolv lignin was utilized to partially replace phenol at up to 40 wt% for synthesis of LPF resins as adhesives for particleboards [48]. In synthesis process, the organosolv lignin first reacted with a partial amount of formaldehyde at 70 °C for 1 h under alkaline condition. Then, the rest of formaldehyde, phenol and sodium hydroxide were added at 85 °C to continue the resinification reaction for 1–3 h to achieve a desired viscosity (250–300 cP) of the final resin products. Final, a small amount of urea (5% of the total solution) was added as the cook cooling. Usually urea is added into PF resins (at <2–4 wt% of total solids) at the final stage of the synthesis to catch free formaldehyde or to substitute phenol in order to address the free formaldehyde emission issue and or to reduce the total cost of the PF resin production [39]. It was found that LPF resins at a phenol replacement ratio of 10–30 wt% have bonding strength comparable or even better than that of a neat PF resin, suggesting that organosolv lignin is a feasible phenol substitute for the synthesis of LPF adhesives for manufacturing particleboard panel.

A study was conducted on utilization of bagasse lignin for synthesis of LPF adhesives [49], where various synthesis parameters, including phenol substitution ratio, F/P molar ratio, catalyst concentration, reaction time, and reaction temperature, have been optimized. With increasing the lignin concentration up to 50 wt% of the total phenolics, the gel time decreased due to an increase in the rate of polycondensation and crosslinking of resins, resulting in improving adhesive strength and shear strength of the LPF resins. The results from the work revealed that the optimum conditions of preparation of LPF adhesive are phenol substitution ratio

50%, F/P molar ratio 2.0, NaOH addition 10 wt% of phenol, 4 h reaction time and 80 °C reaction temperature.

Two types of organosolv lignin, namely eucalyptus acetosolv lignin (EAc lignin) and eucalyptus Formcell lignin (EFo lignin), were modified via hydroxymethylation reaction using formalin and used to synthesize LPF resoles [17]. A set of experiments were, designed by multivariate factorial design (2^{4-1}), were conducted to investigate effect of four synthesis variables including lignin/phenol molar ratio (2:3, 1:1), F/P molar ratio (1.5:1, 2.2:1), NaOH/phenolics molar ratio (0.7:1, 1:1), solid content in wet resins (%) (38, 44.8) on the final viscosity and the synthesis time. The PF resins synthesized based on EFo lignin had 50% higher viscosity compared with EAc lignin PF resins, and the synthesis time decreased in both systems when increasing the molar ratio of lignin-to-phenol in the resin formula.

Vazquez et al. [50] found that when unmodified eucalyptus/acetosolv lignin was used to substitute 20% of phenol in the PF resin synthesis, the strength of the prepared plywoods reduced because the lignin added acted as a filler. In another work by the same group of researchers [14] demonstrated that methylolated or phenolated eucalyptus/acetosolv lignin could replace phenol by 20–40 wt% in the manufacturing of adhesives for plywood boards. The prepared resins met the EN 314-1:1993 standard for Weather and Boil Proof (WBP) plywood quality and their knife test results were very similar to those of samples made of a commercial PF resin.

A methylolated organosolv lignin was incorporated in synthesis of LPF resins by varying the lignin/phenol ratio (X_1: 20–40%), F/P molar ratio (X_2: 1.8–2.2), and NaOH/phenol molar ratio (X_3: 1–1.4) accordance with a $2 \times 2 \times 2$ factorial design with a repeated central point [51]. The effects of the synthesis parameters on gel time (Y_1), free phenol content (Y_2), and plywood board knife test rating (Y_3) were investigated. The results showed that gel time depended strongly on lignin/phenol ratio and NaOH/phenol ratio, free phenol content was influenced by three independent variables, and some prepared LPF adhesives exhibited better knife test results than a commercial PF resin.

An organosolv lignin with and without phenolation were incorporated in the synthesis of LPF resins as adhesives for the production of particleboard [8]. The physical and mechanical properties (including internal bond, modules of rupture, modulus of elasticity, thickness swell, and water absorption) of the prepared particleboards were investigated to determine the adequate phenol substitution ratio in preparation of LPF resins. The obtained results indicated that the LPF adhesives from phenolated lignin generally showed better physical and mechanical properties than those from unmodified lignin. The LPF resins from organosolv lignin with/without phenolation at a phenol substitution ratio of 20–30% showed comparable properties to those of commercial PF resin, when applied as adhesives for particleboards.

The authors group [26] catalytically degraded organosolv lignin in 50/50 (v/v) water–ethanol media under sub/supercritical condition in hydrogen atmosphere to produce highly reactive low-M_w biophenolic compounds. The optimum condition determined was at 340 °C in presence of Ni10/active carbon (AC), producing depolymerized organosolv lignin (DL) at ~81% yield and with an M_w of

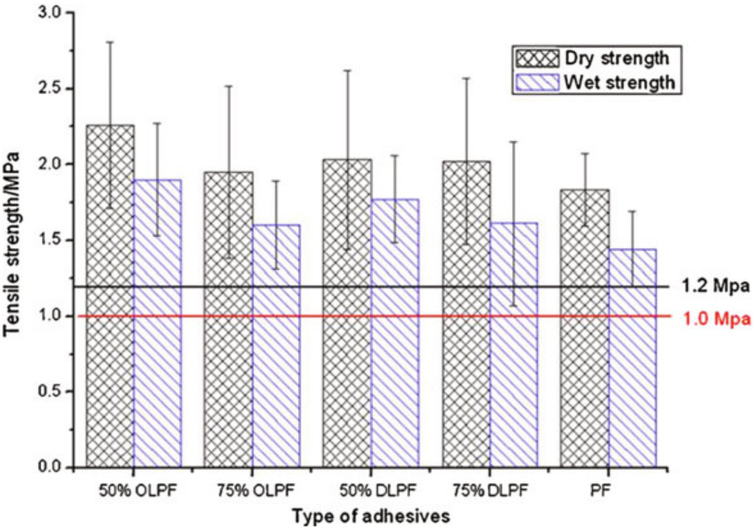

Fig. 6.4 Tensile-strength profile of plywood glued by OLPFs, DLPFs, and PF adhesives, reprinted with permission from Ref. [26]. Copyright (2013) Elsevier

568 g/mol. The depolymerized organosolv lignin (DL) and the original lignin (OL) were used as a substitute for phenol in the synthesis of DLPF or OLPF resins at high substitution ratio up to 75 wt%. The obtained DLPF or OLPF resins showed excellent wet and dry tensile strengths, superior to those of a neat PF resin, as illustrated in Fig. 6.4. Moreover, compared with the OLPF resins, the DLPF resins have lower formaldehyde emission and a lower curing temperature, although the bonding strength and thermal stability of these two types of LPF resins were found to be similar.

6.5 LPF Resins from Hydrolysis Lignin

Enzymatic hydrolysis lignin (EHL) or simply hydrolysis lignin (HL) is extracted from the solid residues from production of bioethanol with sodium hydroxide solution. Qiao et al. [7] modified a HL and bioethanol production residue by phenolation reaction with phenol under an alkaline condition (40 wt% sodium hydroxide aqueous solution) at 90 °C for 1 h. Then these phenolated products were mixed with phenol at different substitution ratios ranging from 10 to 60 wt%, and reacted with formaldehyde (F/P molar ratio of 1.5) in alkaline medium (NaOH) at 80 °C for 2 h. The adhesive strength of the synthesized LPF resins with enzymatic HL and bioethanol production residue-modified PF (RPF) was measured and compared. For the LPF resins with phenol substitution up to 50 wt%, the adhesive strength was higher than that of a commercial PF resin. Further increasing the lignin content, however, reduced the crosslinking of the polymer chain and led to a lower adhesive strength. In general, RPF provided lower adhesive strength in compared with that of LPF resin given a same phenol substitution ratio, but comparable results were obtained when the phenol substitution ratio was <20%. In addition, it was found the free phenol content (%) of the LPF resins decreased with increasing the phenol substitution ratio in the synthesis of LPF resins, which thus has positive impact on the environment.

A novolac-type LPF resin was synthesized using enzymatic hydrolysis lignin (EHL) with a two-step process [52]. First, EHL was liquefied in phenol, at a substrate concentration ranging from 20 to 55 wt%, in the presence of oxalic acid as catalyst, at 115 °C for 2 h. The liquefaction process reduced the weight average molecular weight (M_w) of EHL from 3107 g/mol to 1448 g/mol. While increasing the substrate concentration from 20 to 55 wt%, the solid residue yield increased from 11.9 to 28.1%. Then, novolac resin was synthesized directly with the liquefied EHL lignin at 85–90 °C (at an F/P molar ratio of 0.85:1). Among the synthesized LPF resins, the 55% LPF has lower free phenol content, longer gelation time, and shorter flowing distance in compared with typical neat PF resin, but they are still applicable for the application as a molding powder.

EHL-based PF resoles were produced via a one-step process at F/P molar ratio of 1.5:1 for 1 h at 80 °C [4]. The influences of the partial replacement of phenol by EHL (5–25 wt%) and NaOH concentration (2.5–7.5 wt%) on the bonding strength of the LPF adhesive were investigated. The obtained results showed that the maximum replacement of phenol by EHL was 20 wt% and the loading amount of NaOH should be more than 2.5 wt% to produce a LPF resin to meet minimum requirements as a plywood adhesive.

6.6 LPF Resins from Soda Lignin (Alkali Lignin)

Soda lignin or alkaline lignin, i.e., lignin isolated by alkaline delignification, has also a potential for production of LPF adhesives. During alkaline pulping, the alkyl ether bonds are cleaved, generating more aromatic hydroxyl groups on its structure [9].

Nada et al. [53] investigated the effects of the soda lignin modification process and synthesis parameter (such as lignin concentration, F/P molar ratio, temperature, and reaction time) on the properties of the LPF resins. Lignin was modified by various chemical processes including oxidation in presence of dichromate solution ($NK_2Cr_2O_3$), reduction by sodium hydrosulfite (10% $NaHSO_3$), and hydrolysis by hydrochloric acid (35% HCl). Then, the modified lignins and unmodified lignin were used in the preparation of LPF resins via a two-step process that is illustrated in Fig. 6.5. The effects of lignin modification and lignin content in the mixture of (lignin + phenol) were examined on the properties of LPF resins (i.e., reaction yield, solubility, softening temperature, viscosity, and bonding strength). The results indicate that the modified lignin with HCl and $NK_2Cr_2O_3$ solution achieved a higher yield in comparison with the unmodified lignin, owing to their higher

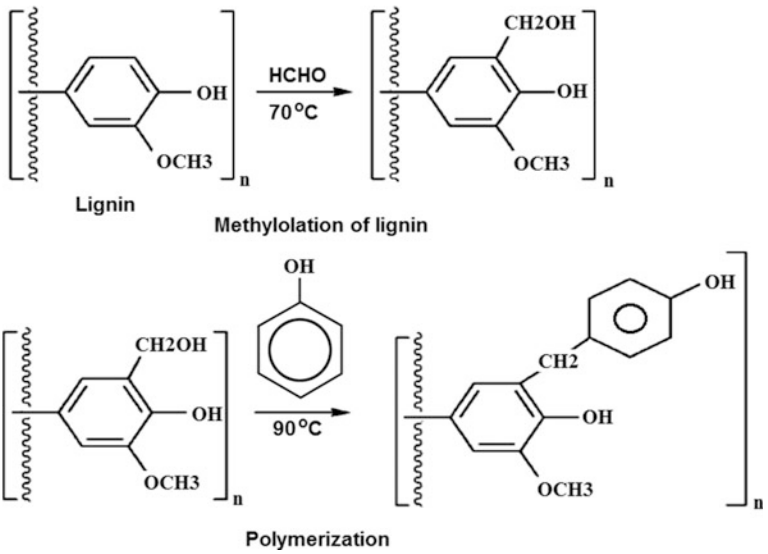

Fig. 6.5 Two-step process to produce LPF resins using soda lignin via a two-step process involving methylolation and polymerization, reprinted with permission from Ref. [53]. Copyright (2003) Taylor and Francis

reactivity ascribing to the modification treatment leading to increased phenolic OH groups and depolymerization of aliphatic chains. With increasing the content of lignin, the solubility of the synthesized LPF resins decreased due to the increase of the molecular weight and ash content in the lignin-based resins. In general, the properties of the synthesized LPF resins improved with the modified lignin, and the hydrolysis treatment of lignin with HCl was found to be the best method, among all the treatment methods tested in their work, for modification of lignin for LPF resins synthesis. In addition, it was observed that the optimum conditions of production LPF resin was 3.5 h reaction at 90 °C with 30% lignin content.

Lee et al. [38] liquefied alkaline lignin in phenol with H_2SO_4 or HCl as a catalyst to prepare feedstock for synthesis of resole-type PF resins. In the synthesis process, the liquefied lignin needed a lower temperature and shorter time to reach an applicable viscosity. Solid content and pH of the liquefied lignin-based PF resins varied in the range of 48.1–50.8% and 9.93–11.26, respectively, which were slightly lower than the values of a commercial PF resin (solid content was 51.4% and pH was around 11.3). In addition, it was observed that the LPF resins from the phenol-liquefied alkaline lignin had higher reactivity than the commercial PF resin, exhibiting a shorter gel time at 135 °C and a lower curing temperature. Khan and Ashraf [9] explored the possibility of using an alkaline lignin derived from coffee bean shell for the synthesis of LPF resin with a high phenol substitution ratio up to 60 wt%. Bonding strength tests for the prepared plywood samples showed that the strength increased with increasing the content of lignin in the formulation up to 50 wt%, while a diverse trend was observed on the gel time.

An alkaline lignin isolated from groundnut shell was incorporated in the synthesis of LPF resole resin at different phenol substitution ratio: 25, 35, 50, and 60 wt% [54] at 80 °C for 4 h in presence of NaOH solution. It was found that, introducing lignin into PF resin up to 50% ratio enhanced the bonding strength owing to better crosslinking density of the LPF resins. For the 50% LPF resin, the nonvolatile content, gel time at 100 °C, and viscosity (at 25 °C) are 34%, 245 s, and 5.5 cP, respectively.

6.7 LPF Resins from Biorefinery Residues

As a by-product of pulping industry, technical lignin has less hydroxyl groups due to the harsh conditions of pulping process, e.g., high-temperature and high-alkaline condition that oxidize hydroxyl groups. As a consequence, LPF adhesives generally have higher free formaldehyde in comparison to the neat PF adhesives. While, biorefinery residues that are rich in lignin and have high reactivity could be utilized as a promising replacement of phenol in the synthesis of PF resins.

