

MRS Bulletin

Technical lignins in polymer materials: A sustainable approach to advanced materials --Manuscript Draft--

| | |
|---------------------------|---|
| Manuscript Number: | MRSB-D-25-00270 |
| Full Title: | Technical lignins in polymer materials: A sustainable approach to advanced materials |
| Article Type: | Impact: Review |
| Abstract: | Lignin, a major component of lignocellulosic biomass, is gaining attention as a renewable alternative to fossil-based materials in polymer composites. Its complex polyphenolic structure imparts antioxidant, antimicrobial, UV-resistant, and biodegradable properties, enabling its integration into thermoplastics, thermosets, and elastomers, often without extensive modification. Technical lignins from industrial processes such as Kraft, sulfite, and organosolv methods offer scalable feedstocks for sustainable materials. In plastics, lignin enhances mechanical, thermal, and aging resistance while supporting biodegradability; in rubber composites, it serves as both a reinforcing agent and a stabilizer against oxidation and UV degradation. Performance can be further improved through plasticization and compatibilization. The review also surveys patents, reflecting the growing industrial interest and commercial potential of lignin valorization. |

1
2
3
4
5
6
7
8

Technical lignins in polymer materials: A sustainable approach to advanced materials

9 Richard Nadányi^{a,c} (ORCID: 0000-0002-2078-2949), Michaela Džúganová^{a,b} (ORCID: 0009-0007-3506-293X),
10 Zuzana Vanovčanová^a (ORCID:), Katarína Tomanová^a (ORCID:), Ján Kruželák^a (ORCID: 0000-0002-2583-
11 1260), Eduard Oswald^a (ORCID:), Zuzana Kramárová^a (ORCID:), Aleš Ház^a (ORCID: 0000-0001-5134-9657),
12 Jozef Feranc^a (ORCID: 0009-0000-9590-0199)

13 ^a Institute of Natural and Synthetic Polymers, Faculty of Chemical and Food Technology, Slovak University of Technology in
14 Bratislava, Radlinského 9, 81237 Bratislava, Slovakia

15 ^b Tomas Bata University in Zlín, Faculty of Technology, Vavrečkova 5669, 760 01 Zlín, Czech Republic

16 ^c Christian Doppler Laboratory for Next-Generation Wood-Based Biocomposite, Institute of Chemical, Environmental and
17 Bioscience Engineering, TU Wien, Getreidemarkt 9, 1060 Vienna, Austria

18 Corresponding author: Richard Nadányi; richard.nadanyi@tuwien.ac.at; Getreidemarkt 9, 1060 Vienna, Austria

Declarations

24 **Funding:** This work was supported by the Slovak Research and Development Agency under the contract No. APVV-
25 22-0011, APVV-22-0388, VEGA 1/0743/24. In addition, the financial support by the Austrian Federal Ministry of
26 Economy, Energy and Tourism, the National Foundation for Research, Technology and Development and the Christian
27 Doppler Research Association is gratefully acknowledged.

28 **Conflict of interest:** The authors declare that they have no conflict of interest.

29 **Availability of data and material:** Not applicable

30 **Code availability:** Not applicable

31 **Financial support:** The authors have no relevant financial or non-financial interests to disclose.

32 **Author contribution:** The idea for this review was conceived by Michaela Džúganová. Literature search and data
33 analysis were performed by all authors. Conceptualization and initial drafting of the manuscript were carried out by
34 Michaela Džúganová, Richard Nadányi, Zuzana Vanovčanová, and Jozef Feranc. Critical revision of the draft was
35 performed by Katarína Tomanová, Ján Kruželák, Eduard Oswald, Zuzana Kramárová, and Aleš Ház. The final revision
36 of the manuscript was completed by Richard Nadányi.

Acknowledgements

40 This work was supported by the Slovak Research and Development Agency under the contract No. APVV-22-0011,
41 APVV-22-0388, VEGA 1/0743/24. In addition, the financial support by the Austrian Federal Ministry of Economy,
42 Energy and Tourism, the National Foundation for Research, Technology and Development and the Christian Doppler
43 Research Association is gratefully acknowledged.

Abstract

44 Lignin, a major component of lignocellulosic biomass, is gaining attention as a renewable alternative to fossil-based
45 materials in polymer composites. Its complex polyphenolic structure imparts antioxidant, antimicrobial, UV-resistant,
46 and biodegradable properties, enabling its integration into thermoplastics, thermosets, and elastomers, often without
47 extensive modification. Technical lignins from industrial processes such as Kraft, sulfite, and organosolv methods offer
48 scalable feedstocks for sustainable materials. In plastics, lignin enhances mechanical, thermal, and aging resistance
49 while supporting biodegradability; in rubber composites, it serves as both a reinforcing agent and a stabilizer against
50 oxidation and UV degradation. Performance can be further improved through plasticization and compatibilization. The
51 review also surveys patents, reflecting the growing industrial interest and commercial potential of lignin valorization.

1
2
3
4 **Keywords:** sustainable polymer materials; lignin valorization; lignin-based polymers; biobased polymer composites;
5 renewable resources
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1 Introduction

With the rise in global population and welfare, consumption has surged, driving the significant growth of polymers (thermoplastics, thermosets, and elastomers) over the past six decades, with thermoplastics being the dominant category. Although polymer production accounts for only about 4–8% of global oil consumption. Roughly half used as material feedstock and the other half as fuel for the production process, there are still concerns about the raw materials used and the end-of-life disposal of these polymers [1]. Research efforts have primarily focused on replacing fossil-based raw materials with renewable alternatives and developing sustainable end-of-life solutions, such as recycling and biodegradation. A key challenge is ensuring that the transformation of renewable resources into polymers is highly efficient to reduce costs. Sustainable polymers must exhibit comparable or enhanced properties relative to existing fossil-based counterparts [2,3].

Naturally abundant and renewable resources, such as lignocellulosic biomass, have been recognized as promising alternatives to fossil-based raw materials. While polysaccharides like cellulose and hemicellulose are fully utilized, lignin remains one of the least used resources of renewable polymers [4]. Lignin, an amorphous and heterogeneous polymer, is a major structural component of vascular plant cell walls, making it the second most abundant biomass on Earth. Due to its unique polyphenolic structure, antimicrobial and antioxidant behaviour, biodegradability, and UV-absorption properties, lignin has attracted attention in the last decades across various fields [5,6]. To illustrate lignin's versatility as a renewable component in polymeric materials, Fig. 1 presents the number of publications retrieved from the *Web of Science* [7] using the keywords “lignin composite.” The exponential increase in publications over the past 20 years highlights significant research efforts aimed at lignin valorization in polymer composites. The global lignin market size was in 2024 estimated at USD 1.32 billion and is expected to grow at a compound annual growth rate of 4.4% by 2030 [8].

Currently, many lignocellulosic biomass-derived materials remain in early-stage development, particularly within academic research, and are not yet ready for industrial-scale production. Therefore, an approach focusing on the utilization of technical lignins in polymer composites, which can already be produced industrially, is of particular interest. This review provides a comprehensive summary of advancements in pulping processes and lignin recovery techniques for the industrial production of technical lignins, along with their potential applications. Furthermore, it examines the incorporation of technical lignins into polymeric materials, including thermoplastics, thermosets, and rubber, without requiring modification methods that involve excessive amounts of solvents and chemicals. The significance of these applications is further emphasized through an overview of relevant patented technologies.

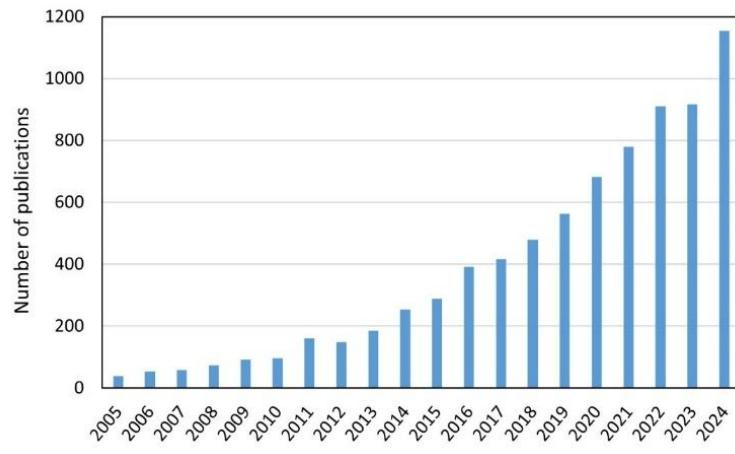


Fig. 1 Number of Publications Searched in the Web of Science with the Keywords “lignin composite” Over the Years [7]

2 Technical Lignins

2.1 Lignin Structure

Lignin is an amorphous, highly irregular polyphenolic heteropolymer derived from the radical polymerization of three primary monolignols: p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol [9–11]. These monomers, presented in Fig. 2, each consist of a phenylpropane (C₆-C₃) unit with differing methoxy substitution on the aromatic ring (none in p-coumaryl, one in coniferyl, two in sinapyl). Upon polymerization, they give rise to p-hydroxyphenyl

(H), guaiacyl (G), and syringyl (S) units in the lignin macromolecule, respectively [9,12–18]. Lignin's biosynthesis involves enzymatic one-electron oxidation of these monolignols to form phenoxy radicals, which then couple in a combinatorial fashion to form a complex, three-dimensional network [12,19–22]. This coupling is largely random, in contrast to the well-defined sequences of other biopolymers, resulting in an extremely heterogeneous structure [19,23–28]. Fig. 2 illustrates the structures of the three canonical monolignols and some common linkage motifs in lignin. Notably, the relative abundance of H, G, and S units varies with plant species and tissue (refer to Table 1): softwood (gymnosperm) lignins are composed predominantly of G units (with minor H and essentially no S), hardwoods (angiosperms) contain a mix of G and S units, and grasses (monocots) incorporate all three units (including a significant H fraction) [9,12,13,29]. This compositional difference is biologically determined and has structural implications (for instance, S-rich lignins tend to be more linear due to fewer cross-linking sites on the aromatic ring). In addition to the primary monomers, lignin often contains a variety of functional groups arising from its composition: abundant hydroxyl groups (both phenolic OH and aliphatic OH on the propyl side chain), methoxy groups on aromatic rings, as well as carbonyl and carboxyl groups in certain units. The exact distribution of these functional groups depends on the lignin's botanical origin and any processing it has undergone [19,30–32]. These functionalities are critical, as they influence lignin's reactivity and interactions in materials (e.g. phenolic OH groups confer antioxidant activity and can participate in cross-linking with polymers in composites). The diversity of linkages and branching leads to lignin's amorphous three-dimensional network structure [33].

Table 1: Distribution of Monolignol Types in Lignin from Various Plant Sources and Comparison of Lignin Linkage Types and Their Abundances in Softwood and Hardwood [34–38]

| Origin of the lignin | <i>p</i> -hydroxyphenyl [%] | Guaiacyl [%] | Syringyl [%] |
|----------------------|------------------------------|---------------------------|---------------------------|
| <i>Softwood</i> | < 5 | < 95 | Not identified |
| <i>Hardwood</i> | 0 – 8 | 25 – 50 | 46 – 75 |
| <i>Grasses</i> | 5 – 33 | 33 – 80 | 20 – 54 |
| Linkage type | Dimer structure | Abundance in softwood [%] | Abundance in hardwood [%] |
| β-O-4 | Phenylpropane β-aryl ether | 45–50 | 60 |
| α-O-4 | Phenylpropane α-aryl ether | 6–8 | 7 |
| β-5 | Phenylcoumaran | 9–12 | 6 |
| 5-5 | Biphenyl and dibenzodioxocin | 18–25 | 5 |
| 4-O-5 | Diaryl ether | 4–8 | 7 |
| β-1 | 1,2-Diaryl propane | 7–10 | 7 |
| β-β | β-β-linked structures | 3 | 3 |

1
 2
 3
 4
 5
 6
 7
 8
 9
 10
 11
 12
 13
 14
 15
 16
 17
 18
 19
 20
 21
 22
 23
 24
 25
 26
 27
 28
 29
 30
 31
 32
 33
 34
 35
 36
 37
 38
 39
 40
 41
 42
 43
 44
 45
 46
 47
 48
 49
 50
 51
 52
 53
 54
 55
 56
 57
 58
 59
 60
 61
 62
 63
 64
 65

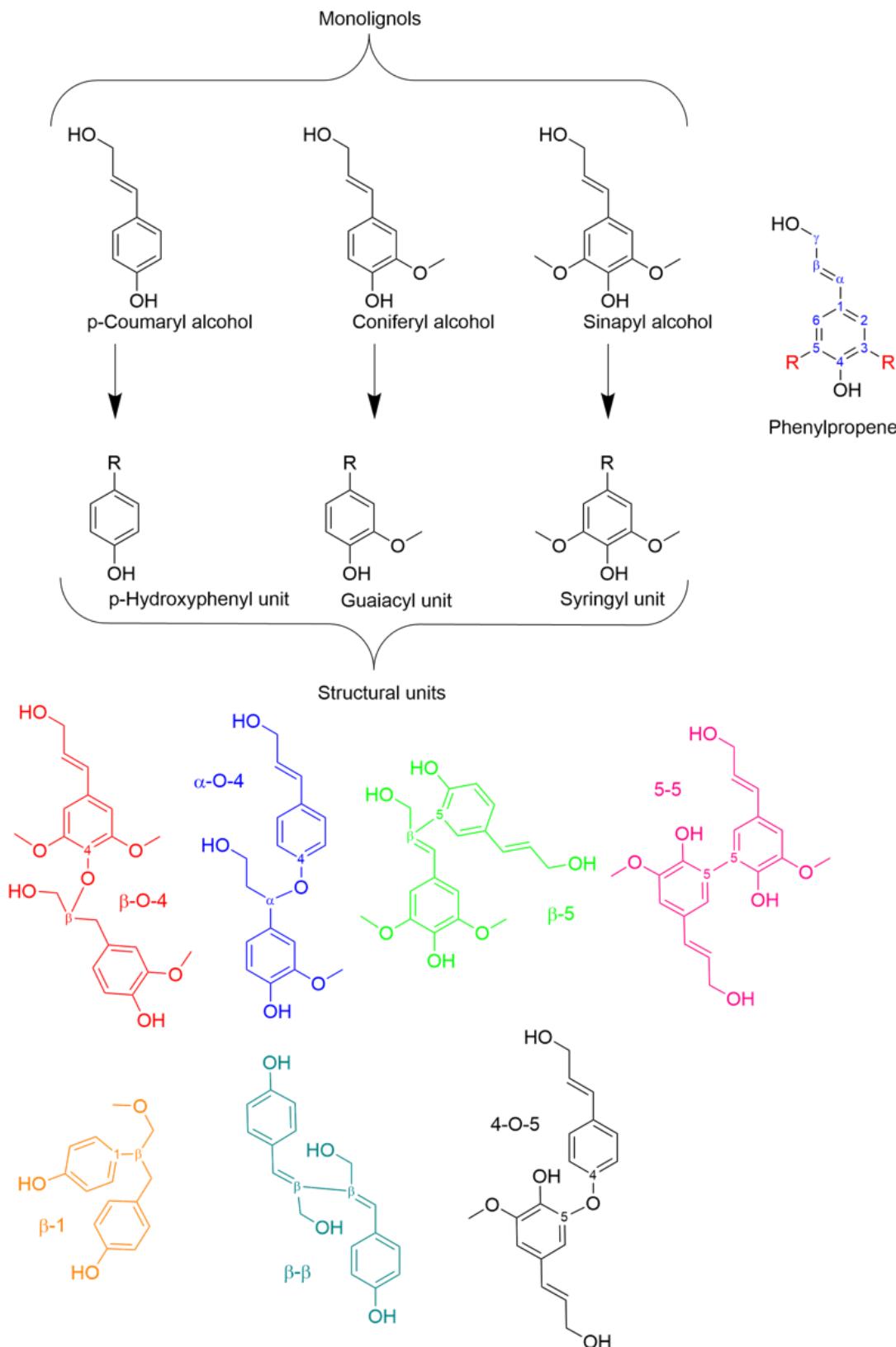


Fig. 2 Structure of Three Monolignols with Corresponding Building Units and Representation of Main Chemical Linkage in Lignin Structure – aryl ether (β -O-4; red), aryl ether (α -O-4; blue), phenylcoumaran (β -5; green), biphenyl (5-5; magenta), spirodienones (β -1; orange), resinol (β - β ; turquoise), diaryl ether (4-O-5; black)

The polymerization of monolignols via radical coupling yields a variety of carbon–carbon and ether (C–O–C) bonds between aromatic units [20]. The result is a highly branched, cross-linked network with no uniform repeating unit. The most prevalent linkage in native lignins is the β -O-4 (arylglycerol- β -aryl ether) bond, which typically accounts for ~45–60% of all inter-unit linkages in both softwoods and hardwoods [14,16–18,20]. This dominant linkage connects the β -carbon of one phenylpropane unit to the 4-O position of another and is critical for the overall linear extension of the polymer. Early degradative studies by *Adler et al.*[34] using acidolysis (producing Hibbert's ketones) estimated the β -O-4 content in spruce (softwood) lignin to be roughly 0.25–0.30 per aromatic unit, corresponding to a substantial fraction of the polymer's connectivity. Modern spectroscopic techniques, such as 2D NMR (HSQC), have corroborated that β -O-4 linkages are predominant in native lignins [20,39,40]. The remaining linkage structure is composed of several secondary linkages that contribute to lignin's branching and cross-linking. These include: β -5 linkages (phenylcoumarans) formed by coupling of a side-chain β -carbon to the 5-position of another unit, β - β linkages (resinol units) resulting from the dimerization of two monolignols at their β -carbons, and 5-5 linkages (biphenyl and associated structures) where two aromatic rings are directly coupled [20,34,35]. Collectively, linkages like β -5 and 5-5 typically make up a significant minority of the polymer (for example, softwood lignins, being G-rich, have a higher fraction of these condensed linkages than S-rich hardwood lignins). The β - β (resinol) structures are often found as branching points: for instance, pinoresinol and related dimers are more abundant in hardwood (S-containing) lignins than in softwoods, whereas grass lignins (which contain H units and special ferulate linkages) show almost no β - β structures [20]. Other linkage types occur in smaller proportions, such as 4-O-5 diaryl ethers, α -O-4 linkages (ether link between the α -carbon of the side chain and an aromatic ring), and β -1 linkages (spirodienones), as well as more complex structures like dibenzodioxocins [20,41–43]. These minor linkages, though less common, further diversify the three-dimensional architecture of lignin. The abundance of different linkages in softwood and hardwood lignins is presented in Table 1. The combination of multiple linkage types means lignin is not a linear polymer but rather a branched network. Some linkages (like 5-5 biphenyl bonds and certain β -5 structures) create junctions where the polymer branches or even forms cyclic structures, contributing to lignin's resistance to depolymerization and its tight, complex packing within the plant cell wall. The overall degree of polymerization and molecular weight of native lignin is not fixed; *in situ*, lignin can be considered an endlessly growing network within the wall. When isolated, lignin typically shows weight-average molecular weights M_w on the order of a few thousand to tens of thousands of Daltons, depending on source and extraction method [20,44]. For example, “milled wood lignin” extracted directly from plants can have M_w in the range of ~5,000–25,000 Da [20]. This polydispersity reflects both the inherent polymerization randomness and any fragmentation during isolation.