Zhang et al. [5] examined the potential of synthesis of bio-based PF resin from cellulosic ethanol production residue and optimized the synthesis parameters with respect to the performance of adhesives (gel time, free formaldehyde content, free phenol content, and bonding strength). With increasing the phenol substitution ratio from 10 to 70%, the viscosity and the free phenol content of the resulted resins decreased, while the free formaldehyde increased and the bonding strength decreased. It was found that 50% substitution of phenol produced an adhesive with acceptable bonding strength (~1.0 MPa) that could meet the requirement of exterior grade plywood adhesives as per the Chinese National Standard (GB/T 9846.3-2004). The results demonstrated that the optimum conditions of synthesis of PF using the residue replacing 50% phenol were: F/P molar ratio of 3.0, and 20 wt% catalyst concentration, obtaining a resin with 0.3 wt% free formaldehyde content, 0.2 wt% free phenol content, and ~1.0 MPa bonding strength.

Table 6.1 The chemical characteristics of biorefinery residues, reprinted with permission from Ref. [3]. Copyright (2013) Elsevier

Properties	ER	BR	XR	LR
Moisture	11.3	5.3	5.1	12.8
Ash	22.7	3.9	5.1	21.5
Acid-insoluble lignin	38.8	78.2	61.1	52.3
Acid-soluble lignin	3.7	2.8	3.2	4.2
Holocellulose	25.2	11.9	25.2	2.1
Polysaccharide	1.1	1.5	1.8	1.4
Total hydroxyl	23.2	20.9	4.7	11.2
Phenolic hydroxyl	1.6	3.3	1.9	1.5
Aliphatic hydroxyl	21.6	17.6	2.8	9.7
Methoxyl	8.8	2.7	3.7	3.9

Table 6.2 The properties and performance of biorefinery residue-based PF resins, reprinted with permission from Ref. [3]. Copyright (2013) Elsevier

Adhesive	Mass ratio Phenol: residue	Resin performances					Plywood performances	
		pH	Viscosity (mPas)	Solid content (%)	Free formaldehyde (%)	Free phenol (%)	Bonding strength (MPa)	Formaldehyde emission (mg/L)
PF	100:0	12.1	100	48.90	0.10	0.65	1.65 ± 0.21	0.13 ± 0.01
30% ERPF[a]	70:30	11.0	175	47.30	0.23	0.15	1.06 ± 0.12	0.11 ± 0.05
30% ERPF[b]	70:30	11.2	100	48.71	0.31	0.13	1.32 ± 0.25	0.10 ± 0.02
50% ERPF	50:50	11.5	235	50.02	0.32	0.24	0.98 ± 0.10	0.23 ± 0.04
50% ERPF[b]	50:50	11.6	160	49.52	0.47	0.26	1.31 ± 0.22	0.11 ± 0.04
50% BRPF	50:50	10.9	300	48.05	0.54	0.49	0.88 ± 0.12	0.23 ± 0.02
50% XRPF	50:50	11.1	1080	47.95	0.76	0.49	0.84 ± 0.09	0.32 ± 0.03
50% LRPF	50:50	11.8	>20,000	46.60	1.10	0.74	1.52 ± 0.20	0.14 ± 0.05
GB/T 14,732	–	≥ 7	≥ 60	≥ 35	≤ 0.3	≤ 6	0.7	0.50

[a] 30% ERPF is the resin of ethanol biorefinery residue substituted phenol by 30 wt%. The following 50% ERPF et al. are the same meaning

[b] The RPF resins were produced in large scale (100L)

Zhang et al. [3] utilized four types of biorefinery residues, including ethanol residue (ER), butanol residue (BR), xylitol residue (XR), and lactic acid residue (LR) to produce bio-based PF resins. The chemical characteristics of the biorefinery residues are presented in Table 6.1. The resin synthesis parameters were: 2:1 F/P molar ratio, 30–50% phenol substitution ratio, under alkaline condition (with NaOH 20 wt% loading with respect to the total mass of phenol/residue) at 80 °C for 3 h. The properties and performance of the synthesized PF resins as plywood adhesives are summarized in Table 6.2. Apparently, the performances of all residue-based PF resins were inferior to that of a neat PF resin due to less reactivity of lignin in reaction with formaldehyde, also resulting in a higher free formaldehyde content in the residue-based PF resins than that of the neat PF resin. Among all different biorefinery residues tested, ER demonstrated to be the best phenol substitute for production of PF resins, likely owing to due to its lower polysaccharide content and higher hydroxyl content (Table 6.1).

6.8 Summary

The phenolic structure of lignin made it a promising substitute for phenol in the synthesis of lignin-based phenol–formaldehyde (LPF) resins as adhesives for engineered wood products. Various types of technical lignin, including lignosulfonates, kraft lignin, organosolv lignin, soda lignin and enzymatic hydrolysis lignin, without treatment have been utilized to substitute phenol up to 30–50 wt% in manufacturing of LPF resins. Technical lignin has larger molecular structure and less reactivity toward formaldehyde in compared with phenol. Therefore, it is required to conduct some chemical/thermal modifications on lignin prior to the resin synthesis process to improve the reactivity of the lignin. It was found the performance of ultimate wood adhesive depended on lignin properties (types of lignin, source of lignin (softwood/hardwood), type of pretreatment, and molecular weight) and the synthesis conditions (phenol substitution ratio, F/P molar ratio, NaOH loading for resole synthesis, reaction temperature, and reaction time).

Various modifications have been developed, such as methylolation, demethylation, phenolation and, sulphonation. Besides chemical modifications of lignin, thermochemical processes, e.g., pyrolysis and depolymerization of lignin proved to be an effective way to enhance the reactivity of lignin, as the thermochemical processes produce degraded lignin with smaller molecular weights and more reactive sites. The hydrogenolysis (reductive depolymerization) and hydrolysis (or hydrolytic depolymerization) processes were found to be promising methods to produce biophenolic species from lignin for LPF resins synthesis. For instance, catalytically degraded organosolv lignin in 50/50 (v/v) water–ethanol media under sub/supercritical condition in hydrogen atmosphere produced highly reactive low-M_w depolymerized organosolv lignin (DL) that was used in synthesis of LPF resins at high substitution ratio up to 75 wt%. The obtained DLPF showed excellent wet and dry tensile strengths, superior to those of a neat PF resin. The DLPF resins have lower formaldehyde emission and a lower curing temperature than the neat PF.

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Chapter 7
Lignin-Based Epoxy Resins

Abstract This chapter focuses on the utilization of lignin in the production of epoxy resins. The incorporation methods of lignin in manufacture of epoxy resins can be classified into three categories: (i) physical blending of lignin and epoxy resin, (ii) pre-modification of lignin before epoxidation, and (iii) direct epoxidation of lignin. The presence of lignin in epoxy resin changes the chemistry of the resultant product and hence affects the thermal and mechanical properties of the epoxy resin. Furthermore, the curing kinetics, mechanical and thermal properties of the synthesized lignin-based epoxy resins were compared with the conventional petroleum-based epoxy resins. The results indicated that lignin could be a promising bio-replacement of bisphenol-A in the production of various epoxy resins with acceptable performance.

Keywords Lignin-based epoxy resins · Physical blending · Pre-modification of lignin · Direct epoxidation of lignin · Thermal and mechanical properties · Curing

7.1 Epoxy Resins and Its Synthesis

Epoxy resin is defined as a component with an average of more than one epoxy group per molecule [1]. The world current epoxy market is estimated to be more than \$20 billion, and market in China has been growing rapidly, accounting for more than 30% of the total worldwide market. The market value is expected to reach \$25.8 billion by 2018 and \$33.6 billion by 2022, following the annual growth rate of 6.8% in the coming years, due to the strong demands in epoxy composite and epoxy adhesives [2].

Over 90% of glycidyl epoxy resins are diglycidyl ether of bisphenol-A (DGEBA or bisphenol-A type epoxy resins), synthesized by reacting bisphenol-A (BPA) with

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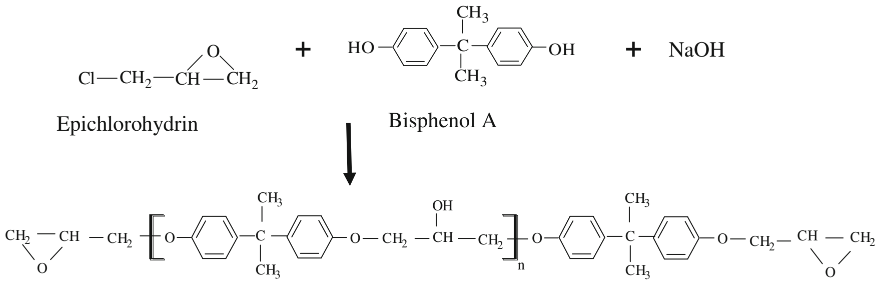


Fig. 7.1 Chemical structure of DGEBA epoxy resin

epichlorohydrin [3, 4]. Figure 7.1 shows the general structure of BPA-type epoxy resin. With increasing the number of repeat unit "n" in the epoxy polymer, the physical state of epoxy resin could transform from liquid resins to solid ones. On the other word, the weight average molecular weight of 380 is liquid at ambient temperature, while an epoxy resin with the weight average molecular weight of 1000 and above would be solid at room temperature.

At present, 80–90% of commercial epoxy resins are prepared from bisphenol-A reacting with epichlorohydrin. Grafting of epoxy groups on phenolic hydroxyl groups (AR-OH) takes place through the following reaction mechanism as illustrated in Fig. 7.2 [5].

NaOH is used as a catalyst for the nucleophilic ring-opening of the epoxide group on the primary carbon atom of epichlorohydrin and as a dehydrochlorinating agent for conversion of the chlorohydrins to epoxide group [6]. Also quaternary ammonium salts (QAS) and phosphonium salts can be used as a catalyst to promote the condensation reaction of epichlorohydrin with bisphenol-A [6]. Besides the major reaction of epoxy resins production, some side reactions can take place and may have an effect on the final properties of epoxy resins. The side reactions, as shown as bellow, should be prevented by optimization of reaction conditions [4]:

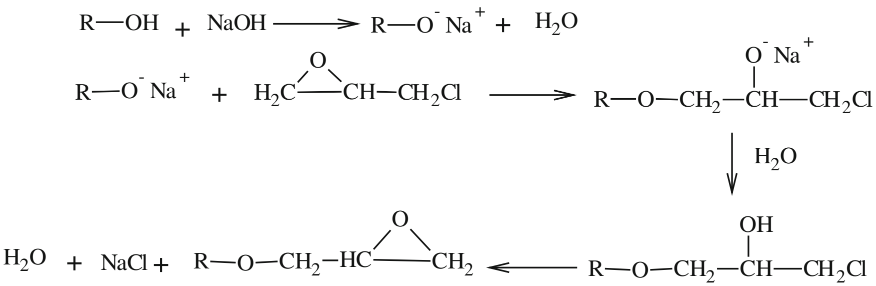
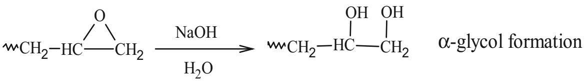


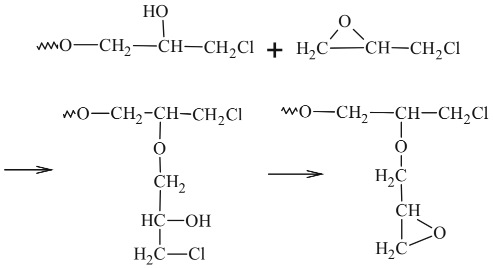
Fig. 7.2 Major reaction scheme in epoxy resin production from bisphenol-A, modified from Ref. [5]

1. *Hydrolysis of epoxy groups*

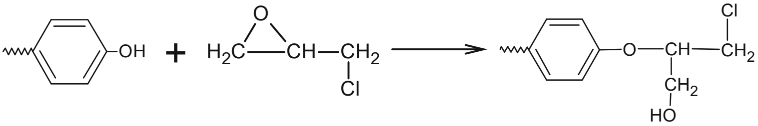


2. *Formation of bound chlorine*

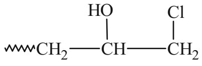
   (a) Reaction of epichlorohydrin with secondary alcohol



   (b) Abnormal addition of phenolic hydroxyl



3. *Incomplete dehydrochlorination*



$$\sim\!\!\sim CH_2-\overset{\overset{HO}{|}}{CH}-\overset{\overset{Cl}{|}}{CH_2}$$

The effective factors that influence the properties of low molecular weight epoxy resin, including reaction time, reaction temperature, propan-2-ol presence, and quantities of water present in the reaction mixture, were investigated by Krol et al. [7]. The optimal conditions for the epoxy resin synthesis were determined to be 40 °C, 90 min reaction time, 5.5 wt% adding amount of water, 16 wt% adding amount of 2-propanol additive, with 45% NaOH aqueous solution as a catalyst. Another factor that has marked effect on molecular weight of the obtained epoxy resins is molar ratio of epichlorohydrin/bisphenol-A. An excess of epichlorohydrin is usually used to control the molecular weight of the resin products [5]. The effects of molar ratio of epichlorohydrin on molecular weight and softening point of epoxy resins are presented in Table 7.1.

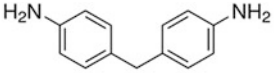
Table 7.1 Effects of molar ratio epichlorohydrin/bisphenol-A on molecular weight and softening point of epoxy resins, modified from Refs. [8, 9]

Molar ratio of epichlorohydrin: bisphenol-A	Molecular weight (M_w) (g/mol)	Epoxide equivalent[a]	Softening point (°C)
10:1	370	192	9
2:1	451	314	43
1.4:1	791	592	84
1.33:1	802	730	90
1.25:1	1133	862	100
1.2:1	1420	11,776	112

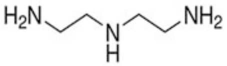
[a] Pure diglycidyl ether (mol. Wt. 340) with two epoxy groups per molecule, epoxide equivalent = 340/2 = 170

7.2 Curing and Applications of Epoxy Resins

A wide range of reagents as curing agents could react with epoxy resins to form three-dimensional crosslinked thermoset structures [10]. The common curing agents for epoxy resins include amines (aliphatic amine, aromatic amine, and modified amines), polyamide resin, imidazoles, polymercaptan, and anhydrides [11, 12]. Typical curing agents are 4,4′-diaminodiphenylmethane (DDM) and diethylenetriamine (DETA).