Although lignin is conventionally described as being built from three monolignols, research has revealed remarkable flexibility in its molecular composition. The polymer's structure can vary not only between species but also with developmental stage, environmental conditions, and genetic modifications [12,19,45–48]. In softwoods (e.g., pine or spruce), lignin is almost entirely guaiacyl-type (G) units, which leads to a highly cross-linked structure due to the free 5-position on the aromatic ring of G units that can participate in bonding (e.g., forming 5-5 and β -5 linkages) [34,35]. Hardwoods (e.g., oak, birch, poplar) produce lignins that are composed of both G and S units, with S units (syringyl) carrying two methoxy groups and lacking a free 5-position. The introduction of S units tends to limit cross-linking, since S units can only link through β -O-4 and β - β (and not 5-5 or β -5 with another S). As a result, hardwood lignins are often somewhat less condensed (more linear) than softwood lignins, which has implications for their reactivity and ease of processing [37,38]. Grass lignins (found in cereals, bamboo, etc.) are even more complex: they contain a mixture of H, G, and S units and are typically enriched in hydroxycinnamate ester residues such as p-coumaric acid and ferulic acid. These hydroxycinnamates are produced via the monolignol pathway and can become covalently attached to lignin or to carbohydrates. In many grasses, p-coumarate esters are grafted onto lignin side chains (especially on S units) at the γ -hydroxyl position, sometimes comprising 5–10% of the lignin mass. This means grasses have a lignin that is acylated – a feature much less common in woody lignins. Similarly, some angiosperm species (e.g., willow, aspen) incorporate p-hydroxybenzoate groups on their lignin (via sinapyl p-hydroxybenzoate as a precursor). These modifications introduce additional functional groups and can influence lignin's glass transition and reactivity (acylated lignins are often more hydrophobic and somewhat less hydrogen-bonded). Importantly, studies show that such acyl groups are built-in during polymerization, i.e. pre-acylated monolignols are polymerized into the lignin, rather than lignin being acylated post facto [20,34–36]. This expands the traditional view of lignin's building blocks beyond just the three alcohols.

Over the past decade, evidence has emerged that plants (especially under certain evolutionary or engineered conditions) can polymerize alternative phenolic monomers into lignin, effectively breaking the “three monomers”

1 paradigm. For instance, some unusual plant species produce catechyl lignin (C-lignin), a polymer derived almost
2 exclusively from caffeic alcohol (3,4-dihydroxyphenylpropane-1-ol). C-lignin was discovered in the seed coats of
3 plants like Vanilla orchid and Cleome, and it forms a linear, condensation-free polymer in which units are linked
4 primarily by benzodioxane bonds. In C-lignin, each caffeic unit couples at its 4-O and β positions to form stable
5 benzodioxane rings, yielding a structure that is far less branched than typical H/G/S lignins. This homopolymer has
6 unique properties (e.g., a more uniform structure and easier depolymerization to single monomers) and highlights
7 nature's ability to produce lignin variants with distinct linkage patterns. Another example of non-canonical monomers
8 is 5-hydroxyconiferyl alcohol (also known as 5HG), which can be incorporated into lignin in certain mutant or
9 engineered plants, leading to the formation of benzodioxane units in the presence of normal monomers [9,14,16–
10 18,26,49–54]. Moreover, flavonoids have been identified as genuine lignin components in some cases: tricin, a
11 methoxylated flavone, is naturally incorporated into grass lignins (particularly in cereal straws and bamboo) as a
12 terminator unit that caps lignin chains. Tricin's structure (already containing multiple OCH₃ substitutions) means it
13 can only form ether linkages (4'-O- β) and thus typically appears at lignin chain ends. Similarly, recent studies have
14 shown other flavonoids (e.g., naringenin, chalcones) can participate in lignification in certain plants [55–60].
15 Additional phenolic compounds such as ferulate conjugates can also integrate into lignin. For example, coniferyl
16 ferulate (a ferulic acid ester of coniferyl alcohol) and tyramine ferulate have been reported as lignin-building units in
17 some species [9,61]. These findings underscore that lignin's polymer structure is not strictly fixed by a universal
18 formula but can evolve and adapt. From a foundational perspective, the paradigm of lignin has shifted from a polymer
19 of three monomers to a polymer that can potentially include a variety of aromatic precursors available in the cell wall
20 environment [22,55,62,63].

21 The inherent complexity and variability of lignin's structure are directly relevant to its utilization in materials
22 science and sustainable polymer development. Key structural aspects such as the abundance of β -O-4 linkages (which
23 are relatively labile under chemical or enzymatic cleavage) versus condensed linkages (which are more recalcitrant)
24 will influence how easily a given lignin can be depolymerized or chemically modified [20,34,35]. Likewise, the
25 presence of certain functional groups (e.g., phenolic OH content, which is higher in G-rich lignins due to many free
26 C4 positions) affects lignin's reactivity in polymer blends and curing reactions. The branching density (affected by S
27 vs G unit ratio and 5–5 linkages) will impact the melt behaviour and mechanical performance of lignin-based plastics.
28 For example, S-rich lignins (more linear) might be more flexible and easier to process, whereas G-rich lignins (highly
29 cross-linked) are more brittle but confer rigidity and thermal stability [20,34–38]. In summary, lignin is best described
30 as a dynamic, three-dimensional network polymer whose exact structure depends on its biological source. Table 1 can
31 be used to summarize the typical compositional differences and linkage distributions among various lignin types (e.g.,
32 softwood vs. hardwood vs. grass). Maintaining a clear picture of lignin's structure – from the molecular level
33 (monomers, linkages, functional groups) to the macromolecular architecture – is crucial for rationally designing
34 strategies to integrate lignin into bioplastic and rubber composites. This understanding allows researchers to predict
35 how lignin will behave as a polymeric additive or precursor, and to devise chemical modifications that improve
36 compatibility and performance in sustainable material applications [18,36,64,65]. The following sections will build on
37 this structural foundation to explore how lignin can be functionalized and utilized in bioplastic and elastomer contexts.

45 2.2 Pulping Processes

46 The complex, randomly cross-linked structure of lignin (rich in aryl-ether and carbon-carbon bonds) provides
47 rigidity and hydrophobicity to wood fibres but also makes lignin chemically recalcitrant. In the pulp and paper industry,
48 removing lignin (a process called delignification) is essential to free cellulose fibres for papermaking [66].
49 Delignification is achieved by various pulping processes, whose differing mechanisms impact the structure and
50 properties of the resulting lignin. Below we review lignin's behaviour in different pulping processes and how it can be
51 recovered as a value-added product. As discussed in previous chapter, complex and heterogeneous lignin's structure
52 influences lignin's molecular mass and reactivity. Lignin is thermostable and insoluble in water (under neutral pH) due
53 to its aromatic structure and high molecular weight. It must be chemically modified (e.g. by introducing hydrophilic
54 or charged groups) or subjected to extreme conditions to become soluble or reactive. During pulping, lignin's structure
55 is fragmented and modified: for example, in alkaline processes many β -O-4 ether linkages are cleaved, reducing the
56 polymer size, while in sulfite pulping lignin is chemically sulfonated to increase its solubility. The balance of lignin's
57 functional groups (phenolic hydroxyl, methoxy, carbonyl, etc.) and molecular size after pulping will determine its
58 properties (such as solubility, glass transition, and reactivity) and thus its suitability for further applications
59 [23,26,34,35,43]. High-purity lignin (with low sugar and ash content) is particularly desirable for value-added uses
60 [67], whereas lignin with more impurities or structural modifications may be limited to energy recovery or low-grade
61 uses [68].

products [68–71]. In summary, the structure and properties of lignin are strongly influenced by its source and the pulping process, which is why understanding these factors is crucial when developing lignin recovery and utilization strategies.

Wood pulping processes are generally classified into three main categories – mechanical, chemical, and semi-chemical – based on how they remove lignin to liberate cellulose fibres. An additional category, organosolv pulping, has gained attention for its environmentally friendly approach and high-purity lignin by-product. Each process leads to a different outcome in terms of lignin removal, lignin chemistry, and pulp properties (detailed comparison and characterization of different pulping methods is presented in Table 2):

Mechanical pulping uses mechanical force (grinding or refining) to physically separate wood fibres with minimal chemical change to lignin. This method retains most of the wood components, resulting in a high pulp yield (often up to ~90–95% of the original dry wood) since lignin largely remains in the fibres. Because the lignin is not removed, mechanically pulped fibres are stiff and discolour easily: the pulp has lower strength and tends to yellow over time due to the high lignin content. Mechanical pulps are used in products with short life spans or lower strength requirements (e.g. newsprint, magazines, and catalogue papers) where high yield is advantageous. A benefit of mechanical pulping is that it produces no spent cooking liquor (since no chemicals are used to dissolve lignin), avoiding liquid waste [72–77]. However, the lignin remains in the paper, which limits the brightness and permanency of mechanical paper products.

In **chemical pulping**, wood chips are cooked with chemicals to dissolve most of the lignin, freeing nearly pure cellulose fibres. The two primary chemical pulping methods are the Kraft (sulfate) process and the sulfite process. Kraft pulping uses a strongly alkaline white liquor containing NaOH and Na₂S to cleave lignin bonds (especially β-aryl ether linkages) and form soluble sodium lignates [73,78–80]. Sulfite pulping, by contrast, uses sulfurous acid and bisulfite salts (e.g. Ca, Mg, Na, or NH₄ bisulfite) to sulfonate lignin, generating water-soluble lignosulfonates. Chemical pulps have lower yield (typically only ~35–55% of the wood is retained as pulp) because most lignin (and hemicellulose) is removed during cooking. However, the resulting fibres are stronger and brighter, making chemical pulps suitable for high-quality paper and board. Kraft pulp in particular is known for its strength and versatility, and it dominates global pulp production (the Kraft process alone accounts for the majority of the ~158 million tons of chemical pulp produced annually) [73,78–82]. Sulfite pulp is easier to bleach and can be used to produce specialty products like dissolving pulp (for rayon or cellulose derivatives), but the process is less common today due to feedstock limitations and environmental challenges with sulfite effluents. Importantly, chemical pulping significantly alters lignin's structure: in Kraft pulping, lignin fragments precipitate as sodium lignate and some lignin chemically binds with sulfur (thiol groups), whereas in sulfite pulping lignin is heavily sulfonated. These “technical lignins” (Kraft lignin and lignosulfonates) are recovered in spent liquor and have distinct properties: Kraft lignin is hydrophobic and can be precipitated by acidification (see recovery techniques below), while lignosulfonates remain water-soluble and are often used directly in applications like dispersants and binders [67,68,83–85].

Semi-chemical pulping combines a mild chemical pretreatment with mechanical fiberization. One common example is the Neutral Sulfite Semi-Chemical (NSSC) process, which treats wood with sodium sulphite (at neutral pH) to soften the lignin, followed by mechanical refining to separate fibres [77,86,87]. The result is an intermediate approach: moderate delignification with higher yield (typically 65–85% yield) than fully chemical pulping, and pulp strength and brightness between that of mechanical and chemical pulps. Semi-chemical pulp (often from hardwoods) is widely used for corrugating medium and other paperboard products, where a balance of strength and yield is desired. By partially dissolving or plasticizing lignin in the pretreatment, semi-chemical processes make the subsequent fibre separation easier than purely mechanical methods, yet they do not remove as much lignin as a full chemical cook. Thus, semi-chemical pulps contain more lignin than Kraft pulps but less than groundwood, giving them moderate strength and stability. The spent liquor from semi-chemical processes (e.g. NSSC liquor) contains dissolved lignin, but in smaller amounts and different form (e.g. sodium lignosulfonates) than Kraft black liquor. Mills often recover and reuse chemicals from NSSC liquor, but lignin isolation from these streams is less common than from Kraft liquor [87–90].

Organosolv pulping uses organic solvents, often in combination with water and an acid catalyst, to solubilize lignin and hemicellulose from wood [91]. Common organosolv methods use solvents such as ethanol, methanol, acetic acid, or formic acid at elevated temperatures. For example, the *Alcell* process uses ethanol-water, while others use acetic acid or acetone with a catalyst [92]. Organosolv processes are not yet widely employed on a large scale, but they are notable for producing a high-purity, sulfur-free lignin as a co-product. The lignin obtained from organosolv pulping is typically precipitated by diluting the spent solvent or by water addition, yielding a relatively unmodified lignin that

is easier to valorise (e.g. for materials or chemicals) compared to Kraft lignin [93–97]. Organosolv pulping also has environmental advantages: it avoids the sulfurous emissions of Kraft and sulfite processes and can recover and recycle the organic solvents, resulting in low effluent pollution [98]. However, the process requires higher capital and operating costs, and solvent recovery systems must be efficient, which has limited its commercial adoption [99]. In summary, organosolv pulping demonstrates an innovative approach to delignification that facilitates lignin recovery (yielding lignin of exceptional purity), but its complexity and cost have so far confined it to pilot and niche operations.

Understanding these differences is important when developing downstream uses for lignin, as the functionality, purity, and molecular size of lignin will determine its suitability for applications such as adhesives, carbon fibres, resins, fuels or fillers in polymer composites (Fig. 3).



Fig. 3 Overview of the Most Common Applications of Lignin [100–102]

Table 2: Overview of Common Pulping Techniques

| Pulping technique | Overview | Key features | Applications | Advantages | Disadvantages | Lignin fate | Ref |
|--------------------|---|--|--|--|--|--|---------------------------------|
| Kraft pulping | Kraft pulping, also known as the sulfate process, is the most dominant chemical pulping method. It involves the use of a highly alkaline cooking liquor composed of sodium hydroxide (NaOH) and sodium sulfide (Na_2S) to break down lignin and separate cellulose fibers. | High Strength: Pulp: Produces strong and durable pulp suitable for a wide range of paper products. Flexibility: Can process both hardwoods and softwoods, with high efficiency. Recovery: Efficient recovery of cooking chemicals and energy from black liquor. | - Packaging materials (e.g., corrugated boxes, linerboard) - Printing and writing papers - Tissue and hygiene products | - High pulp strength and quality - Effective chemical recovery system - Ability to handle various wood types | - High capital and operating costs - Environmental challenges due to sulfur emissions - Intensive bleaching required for high brightness | Lignin is depolymerized in black liquor (sulfur-containing fragments), then combusted for energy; acid-precipitated kraft lignin can be recovered as a moderately condensed, phenolic polymer. | [72–74, 76–80, 86, 91, 103–108] |
| Sulfite pulping | Sulfite pulping uses sulfurous acid (H_2SO_3) and bisulfite ions (HSO_3^-) to dissolve lignin and separate cellulose fibers. It operates under acidic, neutral, or alkaline conditions depending on the base used (e.g., calcium, magnesium, sodium, or ammonium). | Brightness: Produces brighter pulp than Kraft, easier to bleach. Specific Applications: Suitable for producing dissolving pulp for rayon and other cellulose derivatives. | - Fine papers - Tissue papers - Dissolving pulp for cellulose derivatives | - High brightness and ease of bleaching - Effective for certain specialty pulps - Lower sulfur emissions compared to Kraft | - Weaker pulp compared to Kraft - Limited raw material flexibility - Environmental concerns with waste disposal | Lignin ends up as water-soluble lignosulfonates in spent liquor; often burned on-site but can be recovered for dispersants and adhesives. | [72–74, 76–80, 86, 91, 103–108] |
| Mechanical pulping | Mechanical pulping involves physically grinding wood to separate fibers without significant chemical alteration. Common | High Yield: Retains most of the wood components, resulting in high yield. | - Newsprint - Magazine papers - Catalogs and directories | - High pulp yield (up to 95%) - Lower chemical use | - Lower pulp strength and durability - Higher energy consumption | Most lignin remains bound in the fiber network, giving very high yield but accelerating paper | |

| | | | | | |
|----|--|---|--|---|---|
| | | | | | |
| 20 | methods include groundwood pulping and refiner mechanical pulping (RMP). | Lower Strength: Pulp has lower strength compared to chemical pulps. | - Suitable for short-lifespan paper products | - Yellowing over time due to lignin content | yellowing and reducing durability. |
| 21 | | | | | |
| 22 | Semi-chemical pulping | Balanced Properties: Combines the high yield of mechanical pulping with improved strength from chemical pulping. Versatility: Suitable for various paper products. | - Corrugating medium for cardboard - Various grades of paperboard | - Good balance of yield and strength - Lower chemical consumption compared to full chemical processes - Flexibility in raw material use | Partial sulfonation / extraction of lignin into liquor (some recovered as lignosulfonated fragments), with the balance left in the pulp for strength and yield trade-off. |
| 23 | | | | | |
| 24 | | | | | |
| 25 | | | | | |
| 26 | | | | | |
| 27 | | | | | |
| 28 | | | | | |
| 29 | | | | | |
| 30 | | | | | |
| 31 | | | | | |
| 32 | | | | | |
| 33 | | | | | |
| 34 | | | | | |
| 35 | | | | | |
| 36 | | | | | |
| 37 | | | | | |
| 38 | | | | | |
| 39 | | | | | |
| 40 | | | | | |
| 41 | | | | | |
| 42 | | | | | |
| 43 | | | | | |
| 44 | | | | | |
| 45 | | | | | |
| 46 | | | | | |
| 47 | | | | | |
| 48 | | | | | |
| 49 | | | | | |
| 50 | | | | | |
| 51 | | | | | |
| 52 | | | | | |
| 53 | | | | | |
| 54 | | | | | |
| 55 | | | | | |
| 56 | | | | | |
| 57 | | | | | |
| 58 | | | | | |
| 59 | | | | | |
| 60 | | | | | |
| 61 | | | | | |
| 62 | | | | | |
| 63 | | | | | |
| 64 | | | | | |
| 65 | | | | | |

2.3 Industrial Lignin Recovery Techniques

With growing interest in lignin valorization, modern pulp mills employ lignin recovery processes to extract lignin from spent pulping liquors (particularly Kraft black liquor) as an alternative to burning it in the recovery boiler [109]. Recovering lignin can alleviate bottlenecks in the recovery boiler (allowing increased pulp production) and provides lignin as a renewable feedstock for chemicals and materials. Several industrial technologies have been developed to precipitate and recover lignin from Kraft black liquor. The most established of these are LignoBoost, LignoForce, Sequential Liquid-Lignin Recovery and Purification (SLRP), and the historic WestVaco (Indulin) process [110–115]. Each of these processes involves acidification of the alkaline black liquor to precipitate lignin, but they differ in specific conditions and steps to improve lignin purity and filterability.

2.3.1 LignoBoost Process

The LignoBoost™ process is a two-stage acid precipitation method for recovering high-purity lignin from Kraft black liquor. Developed by Innventia and Chalmers University in Sweden, it was the first modern process to produce lignin with low ash and impurity content at commercial scale. In the Kraft mill, a portion of the black liquor (after the evaporators) is diverted to the LignoBoost system. The process has several key steps:

1. *CO₂ Acidification & First Precipitation:* Black liquor (pH > 13, containing dissolved sodium lignate) is acidified with carbon dioxide gas. CO₂ reacts with water to form carbonic acid (H₂CO₃), releasing H⁺ that protonates phenolate groups on lignin. As the pH drops to ~9–10, the lignin aggregates and precipitates as solid particles (since lignin is no longer soluble at lower pH). This step is typically done at elevated temperature (~60–80 °C) to promote larger particle formation for easier filtration. The slurry is then filtered using a pressure filter, yielding a filter cake of crude lignin (often called “LignoBoost crude lignin”) and a filtrate (spent liquor that returns to the recovery cycle). The CO₂ addition is carefully controlled to avoid overshooting pH and to form easily dewaterable lignin. (In LignoBoost, CO₂ from a later stage is often recycled to improve efficiency.)
2. *Lignin Cake Re-slurrying:* The crude lignin filter cake is then re-slurried in acidic water. In practice, the cake is mixed with a solution of sulfuric acid (H₂SO₄) or acidic filtrate to a low pH (~2–4). This washes the lignin and further protonates acidic groups, helping to remove inorganic contaminants (like sodium salts). Essentially, this step redisperses the lignin in a clean acidic medium.
3. *Second Acidification & Filtration:* After re-slurrying, the lignin suspension is filtered again (second filtration). Additional sulfuric acid may be added during this stage to ensure the pH is low enough (around 2.5) to convert lignin to the fully protonated (acidic) form. The second filtration produces a much purer lignin cake, as much of the salts and impurities remain in the filtrate. The lignin is then washed on the filter with acidified water to remove remaining salt (e.g., sodium, potassium) and to reduce ash content to a very low level. This yields the final LignoBoost lignin, which is typically then dried or sent to storage.
4. *Gas Handling & Recycle:* The CO₂ used for the first precipitation can be sourced from mill flue gases or an external supply. LignoBoost cleverly recycles CO₂ from the lignin slurry acidification vents: CO₂ released when the lignin cake is acidified with H₂SO₄ (which drives off dissolved CO₂) is captured and reused for the initial black liquor carbonation. This integration reduces the net CO₂ consumption and lowers operating cost. Off-gases (including any malodorous compounds stripped from black liquor) are collected and treated as part of the mill’s non-condensable gas system.

The outcome of LignoBoost is a high-purity solid Kraft lignin (often >98% dry lignin, <1–2% ash). By removing most ash, sugars, and other impurities, LignoBoost lignin has much better properties for downstream use: for instance, it has been successfully used to produce carbon fibers and as a replacement for phenol in phenolic resins. The process was first demonstrated commercially at the Domtar Plymouth Mill (USA) and later at Stora Enso’s Sunila Mill in Finland, each producing tens of thousands of tons of lignin per year [116,117]. Integration with the mill is a strength of LignoBoost – it operates on sidestream black liquor, and the filtrates (after lignin removal) are returned to the recovery cycle, so the cooking chemicals are not lost. Notably, extracting lignin can relieve the recovery boiler load, enabling increased pulp production or reduced energy use at the mill.

LignoBoost produces exceptionally pure lignin, enabling high-value applications [116–118]. It significantly reduces the ash (inorganic) content of lignin by the two-stage washing, addressing a major issue in earlier lignin recovery attempts. The process is proven at commercial scale and can be retrofitted to existing Kraft mills with relatively modest changes, using mostly standard equipment (tanks, filters, etc.). It improves overall mill sustainability by converting a waste stream into a saleable product and reducing sulfur emissions (since less black liquor is burned). The lignin’s low sulfur and clean composition make it suitable for producing carbon fibers, bioplastics, and other materials that were previously infeasible with crude Kraft lignin. Furthermore, LignoBoost’s

design (recycling CO₂, integrating with mill streams) makes it economically attractive by lowering chemical costs and maintaining chemical recovery [112,119,120].

The LignoBoost process involves multiple steps (two acidification and filtration cycles) and thus is more complex than simply acidifying and filtering once. This added complexity means higher capital and operating costs, and careful control is needed at each stage (pH control, filter handling) to achieve consistent results [116,121]. The requirement for CO₂ and sulfuric acid introduces additional utilities; although CO₂ can be sourced from flue gas, an external supply might be needed if flue CO₂ is insufficient or impure. Handling the acids and the CO₂ off-gas necessitates appropriate safety measures (to manage asphyxiation risk from CO₂ and corrosion from acids). Energy consumption is also a consideration: while LignoBoost typically operates at near-ambient temperature (aside from using hot black liquor), the filters and pumps add some energy overhead, and drying the lignin requires energy. Another limitation is that removing lignin from black liquor reduces its calorific value for the recovery boiler – mills must balance energy needs versus chemical recovery benefits. Overall, LignoBoost is a trade-off between complexity/cost and lignin quality. It has been successful, but its adoption requires confidence in long-term markets for the lignin to justify the investment [112,116,122,123].

2.3.2 *LignoForce Process*

The LignoForce™ process (developed by FPIInnovations and NORAM Engineering, Canada) is an improved variant of lignin recovery that builds upon LignoBoost's concepts with some key modifications. Implemented commercially at West Fraser's Hinton mill in 2016, LignoForce introduced an oxidation pre-treatment of black liquor and a simplified single-stage filtration [103,104]. The main steps of LignoForce are:

1. *Black Liquor Oxidation:* Before any acidification, the black liquor (from the evaporator, ~20–30% solids) is sparged with air or oxygen at ~80 °C. This oxidizes various reduced sulfur species (like sulfide and mercaptans) present in Kraft liquor to sulfate or other stable forms. By doing so, LignoForce eliminates malodorous gases (total reduced sulfur, TRS) that would otherwise be released upon acidification. It achieves roughly a 50% reduction in TRS emissions compared to non-oxidized liquor. Oxidation also consumes some of the alkali in the liquor (since Na₂S is converted to Na₂SO₄ and organic sodium salts to organic acids). This has two benefits: (1) it lowers the initial pH of the liquor slightly, reducing the amount of CO₂ needed later to reach the precipitation pH, and (2) the exothermic oxidation reaction raises the liquor temperature (close to 80–85 °C), which can promote larger lignin particle formation (improved filterability). Overall, this step prepares a cleaner and more filterable liquor for lignin precipitation [105,124,125].
2. *CO₂ Precipitation:* After oxidation, the hot black liquor is acidified with CO₂ under pressure. In LignoForce, CO₂ is often applied at a slightly higher pressure (~0.8–1.0 MPa) and the reaction is done in a pressurized vessel. The pH is lowered to around 9.5–10 (similar endpoint as LignoBoost) and the temperature during CO₂ injection is about 65–75 °C. Lignin precipitates out as the pH drops, forming coagulated particles. The combination of oxidation and the controlled CO₂ addition allows the lignin particles to “age” and grow (a process sometimes called maturation or controlled coagulation) even without an explicit separate maturation tank. The precipitated slurry is held briefly to ensure lignin aggregation is sufficient for filtration [103–105,113].
3. *Filtration and Washing:* LignoForce uses a single filtration stage. The lignin precipitate is filtered (often using a rotary drum vacuum filter or a filter press). Because of the preceding oxidation, the filtered lignin cake is reported to be lower in odour and easier to handle. After the cake is formed, it is washed in situ on the filter with a combination of sulfuric acid and water. This wash converts the lignin to its acid form (if any lignate salt remains) and removes residual inorganic material, similar to the second stage of LignoBoost. The washing reduces the ash content of LignoForce lignin to around 0.1–0.7%, comparable to LignoBoost purity. The filtrate (acidified, lignin-lean black liquor) is returned to the recovery system [103].

Introducing an oxidation reactor adds its own complexity: it requires an oxygen (or air) supply, off-gas management, and careful control to avoid over-oxidation or foaming. Oxidation is exothermic, so heat management is necessary, and the step consumes some of the lignin's calorific value (though that is not a major issue if the lignin is being removed anyway). There is a trade-off in complexity: while LignoForce simplifies filtration, the oxidation step is another unit operation with associated controls and equipment (compressors, reactors). Additionally, the process still requires handling of CO₂ and H₂SO₄ for precipitation and washing, so those costs remain. The oxidation step, being done at ~80 °C with caustic liquor, can cause corrosion and equipment wear if materials are not chosen carefully. Robust metallurgy (e.g., stainless steels or specialty alloys) is needed for long-term operation, potentially raising capital costs. Energy demand is slightly higher due to running

an agitator and blower for oxidation and maintaining temperature. Also, as with any lignin removal, variations in black liquor composition (e.g., seasonal wood changes or different pulping conditions) can affect the process; operators must adjust CO₂ addition or oxidation time to achieve consistent lignin quality. In essence, LignoForce trades one type of complexity for another, but it has proven effective. Its adoption may be favoured by mills particularly concerned with odour emissions or those looking to minimize equipment count while still obtaining high-purity lignin.

2.3.3 Sequential Liquid-Lignin Recovery and Purification (SLRP)

The SLRP process (Sequential Liquid-Lignin Recovery and Purification), developed by the Liquid Lignin Company (USA)[126], is a newer lignin recovery method that operates under elevated temperature and pressure to recover lignin in a unique form. Unlike LignoBoost or LignoForce, which precipitate lignin as a solid directly, SLRP first separates lignin as a dense liquid phase from black liquor. The process builds on earlier work by G.H. Tomlinson Sr. and Jr.[127], who in the 1940s used high-pressure CO₂ (from lime kiln flue gas) to acidify black liquor in a continuous manner. SLRP has modernized this concept and demonstrated it in continuous pilot operations [128,129].

In SLRP, black liquor (at 30–50% solids) is contacted with CO₂ under high pressure (5–15 bar) at an elevated temperature (100–150 °C). Instead of immediately forming a filterable solid, the lignin agglomerates into an oily, highly hydrated “liquid lignin” phase that separates by gravity from the lighter spent liquor (called lignin-lean liquor). This occurs because under these conditions, lignin becomes hydrophobic enough to coalesce, but water in the system plasticizes the lignin, preventing it from solidifying into particulate form [128–130]. The liquid-lignin phase typically contains about 50–70% lignin, 30–50% water, and entraps very little inorganic material (since salts stay in the aqueous phase). The dense lignin-rich phase can be pumped out of the reactor, which is a unique advantage: SLRP does not initially require filtration; lignin is collected as a liquid. The remaining liquor (now low in lignin) can be returned to the chemical recovery cycle, similar to other processes [107,129].

After the CO₂ carbonation step (often termed “primary acidification” or carbonization), the liquid lignin is separated and then subjected to a secondary acidification using sulfuric acid. In this second step, the pH of the liquid lignin phase (and any residual liquor in it) is further lowered to ~2.5 with H₂SO₄. This causes the liquid lignin to precipitate/solidify into fine particles (or a granular solid) as it fully converts from sodium lignate to lignin acid (R-ONa → R-OH). Essentially, the H₂SO₄ treatment “fixes” the lignin by removing remaining sodium and freeing protonated lignin, yielding a solid that can be filtered and washed. The final lignin is then obtained by filtration of this slurry and washing with water or dilute acid [110,128,129,131].

By operating at high pressure and temperature in the first stage, SLRP achieves very rapid lignin aggregation and uses CO₂ more efficiently (gas dissolution in the liquor is enhanced at high pressure). The CO₂ consumption per ton of lignin is thus lower than atmospheric processes [129]. Moreover, direct liquid-phase separation means that the bulky solids separation is deferred to the second stage where the volume is much smaller (only the lignin-rich phase is handled, not the entire liquor). This can simplify equipment requirements and potentially allow continuous operation. SLRP is essentially continuous: the high-pressure reactor can be run in steady state with continuous CO₂ input and continuous withdrawal of liquid lignin and lignin-lean liquor. The process also operates with a relatively high solids content, meaning less water to heat and handle [67,114,132,133].

The lignin produced by SLRP is very pure. Because the lignin is never exposed to extensive washing in the first stage, one might expect high inorganic contamination, but in practice the liquid lignin carries out very little salt [129]. Most of the sodium and other inorganic constituents prefer the aqueous phase, so the liquid lignin is relatively low in ash even before washing. After the sulfuric acid precipitation and washing, SLRP lignin has been shown to have exceptionally low sodium content (often <0.5% Na₂O) and low carbohydrate content, comparable to or better than LignoBoost lignin [128,134,135]. Importantly, the high-pressure operation does not chemically modify the lignin aside from protonating it – the lignin recovered is similar to Kraft lignin in functional groups, without any sulfomethylation or excessive condensation. One notable difference is that the particle morphology of SLRP lignin can be different (it can form a granular solid), which might influence downstream handling (filtration and drying properties). Overall, SLRP yields a high-purity lignin suitable for most applications requiring technical lignin [67,67,128,135].

SLRP’s continuous operation and liquid-phase separation bring several advantages. Continuous processing can lead to higher throughput and easier scaling in large mills compared to batch filtration cycles. The ability to pump lignin as a liquid can simplify material handling and potentially integrate with continuous dewatering equipment (e.g., centrifuges) instead of batch filters. The efficient use of CO₂ at high pressure reduces reagent costs and the carbon footprint of the process (especially if flue gas is used directly as the CO₂ source, as originally conceived by Tomlinson). SLRP lignin is obtained in a very pure form with low ash (low salt) and low

sugar content, making it attractive for high value uses [67,114,135]. The process also significantly debottlenecks the recovery boiler if implemented, by removing a large portion of combustible solids from black liquor in liquid form – this can allow a mill to increase production without a recovery boiler upgrade, similar to other lignin recovery tech. Another advantage is that less acid is required overall: CO₂ does much of the work in the first stage, and sulfuric acid is only used on the smaller volume of liquid lignin phase (reducing acid consumption compared to acidifying the whole liquor). Additionally, operating at higher temperature means the lignin comes out already hot, which can aid in its subsequent processing (e.g., easier to filter or spray dry when warm) [67,114,124,128,129,135].

The conditions of SLRP (high temperature and pressure) demand specialized equipment. The primary reactor must be a pressure vessel with robust corrosion-resistant construction (black liquor and CO₂ can form carbonic acid, plus the liquor is hot and caustic). This raises the capital cost compared to atmospheric systems. High-pressure pumps and compressors are needed for the CO₂ and liquor circulation. There is also an energy cost to maintain the system at 100–150 °C and to compress CO₂, although some of this heat may be recoverable. The requirement for precise control at elevated pressure adds operational complexity. Another consideration is safety and training: handling pressurized caustic fluids and gases requires stringent safety measures. SLP also produces CO₂-rich off-gas when the pressure is let down after lignin separation; this must be managed or recycled. Furthermore, if flue gas is used directly (to source CO₂), any impurities in the flue gas (NO_x, SO_x, particulates) could potentially contaminate the lignin or cause operational issues, so gas cleanup might be needed. Scaling down can be a challenge: SLP is best suited for large continuous operations; implementing it at a small scale (e.g., a small mill or demo plant) might be less efficient. Lastly, while continuous, the process may still need periodic maintenance shutdowns for scaling or fouling (e.g., any precipitation of inorganics in the reactor or piping). In summary, SLP offers a novel and highly effective approach to Kraft lignin recovery, trading off higher complexity and capital requirements for greater efficiency and purity. It is particularly promising for large mills aiming to maximize lignin extraction while maintaining throughput.

2.3.4 WestVaco (Indulin) Process

The WestVaco process (also known as the Indulin process) is one of the earliest commercial lignin recovery methods, developed in the 1940s–1950s by the West Virginia Pulp and Paper Company (later Westvaco, and now Ingevity). It was the method used to produce the well-known “Indulin AT” Kraft lignin. The WestVaco process laid the groundwork for modern lignin recovery, employing acidification and careful conditioning of black liquor to recover lignin on a continuous basis. Many of the innovations in WestVaco’s patents (e.g., staged acid addition, heating/cooling cycles, dewatering techniques) anticipated features of later processes [136–139].

In the classic WestVaco process, CO₂ from combustion flue gas is used to acidify concentrated black liquor. Black liquor at ~20–30% solids is taken from the evaporation train and fed into a series of treatment tanks. Carbonation with CO₂ (often directly using flue gas rich in CO₂) is the first step, typically done in a packed column or sparged vessel to ensure good gas-liquid contact. The pH is gradually brought down to around 9–10 (similar range as other processes) through multiple passes of CO₂ injection. This precipitates lignin as fine particles. What’s distinctive in the WestVaco process is the next step: the acidified slurry undergoes a “maturation” or digestion phase in a heated tank. The slurry is heated to about 75–95 °C (e.g., 80 °C is common) for a period of time (on the order of 0.5–1 hour) and then slowly cooled. This heating and cooling treatment helps the tiny lignin particles to coalesce and form larger, more filterable particles, and it also expels some trapped liquor from the lignin (improving purity). Essentially, the maturation step enhances filterability of the precipitated lignin, similar in purpose to the aging done in LignoForce (though WestVaco did it by heating rather than oxidation) [140,141].

After maturation, the slurry is sent to a filter (in early days, rotary vacuum filters were used). The lignin is filtered and washed. In the original WestVaco process, sulfuric acid was used in washes or secondary precipitation steps to further lower pH and remove impurities, analogous to LignoBoost’s second stage. One of WestVaco’s patents describes adding acid to achieve “free lignin” – essentially fully protonated lignin that is easier to wash and low in ash. The filtered lignin (Indulin) is then spray-dried to a powder for sale. The mother liquor (filtrate), now reduced in lignin, is returned to the recovery cycle. Over the years, WestVaco implemented various refinements: for instance, using higher solids black liquor (~50% solids) in a continuous precipitation reactor for higher throughput, or employing pressure and heat to speed up coagulation. The end product Indulin AT (a trademark Kraft lignin) became a commodity sold for uses like oil well additives, inks, dyes, and rubber additives [137–139].

Indulin lignin from the WestVaco process is a relatively pure Kraft lignin (typically >95% lignin, 1–3% ash, a few percent sugars). It contains sulfur (1–3% sulfur, as thiol/organosulfide structures inherited from pulping) and has moderate molecular weight (~1000–4500 g/mol typical)[142]. Because it is sulfur-containing, Indulin (like

other Kraft lignins) has some limitations in applications (for instance, it's less suitable for high-grade carbon fiber without further purification due to sulfur). Nonetheless, Indulin has been used for decades in industrial formulations, showcasing the feasibility of large-scale lignin recovery. The process yields lignin in powder form, which is convenient for shipping and storing.

The WestVaco process was pioneering and demonstrated that lignin recovery could be integrated into a Kraft mill. It used mostly readily available inputs (flue gas CO₂ and sulfuric acid) rather than exotic chemicals. The use of flue gas is environmentally savvy, essentially capturing CO₂ that would otherwise be emitted to precipitate a useful product. The process is versatile: by adjusting CO₂ flow, temperature, and acid dosages, it can handle liquors of different wood sources and conditions. It operated in a continuous or semi-continuous mode, aligning with mill operation. Over decades of use, it proved to be reliable and robust, producing lignin that found a stable market. The maturation (heat treatment) is a particularly effective step to get a filterable product, and this concept is employed (in various forms) in nearly all modern processes – it improves lignin yield and dewatering significantly. WestVaco's process also integrated chemical recovery: it tried to minimize chemical loss by only partially neutralizing black liquor (pH ~9) with CO₂, so the filtrate still contained enough alkalinity (carbonate, etc.) to be recovered in the recovery boiler without causing issues. Moreover, being an early mover, WestVaco patented a broad range of innovations, essentially covering the whole spectrum from black liquor to purified lignin. This established a foundation for others and gave WestVaco a long period of proprietary technology advantage [137–140,143].