4,4′-Diaminodiphenylmethane
(DDM)



Diethylenetriamine
(DETA)

Curing of bisphenol-A type epoxy resin by DDM can be illustrated in Fig. 7.3. In addition, epoxy resins have tendency to form cured structure by reacting between itself in the presence of an anionic or cationic catalyst. This reaction is known as catalytic homopolymerization, as schematically illustrated in Fig. 7.4.

The homopolymerization reaction leads to generation of the polyether systems with great thermal and chemical resistance. The homopolymerization of epoxy occurs at a high temperature and the obtained network is, however, very brittle, thus with limited applications [4].

Epoxy resin is one of the most popular synthetic thermosetting polymers owing to its superior properties such as great chemical resistance, high adhesion strength to various substrates, low curing contraction, high moisture and solvent resistances, good thermal and dimensional stabilities, and superior electrical properties [14–16]. These properties provide diverse applications of epoxy resins, which are summarized as follows [4, 8, 10, 17–20]:

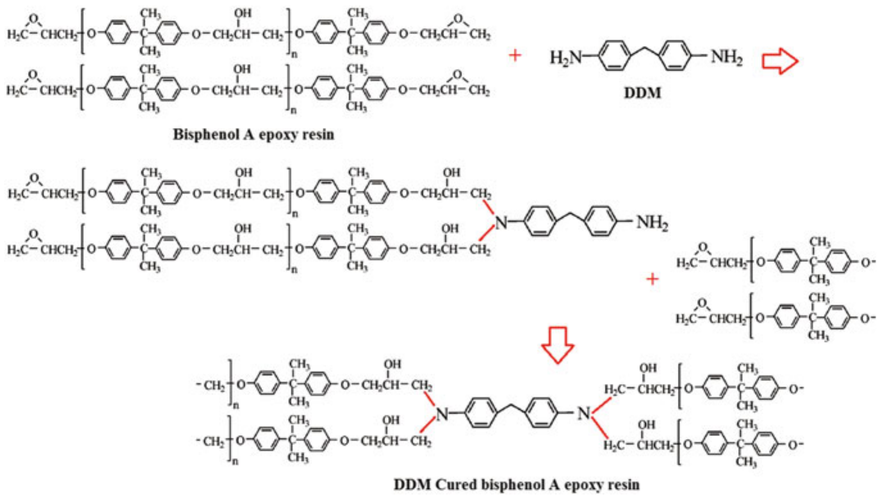


Fig. 7.3 Curing of bisphenol-A type epoxy resin by DDM

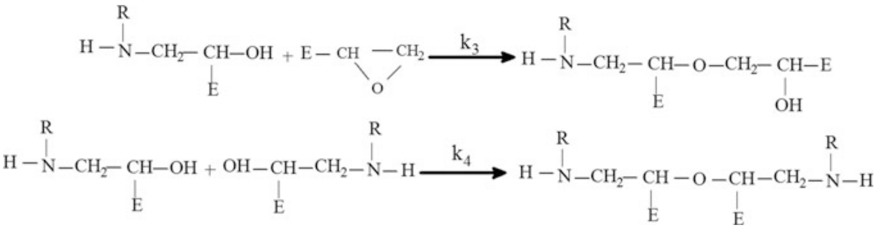


Fig. 7.4 Etherification reaction and homopolymerization of epoxy resins, reprinted with permission from Ref. [13]. Copyright (2013) Elsevier

(1) Adhesives and bonding;
(2) Surface (protective) coatings;
(3) Electrical and electronic applications;
(4) Composites (reinforced resins);
(5) Other applications, e.g., polymer stabilizers, plasticizers, and plastics for pipes.

7.3 Synthesis of Lignin-Based Epoxy Resins

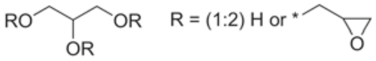
Various natural resources, such as vegetable oils (i.e., soybean oil, linseed oil and palm oil) [21–27], tannins [28–30], rosin [31–33], bark [34], liquefied biomass [35–37], lignin [38, 39], and woody biomass [21], have been used as the precursor for the synthesis of bio-based epoxy resins. The main advantage of these kinds of epoxy resins is biodegradability. Among these bio-based epoxy resins, the vegetable oil-based epoxy resins have limited applications in the industry due to the nonaromatic backbone structure, resulting in poor heat endurance, mechanical, and other performance properties. Therefore, they were used only as plasticizers and modifiers in some industries [21, 40–42]. For instance, adding the epoxidized soybean oil to petroleum-based bisphenol-A with isophorone diamine system effectively reduced the maximum curing peak temperature, and promoted the performance of the resulted epoxy resins with respect to water adsorption and chemical resistance [40]. New bio-based epoxy clay nanocomposites (organo-montmorillonite clay) were produced with diglycidyl ether of bisphenol F (DGEBF), epoxidized linseed oil (ELO) and methyltetrahydrophthalic anhydride (MTHPA) [43]. These new bio-based nanocomposites exhibited high elastic modulus, glass transition temperature, and fracture toughness, thus they might provide potential applications in various industries. A novel bio-based epoxy resin with curable double bonds was developed from itaconic acid [44]. To improve the final properties of the cured resin, divinyl benzene, and acrylated epoxidized soybean oil were incorporated in the cured network, and the results demonstrated that its glass transition temperature, tensile strength, flexural strength, and flexural modulus were comparable with those of the conventional BPA-based epoxy resins [44]. Dimer acid (the dimer of C18 non-saturation fatty acid) is another bio-based material that was applied to epoxy resins systems. Similar to the vegetable oil-based epoxy resins, the dimer acid-based epoxy resin exhibited poor mechanical, electrical properties, and heat resistance due to its nonaromatic structure and long side chain [21].

As discussed previously, lignin is a natural phenolic polymer. The presence of the phenolic hydroxyl groups in lignin enables its utilization in the synthesis of various polymers such as phenolic resins [45], epoxy resins [43, 46], polyurethanes [47–49], and polyesters [49, 50]. It is expected that the lignin-based epoxy resin can have properties equivalent to those of the conventional petroleum-based epoxy resins. Lignin-based epoxy resins can be prepared by three different methods [51]:

1. Physically blending of petroleum-based epoxy resins with lignin [39, 52],
2. Epoxidation of lignin after pretreatment [53], and
3. Direct epoxidation of lignin with epoxides [54–59].

7.3.1 Physical Blending of Lignin and Epoxy Resin

In this method, lignin is simply blended with a petroleum-based epoxy resin and curing agent to prepare composite materials. Lignin will react with the epoxy resin upon curing. The obtained lignin-epoxy composites show good compatibility with other materials and good mechanical and dielectric properties after curing at elevated temperatures [52]. In a study, low molecular weight kraft lignin was blended with an epoxy (1,3-glycerol diglycidyl ether whose structure is illustrated below) and imidazole (a curing agent) for preparation of bio-based epoxy resin [60].



1,3-glycerol diglycidyl ether

The content of lignin in the composites varied in the range of 20–50 wt%, and the best thermoset had the tensile strength and Young's modulus of 37 MPa and 2.2 GPa, respectively. In some studies, lignin was used as a curing agent for epoxy resins. Reinforced green composites were developed by curing DGEBA (bisphenol-A type epoxy resin) with lignin (as a curing agent) at a lignin content varying from 15 to 30 wt%, and the effects of lignin content on thermal and mechanical properties of the composites were investigated and compared with the system of the same epoxy resin cured with isophorone diamine. The optimum properties were obtained from a system comprising 25 wt% of lignin [14]. Pan et al. [51] used aminated lignin as a curing agent for epoxy resin, where the aminated lignin was synthesized based on a two-step process using alkaline lignin. Step 1: The alkaline lignin was first dissolved in sodium hydroxide solution, then epichlorohydrine was added and mixed at 50 °C for 8 h to epoxidize the lignin; Step 2: the epoxidized lignin reacted with propane diamine under 80 °C for 4–6 h to prepare the aminated lignin [61]. The aminated lignin was found to be a more reactive crosslinker for epoxy resins owing to its primary and secondary amine groups, and the cured epoxy resin has uniform and stable structure [51].

However, the limitation of the simple blending approach is that lignin can substitute only a small percentage (<20–30 wt%) of epoxy resins. In contrast, the other two methods as discussed in the following sections make it possible to achieve a high substitution ratio up to complete substitution of petroleum-based materials (such as bisphenol-A) with lignin.

7.3.2 *Epoxidation of Lignin After Pretreatment*

In one study, kraft lignin was reacted first with unsaturated carbonyl groups or unsaturated nitrogen containing compounds to produce alpha- or beta-unsaturated reactive end groups on the lignin molecule. Then, these unsaturated groups were epoxidized by reacting with hydrogen peroxide or sodium peroxide [53].

Several studies were performed on epoxidation of lignin after pretreatment. Sulfuric acid or hydrochloric acid treatment was used to cleave the intermolecular bonds of a kraft lignin to increase the phenolic hydroxyl groups in the lignin molecules, followed by grafting the lignin molecules by epichlorohydrin under sodium hydroxide condition [21]. To the similar end, ozone oxidation was performed on kraft lignin by dissolving the lignin in the dioxane/water mixture followed by oxidation with ozone-containing oxygen. This oxidative treatment could cleave the aromatic ring of lignin and generate muconic acid derivatives with carboxyl groups on both ends of the conjugate double bond. The ozonized lignin was then dissolved in alkaline water to crosslink with the water-soluble petroleum-based epoxy resins. The crosslinked product has intermolecular penetrating network (IPN) structure with superior adhesion ability on wood substrates [21]. In another modification, alcoholysis lignin was dissolved in ethylene glycol at 80 °C and reacted with succinic anhydride and dimethylbenzylamine for 6 h. The obtained mixture of ester–carboxylic acid derivatives of alcoholysis lignin and ethylene glycol was reacted with various molar ratios of ethylene glycol diglycidyl ether (EGDGE) at 130 °C for 5 h to synthesize lignin-based epoxy resin [62, 63]. Hofmann et al. [38] prepared epoxy resins from hydroxyalkyl lignin derivatives from organosolv lignin with varying degrees of alkoxylation. In the study of Hofmann et al. [38], hydroxyalkylation of organosolv lignin was conducted by reacting it with propylene oxide to improve the solubility and then with ethylene oxide to convert secondary hydroxyl groups into primary hydroxyl groups, followed by epoxidation of the pretreated lignin with epichlorohydrin. The epoxidized lignins have an average molecular weight from 1000 to 30000 g/mol and an epoxy index from 200 to 700 g/eq. The epoxy-lignin was then crosslinked with meta-phenylene diamine and the epoxy-amine network that contains more than 50% lignin exhibited tensile strengths and moduli in a similar order of the conventional DGEBA–amine networks [38].

Simionescu et al. [64] modified an iron-lignosulfonate by phenolysis reaction with phenol, beta-naphthol, bisphenol-A, and a novolac phenol formaldehyde resin. Then these phenolated products were reacted with epichlorohydrin in alkaline medium (NaOH) at 75 °C for 6 h with different molar ratios of epichlorohydrin-to-phenolated compounds, and the obtained liquid and solid lignin-epoxy resin products showed good thermal stabilities. Zhao et al. [58] synthesized epoxy-lignin resins from calcium lignosulfonate after pretreatment using sulfuric acid to convert it into lignosulfonic acid in excess phenol at 95 °C for 3 h, which generated phenolated lignosulfonate. With such modification, the content of phenolic hydroxyl groups was improved and the phenolated lignosulfonate was then epoxidized by epichlorohydrin in the presence of NaOH as a catalyst. An interesting point of the above epoxy-lignin synthesis method is that two types of epoxy resin (solid phase and liquid phase) were simultaneously produced. The C-NMR spectroscopy analysis evidenced epoxy groups on the structure of liquid epoxy and solid epoxy with peaks in the chemical shift from 80 ppm to 40 ppm [58]. The proposed structure of the solid lignin-epoxy is illustrated in Fig. 7.5.

Huo et al. [65] synthesized a lignin/cardanol-based novolac epoxy resin. Cardanol was treated with sulfuric acid for 3 h at 150 °C, cooled to 90 °C and reacted with lignin, hydrochloric acid, and the water solution of formaldehyde for 3 h. The obtained product was neutralized with NaOH solution and dried, followed by reacting with epichlorohydrin in the presence of benzyltriethylammonium chloride (BTEAC) at 70 °C for 4 h. Then NaOH solution in 8 times of stoichiometric amount was added and allowed for 4 h reaction, producing a viscous lignin/cardanol-based epoxy resin. Figure 7.6 shows the possible structure of LC-novolac epoxy resins.