Compared to newer methods, the WestVaco process can seem energy-intensive and somewhat cumbersome. The maturation step requires heating a large volume of slurry to ~80 °C and then cooling it, which consumes steam and cooling water (energy that newer processes like LignoBoost avoid by precipitating near ambient temperature). The process also used large equipment (multiple tanks for carbonation and maturation, big rotary filters, etc.), which could be a footprint issue. Filtrate from CO₂ precipitation at pH 9 still contains a significant amount of dissolved lignin (not all lignin precipitates until lower pH), meaning lignin recovery yield was not complete; some lignin remains in the liquor that goes to the boiler. To get more lignin out, WestVaco had to add sulfuric acid to drop pH further, but doing so too much could interfere with recovery boiler chemistry (excess sulfate) and increase corrosion. Thus, there was a careful balance, and usually a compromise that not all lignin is removed. The product lignin still contained some sulfur and residual salt, as complete removal was difficult; WestVaco's later steps (acid hydrolysis and washing) improved purity but added complexity. Another drawback is operational complexity and safety: handling large volumes of CO₂ (as flue gas) means potential asphyxiation hazards and the need for robust gas distribution. CO₂ can also cause foaming in black liquor, which operators had to manage. The process uses acid and creates acidic filtrates, which are corrosive to equipment; materials of construction had to accommodate both high-pH and low-pH streams in different parts of the system, complicating design. In comparison to LignoBoost, WestVaco's lignin typically had higher ash content (because the single-stage washing was less effective than LignoBoost's two-stage wash) and somewhat lower purity, which can limit some high-end applications. Finally, while the WestVaco process was successful in its time, it might be less economically attractive today unless paired with upgrades – newer processes have shown higher yields or lower costs. Nonetheless, WestVaco's approach remains instructive and forms the basis for many current lignin recovery practices [110,126,137,139,144].

Overview of different recovery techniques and approximate properties of different lignins is in Table 3 and Table 4. Modern processes like LignoBoost and LignoForce can be viewed as refinements of the principles first implemented in the WestVaco process. All use CO₂ to precipitate lignin and then a stronger acid to wash/precipitate further. LignoBoost's innovation was the dedicated re-slurry and second filtration (improving purity), while LignoForce's was oxidizing first (improving environmental performance and filterability). SLP took a different path by altering physical conditions to create a liquid lignin phase. The WestVaco process, being the earliest, lacks some of these optimizations, but it proved the concept on an industrial scale. In summary, WestVaco (Indulin) demonstrated that high-quality lignin could be recovered and sold, and although it has been largely supplanted by newer methods, it is the direct ancestor of today's lignin recovery technologies.

Table 3 Overview of Common Lignin Recovery Techniques.

| Recovery Technique | Overview | Key Features | Applications | Advantages | Disadvantages | Ref |
|-----------------------|--|---|---|--|--|---------------------|
| LignoBoost™ | A two-stage acid precipitation process that uses CO ₂ to lower the pH of Kraft black liquor, followed by re-slurrying and a secondary acid wash (typically with H ₂ SO ₄) to yield high-purity Kraft lignin. | - Dual-stage filtration with re-slurrying - CO ₂ recycling from acidification off-gas - Mild operating temperatures (\approx 60–80 °C) | Production of high-purity Kraft lignin for carbon fibers, phenolic resins, and other specialty chemicals. | - Exceptional lignin purity (low ash) - Efficient removal of inorganic salts - Scalable and integrated with existing mill processes | - Complex multi-step process - Higher capital and operating costs - Sensitivity to fluctuations in black liquor concentration | [112,116,117,121] |
| LignoForce™ | An advanced process that builds on LignoBoost by incorporating an oxidation step prior to acidification, using pressurized CO ₂ to precipitate lignin in one filtration stage. | - Oxidation of black liquor (at \approx 80 °C) to convert sulfide/mercaptans into sulfate - Single-stage filtration after controlled CO ₂ acidification - Enhanced particle maturation without a separate aging tank | Recovery of low-odor, high-solids lignin for use in phenolic resins, activated carbon, and other high-value applications. | - Reduced odorous emissions (\approx 50% reduction in TRS) - Lower CO ₂ and acid consumption - Simplified filtration (single stage) | - Additional complexity from the oxidation step - Higher energy demand and potential equipment wear - Operational sensitivity to liquor quality | [103,104,113,145] |
| WestVaco (Indulin AT) | A historic, continuous lignin recovery process that uses plant-derived CO ₂ for acidification, followed by a maturation (heat treatment) step to coalesce lignin particles before filtration and spray drying. | - Use of flue gas CO ₂ for acidification - Maturation phase (heating to 71–93 °C) to improve filterability - Continuous operation with integrated acid washing | Production of “Indulin” lignin for adhesives, dispersants, and specialty chemical formulations. | - Established, proven technology - Effective and environmentally friendly use of flue gas CO ₂ - Versatile with varied black liquor streams | - Energy-intensive maturation phase - Generally higher ash content compared to newer methods - Complex multi-step process with significant equipment and safety requirements | [24,67,127,135,146] |

| | | | | | | | |
|----|---|---|--|---|--|--|-----------------------|
| 22 | SLRP (Sequential Liquid-Lignin Recovery and Purification) | A novel continuous process operating at elevated temperatures (100–150 °C) and pressures (5–15 bar) to first separate lignin as a dense liquid phase from black liquor, then perform a secondary acidification (with H ₂ SO ₄) to yield a solid, high-purity lignin product. | - Operation under high temperature/pressure to form a “liquid lignin” phase - Direct pumping of liquid lignin, reducing the need for extensive filtration - Two-step acidification for enhanced purity and low ash content | Production of high-purity lignin for advanced applications (e.g., bio-based polymers, high-end carbon materials) with very low inorganic contamination. | - Continuous operation and high throughput - Efficient CO ₂ utilization at high pressure - Reduced filtration requirements due to liquid-phase separation | - Requires specialized, high-pressure equipment - Increased energy consumption and potential corrosion - Complex control of phase separation and acidification | [110,114,128,129,133] |
|----|---|---|--|---|--|--|-----------------------|

34 *Table 4. Overview of Typical Technical Lignins' Properties.*

35

| Lignin | Process / Source | M _w and D | Phenolic OH [mmol/g] | Aliphatic OH [mmol/g] | Sulfur [wt%] | Ash [wt%] | Tg [°C] | Ref. |
|------------------------------|-----------------------------|--|----------------------|-----------------------|--------------|-----------|-----------------|----------------------|
| BioPiva 100 | Softwood kraft (LignoBoost) | M _w = 4–13 kDa; D = 2–4 | 2–4 | 1–2.5 | < 1 | < 2 | 140–160 | [147–150] |
| BioPiva 395 | Softwood kraft (LignoBoost) | M _w = 6.6–13.8 kDa; D ≈ 2.1 | 2.5–4.8 | 1.5–2.5 | ~ 1 | < 2 | 140–150 | [148,151,152] |
| Indulin AT | Softwood kraft | M _w = 4–8 kDa; D = 2.4–9.9 | 1.8–3.8 | 1.8–2.4 | 1.3–3.3 | 2–3 | 150–160 | [37,148,153–156] |
| BioChoice™ | Softwood kraft (LignoBoost) | M _w = 5–8 kDa; D = 2–7.1 | 2.5–3.5 | ≈ 2 | 0.1–1.6 | 0.5–2 | 140–150 | [148,155,157] |
| Protobind 1000 | Wheat-straw soda | M _w = 2.4–4 kDa; D = 3–4 | 2.7–3.1 | 1.8–2.1 | ≈ 0 | < 3 | 130–150 | [148,158–161] |
| Borregaard Lignosulfonate | Softwood sulfite | M _w = 1–10 ³ kDa; D > 10 | ~ 1 | 2–4 | 4–8 | 6–18 | 100–150 (broad) | [148,154,162,163] |
| Alcell® | Hardwood organosolv | M _w = 1–6.8 kDa; D = 1.5–3.6 | 2.4–5 | 1–2 | ≈ 0 | < 1 | 90–120 | [37,148,153,154,164] |

2.4 Patented Lignin Recovery and Isolation Techniques

In recent decades, the valorization of lignin through innovative isolation and recovery techniques has garnered significant attention, culminating in a multitude of patents covering methods such as acid precipitation from black liquor streams [126], organosolv-based solvent fractionation [165], and depolymerization approaches using kraft-recovery chemicals. This sub-chapter introduces the chronological progression of these key patented technologies - from early Kraft process adaptations through acid-induced precipitation and solvent-based fractionation to advanced chemical depolymerization and protective-chemistry stabilization - laying the groundwork for a comprehensive tabulated overview of patent developments across diverse process classes and industrial jurisdictions. The overview is presented in Table 5. The table contains the most important and breakthrough patents retrieved from *World Intellectual Property Organization* using the keywords “lignin and (recovery or isolation)”.

Table 5. Overview of Patented Lignins' Recovery and Isolation Techniques

| Year | Title | Description | Applicant | Ref |
|------|--|--|-------------------------------|-------|
| 1942 | Recovery of cellulose and lignin | A method for extracting high-quality cellulose pulp and recovering native lignin from lignin-rich biomass such as wood by cooking in aqueous hydrotropic salt solutions (e.g., sodium xylene sulfonate) at around 150 °C for about 12 hours. The process dissolves lignin without degrading cellulose, allows repeated solvent reuse, and yields bleachable pulp with high α-cellulose content. Lignin is precipitated by dilution and recovered in fusible and non-fusible fractions for industrial use. | RALPH HARPER MCKEE | [166] |
| 1944 | Method of treating lignocellulosic material | An improved cyclic process for treating alkaline pulp black liquor combines flue-gas carbonation, heat recovery, and lignin isolation. Weak liquor is continuously sprayed counter-current to hot flue gas, precipitating finely divided lignin. The carbonated liquor is then heated to melt the lignin, which settles as a viscous liquid and is decanted. The residual liquor is evaporated and burned to regenerate cooking chemicals, while the liquefied lignin is recovered. | SMITH PAPER MILLS LTD HOWARD | [127] |
| 1944 | Improvements in the recovery of lignin from black liquor | Describes a cyclic recovery process for isolating non-oxidized lignin from soda or kraft black liquor via rapid carbonation in multiple spray towers, causing lignin acid salt to precipitate without filtration. The hot suspension is heated to melt the lignin, which is decanted, redissolved, and acidified at ~80 °C to yield fine, thermoplastic lignin particles. The process integrates liquor concentration, heat and salt recovery, and yields high-quality lignin for plastics and papers. | SMITH PAPER MILLS LTD HOWARD | [167] |
| 1944 | Method of producing lignin from black liquor | This patent introduces an industrial method for isolating lignin from concentrated pine wood black liquor using a packed carbonation tower. Prior to CO ₂ treatment, soaps are skimmed off to avoid contamination. Cleaned CO ₂ -rich gas is then used to carbonate the liquor to ~pH 9 at ~150 °F. After carbonation, lignin is coagulated by heating, filtered, and optionally dried. The process is efficient, continuous, and minimizes clogging. | WEST VIRGINIA PULP & PAPER CO | [140] |
| 1950 | Method of coagulating colloidal lignates in aqueous dispersions | Improves lignin recovery by controlling coagulation of sodium lignate. After acid-precipitating black liquor, the suspension is passed through a pressurized tubular heater at 170–220 °F, using a flow rate yielding Reynolds 700–1500. This creates filterable lignate particles. The hot stream is then cooled in motion to prevent fusion, and the coagulated lignate is filtered, yielding consistent, readily separable particles. | WEST VIRGINIA PULP & PAPER CO | [137] |
| 1958 | Decantation of lignin | A process for recovering lignin salts, e.g. sodium lignate or hydrogen lignin, from acidified black liquor (or other lignate-bearing solution) by heating the slurry under superatmospheric pressure at temperatures above the lignate's melting point, so that the precipitated lignate fuses into a viscous liquid layer beneath the mother liquor. That fused layer is then decanted off and, if desired, flashed through a nozzle to yield a dry, finely divided lignin powder. This avoids filter clogging, handles higher-solids liquors, and gives purer, less occluded lignin than conventional atmospheric methods. | WEST VIRGINIA PULP & PAPER CO | [138] |
| 1958 | Continuous acidulation and coagulation of lignin in black liquor | The patent streamlines kraft lignin recovery by simultaneously acidulating and coagulating black liquor in one heated, pressurized pass. 60 °Bé sulfuric acid is metered into 175–205 °F liquor, immediately triggering lignate precipitation and coagulation. The mixture is held from 20 s to 10 min to complete particle growth, then cooled and continuously filtered, yielding cleaner, higher-yield sodium lignate even from >30% solids liquors, avoiding fouling and extra heating/cooling steps. | WEST VIRGINIA PULP & PAPER CO | [139] |

| | | | |
|------|--|--|---------------------------------|
| 1968 | Organosolv pulping and recovery process | Kleinert's organosolv process continuously digests wood chips in a hot (180 °C), pressurized ($\approx 17 \text{ kg/cm}^2$) ethanol–water pulping liquor ($\approx 46 \text{ wt.\%}$ ethanol) without pre-impregnation. Spent liquor is fed, still at cooking conditions, into a multistage flash evaporator, recovering ethanol for reuse. The final concentrate spontaneously separates into a dense, molten lignin phase (recoverable as plasticized lignin) and a lighter aqueous phase of sugars/organic acids, enabling efficient, integrated lignin recovery. | THEODOR N KLEINERT [98] |
| 1986 | Recovery of lignin | Proces' solvent-pulping "black liquor" (an ethanol–water extract of wood) is first flashed to recover most alcohol and cool it to $\sim 70\text{--}95^\circ\text{C}$ without precipitating lignin. The residual liquor ($\approx 35\text{--}45 \text{ wt.\% EtOH}$) is then rapidly and intimately mixed with cold, acidified liquor (from the previous batch's spent liquor bottoms), yielding a diluted solution ($<30 \text{ vol\% EtOH}$, pH <3 , $<75^\circ\text{C}$) in which lignin precipitates nearly quantitatively as fine solids, without tarring. These solids settle, are centrifuged to $\sim 30\text{--}40 \text{ wt.\%}$ cake, then dried to a free-flowing powder ($\sim 800\text{--}1500 \text{ g/mol molecular weight}$, narrow polydispersity), ready for use. | Rerap Technologies Inc. [168] |
| 2005 | Method for separating lignin from black liquor | A multi-stage washing process prevents filter-cake clogging and acid overuse when extracting lignin from black liquor. First, lignin is precipitated by mild acidification and dewatered (e.g. in a filter press). The filter cake is then re-slurried, its pH (and optionally ionic strength) brought to match the wash liquor (pH 1–3.5) and dewatered again. Finally, the cake is displacement-washed at essentially constant pH/ionic strength and dewatered to high dryness, yielding a clean, low-ash lignin fuel or chemical feedstock. | LIGNOBOOST AB [169] |
| 2008 | Method for separating lignin from black liquor, a lignin product, and use of a lignin product for the production of fuels or materials | This invention improves kraft-mill lignin recovery while stabilizing the Na/S balance by recycling wash filtrate back into both the initial acidification and a re-slurry of the precipitated cake. After CO ₂ -precipitating lignin and dewatering, the dry cake is resuspended in a filtrate whose pH and ionic strength have been raised (e.g. with ESP dust). This "matched" filtrate both dilutes and washes the cake, cutting sulphuric-acid use by up to 50% and producing a high-purity, low-ash lignin. | Valmet AB [170] |
| 2010 | Process for recovering lignin | This invention provides a continuous method for recovering high-purity lignin from papermaking or biomass black liquor. Pressurized black liquor is carbonated with CO ₂ (80–150 °C, 50–200 psig) to pH 9–10, separating a dense liquid-lignin fraction. That phase is acidified (H ₂ SO ₄ to pH <4) at elevated temperature to convert residual Na ⁺ salts, then water-washed counter-currently to remove ash. The result is a low-salt, high-energy lignin powder or pellet suitable for fuel or green-chemical applications. | LIQUID LIGNIN COMPANY LLC [126] |
| 2011 | Method for separating lignin from black liquor | This invention improves standard lignin-from-black-liquor recovery by first oxidizing the liquor, e.g. sparging O ₂ at 75 °C, to destroy odorous reduced S-species (H ₂ S, mercaptans, etc.) and convert sulfides to sulphate and organic polysaccharides to carboxylic acids, releasing heat. The hot, neutralized liquor is then acidified (CO ₂ and/or H ₂ SO ₄ to pH ≤ 10.8) to precipitate lignin, whose larger 5–10 μm particles filter 2–3 times faster and wash more cleanly ($\approx 0.2\%$ ash) than unoxidized liquor, while using 10–40% less acid. | FPIinnovations [105] |
| 2020 | Methods for lignin extraction | This disclosure describes a scalable process for extracting high-purity, nanoscale lignin from agricultural and food waste (e.g., peanut shells) using a choline-chloride-based deep eutectic solvent (DES). Ground biomass is incubated with a DES (choline chloride + formic acid, 1:2–1:6 molar) at 90–120 °C (1–4 h), then the solids are filtered off and lignin is precipitated by water addition. Recovered lignin nanoparticles average $< 900 \text{ nm}$ (often $< 550 \text{ nm}$) with up to 100% yield of available lignin. | CANON VIRGINIA, INC. [171] |

3 Application of Technical Lignins in the Rubber Industry

3.1 Technical Lignins and Rubber Reinforcement

Given the widespread use of rubber in industrial applications, including automotive, aerospace, gloves, footwear etc., optimizing its performance is essential. Crosslinked rubber without a filler is generally weak, so fillers are used to enhance reinforcement, modulus, tensile strength, abrasion resistance, tear strength, and other mechanical properties. While the choice of filler depends on the desired properties and application, reinforcing fillers — particularly carbon black (CB) — are critical for mechanical strength. Global CB production reaches 15 million metric tons annually, with 93% used in rubber applications [172]. However, CB is a petrochemical-based, non-degradable material with high energy consumption during production. Its environmental impact is significant, contributing to carbon dioxide emissions and posing health risks [173,174]. Non-reinforcing fillers are also used to reduce production costs. Growing concerns over resource depletion, pollution, and global warming have spurred research into sustainable alternatives. Green rubber innovations focus on eco-friendly alternatives, with lignin emerging as a promising substitute [175–177].

The integration of lignin into rubber compounds emerged as a promising pathway to enhance the sustainability and performance of rubber-based materials as early as 1947 [178], with a subsequent patent titled “Lignin Reinforced Rubber and Method of Making Same” [179], laying the foundations for this research. These early publications described *coprecipitation* as the primary method of compounding lignin with rubber. This method involves suspending lignin in aqueous alkali solutions, which are compatible with latex emulsions, and subsequently precipitating the two materials together to achieve a more uniform distribution of lignin within the rubber matrix. Previous research proves that this method provides improved distribution and dispersion of lignin particles in the rubber matrix and subsequently enhanced mechanical properties in contrast to the method of *dry mixing* [180–182]. On the other hand, neutralization and disposal of the resulting alkaline waste, as well as high water usage, pose environmental challenges and may not be sustainable in large-scale applications, although limited research has been conducted on this topic to date.