In our own work published recently by Ferdosian et al. [66, 67], a novel method was developed for synthesis of lignin-based epoxy resin from depolymerized

Fig. 7.5 The proposed structure of solid lignin-epoxy resin, reprinted with permission from Ref. [58]. Copyright (2001) Springer

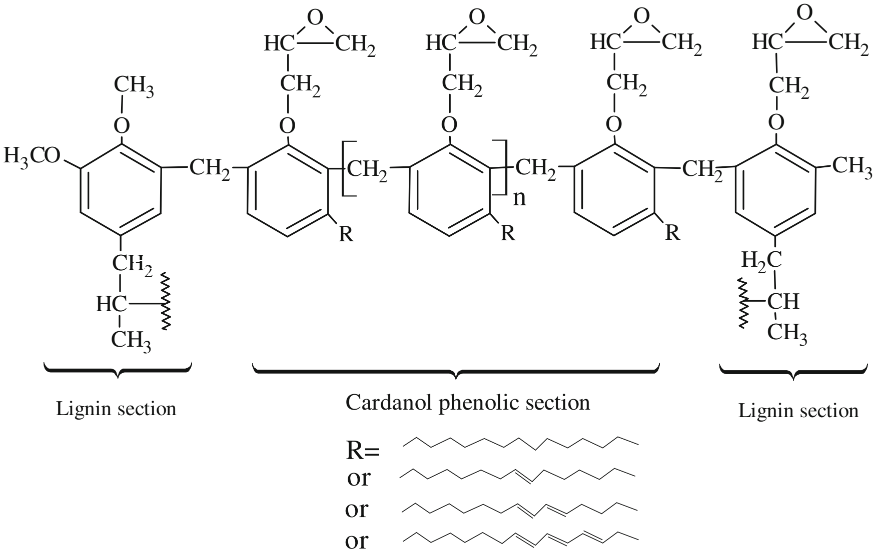


Fig. 7.6 Schematic structure of lignin/cardanol-based epoxy resin, reprinted with permission from Ref. [65]. Copyright (2014) Elsevier

organosolv lignin. First, organosolv lignin (OL) was depolymerized by reductive depolymerization in supercritical acetone at 350 °C in the presence of Ru/C catalyst and 10 MPa H_2. The obtained depolymerized organosolv lignin (DOL), with a low

Table 7.2 Average molecular masses, polydispersity index, and epoxy content of the lignin-based epoxy resins, reprinted with permission from Ref. [68]. Copyright (2015) Elsevier

Sample	M_n (g/mol)	M_w (g/mol)	PDI	Epoxy content wt%
DKL	580	1400	2.4	–
DKL-Epoxy	790	2800	3.5	5.6
DOL	370	760	2.0	–
DOL-Epoxy	500	1400	2.8	8.0

average molecular weight (M_w < 1000 g/mol) and high hydroxyl number, was then used to synthesize lignin-based epoxy resin. The effects of the process parameters including reaction time, reaction temperature, and NaOH/DOL molar ratio on the reaction yield and epoxy content were investigated using central composite design (CCD) to obtain the optimum conditions that were further validated by the experimental data. The optimum conditions determined are 8 h at 55 °C with 6.3 NaOH/DOL molar ratio, obtaining an epoxy resin with a high epoxy content of ~8, and 99% product yield. In a continuing work [68], a depolymerized kraft lignin (DKL)-based epoxy resin was also synthesized at optimum conditions with 97% product yield. The GPC measurement results for the raw materials (depolymerized lignins) and the two lignin-based epoxy resins are summarized in Table 7.2. The M_w of the DKL is 1400 g/mol and its polydispersity index (PDI) is 2.4. After the epoxidation reaction, the M_w of product was doubled (2800 g/mol) with an appreciable increase in PDI (3.5). Similarly, the M_w and PDI of the DOL increased from 760 to 1400 g/mol and from 2 to 2.8, respectively, after the epoxidation reaction. These results suggest that several lignin molecules attached together during the epoxidation reaction, leading to significant increase in the average molecular masses of the epoxidized samples.

The synthesized DKL or DOL lignin-based epoxy resins were blended with a conventional BPA-based epoxy resin at a blending ratio of 0–100 wt% and used as polymer matrixes for manufacturing fiber-reinforced plastics (FRPs). The thermal stability of the obtained lignin-based epoxy resins was also characterized using TGA–FTIR analysis. The mechanical/thermal characterization results indicated that the DKL or DOL lignin-based epoxy resins have excellent mechanical/thermal properties and can be used as a substitute for conventional BPA-based epoxy resins at a ratio up to 75 wt% in FRPs without compromising their properties.

7.3.3 Direct Epoxidation of Lignin

As reported by Simionescu et al. [46], calcium lignosulfonate was reacted directly with epichlorohydrin under alkaline conditions at 70–75 °C for 4.5–7.5 h and various compositions of sodium hydroxide and various molar ratios of epichlorohydrin. The use of highly concentrated sodium hydroxide and low molar ratio of epichlorohydrin led to a prepolymer with high viscosity and high epoxy equivalent. Although the curing of the lignin-based epoxy resin with diaminodiphenyl methane was slower than that of conventional petroleum-based epoxy systems, the shear strengths of lignin-based epoxy films were found to be comparable to those of the conventional epoxy resin films. Hirose et al. [56] synthesized epoxy prepolymer from alcoholysis lignin and lignin-related phenol such as p-hydroquinone (HQ) and methoxy-p-hydroquinone (MHQ) via reaction with epichlorohydrin in a NaOH aqueous solution at 100 °C for 5 h, and the synthesized epoxy resins were curable with poly-(azelaic anhydride). Delmas et al. [54] used lignin as a substitute for bisphenol-A in synthesis of epoxy resin. The epoxidation reaction was carried out first by dispersing lignin in water in the presence of an Ultra-Turrax T18 disperser (IKA, Staufen, Germany), then, adjusting the pH of the system to around 12 with aqueous NaOH, and lastly, and adding poly (ethylene glycol) diglycidyl ether (PEGDGE) as an epoxide agent while heating the mixture up to 60 °C and keeping the reaction at this temperature for 2 h. The chemical structure of the obtained lignin-based epoxy resins was confirmed by solid state ^{13}C NMR. In another research, glycidyl etherification of liquefied wood was achieved with 10 molar ratio of epichlorohydrin and twofold of sodium hydroxide at 100 °C for 2.5 h [35, 37].

Malution et al. [59] reported epoxidation of both unmodified lignin and methylolated lignin (reaction of lignin with formaldehyde in alkaline medium) at varying reaction parameters, e.g., reaction temperature, reaction time, epichlorohydrin/lignin molar ratio, and NaOH/lignin molar ratio. The results indicated that increasing temperature and reaction time had a negative effect on the epoxy index of the product due to crosslinking reactions. The epoxy resins from the modified lignin (methylolated lignin) had a lower epoxy index in comparison to that of the one derived from unmodified lignin. El Masouri et al. [57] epoxidized kraft lignin to improve its application potential. Before epoxidation, two different treatments were performed on the kraft lignin: methylolation via reaction with formaldehyde and glyoxalation by glyoxal. Epoxidation was then carried out on the unmodified kraft lignin (KL), methylolated kraft lignin (MKL), and glyoxalated kraft lignin (GKL). H-NMR results indicated that the MKL has more aliphatic hydroxyl groups than KL and GKL. Hence, the methylolated lignin with higher content of hydroxyl group could be resinified to form more useful materials, especially epoxy resins. Their results suggested that the best condition for the synthesis lignin-based epoxy resin is 70 °C for 3 h in the presence of 1/3 lignin/NaOH ratio (w/w). If the value of each of these parameters increased, the epoxy index could decrease due to the possibility of secondary reaction occurring between the formed epoxy groups and the free phenolic hydroxyl groups. Epoxy resins from the epoxidized MKL and the epoxidized GKL have a higher value of epoxy index in comparison with the epoxidized KL because of their higher contents of aliphatic hydroxyl groups in both lignin samples.

Sasaki et al. used steam-exploded bamboo lignin as a replacement for bisphenol-A in synthesis of epoxy resins [69] employing a two-step epoxidation reaction of the bamboo lignin with epichlorohydrin in the presence of a phase transfer catalysis, i.e., tetrabutylammonium bromide (TBAB), first at 80 °C for 4 h under nitrogen, and then at 10 °C for 12 h in aqueous NaOH and dimethylsulfoxide (DMSO). In another research, a methanol soluble lignin was epoxidized directly with epichlorohydrin in alkaline condition for 3 h at 110 °C [36]. Similarly, Singh et al. [70] synthesized lignin-based epoxy resin by directly reacting lignin and epichlorohydrin in the ratio of 2:3 (w/v) in alkaline condition at 80 °C for three hours reaction. The synthesized lignin-based epoxy was blended with a conventional epoxy primer in different weight % from 5 to 20 wt%. It was found that 5 wt % of epoxidized lignin in the primer led to increased pot life of the paint, while the pot life was reduced with a higher content of epoxidized lignin in the primer, and increasing the lignin-based epoxy resin in formulation increased the corrosion rate of the paint.

7.4 Curing Kinetics of Lignin-Based Epoxy Resins

The ultimate properties of an epoxy resin depend on both its chemical composition and the curing process (related to the crosslinked structure of the cured resins) [71, 72]. Therefore, it is essential to investigate the curing process of epoxy resin and the crosslinked structure of the cured resin. In comparison with thermoplastics, processing of thermosets composites is more complicated and less controllable because in processing of a thermoset composite, polymer reactions, and shaping occur at the same time. During the curing process of fiber-reinforced composites, two major physical transformations of the corresponding thermoset polymers, i.e., gelation and vitrification, take place [73]. The mechanism and kinetics of the thermoset polymer curing determine the network morphology, which in turn, dictates the physical and mechanical properties of the cured products [74]. For instance, polyblending an epoxy resin and a lignin increased the mechanical properties of the resin owing to an increased crosslinking density, caused by the reaction between epoxy groups and the hydroxyl and carboxyl functional groups [16]. In the studies of Kishi et al. [35, 37], lignin-based epoxy resins were cured with diaminodiphenyl sulphone (DDS) or diaminodiphenyl methane (DDM). The cured lignin-based epoxy resins exhibited a lower glass transition temperature, a higher storage modulus of elasticity at room temperature and higher flexural modulus of elasticity as well as higher flexural strength, in comparison with a BPA-based epoxy resin.

The curing process can be monitored by different techniques such as DSC, dynamic torsional vibration method (DTVM) [75–77], FTIR [78], rheokinetic measurements [79], dielectric measurements [80, 81], etc. Curing kinetics of lignin-based epoxy resins have been widely studied in the literature. For instance, Sun et al. investigated curing kinetics of a liquid lignin-based epoxy resin cured with three different curing agents including methylhexahydrophthalic anhydride (MTHPA), maleic anhydride (MA), and 2-methyl-4-methylimidazole (EMI-2,4) [71, 72]. The kinetic parameters were evaluated based on Kissinger method and autocatalytic kinetics. The apparent activation energies calculated from Kissinger method for the cured resin system with the curing agent of MTHPA, MA and

EMI-2,4 are 76.54, 56.35, and 47.22 kJ/mol, respectively. The curing kinetic of the resin followed approx. first-order model with MTHPA, while the two other systems had autocatalytic kinetics with overall order of 1.47 with MA and 1.15 with EMI-2,4. Hirose et al. [15] reported the activation energy to be around 83.5 kJ/mol when the extent of curing was below 60%, and it increased to 110 kJ/mol at higher curing extent >80%, likely due to a reduced diffusion rates for various synthesized epoxy resins derived from biomass components such as saccharides, lignin, and glycerol.

The curing kinetics of lignin–cardanol-based novolac epoxy resin with methyl tetrahydrophthalic anhydride (MeTHPA) was studied by DSC and evaluated by Friedman method and Malek method [65]. Being different from what described above, the activation energy increased with the curing extent up to 50% extent, but remained constant approx. 52 kJ/mol up to the completion of the curing process. The reaction of epoxy group and curing agent can be catalyzed in the presence of tertiary amine. The tertiary amine reacts with the anhydride groups of the curing agent to generate a Zwitterion. The carbonyl anion on the zwitterion quickly reacts with the epoxy group to form a new alkoxide anion that can attack the anhydride to form new Zwitterions. The above propagation mechanism for epoxy resin curing may account for the increased activation energy at its initial curing stage, and the constant activation energy at a higher curing extent.

The curing kinetics along with the mechanical properties of lignin blended by epoxy resin were reported by Kong et al. [16], where a polyblended lignin-epoxy resins as adhesives were prepared with a hydrolysis lignin. The results demonstrated that introducing lignin into the epoxy resins could promote the curing reaction and improve the shear strength. Yin et al. [82] studied the mechanical properties and curing reaction of an epoxy resin blended with enzymatic hydrolysis lignin from cornstalk. The hydroxyl and carboxyl groups of lignin could react with epoxy groups, and lignin's polyphenol structure could catalyze the epoxy curing reaction. In another study, an epoxy resin blended with carboxylic acid functionalized alkali lignin (AL-COOH) at three blending levels, 0.5, 1, and 2%, was cured by anhydride [83]. The results revealed that the AL-COOH did not change the primary mechanism of the curing reaction, evidenced by the consistent main exothermic peak for all samples, while a new exothermic peak appeared in the range of 130–140 °C, attributed to the curing reactions between the epoxy groups and carboxyl groups on the AL-COOH. On one hand, introduction of lignin into an epoxy resin changes the chemistry of epoxy resin, and hence would change the mechanical properties of the epoxy resin. On the other hand, however, performance of the final epoxy resins depends on both the chemical composition and the curing process. Thus, the curing of epoxy resin provides an effective way to control its manufacturing process to produce a high-performance finished product [84–86].

Komiya et al. [19] studied the mechanical (by DMA) and dielectric properties of cured DGEBA epoxy resins blended with soda lignin and methanol extracted soda lignin. The DMA results showed that both samples have one glass transition temperature, suggesting that the epoxy resins cured with lignin derivatives have a homogeneous structure. The methanol extracted soda lignin has a lower molecular weight and more reactive hydroxyl groups in comparison with the unmodified soda lignin. Hence, the DGEBA–methanol extracted soda lignin has a lower initial viscosity and a higher T_g in comparison with the DGEBA–soda lignin. Feldman [87] investigated effects of different types of lignin on the adhesion properties of epoxy resin. It was reported that the hardwood lignin enhanced the adhesion of epoxy resin more than the softwood lignin (Indulin). Adding 20% hardwood lignin to an epoxy resin provided the highest adhesive joint shear strength for the epoxy resin, and it was concluded that the kind and content of functional groups of the lignin added and its molecular weight are the main factors that influence the final performance of a lignin-based epoxy resin. It was also observed that blending up to 20 wt% kraft lignin with a liquid epoxy resin and a curing agent, the cured samples showed one glass transition temperature, suggesting a homogeneous structure of the blended epoxy resins, but two T_g's were observed if increasing the content of lignin to 20 wt% or higher [88].