The addition of dry lignin powder during rubber processing is referred to as the dry mixing method, the industry-standard technique for rubber compounding using an internal mixer and an open two-roll mill. However, due to lignin's chemical structure, the direct mixing of lignin powder shows little reinforcing effect because of the formation of large agglomerates and the incompatibility between lignin and the rubber matrix at the interface [182]. The ultimate properties of rubber/lignin composites critically depend on the processing method, as it determines the dispersion state within the rubber matrix, so the mixing parameters are of great importance, particularly the distinction between mixing at a temperature below or above the glass transition temperature T_g of a specific lignin. Lignins in general have a high T_g due to their stiff aromatic backbone and secondary interactions, however this varies based on their botanical origin and extraction methods. T_g values of technical lignins typically fall within the range of 90–170 °C [183,184], which overlaps with possible rubber mixing temperatures when using an internal mixer [185], following the process to be set up for lignin macromolecules to soften and increase processability in melt-compounding processes [186]. Koskinen et al.[187] reported a significant influence of mixing temperature on Kraft lignin dispersion in BR but observed no clear improvement around the T_g of the lignin used in this study. Varying the mixing temperature affected the macro-dispersion of lignin, with higher temperatures reducing the number of large particles and consequently increasing the tensile strength. Hait et al.[188,189] reported a comparison of reactive mixing at 120°C (below T_g) and 155°C (above T_g), which demonstrated a distinct improvement in tensile properties at the higher temperature. The reactive mixing above the lignin's T_g , in the presence of a suitable coupling agent, yielded Kraft lignin/BR composites with mechanical properties comparable to CB-filled composites at similar loadings. Additionally, mixing time is of importance in specific cases. Bova et al.[186] used reactive melt-mixing of lignin/NBR binary blends, hypothesizing that extending the mixing time beyond 30 minutes at 160°C was necessary to achieve sub-micron lignin domains. This approach effectively tuned the final material's mechanical properties, as crosslinking occurred between lignin and rubber phases when crosslinking agent was incorporated. Similarly, Tran et al.[190] reported findings consistent with evidence of an exothermic reaction occurring between softwood Kraft lignin and NBR, as indicated by a significant increase in torque after 10 minutes of mixing.

A wide range of rubbers is used in the industry, with the most common elastomers being natural rubber, butadiene rubber, styrene-butadiene rubber, ethylene-propylene diene rubber, and nitrile rubber. The mechanical properties of rubber composites depend on the size and dispersion of filler particles, requiring homogeneous distribution through effective mixing. This necessitates high rubber/filler - in this case rubber/lignin compatibility - often achieved by lignin modification or the use of compatibilizers before or during mixing. Due to the high

polarity of pristine lignin, effective dispersion via dry mixing is only feasible for polar rubbers, such as nitrile rubber [191].

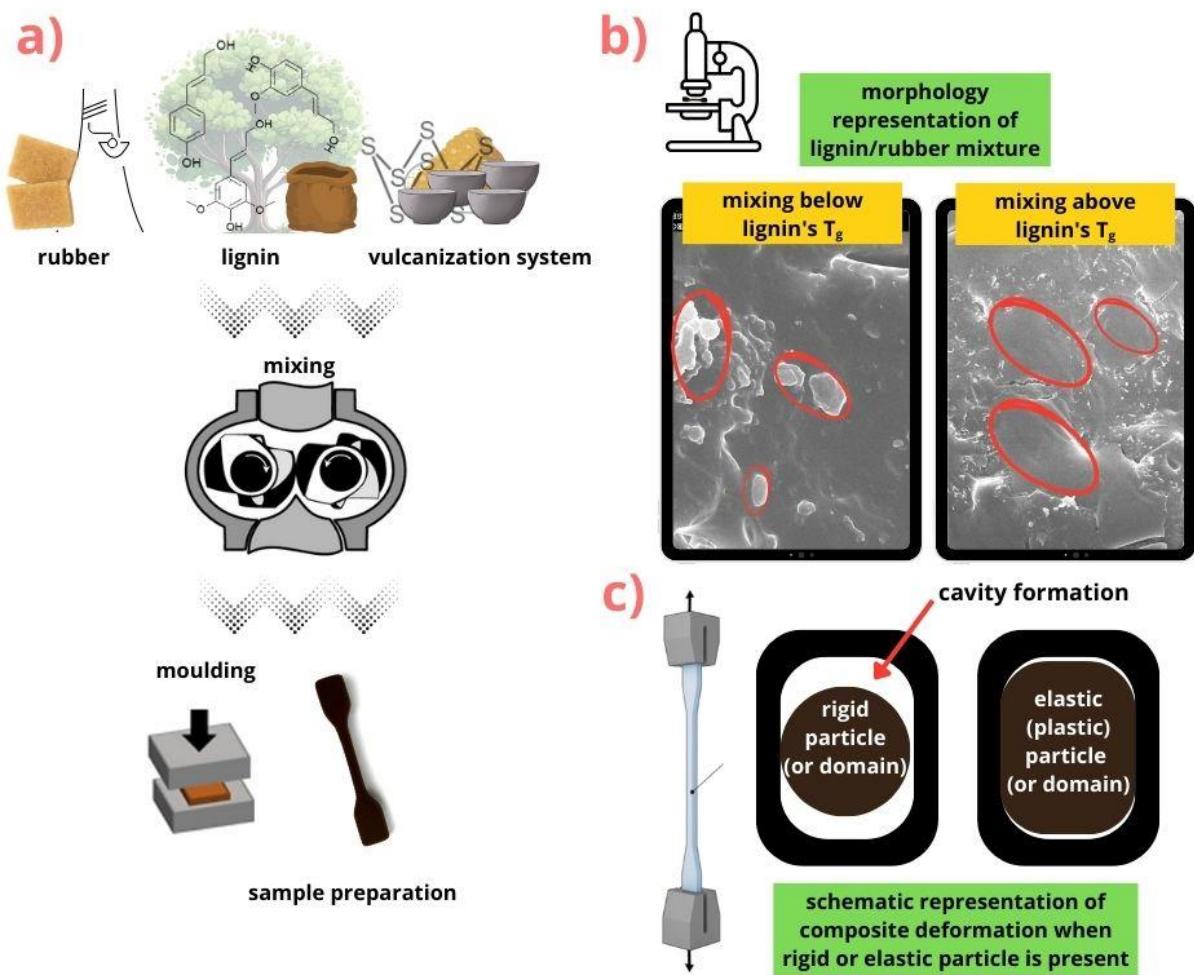


Fig. 4 a) Schematic Representation of Lignin/Rubber Composite Preparation, b) SEM Photograph of NBR/Lignin Composites as Morphology Representation of Lignin/Rubber Composites Described as “Islands In The Sea” & c) Schematic Representation of Composite Deformation Under Tension When Rigid or Elastic (Plastic) Particle or Domain is Present

Interface conditions play a crucial role in determining the performance of polymer composites. Poor interfacial bonding can significantly degrade mechanical properties, highlighting the importance of optimizing the conditions for lignin/rubber interface adhesion. The coarse morphology of lignin/polymer systems can be described as “islands in the sea” (Fig. 4b). Flexible polymers do not adhere to lignin without some sort of dipole, ionic, or covalent bonding interaction; without it, composites easily fall apart under thermal, shear, or mechanical strain. When a rigid lignin particle (or domain) is embedded in an elastomer and subjected to deformation forces, a cavity is formed regardless of the adhesion strength between the lignin particle surface and the elastomer chains or the lignin particle size (Fig. 4c). Larger lignin particles create larger cavities, which leads to a deterioration in mechanical properties. However, when the rigid particles are replaced with plastic or elastic domains that are properly bound, lignin can impart significant rigidity to the softer polymer, improving mechanical properties by preventing or significantly reducing cavity formation [192,193].

In order to enable the use of lignin powder in thermal compounding, plasticizers are required [194]. Plasticization is among the most cost-effective and straightforward methods to improve polymer processability and interfacial adhesion. In lignin/rubber blends, plasticizers reduce the T_g of lignin, enhancing processability and flexibility within the elastomeric network. Additionally, plasticizers can influence lignin's chemical reactivity by lowering its viscosity; however, they may also dilute reactive components [195]. Hydrophilic, low-molecular-weight substances, including water, can act as plasticizers for lignin due to their ability to disrupt intermolecular hydrogen bonding. When lignin is in a dry, unsaturated state, plasticization becomes more effective when molecules capable of participating in hydrogen bonding—such as short-chain alcohols—are introduced [196]. Various compounds can be used for lignin plasticization, but their effectiveness depends on the specific type of

lignin used [197]. The influence of such plasticizers was investigated by *Kruželák et al.*[197]. In this study, the effects of 1,4-butanediol, ethylene glycol, and glycerol on the plasticization of calcium lignosulfonate in NBR based composites were examined. It was reported that the plasticizing effect increased in the same order as the listed plasticizers, which correlates with the corresponding increase in polarity and their solubility parameters [198] which is very similar to calcium lignosulfonate [199]. Good compatibility at the lignin/rubber interface was observed; however, it was noted that the smaller the plasticizer molecule, the greater the blooming. This suggests that the plasticizer migrates into the rubber matrix rather than remaining physically bonded within the calcium lignosulfonate domains. Although this migration cannot be entirely avoided, it is undesirable. Since the general goal of researchers is to maintain an environmentally friendly approach, the choice of plasticizer should prioritize bio-based, non-toxic, and biodegradable alternatives. Glycerol was used as a plasticizer of calcium lignosulfonate in several other studies [200–202], where it provided finer and more compact morphological structure in NR, SBR and NBR based composites. Alternatively, *Datta et al.*[203,204] presented the use of glycerolysate, a product of thermo-mechanical recycling of polyurethane waste on the plasticization of softwood Kraft lignin in NR composites. It was reported that the presence of glycerolysate suppressed the accumulation of lignin into larger agglomerates. When compared with commonly used naphthenic oil, the utilization of glycerolysate showed similarity in agglomerate formation. A patent application from 2019 [194] describes *meltable lignin* as a composition that is liquid, viscous or a dense solid material, achieved by blending lignin powder with a molecule that interferes with lignin's intra- and intermolecular hydrogen bonding and π - π interactions. Here, as plasticizers are listed polyethers, polypropylene glycols or polyols. Encompassed are also molecules that can chemically react and bind with lignin, enhancing its interaction, reactivity, and compatibility with, but not limited to, composites. Examples of such molecules listed in this patent application belong to the family of carbonate esters, amides and cyclic urea derivates, aldehydes and ketones, conjugated systems with carbon-carbon and carbon-nitrogen bonds, (di)carboxylic acids, acrylic acid, and acrylates, halogenated acetic acid, cyclic compounds with hydroxyl and carbonyl groups, carboxylic acid anhydrides, acyl halides, carboxylic acid esters, furans, isocyanates, polyethylene glycol-based polymers, substituted silanes, sulfones and sulfoxides. Several other researchers also introduced coupling agents as another approach for inducing compatibility between lignin and rubber. *Bahl et al.*[205] reported the results of non-covalent coupling between Kraft lignin and SBR using polybutadiene-g-polypentafluorostyrene graft copolymer as a coupling agent. However, the improvements were not as significant as those achieved with covalently coupled systems, such as the one studied by *Hait et al.*[188,189], due to the lower strength of π - π stacking interactions compared to covalent bonds. Here a commonly used silane coupling agent - bis(3-triethoxysilyl propyl) tetrasulfide - was used for Kraft lignin/BR composite, achieving an overall homogeneous dispersion of Kraft lignin. This resulted in enhanced mechanical properties, even when compared to the reinforcing CB (N330) and silica systems.

As discussed in the preceding sections, numerous researchers have investigated the incorporation of lignin as a biopolymeric component in rubber composites, employing various lignin types and elastomeric matrices. Table 6 presents an overview of the mechanical properties of rubber composites containing technical lignins in combination with commonly used elastomeric matrices.

Table 6: Mechanical Properties of Various Lignin / Rubber composites. T_s – Tensile Strength; E_b – Elongation at Break; HTDHT – High Temperature Dynamic Heat Treatment

| Rubber | Lignin [trade name] | Lignin content | Properties | Extra notes | Ref. |
|-----------------------------------|---|-------------------|--|---|-----------|
| Kraft lignin <i>INDULIN AT</i> | | up to 40 phr | ✓ gradual decrease from 5phr to 40 phr of T_s from 15.16 to 8.39 MPa; hardness from 45.5 to 38.3 °ShA; crosslink density from 5.07 to 3.88×10^{-3} mol/cm ³ ; abrasiveness increases from 0.085 to 0.2 cm ³ | samples containing 5 and 10 phr of lignin showed best thermal properties | [203] |
| Kraft lignin <i>REAX 910</i> | | 10 phr | ✓ T_s 15.17 MPa; E_b 672% | | |
| | | 40 phr | ✓ abrasiveness 0.0988 cm ³ ✓ T_s 10.61 MPa; E_b 630% ✓ abrasiveness 0.2397 cm ³ | addition of glycerolysate as plasticizer | [204] |
| NR | Sodium lignosulfonate <i>Pearllex NP</i> | up to 40 phr | ✓ maximum T_s of 27.2 MPa at 5 phr ✓ stretching ratio 7.8 ✓ maximum T_s of 19.2 MPa at 10 phr ✓ stretching ratio 8.8 | | [206] |
| | Sodium lignosulfonate <i>Borresperse NA220</i> | | ✓ gradual increase of T_s to 10 MPa and E_b to 400% at 40 phr | | |
| | Calcium lignosulfonate <i>Borrement CA120</i> | up to 40 phr | ✓ maximum T_s of 14 MPa at 20 phr | glycerol greatly improved T_s up to 25 MPa | [201] |
| | Magnesium lignosulfonate <i>Vianultra</i> | | ✓ maximum E_b ca. 600% at 20-40 phr | and E_b up to about 650% at 10 phr of lignin | |
| | | | ✓ T_s 19 MPa; E_b 700% ✓ hardness 47.5 °ShA ✓ mechanical properties remained robust after exposure to UV, humidity & elevated temperature | reactive mixing of ENR/lignin masterbatch at 140°C resulted in covalent ether bonds; NR/ENR/lignin composites have potential for application in footwear industry | [207] |
| NR/ENR | Kraft lignin | 20 phr | ✓ T_s 11 MPa; E_b 425%; hardness 51 °ShA | | |
| | | 35 phr | ✓ T_s 9 MPa; E_b 390%; hardness 56 °ShA | | |
| ENR | Kraft lignin | up to 40 phr | ✓ gradual decrease of T_s from 15 MPa to 6 MPa (0 to 40 phr of lignin) ✓ slight decrease of T_s from 16 MPa to ca. 14 MPa & gradual decrease of E_b by 250% (0 to 40 phr of lignin), by HTDHT the M300 increased by ca. 400% | reactive mixing of ENR/lignin at 160°C via ring opening reaction, thus perfect lignin dispersion (HTDHT) | [208,209] |
| | Kraft lignin <i>BioPiva395</i> | 50 phr | ✓ T_s gradually increased with mixing temperature up to 4 MPa (mix. at 200°C), on the contrary E_b decreases | mixing temperatures of 180°C & 200°C are presented as a milestones where the best possible dispersion of lignin is achieved | [187] |
| BR | Magnesium lignosulfonate <i>Lignex MgF</i> | 50 phr | ✓ T_s of ca. 2 MPa - marginal increment in T_s vs. ref. sample | MgL & NaL showed cracks and voids in morphology, KL resulted in better | [188,189] |

| | | | | |
|-----|---|------------------------|---|--|
| | Sodium lignosulfonate <i>Hansa 201</i> | 50 phr | ✓ T_s of ca. 2 MPa - marginal increment in T_s vs. reference sample | mechanical properties than silica-silane or CB systems at equivalent loading |
| | Kraft lignin <i>BioChoice</i> | 50 phr up to 90 phr | ✓ improvement in T_s by 180% (to ca. 5 MPa) ✓ maximum T_s & E_b of ca. 9 MPa & 270% at 50 phr (comparable properties at 70 and 90 phr loading) | TESPT coupling agent enabled efficient dispersion of lignin |
| | Calcium lignosulfonate <i>Borrement CA120</i> | | ✓ maximum T_s & E_b 2.8 MPa & 180% at 30 phr | glycerol greatly improved T_s up to 5 MPa and E_b up to about 200% at 30 phr of lignin |
| SBR | Sodium lignosulfonate <i>Borresperse NA220</i> | up to 40 phr | ✓ slight increase in T_s (ca. 2 MPa) and E_b (ca. 120%) with the increasing content of lignin | [201,210] |
| | Magnesium lignosulfonate <i>Vianultra</i> | | ✓ T_s and E_b are not affected by the lignin content | |
| | Calcium lignosulfonate <i>Borrement CA120</i> | up to 60 phr | ✓ sulfur v.s. T_s 4MPa (from 30 phr up) ✓ E_b increases up to 800% at 60 phr ✓ peroxide v.s. T_s 5 MPa (at 20-60 phr) ✓ E_b stays below 200% | necessity to use co-vulcanization agent [211] |
| NBR | | 30 phr | ✓ sulfur v.s. T_s ca. 3 MPa; E_b ca. 400%; hardness 58°ShA | glycerol improved T_s to ca. 9 MPa, E_b to ca. 600%, hardness to 55 °ShA [200] |
| | Industrial alkali lignin | 40 phr | ✓ T_s 12.8 MPa; E_b 702%; hardness 63°ShA; energy dissipation 33.8 MJ.m ⁻³ | [212] |
| | Kraft lignin | 120 phr | ✓ peroxide v.s. T_s 8.82 MPa; E_b 126% | reactive melt-mixing at 140°C [186] |
| | Kraft lignin | 100 phr | ✓ T_s over 30 MPa; E_b ca. 180% (NBR with 41% of acrylonitrile) | reactive melt-mixing at 160°C, without vulcanization system [190] |

Lignin-based organic–inorganic hybrid fillers have been developed to reinforce rubber composites, suppressing filler network formation and improving dispersion within the rubber matrix. CB and silica are the most common fillers in rubber compounds, though they differ in their properties. CB, with its low polarity and small particle size, disperses well and strongly interacts with rubber, providing better reinforcement. Silica, on the other hand, contains hydroxyl and siloxy groups that form hydrogen bonds, causing poor compatibility with non-polar rubbers but enhancing properties like tear strength, wet skid resistance, and lower rolling resistance [213]. Although lignin is less reinforcing than CB or silica, their hybridization can partially mitigate performance loss. *Bahl et al.*[214,215] reported the hybridization of CB with Kraft lignin and calcium lignosulfonate for use in SBR composites. The study revealed that π – π interactions between lignin and CB enable the formation of hybrid filler particles, with surface characteristics and morphology controlled by the material ratio. Both lignin types form coating layers on CB aggregates, preserving their fractal structure and leading to lower energy dissipation. The study provides data in support of partial replacement (up to 10 wt.%) of CB with lignin, potentially saving 300 million pounds of CB annually just for the tire industry. *Liu et al.*[216] subsequently proposed reinforcement mechanisms for CB/lignin and silica/lignin hybrid fillers in NR composites. The study also demonstrates that π – π stacking interactions between lignin and CB suppress filler network formation, while increasing lignin content enhances CB/lignin – rubber interactions through greater chain entanglements. In silica/lignin systems, lignin weakens filler network formation, improving dispersion, while the silane coupling agent strengthens filler–rubber interactions through silylation. As a result, superior reinforcing effects of lignin at different contents were clearly apparent in the silica/lignin NR composites. While the above-mentioned studies prepared the hybrid filler systems by dissolving the lignin in a solvent, several studies reported direct mixing of rubber, CB and lignin in an internal mixer, with the purpose of partially replacing CB with lignin and reducing costs while maintaining material properties. *Kubačková*[217] reported, that up to 25 vol.% of CB can be replaced by calcium lignosulfonate in real rubber formulas used for tire production, without the loss of mechanical properties. *Džuganová et al.*[202] combined 25 phr of CB with 30 phr of calcium lignosulfonate in NBR and SBR based composites, achieving tensile strengths of 16 MPa and 13 MPa, respectively, along with a five-fold increase in tear strength compared to CB-only composites.