In our own recent work by Ferdosian et al. [68], we investigated the curing behavior and kinetics of lignin-based epoxy resins derived from depolymerized organosolv lignin (DOL) and depolymerized kraft lignin (DKL). The synthesized lignin-based epoxy resins were cured with 4,4′-diaminodiphenyl methane (DDM, an aromatic amine) and diethylenetriamine (DETA, an aliphatic amine) to generate a three-dimensional crosslinked structure. The effects of curing agents on the curing

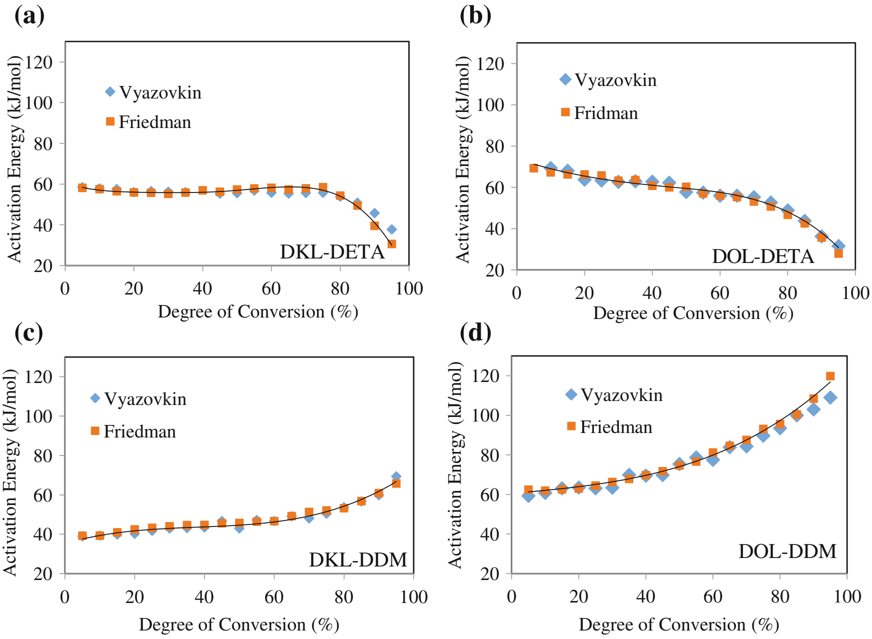


Fig. 7.7 Activation energy of the curing reaction versus conversion based on Friedman and Vyazovkin methods, reprinted with permission from Ref. [68]. Copyright (2015) Elsevier

process were investigated by non-isothermal differential scanning calorimetry (DSC). The dependency of activation energy of the curing reaction on the extent of curing (conversion) was determined in this study by model-free kinetics based on the DSC results (Fig. 7.7). As shown in the figure, the activation energy increases with increasing the curing extent for the lignin-based epoxy resins cured with DDM, which could result from the reduced molecular mobility due to higher crosslinking at higher curing extent. Interestingly, the activation energy of curing DKL-epoxy or DOL-epoxy with the DETA generally decreases along with the curing extent, suggesting an autocatalytic mechanism.

7.5 Thermal Properties of Lignin-Based Epoxy Resins

Thermal stability of polymeric materials plays an important role in their final applications. Thermal stability of a polymeric material can be characterized by thermogravimetric analysis (TGA) measuring the weight loss of the sample as a function of temperature or time.

Generally, introduction of lignin into a polymeric matrix could promote the thermal stability due to the aromatic structure of lignin and lots of polar bonds on the structure of lignin [51, 89–92]. Lignin was considered as a thermal stabilizer for cellulose against thermal oxidation at low temperature due to its tendency of radical scavenging [93]. Thermal stability of extracted lignin from sal (*shorea robusta*) leaves was evaluated by TGA, and it was observed that following the first weight loss peak happened at around 110 °C (believed associated to the moisture loss), the second peak was detected at around 440 °C, which can be corresponding to the start of thermal degradation [70]. Thermal decomposition of lignin-brominated epoxy flame-retardant system was analyzed by pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS) and thermogravometry/mass spectrometry (TG/MS) [93]. It was realized that the brominated epoxy with lignin shifted the decomposition temperature into a higher temperature. The thermal stability of lignin can be improved further by the acetylation of hydroxyl groups on the structure of lignin [15], and the thermal decomposition temperature of a lignin shifted from 230 to 289 °C after modification of the lignin via acetylation. As commonly observed in literature, the thermal stability of lignin depends on its plant source, the extraction process, and the operating parameters of the extraction process such as reaction temperature, pressure, heating rate, and degradation atmosphere [70, 94–97].

Typical degradation of a lignin shows the first mass-loss peak in the range of 100–180 °C due to elimination of humidity, the second mass-loss peak at 280–390 °C, and the third peak at around 420 °C, leading to a char yield of around 45% [94, 96]. More studies were reported on thermal stability of lignin-based epoxy resins and the results are summarized as follows: Thermal properties of epoxy resin cured by different contents (20–100%) of aminated lignin and W39 amine curing agent demonstrated that with increasing the content of aminated lignin, the thermal stability improved [51]. Petreus et al. [98] synthesized a new phosphorus containing lignin-based epoxy resin from aspen wood lignin, and the prepared prepolymer was cured with [2-(6 oxide-6H-dibenz(c,e)(1,2)oxaphosphorin-6-yl)]-1,4naphtalendiol (NBQ). The phosphorus modified lignin-based epoxy has higher thermal stability. On the other hand, however, Sasaki et al. [69] reported that cured bamboo lignin-epoxy resin (BL-epoxy) had lower thermal stability compared to the conventional BPA-type epoxy (DGEBA), although the thermal stability of lignin-based epoxy systems can still meet the minimum requirements for being used as a solder-dip resistant in printed circuit boards (250–280 °C). The thermal stability of lignin-based epoxy resins derived from depolymerized kraft lignin (DKL) and depolymerized organosolv lignin (DOL) cured with two curing agents, i.e., 4,4′-diaminodiphenyl methane (DDM, an aromatic amine) and diethylenetriamine (DETA, an aliphatic amine) was investigated by TGA [68]. The DKL-based epoxy resins are more thermally stable than the DOL-based epoxy resins. The lignin-based epoxy samples cured with DDM curing agent have higher thermal stability than those cured with DETA. However, the thermal stability of all lignin-based samples is comparable to the thermal properties of petroleum-based BPA-type epoxy resins. The char yields at 800 °C for all the lignin-based epoxy resins were in the range of 23–38%, much higher than that of conventional BPA-based epoxy resins. The char yield of DKL–DDM at 800 °C was as high as 38%, suggesting that the DKL–DDM can be a promising substitute for BPA-based epoxy for some high-temperature applications.

7.6 Summary

Production and properties of lignin-based epoxy resins are overviewed in this chapter. The production of lignin-based epoxy resins can be divided into three categories: (1) physical blending of lignin and epoxy resin, (2) epoxidation of pretreated lignin, and (3) direct epoxidation of lignin. The limitation of the simple blending approach is that lignin can substitute only a small percentage (<20–30 wt%) of epoxy resins. In contrast, the other two methods as discussed in the following sections make it possible to achieve a high substitution ratio up to complete substitution of petroleum-based materials (such as bisphenol-A) with lignin.

Introduction of lignin into an epoxy resin changes the chemistry of epoxy resin, and hence would change the mechanical and thermal properties of the epoxy resin, and the performance of final epoxy resins depends on both the chemical composition and the curing process. It was concluded that the kind and content of functional groups of the lignin added and its molecular weight are the main factors that influence the final performance of a lignin-based epoxy resin. For instance, the lignin-based epoxy resins from low M_w depolymerized kraft lignin (DKL) and depolymerized organosolv lignin (DOL) were blended with a conventional BPA-based epoxy resin at a blending ratio of 0–100 wt% and used as polymer matrixes for manufacturing FRPs. The mechanical/thermal characterization results indicated that the DKL or DOL lignin-based epoxy resins have excellent mechanical/thermal properties and can be used as a substitute for conventional

BPA-based epoxy resins at a ratio up to 75 wt% in FRPs without compromising their properties. Generally, introduction of lignin into a polymeric matrix could promote the thermal stability due to the aromatic structure of lignin and plenty of polar bonds on the structure. Moreover, lignin can be a thermal stabilizer for cellulose against thermal oxidation at low temperature due to its tendency of radical scavenging.

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Chapter 8
Lignin-Based Polyurethane (PU) Resins and Foams

Abstract This chapter overviews the production and properties of lignin-based polyurethane (LPU) for various applications such as elastomers, coatings, adhesives, flexible foams, and semi-rigid or rigid foams. Lignin with hydroxyl groups on its structure could be used as a substitute for polyol in the synthesis of polyurethane. Lignin can be incorporated in polyurethane without pre-treatment or with chemical modifications, e.g., oxypropylation, esterification, etherification reactions, and depolymerization. Chemical modifications of lignin produce modified lignin with enhanced reactivity, which enables synthesis of LPU at a higher biosubstitution ratio, and the resulted LPU products demonstrated acceptable performance in various industrial applications.

Keywords Lignin-based polyurethane (LPU) · Elastomers · Coatings · Adhesives · Flexible foams · Semi-rigid or rigid foams · Chemical modifications · Oxypropylation · Esterification · Etherification reactions · Depolymerization

8.1 Polyurethane

Polyurethane (PU) is among the most commonly used synthetic polymers, containing a majority of urethane functional groups in the molecular backbone, resulting from a poly-addition reaction between NCO groups from polyisocyanate with compounds containing active hydrogens or polyols (i.e., polyether and polyesters) [1–4]. According to transparency market research analysis, the global PU market was valued at US$ 48.29 billion in 2014 and is expected to reach US$ 80.76 billion in 2023, expanding at CAGRs of 5.9% between 2015 and 2023 [4]. The global consumption of PU in different segments is shown in the figure in 2014. The worldwide demand for PU was around 8 million tons in 2010, accounting for 5% of total global consumption of plastics [1]. The global usage of PU in various product segments in 2014 is illustrated in 8.1 [4]. As shown in the figure, the majority of PU is consumed for the production of flexible and rigid foams, and a large portion of PU is for protective and decorative coatings on a wide variety of

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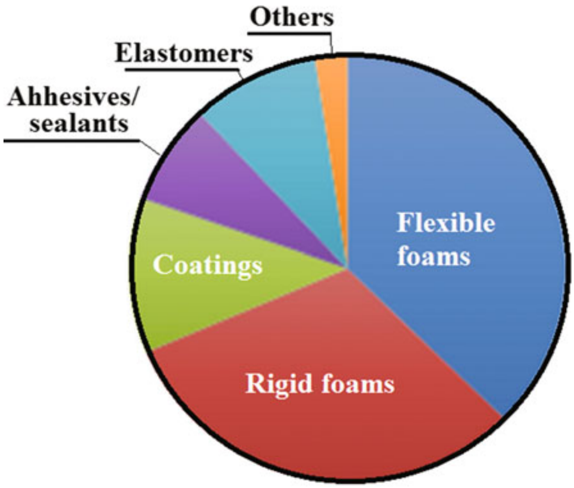


Fig. 8.1 Global PU market volume share, by product segment in 2014, modified from Ref. [4]

substrates such as wood, metal, plastics, leather, and textiles. The rest of PU is consumed as elastomers, adhesives, sealants, and others [1–3]. Polyurethane rigid foams are widely used as insulation and structural materials for construction, transportation, and decoration. Those foams account for almost one-third of the polyurethane market. Out of annual 1.3 million tons of North American polyol market, approximately 50% is used for the manufacturing of polyurethane rigid foams [5] (Fig. 8.1).

8.2 Biopolyols and Bio-based Polyurethane

PU is made from a poly-addition reaction between a polyisocyanate and a polyol. Two major kinds of polyols in the global polyols market are polyether polyols and polyester polyols. Nearly 90% of PU in the US was based on polyethers, 9% on polyesters, and 1% on other specialty polyols [1]. The chemical structure of polyurethanes varies widely depending on the specific isocyanate and polyols in its production.

In the recent years, prices of petroleum-based polyols have escalated, and there is a growing concern on the depleting petroleum resources and their adverse effects on the environment like emissions of greenhouse gas and VOC's, bio-based polyols have attracted increasing attention [6, 7]. Various natural resources such as vegetable and seed oils (soybean oil [8], Caster oil [9–12], palm oil [13, 14], canola oil [15], rapeseed oil [16]), starch [17], gallic acid [18], cardanol [19, 20], wheat straw [21], and unmodified and modified lignins [22–25] have been used as the biopolyols for the production of bio-based PU. On the other hand, bio-based isocyanates were also produced from renewable resource in the synthesis of polyurethanes [9, 26, 27]. For instance, a commercialized process produces aliphatic isocyanates from dimerized fatty acid, but the bio-based isocyanates are not suitable for foam formation due to their lower activity, although they can be widely used for manufacture of PU for coatings and other applications [28].

Among the above-mentioned biopolyols resources, lignin has aroused an extensive interest due to its availability and aromatic nature. The presence of free phenolic, aliphatic, and carboxylic groups being able to interact with isocyanate allows lignin application as effective biopolyols for PU production. Lignin can be incorporated in synthesis of PU by two approaches: (1) direct incorporation of crude technical lignin without modification or polyol combination [29, 30]; and (2) incorporation of modified lignin with improved reactivity, via esterification, etherification reactions, and depolymerization processes [31–33]. Lignin can be converted to liquid polyol by modification with alkylene oxides such as oxypropylation (reacting with propylene oxide catalyzed by a base catalyst), as illustrated in Fig. 8.2. The obtained products contain either or both hydroxyl alkyl lignins soluble in low molecular weight poly(oxyalkylene glycols) and chain-extended lignin-poly(oxyalkylene ether) copolymer [34–36].

A systematic study was reported on lignin-based PU [38, 39], where effects of some synthesis parameters such as temperature, NCO/OH ratio, type and average molecular weight of the polyol, type of isocyanate, and type and weight content of lignin on the polymerization process were investigated in detail. The FTIR results demonstrated the chemical interaction of lignin with isocyanate through the formation of urethane linkages, as confirmed with the results of swelling tests. Lignin could effectively replace up to 25 wt% of polyols in resinification with a low molecular weight polyol (polycaprolactone diol (PCL) with M_w of 400–1000 g/mol), but the obtained PU samples are brittle with limited applications. Furthermore, it was found that the lignin resinification reaction was affected by lignin type, Alcell lignin (organosolv lignin), and Indulin AT (kraft lignin). With the Indulin AT, it showed lower isocyanate conversions compared to the Alcell lignin-based systems. Alcell lignin, with a lower molecular weight and total hydroxyl content, can act as a chain extender in the PU networks, while Indulin AT could play effectively as a crosslinker. Kraft lignin can be a good source of polyols,

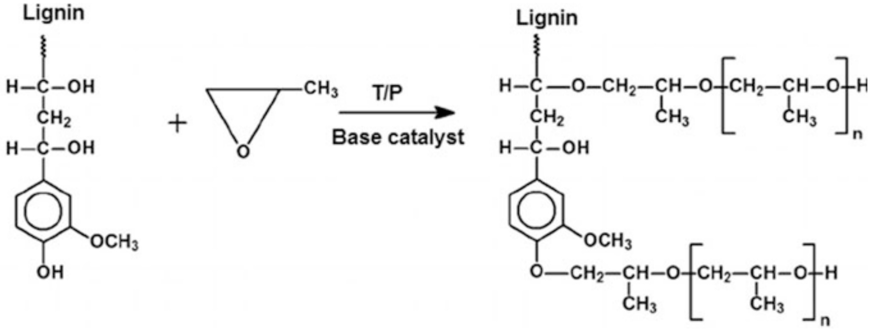


Fig. 8.2 Oxypropylation of lignin to form a liquid polyol, modified from Ref. [37]

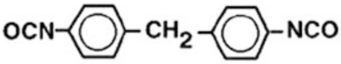
although it has relatively low reactivity due to its high M_w and the steric hindrance effects. Kraft lignin can be incorporated directly into PU formulations due to the presence of aliphatic and aromatic hydroxyl groups as the reactive sites for isocyanate groups for urethane linkage formation, while the major drawback of kraft lignin-based PU is that the products are rigid and brittle.

The following section overviews synthesis and properties of lignin-based PU materials for various applications including elastomers, coatings/adhesives/sealants, flexible foams, and rigid foams.

8.3 Lignin-Based Polyurethane

8.3.1 Lignin-Based Polyurethane Elastomers

Lignin has been incorporated as a starting material in manufacturing of PU elastomers and much work has been published in this field [30, 40–43]. Ciobanu et al. [22] investigated the effect of flax soda lignin content on mechanical and thermal properties of a PU elastomer film. The PU elastomers were made from the reaction of 1:5:6 mol ratio of poly(ethylene adipate), ethylene glycol, and 4,4′-methylene diphenyl diisocyanate (MDI, as illustrated below) and then blended with the lignin at an amount ranging from 4.2 to 23.2 wt% in dimethylformamide (DMF) solutions.



4,4'--methylene diphenyl diisocyanate (MDI)

The FTIR results confirmed the chemical interaction between the urethane groups and the functional groups of lignin when the concentration of lignin exceeded approximately 9.3 wt%. The presence of metal ions in the technical lignin showed a catalytic effect through auto-oxidation processes, complex formation, and enhancing of lignin–PU interaction. It was suggested that the addition of lignin should be less than 10 wt% and preferably 5 wt% to enhance the strength and biodegradability of PU elastomers. Meanwhile, the obtained lignin-based PU elastomers have reduced elasticity and a lower degradation temperature. Borges da Silva et al. [44] studied the incorporation of a kraft lignin (Indulin AT) in preparation of PU elastomers. The lignin was blended with a linear polycaprolactone (PCL, M_w of 750 g/mol) at different contents of 10–25 wt% to prepare PU elastomers. The storage modulus (E′) and loss tangent (tanδ) of the prepared elastomers are shown in Fig. 8.3. With increasing the content of lignin, the maximum of tanδ shifted to a higher temperature

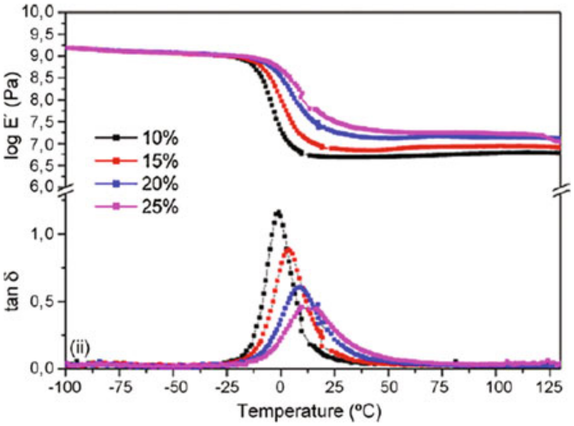


Fig. 8.3 Storage modulus (E') and loss tangent (tanδ) as a function of temperature for lignin-based PU elastomers, reprinted with permission from Ref. [44]. Copyright (2009) Elsevier

with a broader peak. It indicated that the glass transition temperature (T_g) increased, likely due to the higher incorporation of lignin. Furthermore, the storage modulus at the rubber region increased with the increase of lignin contents up to 20 wt%, and then remained constant at the higher lignin content (25 wt%).

Oxygen-organosolv lignins were employed as starting materials in the synthesis of elastomeric PUs [45], where oxygen-organosolv lignins were isolated from a spent liquor arising from the oxidative delignification of aspen or spruce chips in different acidic–organic solvent–water media. Then, the lignin reacted with an oligoethyleneoxide diisocyanate (ODI) as a flexible segment in the presence of dibutyltin dilaurate catalyst to yield elastomeric products with a glass transition temperature below room temperature (−38 to −44 °C). The effects of delignification method and lignin type on the PU yield and the glass transition temperature are presented in Table 8.1. It was proposed that the optimum [NOC]/[OH] ratio was 1.5, which leaded to a higher polyurethane yield. Moreover, the oxygen–acetone and oxygen ethanol lignins gave the best results, whereas oxygen–acetic acid lignin had the lowest conversion. In addition, the hardwood lignin (aspen) was more reactive than the softwood lignin (spruce) toward ODI.

Yoshida et al. [29] investigated the effects of molecular weight of lignin on the structure of the prepared PU elastomer films. At a low lignin content (<30 wt%), the prepared PU films from low M_w lignin (M_w = 620 g/mol) were more flexible compared to PUs derived from lignins with medium M_w (=1290 g/mol) and high M_w (=2890 g/mol). However, the PUs with a high content of lignin (>30 wt%) were rigid and brittle, regardless of the molecular weight of the lignin and the [NOC]/[OH] ratio used. Thermal and mechanical properties of solvolysis lignin–PU films could be controlled by varying the content of lignin as a hard segment in PU elastomers [46, 47]. For instance, versatile PU films could be obtained with a glass transition temperature of −10 to 130 °C and ultimate strength from 1 to 75 MPa.

Table 8.1 Effects of lignin origin and delignification method on PU elastomer properties, reprinted with permission from Ref. [45]. Copyright (1998) Elsevier

Lignin sample	Yield after extraction (%)	Glass transition temperature (°C)	
		Lignin	Polyurethane
Aspen oxygen–acetone	82.9	130	−41
Spruce oxygen–acetone	75.6	121	−42
Spruce oxygen–ethanol	75.5	116	−44
Spruce oxygen–acetic acid	68.4	122	−38

Demethylation of lignin by acid (e.g., hydrogen bromide or HBr) treatment can be used to improve the mechanical properties of lignin-based PUs [48]. The chemical treatment of lignin with HBr resulted in 28% enhancement in hydroxyl content of lignin with an improvement in hydrophilicity of solvent-cast thin film. In addition, the mechanical properties increased significantly, with a 6.5-fold increase in modulus.

More interestingly, Lee and Deng [49] reported an innovative procedure for synthesis of PU elastomer from lignin and soybean oil via non-isocyanate reactions. In this process, carbonated soybean oil was reacted with 3-aminopropyltriethoxysilane as a coupling agent to produce urethane linkages, followed by reaction with lignin to form bio-based polyurethane with up to 85 wt% biomass content. The novel reaction route of synthesis of bio-based polyurethane using lignin and vegetable oil without using isocyanate is illustrated in Fig. 8.4.

8.3.2 Lignin-Based Polyurethane Coatings/Adhesives/Sealants

Chahar et al. [50] reported the synthesis of PU coatings and adhesives with waste black liquor lignin (kraft lignin), where effects of lignin concentration [ranging from 5 to 70 w/v in poly ethylene glycol (PEG)] and the PEG M_w (200, 600, 1000, 1500, and 4000 g/mol) on shear strength, adhesion, and thermal stability of the resulted PU resins were investigated. The lignin-based PU adhesive with optimal combination of thermal and mechanical properties, with shear strength as high as 3.6 N/mm^2, was prepared using 50% w/v lignin in PEG (M_w 200 g/mol). In another study, a carboxyoxylated lignin pre-polymer (polyester–polyether polyol) was reacted with various types of isocyanates including hexamethylene diisocyanate (HDI), methylene diphenyl diisocyanate (MDI), and toluene diisocyanate (TDI) to form polyurethane wood adhesives [51]. The shear strength and percentage of wood failure of lignin-based PU adhesives were found to be comparable with resorcinol–formaldehyde and epoxy resins. A novel series of bio-based thermoset PU coatings containing with a high lignin content (70–90 wt%) was developed and characterized

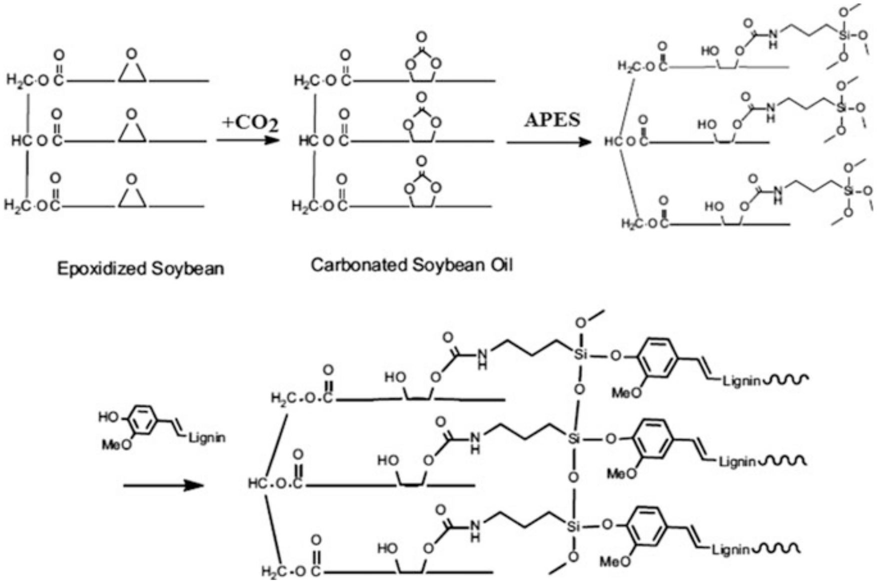


Fig. 8.4 Schematic reaction route of synthesis of bio-based polyurethane using lignin and vegetable oil without using isocyanate, reprinted with permission from Ref. [49]. Copyright (2015) Elsevier

by Griffini et al. [52]. In this work, a sol fraction of kraft lignin (S-lignin) was extracted by a bio-derived solvent 2-methyl-tetrahydrofuran, subsequently reacted with a toluene diisocyanate (TDI)-based polyisocyanate. The obtained lignin-based PUs showed better thermal stability, film formation ability, and higher hydrophobic character, compared with the un-crosslinked lignin precursor. The measured physical and thermal properties are summarized in Table 8.2. The results indicated that the lignin-based PUs had great adhesion to different substrates such as glass, metals, and wood. Thus, the lignin-based PUs can be used as high-performance coatings or adhesives.

8.3.3 Lignin-Based Flexible Polyurethane Foams

Flexible PU foams are commonly named as visco-hyperelastic, memory, slow recovery, controlled recovery, or low resilience foams [53]. Flexible PU foams could be used as thermal insulation as well as acoustic absorbing materials for reduction of noise and vibration due to their high potential of damping the mechanical vibrations [53]. Flexible PU foams are block copolymer with elastic properties, consisting of two phases: “hard block” and “soft block”. Hard blocks are rigid with crosslinked structure which give the firmness into the materials, while soft blocks are stretchable

Table 8.2 Thermo-mechanical properties and pull-off adhesive strength of the thermoset lignin-based PU coatings, reprinted with permission from Ref. [52]. Copyright (2015) American chemical society

S-lignin/TDI (w/w)	Surface roughness (μm)	Elastic modulus (GPa)	$T_{50\%}$ (°C)	Char residue at 750 °C (%)	$T_{DTG\ max}$ (°C)	Pull-off adhesive strength (MPa)			
						Glass	Wood	Aluminum	Steel
70/30	0.07 ± 0.01	3.7 ± 0.75	373	31	290				
80/20	0.08 ± 0.02	1.93 ± 0.51	434	37	290	7.6 ± 0.5	>9[a]	1.5 ± 0.3	0.9 ± 0.1
90/10	0.11 ± 0.01	2.1 ± 0.57	437	39	379				
S-lignin	0.2 ± 0.01	3.39 ± 1.18	411	35	379				

[a] 9 MPa represents the maximum allowable instrumental reading

chains which give the elasticity to the materials [28]. By manipulating the ratio of the hard and soft blocks, a flexible PU foam is produced with desired properties. The foaming process for flexible PU foams consists of two main reactions: (1) gelation (crosslinking) reaction and (2) blow (gas generation) reaction. If the gelation reaction takes place too fast, close-called foam may be generated. In contrast, if the blow reaction occurs too quickly, cells may open as the strength of the polymer structure is not sufficient to control it, resulting in collapsing the foams.

Cinelli et al. [28] employed a liquefied lignin for the production of lignin-based flexible PU foams with a "one-shot" technique. Lignin was liquefied with polyethylene glycol (molecular weight of 400 g/mol) and glycerol in a microwave oven for 3 min at 135 °C and heat power of 180 W. Then the liquefied lignin was formulated into flexible PU foam by addition of some chain extenders with low OH value such as polypropylene glycol triol (PPG) and castor oil to reduce the viscosity and T_g and to improve the flexibility of the final foams. It was demonstrated that the glass transition temperature of the foams based on PPG was around −50 °C and remained constant with increasing the content of lignin, while the tanδ peak heights reduced significantly when the content of lignin increased. This reduction showed that a large part of soft segment was mixed with lignin polyol with a higher T_g. The foams based on castor oil showed several transitions in the storage modulus (G') due to lower homogeneity of the foam structure and a wider distribution of crosslink density. Flexible PU foams were recently successfully produced with a green synthesis approach based on the use of soda lignin by following a liquefaction process by microwave irradiation [54]. A mixture of glycerol and glycerin polyglycudyl ether was used as the liquefaction solvent in the presence of PPG triol as a chain extender. With increasing the lignin content from 12 to 30 wt%, the properties of the synthesized PU foam varied from 65 to 95 kg/m^{-3} for the apparent density, and from 1.35×10^{-2} to 3.35×10^{-2} MPa for the compression strength.