3.2 Technical Lignins as Additives in the Rubber Industry

To enhance rubber product durability, controlling elastomer degradation is crucial. Antioxidants and antiozonants prevent oxidative damage by neutralizing free radicals and hydroperoxides. While synthetic antioxidants are common, there's growing interest in renewable, plant-based alternatives[218]. Thanks to its phenolic groups, lignin exhibits antioxidant properties, acting as a stabilizer by inhibiting oxidation reactions in rubber compounds [219–222]. However, its effectiveness depends on the lignin's structure, which varies with botanical origin and extraction methods [223]. Research revealed that lignin with less aliphatic hydroxyl groups, more phenolic hydroxyl groups, lower and narrower M_w distribution has greater antioxidant activity [224]. *Aini et al.*[225] reported the lignin content in NR/BR composites to be one of the factors that reduce the rate of oxygen absorption and lessens the deterioration of mechanical properties after thermal aging. *Kubačková et al.*[221] reported the antioxidative effect of three different lignins in NR/SBR composites, where the results indicate that the main factor that establishes the antioxidant properties is the content of phenolic structures. In this study Kraft lignin exhibited antioxidant properties comparable to synthetic antioxidant IPPD. *Nilmini et al. and Gunasekara et al.*[220,226] studied the antioxidative effect of industrial grade lignin on NR and SBR tire tread compounds, revealing that lignin could be used as an efficient antioxidant in tire tread compounds by substituting 6PPD and SKF alone or in combination.

Adhesive bonding of metals has become increasingly relevant in recent years due to the demand for reducing weight and improving performance in structural applications such as automobiles and aerospace. *Kanbargi et al.*[227] developed renewable thermoplastic adhesives from technical organosolv lignin isolated from hardwood biomass and NBR for joining steel substrates. The highest adhesive strength of 13.1 MPa measured in a 60% lignin loading ratio when NBR with acrylonitrile molar ratio of 51% was used. Similarly, *Yu et al.*[228] reported acrylonitrile-butadiene-lignin rubber filled with 5 wt.% of fumed silica and 30 wt.% of epoxidized glass spheres to reach 21 MPa of lap-shear strength - 90% of a commercial epoxy-based adhesive. A 2012 patent [229] demonstrated that incorporating lignin into wire stock compositions enhances rubber-to-metal adhesion, maintaining high performance after 20 days of humidity aging, eliminating the need for cobalt salt in the wire coat stock.

3.3 Patented Applications of Technical Lignins in the Rubber Industry

Growing interest in the incorporation of technical lignins into rubber composites has resulted in practical solutions for manufacturing value-added products, regulated by patents worldwide. Starting since the early 1950s,

the number of patents related to lignin-containing rubber articles has grown exponentially, with over a thousand patented applications retrieved from *World Intellectual Property Organization* using the keywords “lignin and rubber” [230], highlighting the vast application potential of this biopolymer. Lignin has been utilized in rubber compounds as an antidegradant, enhancing ultraviolet and aging resistance, as an adhesive or cross-linking agent, and most commonly as a filler to improve mechanical and dynamic properties or increase wear resistance in applications such as conveyor belts and tires. Table 7 provides an overview of selected patents granted throughout the rubber/lignin age.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Table 7: Overview of Patented Applications of Technical Lignin / Rubber Composites

| Year | Title | Description | Applicant | Ref |
|------|--|---|--------------------------------------|-------|
| 1954 | Lignin reinforced rubber and method of making same | This invention relates to an elastomer made from polymeric butadiene rubber and a reinforcing agent (CB and lignin in a ratio of about 2 to 10 phr). The elastomer achieves a tensile strength greater than that produced by 50 phr of CB alone. The method of making this elastomer is <i>co-precipitation</i> , after which the elastomer is milled, and additional uncured rubber is added during milling to complete the process. | West Virginia Pulp & Paper Co. | [179] |
| 1983 | Lignin reinforced synthetic rubber | The present invention provides a novel reinforced synthetic rubber. The rubber comprises acrylamide-modified SBR alone or in combination with SBR and is reinforced with lignin or a mixture of lignin and CB, wherein said lignin reinforced synthetic rubber is prepared by coprecipitating a latex blend of said monomers. A lignin product successfully employed in the work reported here was INDULIN AT. Such rubber can be employed in the manufacture of tires, conveyor belts and the like. | Bridgestone Firestone Inc | [231] |
| 2009 | Lignin in tire components | The invention features a vehicle tire with a rubber composition containing unsulfonated lignin particles (e.g., INDULIN AT) in the sidewall, undertread, or tread band. The composition includes a diene elastomer, CB, and at least 70 wt.% lignin, with lignin comprising up to 50 wt.% of the total filler. | Societe de Technologie Michelin | [232] |
| 2012 | Wire coat compositions for rubber articles | This invention presents rubber formulations with strong metal adhesion that remains high even after aging in humid conditions. | Goodyear Tire & Rubber | [229] |
| 2013 | Rubber composition for tire, method of preparing the same, and pneumatic tire | The invention provides a rubber composition for tires, consisting of a rubber component, microfibrillated plant fibres, and industrial lignin (0.1 to 50 parts by mass per 100 parts of fibres). This improves the compatibility of the fibres with the rubber, enhancing both rigidity and elongation at break, while maintaining good fuel economy. The resulting pneumatic tire offers improved tensile properties, handling stability, and fuel efficiency in a balanced way. | Sumitomo Rubber Industries Ltd | [233] |
| 2014 | Lignin-containing polymers and compositions including lignin-containing polymers | The composition features a grafted polymer-lignin agent and a compatible component. The method enhances dispersion by introducing the agent into the matrix. | Carnegie Mellon University | [234] |
| 2015 | Lignin derivative, lignin resin composition, rubber composition and molding material | The present invention relates to a lignin derivative, a lignin resin composition, a rubber composition, and a molding material. | Sumitomo Bakelite Co. Ltd. | [235] |
| 2018 | Lignin-reinforced NBR/PVC elastomer and preparation method thereof | The invention uses lignin as an alternative filler to CB, enhancing the anti-ultraviolet and anti-aging properties of the NBR/PVC elastomer. By creating dynamic coordination and hydrogen bonding between lignin and the NBR/PVC interface, the compatibility and dispersion of lignin are improved, reinforcing the elastomer. Additionally, the dynamic coordination network can repeatedly break and reform under external force, absorbing mechanical energy and resulting in an elastomer with excellent overall mechanical properties, including a tensile strength of 25–35 MPa and a break elongation of 150–400%. | South China University of Technology | [236] |
| 2019 | Lignin/nitrile butadiene rubber composite and preparation method thereof | The inventions relate to a lignin/acrylonitrile-butadiene & lignin/ethylene-propylene rubber composites produced by reacting nitrile (or EPDM) rubber, lignin, reactive compatibilizer, and modifiers. The reactive compatibilizer is epoxidized hydroxyl-terminated polybutadiene, which can be modified with chemicals like 3- | South China University of Technology | [237] |

| | | | | | | | |
|----|----|----|----|----|--|---|---|
| 21 | 22 | 23 | 24 | 25 | Lignin/EPDM (ethylene propylene diene monomer) rubber composite and preparation method thereof | amino-1,2,4-triazole, 4-(2-ethylamino)benzene-1,2-diphenol, or 2-amino-3-imidazolylpropionic acid. Modifiers include chemicals like 3-amino-1,2,4-triazole, 4-(2-ethylamino)benzene-1,2-diol, and others or ZnCl ₂ , CaCl ₂ , FeCl ₃ , CuCl ₂ , and zinc acrylate. | [238] |
| 26 | 27 | 28 | 29 | 30 | 2019 Meltable lignin compositions, method for producing them and their uses | The invention involves preparing a meltable lignin composition by blending lignin powder with at least one reactive molecule that disrupts lignin's intra- and intermolecular hydrogen bonding and π-π interactions. The process includes steps such as mixing lignin powder with a reactive molecule at temperatures between 0°C and 120°C, coprecipitating the rubber and lignin to form a coagulum, drying the mixture, and then masticating it to produce a uniform lignin dispersion throughout the rubber. The resulting lignin composition can be in various forms, such as liquid, viscous, or dense solid materials like pellets, granules, or powder. | FPInnovations [194] |
| 32 | 33 | 34 | 35 | 36 | 2019 Nitrile rubber/lignin composition, nitrile rubber/lignin composite material, and preparation method and application thereof | The patent describes a nitrile rubber and lignin (1-150 parts by weight) composite, interface reactants, vulcanization aids, and activation aids. The interface reactants include carboxyl-terminated or epoxy-terminated nitrile rubber, while vulcanization aids may include dicumyl peroxide and triallyl isocyanurate. The composition is mixed in several steps, with specified conditions for each stage. The resulting composite is suitable for applications like automotive hoses, printer rollers, and foamed insulation. | China Petroleum and Chemical Corp [239] |
| 38 | 39 | 40 | 41 | 42 | 2021 Application of lignin in preparation of radial tires | The invention belongs to the field of rubber tire processing and relates to the application of lignin in preparing radial tires. | Nanjing Tech University [240] |
| 43 | 44 | 45 | 46 | 47 | 2023 Rubber/fiber adhesion treating agent and synthetic fiber cord for rubber reinforcement using same | The invention describes a rubber/fibre adhesive agent that enhances adhesion without using resorcin/formaldehyde resin. It includes a lignin derivative, a water-soluble or water-dispersible cross-linking agent, and rubber latex. The lignins solid content makes up 5-50% of the adhesive. The formulation ensures a dry film strength of 0.2-1.6 MPa and elongation of 2-120%. The cross-linking agent may include oxazoline, epoxy, or blocked isocyanate compounds. The adhesive maintains stable viscosity over time and is used for reinforcing synthetic fibre cords. | Toray Industries Inc [241] |
| 48 | 49 | 50 | 51 | 52 | 2024 A pneumatic tyre comprising recovered filler | This invention relates to a pneumatic tire with metal, textile, and cured rubber components. The rubber component includes CB, and a recovered filler derived from pyrolyzed tire rubber containing lignin-based material. The lignin-based filler helps control the morphology and bulk density of the recovered filler during pyrolysis, optimizing its properties for tire reinforcement. | Nokian Renkaat Oyj [242] |
| 53 | 54 | 55 | 56 | 57 | 2024 High-wear-resistance conveyor belt cover rubber and preparation method thereof | The invention relates to the technical field of conveyor belts, and in particular to a highly wear-resistant conveyor belt covering rubber and a preparation method thereof. In this invention lignin has a reinforcing effect, further improving the strength and wear resistance of the conveyor belt covering rubber. | LI QIANG [243] |
| 58 | 59 | 60 | 61 | 62 | 2025 Tires for vehicle wheels | This invention relates to a vehicle tire with a structural component containing a reinforcing element, which consists of an elongate member coated with or embedded in a vulcanized elastomeric compound. The elastomeric composition includes per 100 phr of diene elastomeric polymer, a predisposition of diene elastomeric polymer and at least 25 phr of lignin, 0-90 phr of diene elastomeric polymer, at least 30 phr of CB filler, optionally, a reinforcing resin with a methylene acceptor and donor, and 0.1-12 phr of a vulcanizing agent. At least 50 phr of the diene elastomeric polymer consists of natural or synthetic isoprene rubber. | Pirelli Tyre S.p.A. [244] |

4 Application of Technical Lignins in the Plastics Industry

Lignin has significant potential in the development of sustainable thermoplastic materials. This biodegradable polymer could improve some material properties, by reducing brittleness, improving flexibility of polymer matrices, and lowering the glass transition temperature of polymers, enabling easier processing at lower temperatures. It has been added to a wide variety of polymers from natural to synthetic materials including proteins, starch and other biopolymers, polyolefins, vinyl polymers, polyesters. Its low cost, low density, non-abrasive nature, thermal stability, and high reactivity make lignin a promising filler or additive for polymeric applications [245,246].

Despite its potential, it has several disadvantages:

- Lignin has poor processability because it is typically stiffer and less thermally stable than other thermoplastics, which can make it difficult to process without treatment.
 - The polar nature of lignin can make it difficult to blend with non-polar thermoplastics, limiting its applications unless processing additives or compatibilizers are used.
 - For certain applications, the dark brown colour of lignin is undesirable because it can affect the final appearance of thermoplastic products.

Ongoing research is working to overcome these obstacles, and lignin-based thermoplastics could become a key part of biological materials in the future. Lignin-based thermoplastic materials are expected to show applications such as engineering plastics, polymeric foams, thermoplastic elastomers, and carbon-fibre precursors [247]. These materials are also expected to provide cost-effective and biodegradable alternatives to petroleum-based thermoplastics and address the problem of papermaking waste disposal.

The unique chemical structure and properties of lignin depend on the extraction technology used for its production as discussed in previous chapters. Mixing lignin with polymers is not simple due to the polarity of the lignin molecules, which leads to strong self-interactions. Systematic studies on polymers with increasing polarity—from polypropylene to those capable of forming aromatic π -electron interactions, hydrogen bonds, or electrostatic interactions—have demonstrated that such interactions are critical in determining blend structure and properties. Although complete miscibility was not achieved, lignin was consistently dispersed as droplets within the polymer matrix. Even though lignin's self-interactions hinder full miscibility, competitive interactions with the functional groups of the matrix polymer can alter the structure and properties of the blend—though not enough to achieve complete miscibility [248]. The use of plasticizers, compatibilizers or even chemical modification of lignin is often required to improve its miscibility with other types of plastics or to increase adhesion at the interface [245,247,249]. Plasticization is a widely used method to enhance the thermoplasticity of technical lignin. According to gel theory, a plasticized polymer exists in an intermediate state—neither fully solid nor liquid—held together by a 3D network of weak secondary bonds. These bonds between the polymer and plasticizer are easily disrupted by external stress, allowing the material to flex, stretch, or compress [250]. Water, as the most common plasticizer, plays a key role in many amorphous materials. Studies show that dry lignin is best plasticized by hydrogen-bonding molecules and hydrated lignin responds better to aromatic molecules structurally similar to monolignols, such as vanillin [247].

The use of lignin in *polyolefins* is the subject of growing research interest, even though the compatibility of lignin and polyolefins is low and often leads to poor mechanical properties of the blends [245,251]. The use of unmodified lignin is therefore limited as the products based on the simple addition or incorporation of lignin into the blend are often too brittle [252,253]. Interactions play a decisive role in the determination of the structure and properties of polymer/lignin blends. The blending of lignin with conventional polyolefins – polyethylene (PE) and polypropylene (PP) is a subject of extensive research [254,255]. *Levon et al.*[256] report that lignin protects PE – both low- and high-density types - from UV radiation and found that the thermal oxidative stability of PE is significantly improved after mixing with different lignosulfonates. *Alexy et al.*[257] used the natural polymer lignin of prehydrolysis of beech wood as a filler in low-density polyethylene and polypropylene up to 30% by weight. The influence of lignin was reflected in processing stability, mechanical properties and light and long-term thermal degradation. Lignin concentration affected both tensile strength and melt flow index. The dependence of tensile strength on lignin content continuously decreases for both PE and PP/lignin blends. Based on the obtained results, the authors state, that lignin acts, especially in PP, as a good processing stabilizer and light stabilizer due to lignin's rich aromatic structure. On the other hand, at long-term heat stress lignin acts as an initiator of the degradation process in PP, mainly at higher concentration levels. In PE blends, lignin has no effect on processing stability. It acts as an initiator of the degradation process after short exposure of samples to UV light, if lignin content is more than 10 wt.%. In the case of long-term heat stress lignin in PE acts as a stabilizer mainly at a higher concentration

above 20 wt.%. *Košíková et al.*[258] also support the finding that lignin can act as a stabilizer or an initiator of polymer degradation, depending on the type and content of lignin. *Mikulášová et al.*[259] investigated the biodegradability of blends of PE and PP with different lignin (from beech wood) content. Based on the results of the spectroscopic measurement, they found that the biotransformation of the lignin component during the cultivation process initiates the partial biodegradation of the synthetic polymer matrix.

Lignin is polar and hydrophilic, whereas PE is non-polar and hydrophobic. This leads to weak interfacial bonding, affecting mechanical performance. *Ghozali et al.*[260] prepared ternary blend of PP/PLA/lignin, where lignin can affect several parameters of the resulting blends and can also act as a compatibilizer with increasing interfacial adhesion and interaction between particles or polymer matrices. The addition of lignin to PP/PLA blends increased tensile strength compared to the values measured for PP/lignin and PLA/lignin blends, but reduced the elongation at break, however the amount of lignin added did not significantly affect this characteristic. Enhancement of biodegradability with increasing lignin content and thermal stability was also seen. Another modification method can be the addition of coupling agents such as ethylene vinyl acetate (EVA) [261]. EVA copolymers significantly improved the processing and mechanical properties of the final materials containing lignin amounts of 30%. Even though matrix several lignin-based composites were prepared without lignin modifications [262–264], many authors address these problems by lignin modification, which depends on the origin of the polymer and the modification conditions [251,261,265,266]. Although most of the publications concern lignin modification via esterification, other modification routes are also explored [267]. Modification is a crucial factor for improving the properties of these blends. Chemical treatments can improve lignin's compatibility with PE. *Dehne et al.*[266] investigated the influence of the chemical composition of various types of lignin on the mechanical properties and water absorption of lignin-polyethylene blends. Part of the experiments was devoted to the esterification modification of lignin before its incorporation into polymers to introduce new reactive sites and simultaneously reduce the polarity of lignin. Esterification with anhydrides as a strategy to enhance the compatibility of lignin with polymers was used by *Teramoto et al.*[265] which reports an increase in the miscibility of Organosolv lignin and polycaprolactone after this modification. Based on the experiment described in article [266], it was also confirmed that esterification is a decisive factor for improving the properties of the blends. Lignin derivatives were cleaner and less polar and were shown to exhibit better miscibility with polyethylene than unmodified lignin. The effect of esterification was also confirmed in a study [251,268], where esterified lignin-LDPE composites were prepared.