In another study by Bernardini et al. [55], novel flexible polyurethane foams were developed from soda lignin or oxypropylated soda lignin after liquefaction. Lignin was liquefied with glycerol and PEG 400 as liquefaction solvents using microwave irradiation. The flexible foams were produced from the reaction of protobind lignin or oxypropylated protobind lignin with polypropylene glycol triol (PPG triol) or castor oil as chain extender, water as blowing agent, and polymeric methylene diphenyl diisocyanate (PMDI) via the one-shot approach. In all formulated foams, the molar ratio of NCO/OH was fixed to less than one to reduce the crosslink density and provide more flexibility of the foam. The lignin content varied from 6 to 13 wt%. The foams derived from castor oil consisted more than 45 wt% bio-based materials, and they had open-cell structure with acceptable thermo-mechanical properties for filling and packaging application. The foams derived from PPG triol had an apparent density and compression strength ranging from 70–150 kg/m^3 and 2×10^{-2} to 7×10^{-2} MPa, respectively, while the foams from castor oil showed an apparent density from 130 to 210 kg/m^3 and a compression strength in the range of 7×10^{-3}–3.5×10^{-2} MPa. A comprehensive study was conducted on effects of lignin concentration and molecular weight of polyethylene glycol (PEG) on the compressive viscoelastic properties of kraft lignin-based flexible PU foams. Lignin acted as hard segments and PEG as soft segments in the ultimate structure of PU. The addition of lignin had two distinctive effects on the prepared foams, i.e., filler effect and crosslinking effect. Increasing the content of lignin in the foams led to an increase in crosslink density and viscometric properties ($\tan\delta_{\max}$ and hysteresis loss) of the foams due to the filler-like behavior of the separated lignin-rich phase. Furthermore, it was observed compression strength and Young's moduli of the lignin-based PU foams increased with increasing the lignin content due to enhancement of the foam density.

8.3.4 Lignin-Based Rigid Polyurethane (RPU) Foams

Rigid polyurethane (RPU) foams have a crosslinked network with close-cell structure. RPU foams can be used in a variety of applications such as construction, refrigeration appliance, and technical insulation, accounting for approximately 23% of all PU market, because of such features as low density, low moisture permeability, low thermal conductivity, high dimensional stability, high strength-to-weight ratio, easy construction, high durability, and good adhesion strength [8, 37]. The properties of RPU foams are mainly affected by the formulation, the manufacturing process, and the density [56]. Typical density of RPU foams varies from 30 to 200 kg m^{-3} for applications in a wide range of temperatures between +130 and −196 °C. The properties of different categories foam, namely B2 (ordinary combustible) and B3 (easy to ignite), are summarized in Table 8.3. The B2 foams are mainly consumed for building application such as flat roofs, ceilings, pitched roofs, floors, or walls [56]. For industrial applications, B2 and B3 foams with normal and low-temperature range are used for refrigerated vehicles and containers, pipelines, and liquid gas tanks [56]. The commercial RPU foams are commonly derived from two commercial polyols, i.e., sucrose polyols and glycerol polyols [37].

The developments of rigid and semi-rigid PU have been the main focus of many studies [57–62] and the latest investigation is summarized below. Water is the common chemical blowing agent in the production of PU foams, as it reacts with diisocyanate to generate CO_2 gas [63]. The crosslinking kinetics of the formation of a polyurethane foam by reacting a mixture of lignin-aminated polyol (LAP) and glycol (such as PEG) with MDI-50 in the presence of water as a blowing agent was investigated at constant temperature (60 °C). The results showed that the crosslinking reaction fitted to a first-order reaction. According to Arrhenius equation, the overall activation energy was 16.44 kJ/mol and the frequency factor was 2.69 min^{-1}.

The mechanical and thermal properties of lignin-based RPU foams are controllable by adjusting the foaming reaction rate. Hatakeyama et al. [64] investigated the effects of blending ratio of two different kinds of sodium lignosulfonates (NaLS): acid-based NaLS (LSHW, pH: 3.7) and alkaline-based NaLS (LSN, pH: 8.2), and molecular weight of ethylene glycols: diethylene glycol (DEG), triethylene glycol (TEG), and polyethylene glycol (PEG), on the reaction rate of PU preparation. Foaming reaction rate can be defined by several factors including

Table 8.3 Typical properties of different types of RPU foams, reprinted with permission from Ref. [56]. Copyright (1998) Elsevier

Properties	Unit	Standard	Type of RPU foam						
			B2-32	B2-50	B2-80	B2-145	B3-32	B3-50	B3-200
Density	Kg m^{-3}	DIN 53420	32	50	80	145	32	50	200
Combustibility	–	DIN 4102	B2	B2	B2	B2	B3	B3	B3
Compressive strength	N mm^{-2}	DIN 53421	0.22	0.40	0.70	2.0	0.21	0.40	2.50
Tensile strength	N mm^{-2}	DIN 53292	0.25	0.45	0.80	1.10	0.26	0.50	2.00
Bending strength	N mm^{-2}	DIN 53423	0.30	0.55	1.00	2.6	0.28	0.55	3.50
Shear strength	N mm^{-2}	DIN 53294	0.15	0.28	0.45	0.80	0.18	0.32	1.20
Shear strength	N mm^{-2}	DIN 53427	0.12	0.25	0.38	0.70	0.15	0.23	1.10
Thermal conductivity	mW/m/K	DIN 52612	21.4	22.6	24.8	30.8	22.0	22.3	37.0

mixing time, cream time, and rise time. Mixing time is the interval time from adding isocyanate to detection of elevated heat under string, cream time is defined as the duration from termination of stirring to initiating of foaming, and rise time as the time interval from the starting to completion of foaming. Figure 8.5 shows the influence of LSN content and types of ethylene glycol on the indexes of foaming reaction. In general, the reaction time decreased with increasing the content of lignin. The apparent density, compression strength, and compression modulus of the obtained lignin-based RPU foams linearly increased with lignin content, and the glass transition temperature varied from 310 to 390 K by manipulating the PU formulation. It demonstrates that by manipulating the PU formulation, a designed lignin-based RPU foam can be produced with appropriate thermal and mechanical properties for desired applications.

Thermo-mechanical performance and flame retardancy of a 30% liquefied lignin-based rigid PU foam (Lignin(30%)-RPUF) was improved by employing a flame-retardant polyol (FRP), polyurethane microencapsulated ammonium polyphosphate (MAPP), and organically modified layered double hydroxide (OLDH) [65]. The best formulated RPUF was lignin (30%)-RPUF-FRP(20%)-MAPP(20%)-OLDH(3%). The properties of the optimal formulated foam are presented in Table 8.4, compared with the neat RPUF and the lignin (30%)-RPUF. The lignin-based RPU foams apparently have better thermo-mechanical properties than the neat RPF foam.

Other RPU foam with halogen-free flame retardant was developed by incorporation of polyol modified lignin (PL) [66]. In this work, lignin was functionalized with flame-retardant elements, phosphorous, and ethylene glycol through a three-step reaction, as illustrated in Fig. 8.6. The polyol modified lignin was then used in preparation of lignin-based RPUFs that had finer average cell size with uniform spherical cells. Compared to the neat RPUF, the apparent density,

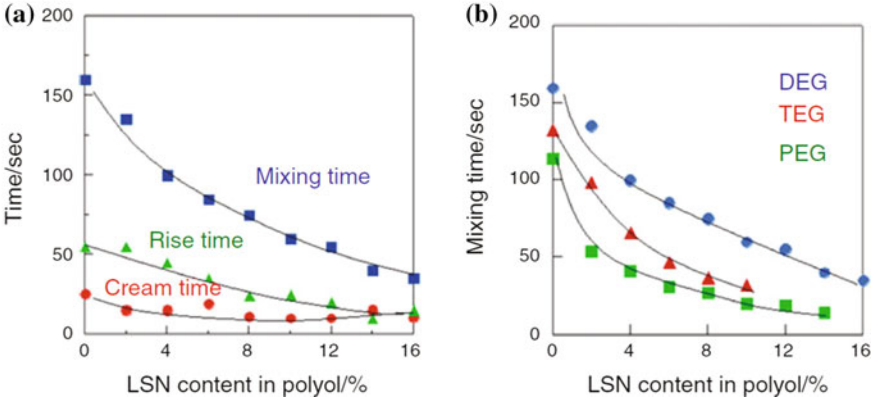


Fig. 8.5 Mixing, cream, and rise times of LSN/LSHW-DEG system as a function of LSN content (**a**), and effects of molecular weight of ethylene glycol on mixing time (**b**), reprinted with permission from Ref. [64]. Copyright (2013) Springer

Table 8.4 Thermo-mechanical properties of various RPU foams, modified from Ref. [65]

Sample	Density (kg/m^3)	T_{Initial}^{a} (°C)	Char$^b_{900}$ (%)	LOI^c (%)	T_g (°C)	Specific compressive strength (MPa g^{-1} cm^{-3})	Thermal conductivity (Wm^{-1} K^{-1})
Neat RPUF	40.1	228	0.6	19	71	10	0.023
Lignin(30%)-RPUF	40.1	241	3.9	19.5	78	10.2	0.023
Lignin(30%)-RPUF-FRP (20%)-MAPP (20%)-OLDH (3%)	42.8	265	15.4	28.1	85	11	0.025

^{a}$T_{Initial}$ Initial decomposition temperature; ^{b}$Char_{900}$ Mass residue at 900 °C; ^{c}*LOI* Limited oxygen index

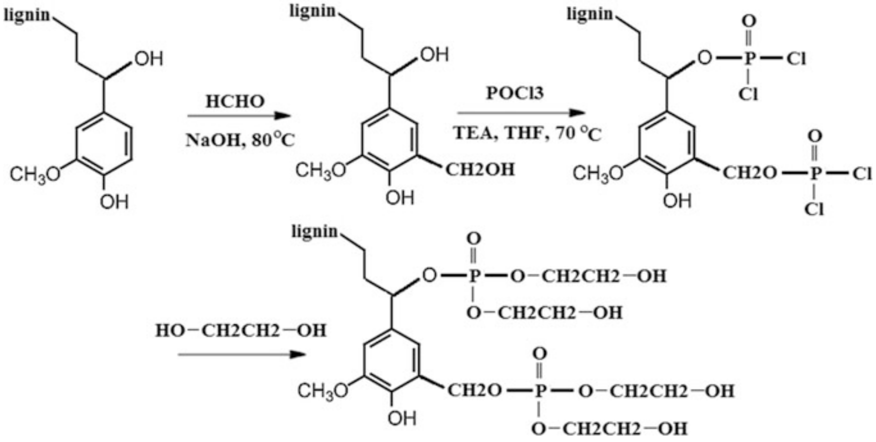


Fig. 8.6 Reaction route to the polyol modified lignin with incorporation of phosphorous flame-retardant element, modified from Ref. [66]

compressive strength, storage modulus, damping properties, thermal stability, and fire-retardant properties of the lignin-based RPUFs all increased owing to the high crosslink density.

Kraft lignin (KL) and organosolv lignin (OL) after propylene oxide modification (or oxypropylation) were employed as a component and extender of a furan polyol-based PU formulated into a class I fire-resistant foam with an aromatic polyisocyanate [67], where the content of lignin derivatives was kept constant at 20 wt%. The results indicated that the OL derivative had better foaming characteristics compared to the KL derivative owing to differences in molecular weight or chemical structure of between of the original lignins. The fire resistance of lignin-based RPU foams increased slightly, whereas the compression strength reduced compared with the control RPU foam.

Liu et al. [23] demonstrated the potential of a refined alkali lignin and a modified alkali lignin with 3-chloro-1,2-epoxypropane as promising feedstocks in the production of RPU foams at 15 wt% replacement of PEG. The mechanical performance of both lignin-based RPU foams was superior to that of the commercial RPU foam. The bending strength of the modified lignin-based RPU foam was around 2 times that of the refined lignin-based RPU foam. The apparent density and heat aging resistance of the modified lignin-based RPU foam were also higher than those of the refined lignin-based RPU foam. Moreover, the thermal conductivity of the modified lignin-based RPU foam was lower than those of commercial RPU foams. These results demonstrated the potential of the modified lignin-based RPU foams for thermal insulation application. RPU foams were prepared from hardwood ethanol organosolv lignin (12–36 wt% replacement) and hardwood kraft lignin (9–28 wt% replacement), and the resultant lignin-based RPU foams showed satisfactory morphology and strength when the lignin replacement ratio is less than 30 wt% [24]. In general, organosolv lignin has a better miscibility with the polyols, resulting better performance of the final RPU foam products. In addition, it was suggested that the strength of the prepared RPU foams could be improved using a chain extender such as butanediol.

Lignin was used as a co-polyol in solvent-free production of tall oil amide-based RPU foams [68]. The apparent density and the closed-cell content increased from 30 to 36 kg/m^3 and 81 to 98%, respectively, when the concentration of lignin varied from 0 to 50 wt% in the formulation of RPUs.

Cateto et al. [69, 70] investigated the oxypropylation reaction of four different types of lignin (Alcell, Indulin AT, Curan 27-11P, and Sarkanda) to generate liquid polyols for production of RPU foams. It was suggested that the adequate polyols in RPU foam formulation should have hydroxyl index in the range of 300–800 mg KOH/g with the viscosity below 300 Pa.s. Li et al. [37] studied the utilization of kraft lignin for production of RPU foams after oxypropylation reaction (as illustrated in Fig. 8.7). The oxypropylated lignin was then blended with sucrose polyol and glycerol polyol at varying combinations for RPU foam formation. The

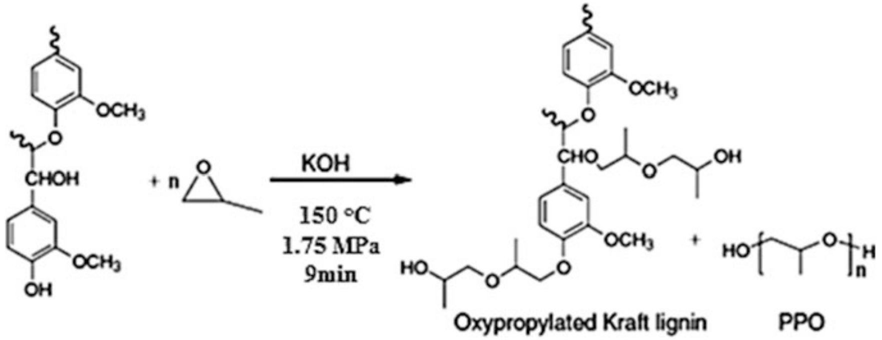


Fig. 8.7 Lignin oxypropylation reaction, reprinted with permission from Ref. [37]. Copyright (2012) Taylor & Francis

corresponding foams exhibited a low density of ~30 kg m^{-3} and most of them have closed cells in approximately 650 μm diameter. It was found the lignin-based RPU foam from 100% oxypropylated lignin polyol had the best compressive properties due to the high functionality of lignin and the rigidity of its aromatic structure.

In a similar study, biopolyols were synthesized from different lignins (soda lignin, organosolv lignin, kraft lignin (KL), and oxidized organosolv lignin) by a chain extension or oxypropylation reaction with propylene oxide (PO) at 180 °C [33]. The lignin/PO ratio strongly affected the viscosity of the biopolyols, varying from 5 cP to infinity, and the hydroxyl index of the biopolyols in the range of 100–200 mg KOH/g. The glass transition temperature of all RPU foams maintained an almost constant value (~60 °C) regardless the lignin type, and a thermal conductivity of the foams was ~20 to 25 mW/m.K.

Lignin chemical modification processes other than oxypropylation, including hydroxymethylation, epoxidation, and phenolation, have been tested to improve the reactivity of lignin towards isocyanate for preparation of lignin-based RPU foams [71]. The modified lignin had a lower impurity and a higher hydroxyl groups compared to the unmodified lignin. It was found that the best formulated of RPU foams with improved mechanical and thermal properties were obtained with 1 wt% of phenolated lignin and 3 wt% of epoxidized lignin. Xue et al. [72] synthesized biopolyols from lignin through microwave-assisted liquefaction of lignin for production of RPU foams. The liquefaction process was conducted using a mixture of polyethylene glycol (PEG-400)/glycerol as the liquefaction solvents and sulfuric acid as a catalyst at 140 °C for 5 min. The liquefaction achieved 97.47% liquefaction yield of liquefied lignin with M_w of 525 g/mol. The liquefied lignin was then coupled with MDI at different molar ratios of [NCO]/[OH]. At the [NCO]/[OH] ratio above 0.6, the compressive strength of the produced RPU foams was higher than 0.1 MPa sufficient for many applications. A biopolyol from lignin, prepared by reacting Biolignin™ with propylene oxide catalyzed by KOH, was used in the production of rigid polyurethane foams at 25–37 wt% polyol replacement [73]. The lignin-based RPU foams exhibited better mechanical and thermal properties in comparison with those of commercial polyether-based RPU foams, and could meet the requirements of EU standard for heat-insulation materials. A bio-based RPU foam was developed from 100% soy polyol for automotive parts, and then lignin (5 wt%) and nanocellulose fiber (1 wt%) were incorporated into the foaming formulation [74]. By addition of lignin and cellulosic fibers into soy-based RPUs, the foam density increased slightly while the open-cell content reduced dramatically from 90% to 12%. An improvement was observed on the compression and impact strengths, owing to the synergic effect of the replacement of isocyanate by lignin and the reinforcement effect of nanofiber on the RPU foams. Semi-rigid PU foams were developed from lignin-molasses-poly (ethylene glycol) polyols with various lignin/molasses polyols [75]. With increasing the percentage of lignin, the apparent density of PU foams increased, consequently the compression strength and elastic modulus improved linearly. The formed bio-based PU foams were thermally stable up to 300 °C.

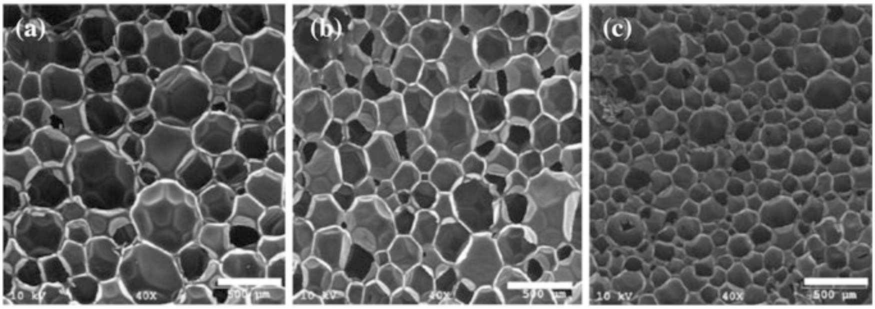


Fig. 8.8 SEM images of the reinforced RPU foams by 0 wt% (**a**), 1 wt% (**b**), and 5 wt% (**c**) of CNWs (Scale bar: 500 µm), reprinted with permission from Ref. [76]. Copyright (2012) Royal Society of Chemistry

An ethanol organosolv lignin polyol was used as a starting material in the preparation of RPU foams and then reinforced by cellulose nanowhiskers (CNWs) at a loading up to 5 wt% [76]. With introducing of CNW into the foaming process, the cell nucleation process was facilitated and a finer cell structure was formed in the resulted lignin-based RPU foams (Fig. 8.8). The compressive strength and the decomposition temperature improved from 4.1 to 12.8 MPa, and from 247 to 296 °C, respectively, by increasing the CNW content from 0 to 5 wt%, which may be attributed to the rigidity of the aromatic structure of lignin and the rigidity of CNWs as well as the induced crosslinking by CNWs.

A series of RPU foams were formulated from oxypropylated lignin at 20 and 30 wt% substitution [44], where the oxypropylation reaction was conducted with lignin and propylene oxide at 160 °C in the presence of KOH catalyst. The produced biopolyols comprising a mixture of oxypropylated lignin, polypropylene oxide oligomers, and catalyst was used for preparation of RPU foams by reacting the lignin-based polyol, a commercial polyether–polyol, a polymeric isocyanate (p-MDI) in combination with glycerol (10% (w/w)) as a co-crosslinker, n-pentane (20% (w/w)) as a physical blowing agent, a mixture of DMCHA and NIAX-A1(2% (w/w)) as a catalyst, SR-321 NIAX (2% (w/w)) as a surfactant, and water (2 wt% with the respect to the total weight of polyols). Although the lignin-based RPU foams showed reduced mechanical properties and density in comparison with those of a reference foam, the presence of lignin did improve the moisture and flame resistance of the final products.

In a later study by the authors' group [31], a hydrolytically depolymerized lignin (DKL, M_w ~ 1700 g/mol and aliphatic hydroxyl number of 365 mg KOH/g) was incorporated into rigid polyurethane foam formulation at high concentration (50 wt%) through direct replacement or oxypropylation, as illustrated in Fig. 8.9.

It was found the compressive strengths and compression modulus of DKL-based RPU foams were comparable with those of the references foams from sucrose polyol and PPG400. The thermal conductivity of DKL-based RPU foams varied in

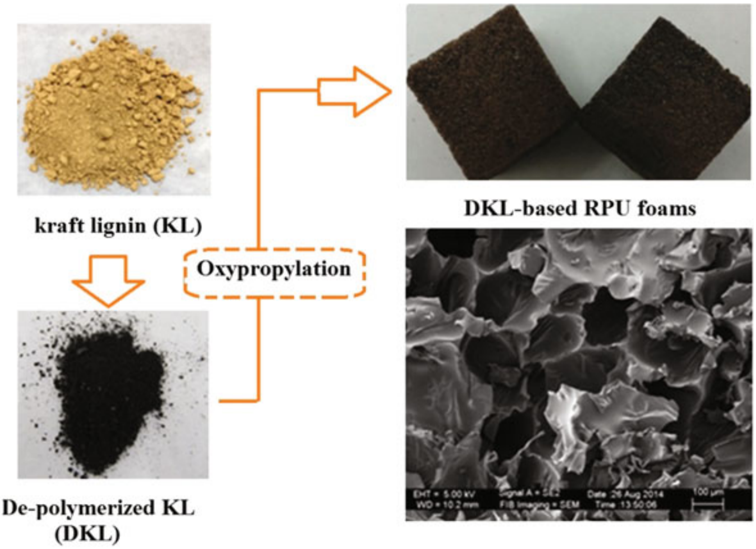


Fig. 8.9 Preparation of lignin-based RPU foams using hydrolytically depolymerized kraft lignin (DKL), modified from Ref. [31]

the range of 0.029–0.038 W/m/k. The oxypropylated DKL showed the best mechanical and thermal properties with the lowest thermal conductivity, which makes it as a suitable candidate for insulation applications.

Hatakeyema et al. [77] studied the thermal performance of lignin-based PU foams with various inorganic fillers such as barium sulfate ($BaSO_4$), calcium carbonate ($CaCO_3$) and talc. The homogeneous dispersions of $BaSO_4$ and talc were confirmed by SEM; however, the dispersion of $CaCO_3$ in the foam was poor. With increasing the talc content, the temperature of thermal decomposition shifted to a higher temperature and the carbon residue at 500 °C linearly increased. A series of RPU resins were produced from the mixture of sodium salt of lignosulfonic acid (LS, 0–33 wt%) and other polyols such as diethylene glycol (DEG) or triethylene glycol (TEG) or polyethylene glycol (PEG200, 200 g/mol) [78]. The phase transition behaviors of the formed RPUs were characterized using TMA and DSC. There is a good agreement between the obtained values from both techniques. The measured glass transition temperatures (T_g) for these foams are illustrated in Fig. 8.10. As can be seen, the T_g increased from 80 to 140 °C with increasing the lignin content and with reducing the oxyethylene chain length.

Water-absorbent polyurethane composite foams were derived from molasses and lignin filled with various particle sizes of microcrystalline cellulose (MCC) powder [79]. With increasing the mixing ratio of lignin/molasses, the compression strength and elasticity increased, whereas the water-absorbing ability reduced due to reduced amount of molasses that has better hydrophilic property. The optimal ratio of 20/80 of lignin/molasses was selected to study the content and particle size of MCC on the

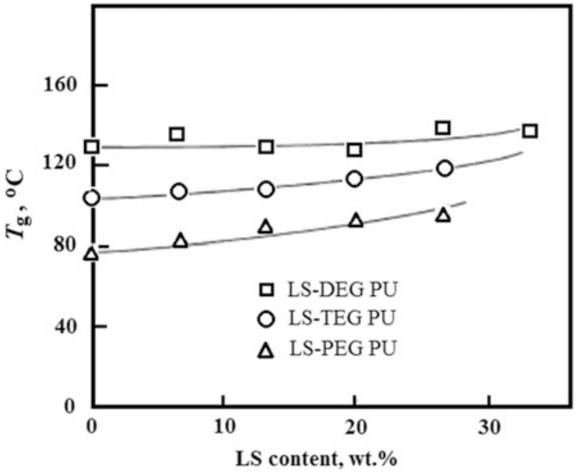


Fig. 8.10 Variation of glass transition temperature of LS-based PUs as a function of LS content, modified from Ref. [78]

water absorption properties of PU foams, and it was observed that water vaporization was retarded using high amount of MCC with large particle sizes.

Biodegradations of lignin-based RPU foams were examined by Cateto et al. [80]. Four different oxypropylated lignins (Alcell, Indulin AT, Curan 27-IIP, and Sarkanda) at 20 and 30 wt% substitutions were used in synthesis of RPU foams. Among all types of lignin-based foams, Alcell-, and Indulin AT-based polyols resulted in foams with comparable properties to the reference foams. The biodegradation of the formulated Alcell- and Indulin AT-RPUFs was then evaluated using respirometry tests in liquid and solid media. Indulin AT-based RPU foams showed higher weight loss in the presence of P. *chrysosporium* and T. versicolor microorganisms due to the production of enzymatic extracts rich in lignin peroxidase (Lip), manganese peroxidase (MnOX), and laccase (Lac) with a well-known combinatory effect on lignin biodegradation.

Polyurethanes can be used in the field of civil construction such as geocomposites. Polyurethane resins are injected into sand by injection force-poling method followed by crosslinking and foaming reactions, to prevent collapse of the ground, when tunnels are excavated [81]. The development of new geostabilizers mainly depends on the physical properties, practical and cost performance, and environmental compatibility of the utilized materials. Lignin-based PU geocomposites were newly developed from two types of lignin, kraft lignin and lignosulfonate [81]. The mechanical and thermal properties of the formed geocomposites were investigated by compression test and TGA. The apparent density of lignosulfonate–PU remained unchanged by varying the types of polyol and the content of lignin up to 30 wt%. On the other hand, a slight increase in the apparent density was observed for the kraft lignin-based PU in which PEG was substituted with lignin at around 16–25 wt % ratio. The decomposition temperature reduced with increasing the content of lignin. The compression strength of the lignin-based RPU foams increased gradually when the content of lignin was low, while reduced linearly with further increasing of the lignin content. All samples showed the mechanical strength higher than 2 MPa, which could meet the requirements of geocomposite applications.

Lignin was incorporated in production of RPU foams through two distinct approaches: as filler without chemical reaction and as biopolyol after oxypropylation in alkali conditions [82]. With increasing the percentage of lignin as filler reduced the compression characteristic, dimension stability, and hydrophobicity of RPU foams, in contrast, the substitution of petroleum-based polyols by lignin–polyol improved the uniformity of cell structure and dimensional stability without compromising the physical–mechanical properties of foams.

8.4 Summary

The majority of polyurethane (PU) is consumed for the production of flexible and rigid foams, and a large portion of PU is for protective and decorative coatings on a wide variety of substrates such as wood, metal, plastics, leather, and textiles. The rest of PU is consumed as elastomers, adhesives, sealants, and others. Polyurethane rigid foams are widely used as insulation and structural materials for construction, transportation, and decoration. Those foams account for almost one-third of the polyurethane market. The aromatic structure and the presence of hydroxyl groups on lignin make it as a suitable substitute of polyol in manufacturing of polyurethanes. Lignin can be incorporated in synthesis of PU by two approaches: (1) direct incorporation of crude technical lignin without modification or polyol combination, (2) incorporation of modified lignin with improved reactivity, via oxypropylation, esterification, etherification reactions, and depolymerization processes. In general, the content of the unmodified lignin in the prepared polyurethane was kept below 15–30 wt% to reach an acceptable performance, while after chemical modifications or thermal degradation of lignin, the lignin substitution levels increased more than 50 wt% with comparable properties.

This chapter summarized the production of lignin-based PU for various applications including elastomers, coatings/adhesives/sealants, flexible foams, and semi-rigid or rigid foams. Generally, the obtained lignin-based PU elastomers have reduced elasticity and a lower degradation temperature. The lignin-based PU adhesive with optimal combination of thermal and mechanical properties, with a high adhesion strength, can be prepared using lignin-based biopolyols containing over 50 wt% lignin even as high as 70–90 wt%. The addition of lignin had two distinctive effects on the prepared flexible or rigid foams, i.e., filler effect and crosslinking effect. Increasing the content of lignin in the foams led to an increase in crosslink density and viscometric properties of the foams due to the filler-like behavior of the separated lignin-rich phase. Furthermore, it was observed compression strength and Young's moduli of the lignin-based PU foams increased with increasing the lignin content due to enhancement of the foam density.

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