Stival Bittencourt et al.[269] added Kraft lignin to poly(vinyl alcohol) (PVA) films at different concentrations. Two lignin samples were used: kraft lignin and acetone soluble fraction of kraft lignin. It was observed that the addition of lignin increased the thermal stability of PVA films. While the blends containing Kraft lignin seemed to have more resistance to photochemical attack, evaluated by changes in crystallinity due to film irradiation – where no change was observed, the blends with the acetone soluble fraction of Kraft lignin showed increased crystallinity and homogeneity. Furthermore, *Kubo et al.*[270] reported the formation of strong intermolecular interactions between the hydroxyl groups of PVA and Kraft lignin, though the PVA/lignin blend remains immiscible in the bulk. The combination of these materials could create environmentally friendly alternatives to conventional plastics, but processing and compatibility issues between the two components need to be addressed to optimize the blend for various industrial applications. Because PVA can form uniform mixture with thermoplastic starch and gain excellent mechanical properties, ternary blend PVA/starch/lignin was studied by *Ratnawati et al.*[271]. The mechanical properties reached at optimum processing conditions with 10% of lignin incorporated reached 7.93 MPa, 143%, and 68.50 N/mm for tensile strength, elongation at break, and tear resistance, respectively.

Lazzari et al.[272] demonstrated the potential use of Kraft lignin in bottle-graded poly(ethylene terephthalate) (PET) blends for enhancing mechanical and thermal properties. The PET/lignin blends were produced by melt extrusion followed by injection moulding. Blends containing a small amount of lignin (up to about 1%) showed improved mechanical properties. Both the modulus of elasticity and maximum tensile strength of PET increased with lignin addition, consistent with the behaviour expected from compatible polymer blends. Kraft lignin was also used as a filler with antimicrobial properties in PET blends by *Minet et al.*[273]. Although the dispersion of Kraft lignin was poor, it had little impact on the tenacity of the monofilament. However, it was concluded that it does not ensure antibacterial activity throughout the multifilament. *Kadla et al.*[274] observed miscibility in PET/lignin and poly(ethylene oxide) (PEO)/lignin blends, revealing strong hydrogen bond between the hydroxyl hydrogen of lignin and the ether oxygen in PEO, though no such bonding was observed in PET/lignin blends. *Yu et al.*[275] used PEO as plasticizer to improve spinnability and mechanical properties of lignin-based filament used in 3D printing. By mixing Kraft lignin with 15% of PEO a very uniform diameter and smooth surface, adequate compression and tensile strength were achieved. To further improve the performance of

lignin/PEO fibres *Ebers et al.*[276] incorporated epoxidized PEO. The fibres exhibited enhanced degree of crystallinity of 70%, doubling of Young modulus to 450 MPa and tensile strength to 12 MPa. It was argued that epoxidized PEO plays the role of a stress transfer agent between the rigid lignin regions and the flexible PEO regions, thereby improving the blend performance.

Barzegari et al.[277] prepared polystyrene (PS)/lignin blends over a wide range of Kraft lignin content (0–80 wt.%) using a laboratory batch mixer at 190 °C for 6 min with and without the addition of a compatibilizer - a linear triblock copolymer based on styrene, ethylene, and butylene (SEBS). The addition of lignin improved some mechanical properties such as flexural and shear moduli, which steadily increased with increasing lignin content while tensile strength, tensile modulus, and elongation at break were all reduced as lignin loading increased. The addition of a SEBS at 1% and 2% improved the tensile modulus and flexural modulus (by 54 and 52% respectively when 60% of lignin was added) due to improved interfacial adhesion between lignin and PS observed through SEM analysis. Plasticization effect was observed at higher SEBS content (5%) leading to lower viscosities and mechanical properties [277,278]. *Ghavidel et al.*[279] polymerized Kraft lignin and PS via free radical polymerization using emulsion process, where lignin enhanced surface area and porosity of PS. The blend was stirred for 18 h at 80°C in an oil bath. The successful incorporation of KL into PS was confirmed by various analyses. The participation of various hydroxyl functional groups, such as aliphatic, guaiacyl and C5-substituted, in the radical polymerization of styrene has been confirmed. Incorporation of Kraft lignin (40 wt.%) in PS increased its surface energy and oxygen content, which led to preparation of material with better compatibility. The material could be used as an adsorbent for the uptake of copper ions from an aqueous medium.

Culebras et. al[280] described the successful preparation of precursor fibres from a blend of lignin (organosolv and Kraft) and thermoplastic polyurethane (TPU) using continuous melt spinning. Subsequently, the fibres were converted to carbon fibres with modified mechanical properties. The differences in structure of each lignin caused differences in the degree of interaction with TPU, with H-bonding interactions more relevant in samples containing organosolv hardwood lignin. Carbon fibres with high mechanical properties were obtained especially for the sample organosolv lignin/TPU: 50/50 (1.1 GPa tensile stress with a modulus of 80 GPa). Such a blend shows great potential as a carbon precursor and could be an alternative to polyacrylonitrile as a precursor material in the future.

Lignin contains reactive phenolic groups that can participate in crosslinking reactions and therefore can also be used as a reactive component of various polymers, for example resins [245]. By incorporating lignin into thermosets, cross-linking density can be increased, which leads to improved thermal stability, resistance to deformation and other desired properties. Given its high carbon content, stiffness, and thermal stability, technical lignin is being explored as a sustainable alternative in thermosetting polymers, where it can act as a reinforcement, crosslinker, or reactive filler. Several reports display the use of renewable methods in the production of lignin-derived polyurethane (PU) foams [246]. It has been shown that by using another bio-component it is possible to modulate the density and thus also the physical properties of PU foams containing lignin. PUs derived from lignin and lignocellulosic biomass have shown improved biodegradation compared to traditional petroleum-derived plastics but have not shown complete biodegradation [281].

In most reports on the use of lignin in phenolformaldehyde (PF) resins, lignin replaces part of the phenolic component, contributing to the production of more sustainable materials, while formaldehyde remains as the crosslinking agent [246,282]. Although great potential has been reported for the use of lignin in PF resins, it must be admitted that lignin incorporation often remains around 50 percent. Lignin incorporation can improve the thermal stability of PF resins, which is particularly advantageous in applications requiring heat resistance. The addition of lignin can affect the mechanical properties of the final resin, although the effects may vary depending on the specific composition and amount of lignin used. However, processing and compatibility issues need to be addressed for successful commercialization. Lignin-based thermoplastic phenolic resins were prepared by the partial substitution of phenol through direct addition, and then lignin-based phenolic fibres were prepared by melt spinning [283]. The effects of different lignin contents on resin structure and fibre properties were investigated by adding lignin directly without treatment. The addition of lignin effectively improved the thermal properties of the fibre but resulted in a decrease in the molecular weight of the resin and increase in dispersity. From the point of view of mechanical properties, the optimal lignin content was 10%, when the tensile strength (160.9 MPa) and elongation at break (1.9%) reached maximum values. When the amount of lignin was 20%, a decrease in fibre strength and toughness was observed [283]. Overall, lignin-based thermoplastic phenolic resins represent a promising area of research and development, especially in the context of sustainable materials and green chemistry. However, lignin has a complex, highly cross-linked structure that can make it difficult to process into thermoplastic materials without treatment. The development of lignin-based phenolic fibres is of interest due to their potential applications in various fields, including sustainable textiles, composites, and engineering materials.

Lignin can be used as a sustainable alternative to bisphenol A (BPA) to prepare lignin-based epoxy resins [284]. Lignin with more content of phenolic hydroxyls is more desirable as a crosslinking filler [285,286]. The structural properties of lignin significantly affect the synthesis and properties of epoxides. Lignin with a lower molecular weight were more reactive in co-curing reactions and was beneficial to generate a denser crosslinking epoxy network with better mechanical properties [287], while its thermal stability showed an opposite trend due to the loss of lignin structural rigidity [288]. The incorporation of lignin with a higher molecular weight would lead to the higher rigidity of epoxy crosslinking network and higher contents of ether bonds in lignin would provide higher structural flexibility epoxy thermosets. These resins could be used as coatings (with anti-corrosion and UV-blocking effects), adhesives and flame retardants (with high charring ability). Resins can be directly produced from lignin glycidylation and can be further used to prepare lignin-based epoxy thermosets through curing process [284]. Lignin-based epoxy resins were prepared using technical lignins from eucalyptus and spruce, obtained from the Kraft process [289]. Mild epoxidation of lignin was carried out followed by curing with flexible, commercially available polyetheramines. Softwood spruce Kraft lignin provides somewhat better thermomechanical properties compared with eucalyptus-based resins. The presence of guaiacyl units leads to the formation of more C5-condensed aromatic units, which reduces molecular mobility of this unit. In hardwood Kraft lignin is dominated by sinapyl units with lower content of condensed units but higher content of flexible methoxy units. The tensile strength reached 66 MPa and was slightly higher for the spruce-based lignin epoxy resin. This thermoset showed unusually high toughness with a strain to failure of 8%. Lignin addition should be controlled because the epoxy composite formed with a high content (e.g. 50 wt.%) of lignin was not easy to shape and would cause a deterioration on structural compatibility [290,291].

4.1 Technical Lignins in Biopolymers and Biodegradability

The push for biodegradable plastics derived from renewable resources has intensified due to rising concerns over the environmental impact of plastic waste. While the term “biopolymer” refers to a group of polymers that are bio-based, biodegradable, or both [292], this chapter will focus solely on biopolymers that are both from renewable resources and are biodegradable. Lignin incorporation in biopolymers such as starch, polylactic acids, plant proteins and polyhydroxybutyrate has significantly improved the mechanical properties of such materials. It has been used in various applications such as antimicrobial, antioxidant, adhesive, adsorbent, energy storage material, flame retardant, flocculant and ultraviolet blocker [293].

The biodegradability of such biopolymer blends is influenced by various factors, including blend and surface composition, miscibility of components, phase structure, and surface roughness. Biodegradable polymers break down into carbon dioxide, methane, water, inorganic compounds, or biomass through microbial activity, schematically shown in Fig. 5. In nature, white-rot fungi (*Basidiomycetes*) play a key role in lignin degradation during wood decay, while in soil, lignin decomposition contributes significantly to humus formation [294,295]. Although lignin has been used for many decades as a biological source of new polymers in academic research, very little effort has been devoted to the biodegradability or recyclability of such polymers [246].

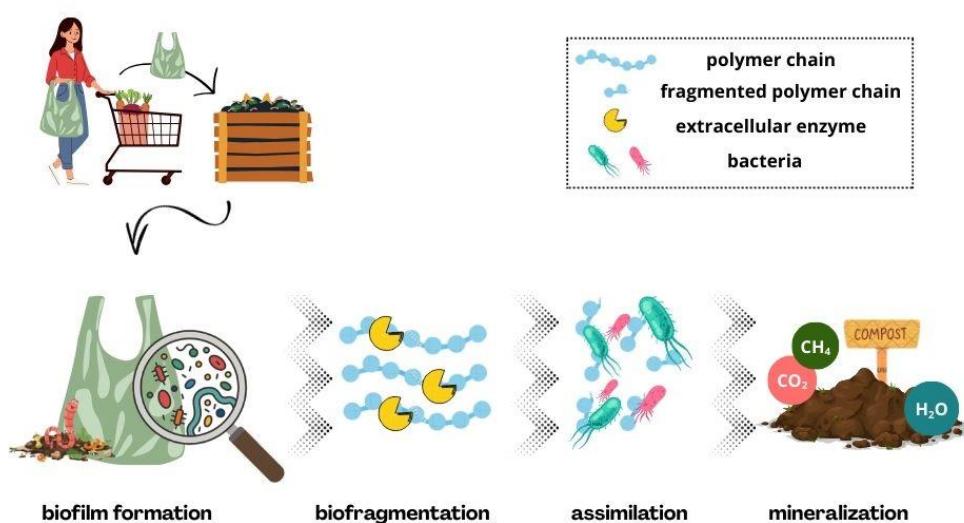


Fig. 5 Schematic Representation of the Biodegradation Process

Poly(lactic acid) (PLA) is a highly versatile aliphatic polyester. High-performance PLA grades are available that can effectively replace PS, PP, and ABS (acrylonitrile butadiene styrene) in more demanding applications. The

properties of PLA depend on the ratio of its D- and L-enantiomers (PDLA and PLLA, respectively)[292]. Nevertheless, compared to conventional synthetic polymers, PLA has some inherent disadvantages, such as brittleness, stiffness, poor elongation at break, limited gas and UV-light barrier properties, low thermal resistance, and poor toughness. These drawbacks have limited its large-scale commercial use. As a result, several researchers have investigated the enhancement of PLA-based bioplastics by incorporating lignin [293]. The blend of PLLA and lignin has material properties, as well as the price at an acceptable level when the content of lignin is less than 20%. The aim of work by *Li et al.*[263] was to develop an economically viable biodegradable thermoplastics in which PLLA should be the main phase (>50%) and percentage of lignin should be as high as possible. In general, lignin is more cost-effective compared to PLA, so incorporating it into blends could lower production costs for PLA-based products. Based on the analyses, the existence of intermolecular interaction between PLLA and lignin was confirmed. The glass transition temperature and melt temperature decreased when lignin content in the blends increased. When lignin content reached 20%, some mechanical properties were worse, but Young's modulus remained constant. Thermogravimetry curves showed that lignin accelerated PLLA degradation at lignin content more than 20%. However, the optimal lignin content was lower than 20%, both in terms of material properties and in terms of material costs. Both PLA and lignin are biodegradable and renewable materials, and their combination is an attractive alternative to commercially produced polymers, so their blends are more eco-friendly compared to petroleum-based plastics. PLA/lignin blends have garnered significant interest in the field of materials science, particularly in the development of biodegradable and sustainable composites. Their combination is an attractive alternative to petroleum-based polymers. By improving processing techniques, these compounds could play a key role in reducing plastic waste. *Mu et al.*[296] prepared fully degradable PLLA/lignin blends using a melt-blending method. The lignin content varied from 5 to 30wt.%. The impact strength of PLLA was improved by about 50% and 35% by adding 5 wt.% and 10 wt.% of lignin respectively, while the Young's modulus was preserved. The lignin in the blend acted as a nucleating agent in the crystallization of PLLA, and therefore the impact strength was improved. Based on thermal analysis, it was found that lignin also promoted the cold crystallization of PLLA. The thermal and photo stability of lignin can provide a synergistic effect with the properties of PLA.

Blends of starch and lignin are being investigated for their potential, especially in the field of sustainable materials, packaging and biomedical products [296]. The reinforcement of starch matrices with lignin is a promising strategy to overcome starch's downsides such as water sensitivity, thermolability and mechanical weakness. However, these materials were mostly prepared with minimal lignin content because the incorporation of higher contents (>10 wt.%) leads to the formation of lignin aggregates and uneven distribution in the starch matrix. Many studies have focused on increasing water resistance and reducing the hydrophilicity of starch-based materials by reinforcing the starch matrix with lignin [297,298]. Therefore, it is also important to choose the right type of lignin for producing starch-lignin materials. For instance, if the aim is to obtain hydrophobic material, lignosulfonates should be avoided, while Kraft lignin would be more suitable. Lignin/starch blends often require plasticizers to reduce brittleness. A starch-Kraft lignin-glycerol blend was therefore investigated, and it was found that glycerol concentration affected the modulus and elongation of the final lignin-starch product [299]. *Baumberger et al.*[264] prepared films from starch and crude commercial lignosulfonates by thermal moulding and also by casting. They found that the glass transition temperature varied from 16 to 40 °C depending on the lignin content. In the presence of lignin, some mechanical properties were also modified compared to the properties of standard starch films. The authors expected that sufficiently strong interactions between lignin and starch would be formed during processing, which would lead to an improvement in mechanical resistance of the material. Blending lignosulfonates into starch does not significantly improve the water resistance of the films, which is consistent with the solubility of lignosulfonates in water. However, the decrease of contact angle suggests that lignosulfonates are still surface active in the materials [264]. Properties of composites based on thermoplastic starch (TPS) and Kraft lignin are described by *de Freitas et al.*[300]. Using thermal analysis, it was confirmed that there is an improvement in the thermal properties of films with the addition of Kraft lignin. The presence of Kraft lignin in the TPS film also showed mechanical improvement in the films, increasing their energy storage property and, consequently, their elastic response. Increase of Kraft lignin in TPS can cause a reduction in mass loss of up to about 30% compared to TPS itself, and thus the use of Kraft lignin in the blend could slow down the biodegradation process of TPS. *Kaewtatip et al.*[298] also investigated TPS/Kraft lignin blends and achieved improvement in tensile strength by 17% as well as significant decrease in the water absorption properties, by incorporating only 5 wt.% of lignin.

Polyhydroxybutyrate (PHB) and related bacterial polyesters have attracted global attention due to their biodegradability, sustainability, and favourable mechanical properties. PHB shares many characteristics with isotactic polypropylene (PP), but it is more expensive, inherently stiff and brittle, and exhibits thermal instability during processing. To address these limitations, various efforts have focused on blending PHB with other

1 biodegradable polymers to improve its physical properties [294,301]. *Mousavioun et al.*[294] investigated
2 degradation mechanisms of lignin/ PHB blends. Based on the results, the authors hypothesized that the presence
3 of lignin in the blends inhibited the colonization of microorganisms and, due to the formation of hydrogen bonds
4 between lignin and PHB, a lower rate of PHB decomposition was observed, and therefore a slower degradation of
5 the blend compared to PHB film without lignin. The presence of hydrogen bonds and the increase in PHB
6 crystallinity at low lignin concentration contribute to the resistance of PHB/lignin films to degradation. The PHB
7 films were disintegrated and lost 45 wt.% of mass within 12 months. This value decreased to 12 wt.% of mass
8 when only 10 wt.% of lignin was added.

9 The effect of sodium lignosulfonate on thermal and morphological properties of the poly(3-hydroxy
10 butyrate-co-3-hydroxyvalerate) (PHBV) copolymer was described by *Lemes et al.*[302]. The melt and glass
11 transition temperatures of the PHBV matrix decrease with the addition of lignosulfonate, as determined by DSC
12 analysis. The addition of lignosulfonate in different amounts affected the morphological and thermal behaviour of
13 the PHBV matrix. Depending on the lignosulfonate concentration, the formation of lignosulfonate domains was
14 observed, which represent a weak interaction with the PHBV matrix. The decrease in thermal stability of PHBV
15 is also related to the content of lignosulfonate.

16 **4.2 Patented Applications of Technical Lignins in the Plastics Industry**

17 Innovative approaches to incorporating technical lignins into thermoplastics have emerged in response to
18 growing interest, resulting in patented solutions for value-added product manufacturing worldwide. Starting since
19 the early 1940s, the number of patents related to lignin-containing thermoplastics has grown, with almost six
20 hundred patented applications retrieved from World Intellectual Property Organization using the keywords “lignin
21 and thermoplastic” [230]. Lignin has been used in thermoplastics as a filler to enhance mechanical properties, as
22 an antidegradant improving resistance to ultraviolet radiation and aging, as well as an antioxidant, pigment,
23 adhesion promoter, and a modifier of rheological behaviour and processability. These functionalities have been
24 demonstrated across a wide range of applications, including packaging technology, injection-moulded products,
25 foamed materials, 3D printing, and others. Table 8 provides an overview of selected patents granted for lignin
26 application in thermoplastics or thermosets.

Table 8: Overview of Patented Applications for Technical Lignin in Thermoplastics and Thermosets

| Year | Title | Description | Applicant | Ref. |
|------|---|---|---|-------|
| 2000 | Starch-based thermoplastic mixture for producing biodegradable shaped bodies | The incorporation of lignin into starch-based thermoplastic biopolymers yields materials with significantly improved mechanical and functional properties. The resulting thermoplastic material is suitable for extrusion and pelletization and can be further processed into biodegradable films, moldings, and shaped articles. Potential applications include biodegradable packaging, agricultural films, food and beverage contact films, food casings, and systems for controlled substance release. The use of lignin plays a key role in enhancing mechanical strength and overall performance characteristics of the final bioplastic products. | Celanese Ventures GmbH | [303] |
| 2012 | Lignin-epoxy resin composite material and preparation method thereof | The lignin–epoxy resin composite material disclosed in the present invention is formulated from the following components: epoxy resin, lignin, curing agent, a reinforcing agent, and a toughening agent. In this invention, lignin is employed as the primary material, with a content exceeding 50%, and is compounded with a high-polarity thermosetting epoxy resin. The composite exhibits mechanical properties suitable for general applications and can be readily shaped by hot pressing. The resulting composite demonstrates excellent heat resistance, UV resistance, high strength, stiffness, and degradability, making it suitable for a broad range of everyday applications. | Northeast Forestry University | [304] |
| 2014 | Blending lignin with thermoplastics and a coupling agent or compatibilizer | The invention describes a composition comprising a modified lignin, a thermoplastic (HDPE, LDPE, LLDPE), and a compatibilizer (e.g., Maleic Anhydride grafted Polyethylene – MAh-g-PE). In a specific example, the composition comprises 45 wt% modified lignin, 50 wt% polyethylene, and 5 wt% PE-grafted lignin compatibilizer. In some cases, the modified lignin is transesterified, which enables stronger interfacial interaction with the polymer matrix. Additionally, the compatibilizer may include a peroxide and a bifunctional compound to promote the formation of branched copolymers within the lignin phase, thereby enhancing the mechanical integration and cohesion of the blend. | Cyclewood Solutions, Inc | [305] |
| 2015 | Thermoplastic polymer compounds with low-molecular-weight lignins, a method for producing same, moulding and uses | The patent describes a thermoplastic polymer compound, comprising a thermoplastic matrix polymer or a blend of at least two thermoplastic matrix polymers and at least one low-molecular-weight lignin and/or low-molecular-weight lignin derivative with a weight-average molecular weight of 200 to 6000 g/mol. Using PA11 as an example, it has been demonstrated that the incorporation of a low-molecular-weight fraction of softwood lignin can significantly enhance the properties of the polymer compound, forming a homogeneous phase with PA11 when the lignin content is 50%. This compatibility allowed for a partial increase in the elasticity of PA11, as indicated by an elongation at break of 135% for neat PA11 and up to 182% when 40% lignin extract was used. Furthermore, tensile strength and stiffness were improved to 56.2 MPa and 2180 MPa, respectively, compared to 43.5 MPa and 1120 MPa for pure PA11. | Fraunhofer-Gesellschaft zur Förderung der angewandten Forschung | [306] |
| 2017 | Lignin poly(lactic acid) copolymers | This invention relates to lignin-grafted poly(lactic acid) (lignin-g-PLA) copolymers produced via metal-free, solvent-free ring-opening polymerization of lactides using lignin and an organic base catalyst. The copolymers contain approximately 1% to 50% lignin by weight. Lignin-g-PLA show improved thermal and physicochemical behavior, including higher glass transition temperatures with more lignin, better dispersion in PLA and other polymers, and solubility in solvents like tetrahydrofuran and chloroform. Lignin-g-PLA also enhances UV absorption, functioning as an effective UV blocker. These materials are suitable for applications | The Board of Trustees of the Leland Stanford Junior University | [307] |

| | | | |
|------|--|--|--|
| | | such as biodegradable packaging, agricultural films, UV-resistant coatings, adhesives, colorants, and performance-tunable polymer blends. | |
| 2018 | Lignin/PVC film and preparation method therefor | The invention discloses a lignin/PVC film, comprising of thermoplastic plastic PVC, lignin, calcium-zinc stabilizer, plasticizer, compatibilizer and lubricant. The lignin/PVC film disclosed by the invention is non-toxic and harmless, is in line with environmental requirements, is uniform in thickness and level and smooth in surface and has the advantages of good toughness, tension resistance, difficulty in rupture, and the like. | Jining Mingsheng New Material Co., Ltd. [308] |
| 2018 | Biodegradable color masterbatch taking lignin as pigment as well as preparation method and application thereof | The invention relates to the field of plastic coloration and provides a fully biodegradable color masterbatch using lignin as a pigment, along with its preparation method and applications. The masterbatch is composed of the following components: carrier resin, lignin, surface treatment agent, dispersing compatibilizer, and other additives. The resulting granules exhibit good flowability, high thermal decomposition temperature, excellent dispersibility, strong tinting strength, and biodegradability. The material is cost-effective and suitable for use as a color masterbatch in thermoplastic processing of biodegradable plastics, including extrusion, injection molding, blow molding, calendaring, and other forming methods. | Beijing Technology and Business University [309] |
| 2019 | Lignin/polyolefin thermoplastic elastomer composite and preparation method thereof | The invention enhances lignin dispersion and interfacial compatibility with polyolefin elastomers using additives A and B, creating a non-covalent energy-sacrificing bond. This bond breaks and reforms under force, efficiently absorbing mechanical energy, improving strength and toughness, and addressing poor compatibility issues. | South China University of Technology [310] |
| 2021 | Polylactic acid and lignin composite thermoplastic for 3D printing | The present invention provides a PLA composite material that includes biodegradable and/or renewable materials such as lignin. The present inventors have determined that PLA blended with purified lignin has advantages over preexisting filaments or pellet material, including reduced material cost, biodegradable properties, adjustable mechanical properties, improved thermal stability, heat shielding, flame retardation, and ultraviolet radiation shielding in 3D printed parts. | WiSys Technology Foundation, Inc. [311] |
| 2021 | Composition comprising polyester and modified softwood lignin | The present invention relates to a thermoplastic composition comprising chemically modified softwood lignin and a biodegradable polyester, such as PBS, PBAT, or PCL, or mixtures thereof. The modified lignin is compatible with these matrices due to the nature of the substituents, improving dispersibility and interfacial adhesion. The resulting compositions possess comparable or superior toughness and strain at break compared to the neat polyester, allowing for their use as drop-in replacements in applications traditionally using pure polyesters. The compositions are processable via extrusion and injection moulding using conventional equipment at temperatures of at least 100°C. They can be extruded into pellets or shaped directly into final products. | Lignin Industries AB [312] |
| 2021 | Lignin-containing bio-based composite material and preparation method thereof | The invention discloses a bio-based composite material containing lignin and polyamide, belonging to the technical field of high polymer materials. The lignin-containing bio-based composite material has the beneficial effects that it still has good toughness when containing 80% of lignin, thereby greatly increasing the utilization rate of lignin and widening its application field. In addition, the material has good ultraviolet radiation resistance, thermal stability, good shape memory performance, and the like, indicating good industrial prospects and high commercial value. A good hydrogen bonding effect can be formed between the lignin and the polyamide. | Anhui Agricultural University [313] |

| | | | | |
|------|--|---|---|-------|
| 2022 | Calcium lignosulphonate thermoplastic elastomer modified polylactic acid material and preparation method thereof | The invention discloses a calcium lignosulphonate thermoplastic elastomer modified polylactic acid material and a preparation method thereof. The resulting material addresses the issues of low mechanical strength and poor thermal stability of PLA, while also reducing cost, utilizing abundant raw materials, and aligning with the principles of sustainable development. The incorporation of modified calcium lignosulfonate improves PLA's thermal and mechanical properties, expands its application range, and significantly increases lignin utilization. | Wuhan Institute of Technology | [314] |
| 2022 | Biodegradable and/or compostable thermoplastic composition comprising lignin, use of said composition and product comprising same | The invention relates to a biodegradable and/or compostable thermoplastic composition comprising rigid polymers, flexible polymers, and lignin, optionally with biodegradation accelerators, formulated to produce rigid parts with good mechanical properties. Lignin plays a key role in reducing the viscosity of the blend, allowing for lower processing temperatures and pressures. Example polymers include PHB and PBAT. The composition is suitable for use in forestry, agriculture, packaging, consumer goods, automotive, and construction industries. | Fundação Universidade Federal de São Carlos Suzano S.A. | [315] |
| 2022 | Lignin hybrid polymers obtained from the reaction of lignin and compatible polymer precursors, and starting compositions for forming lignin hybrid polymers. | The invention provides starting compositions, reaction processes, and final products to produce lignin hybrid polymers formed by reacting lignin with compatible polymer precursors. These lignin hybrid polymers can take the form of polyols, thermoplastic resins, or thermoset resins, and are suitable for a wide range of applications, including coatings, adhesives, sealants, elastomers, binders, and polyurethane systems. The invention offers several key advantages. When polymer precursors are bio-based, the resulting lignin hybrid polymer can be entirely renewable. Additionally, these polymers require less energy to produce than polymers made solely from conventional monomers of similar molecular weight. The aromatic structure of lignin further enhances the performance of the hybrid polymer, imparting mechanical strength, chemical resistance, thermal stability, fire resistance, and water resistance. | Organic Chemical, LLC | [316] |
| 2023 | Lignin/starch/PBAT composite film material and preparation method and application thereof | The main purpose of the invention is to provide a lignin/starch/PBAT composite film material, to solve the technical challenge of incorporating a higher proportion of starch and purified lignin into PBAT plastic as a filler. This significantly reduces the cost of composite film materials while ensuring comprehensive performance. The composite film material achieves a tensile strength of ≥ 13 MPa and elongation at break of $\geq 200\%$, and it remains non-sticky. The application of the material is in the field of agricultural mulch films, plastic bags, and packaging. | Beijing Forestry University | [317] |
| 2023 | Acrylonitrile butadiene styrene copolymer/lignin blends | The present invention relates to ABS/lignin blends, having enhanced ductility, impact resistance, and mechanical properties. Any commercially available lignin can be used, and the presence of compatibilizer boosts performance - 50% greater impact strength and 50% greater elongation at break. These improved composites are suitable for various applications requiring durable thermoplastic materials. | Prisma Renewable Composites, LLC | [318] |
| 2024 | Antioxidant stabilizer in polymers | The present invention relates to the use of a grass lignin and/or a hardwood lignin as an antioxidant in polymers or polymer compositions. The example demonstrates the effect of switchgrass lignin as an antioxidant in polypropylene and compares it to hardwood lignin, Kraft lignin, and a commercially available antioxidant. The data show that at a 1.0 wt.% addition level, all of the lignins show some efficacy as antioxidant stabilizers in that the OOT is elevated compared to the base case, however, the switchgrass lignin provides significantly improved OOT compared to that of Kraft lignin and hardwood lignin, for example, at a 1.0 wt.% level, the switchgrass lignin typically raises the OOT of polypropylene from about 200° C. to about 244° C. | Renmatix, Inc. | [319] |
| 2025 | Composite packaging material | The present invention relates to a biodegradable composite material for use in packaging applications. The composite material comprises a blend of lignin and PBS, which showed excellent behaviour in terms of | University of Limerick | [320] |

| | | | |
|------|------------------------------|--|---------------------------------------|
| | | processing using extrusion and injection moulding. The melting point of PBS clearly decreases with the addition of lignin until it disappears for the Polymer blend 1 comprising 70 wt% lignin. This evidences the good miscibility between lignin and PBS. The processability of the polymer blends improves with increasing PBS content. Based on the testing of hemp and lignin/PBS composites, it was found that the tensile strength values increased with the hemp fiber content. The addition of fibers showed a clear enhancement of the maximum flexural stress and modulus, indicating a reduction in brittleness compared to the polymer blends without hemp fibers. | |
| 2025 | Lignin-containing composites | The aim of this disclosure is to enhance the mechanical properties—especially impact strength—of lignin-based composites by partially replacing conventional plastics with lignin. The composition includes lignin (modified or unmodified), polymer matrix, and additive. Depending on the formulation, the additive is either a thermoplastic elastomer or an ester-containing thermoplastic. The polymer matrix may be selected from polyolefins, styrene-acrylonitrile copolymers, or biodegradable polyesters. The thermoplastic elastomer, such as S-TPE or TPO, is believed to enhance impact strength and strain at yield through interaction with lignin within the matrix. | <i>Lignin Industries AB</i> [321] |

1 **5 Summary and Future Perspectives**

2
3 A broadly conceived review article emphasizes the importance of lignin, the main structural component of
4 the cell walls of vascular plants and the second most abundant polymer on Earth. Its unique polyphenolic structure,
5 along with its antimicrobial, antioxidant properties and natural biodegradability, makes lignin an attractive
6 candidate for diverse applications. Nevertheless, lignin remains primarily the subject of academic research. Its
7 inherent structural complexity and variability are critical factors influencing its use in materials and bioplastics.

8 This review presents a comprehensive summary of the integration of engineered lignins into polymeric
9 materials, including thermoplastics, thermosets, and rubber. It also highlights advances in the industrial production
10 processes of technical lignins and explores their potential applications. The significance of these applications is
11 further underscored through a survey of related patented technologies.

12 Innovative approaches to incorporating technical lignins into thermoplastics have led to patented solutions
13 for the production of value-added products. In thermoplastics, lignin is employed as a filler to enhance mechanical
14 properties, as an antidegradant to improve resistance against ultraviolet radiation and aging, as an antioxidant,
15 pigment, adhesion promoter, and as a modifier of rheological behaviour and processability. These properties have
16 been demonstrated across a wide range of applications, including packaging, injection-moulded products, foam
17 materials, 3D printing, and more.

18
19 The review also examines the use of lignin in rubber for a broad spectrum of industrial applications, notably
20 in the automotive, aerospace, and consumer goods sectors, with a particular focus on optimizing rubber
21 compounds. Despite significant progress, lignin remains a material of ongoing scientific and industrial interest,
22 and further research is crucial to unlocking its full potential.

23
24 **References**

- 25
26 [1] The New Plastics Economy: Rethinking the future of plastics, World Economic Forum, Ellen MacArthur
27 Foundation and McKinsey & Company, 2016.
28 [2] Y. Zhu, C. Romain, C.K. Williams, Sustainable polymers from renewable resources, *Nature* 540 (2016)
29 354–362. <https://doi.org/10.1038/nature21001>.
30 [3] A.K. Mohanty, F. Wu, R. Mincheva, M. Hakkarainen, J.-M. Raquez, D.F. Mielewski, R. Narayan, A.N.
31 Netravali, M. Misra, Sustainable polymers, *Nat. Rev. Methods Primer* 2 (2022) 1–27.
32 <https://doi.org/10.1038/s43586-022-00124-8>.
33 [4] Y. Yang, Y. Guan, C. Li, T. Xu, L. Dai, J. Xu, C. Si, Application and carbon footprint evaluation of lignin-
34 based composite materials, *Adv. Compos. Hybrid Mater.* 7 (2024) 61. <https://doi.org/10.1007/s42114-024-00873-y>.
35 [5] D. Kai, M.J. Tan, P.L. Chee, Y.K. Chua, Y.L. Yap, X.J. Loh, Towards lignin-based functional materials in
36 a sustainable world, *Green Chem.* 18 (2016) 1175–1200. <https://doi.org/10.1039/C5GC02616D>.
37 [6] C. Libretti, L. Santos Correa, M.A.R. Meier, From waste to resource: advancements in sustainable lignin
38 modification, *Green Chem.* 26 (2024) 4358–4386. <https://doi.org/10.1039/D4GC00745J>.
39 [7] Web of Science, (n.d.).
40 <https://www.webofscience.com/wos/?Init=Yes&SrcApp=CR&SID=EUW1ED0AE5x9m1rLtXcMpfbBqxxR> (accessed May 19, 2025).
41 [8] Lignin Market Size & Outlook, 2030, (n.d.). <https://www.grandviewresearch.com/industry-analysis/lignin-market> (accessed May 16, 2025).
42 [9] R.A. Dixon, J. Barros, Lignin biosynthesis: old roads revisited and new roads explored, *Open Biol.* 9
43 (2019) 190215. <https://doi.org/10.1098/rsob.190215>.
44 [10] R. Patt, O. Kordsachia, R. Süttinger, Y. Ohtani, J.F. Hoesch, P. Ehrler, R. Eichinger, H. Holik, U. Hamm,
45 M.E. Rohmann, P. Mummenhoff, E. Petermann, R.F. Miller, D. Frank, R. Wilken, H.L. Baumgarten, G.-
46 H. Rentrop, Paper and Pulp, in: Ullmanns Encycl. Ind. Chem., Wiley-VCH Verlag GmbH & Co. KGaA,
47 Weinheim, Germany, 2000. https://doi.org/10.1002/14356007.a18_545.
48 [11] R. Vanholme, K. Morreel, J. Ralph, W. Boerjan, Lignin engineering, *Curr. Opin. Plant Biol.* 11 (2008) 278–
49 285. <https://doi.org/10.1016/J.PBI.2008.03.005>.
50 [12] R. Vanholme, B. Demedts, K. Morreel, J. Ralph, W. Boerjan, Lignin biosynthesis and structure, *Plant*
51 *Physiol.* 153 (2010) 895–905. <https://doi.org/10.1104/pp.110.155119>.
52 [13] D. Fengel, G. Wegener, Wood: chemistry, ultrastructure, reactions, Walter de Gruyter, 1984.
53 <https://doi.org/10.1002/pol.1985.13023112>.
54 [14] W. Boerjan, J. Ralph, M. Baucher, Lignin Biosynthesis, *Annu. Rev. Plant Biol.* 54 (2003) 519–546.
55 <https://doi.org/10.1146/annurev.aplant.54.031902.134938>.

- [15] J. Ralph, K. Lundquist, G. Brunow, F. Lu, H. Kim, P.F. Schatz, J.M. Marita, R.D. Hatfield, S.A. Ralph, J.H. Christensen, W. Boerjan, Lignins: Natural polymers from oxidative coupling of 4-hydroxyphenyl-propanoids, *Phytochem. Rev.* 2004 31 3 (2004) 29–60. <https://doi.org/10.1023/B:PHYT.0000047809.65444.A4>.
- [16] J. Nakashima, F. Chen, L. Jackson, G. Shadle, R.A. Dixon, Multi-site genetic modification of monolignol biosynthesis in alfalfa (*Medicago sativa*): Effects on lignin composition in specific cell types, *New Phytol.* 179 (2008) 738–750. <https://doi.org/10.1111/j.1469-8137.2008.02502.x>.
- [17] E.N. Uzal, L.V. Gómez Ros, F. Pomar, M.A. Bernal, A. Paradela, J.P. Albar, A. Ros Barceló, The presence of sinapyl lignin in *Ginkgo biloba* cell cultures changes our views of the evolution of lignin biosynthesis, *Physiol. Plant.* 135 (2009) 196–213. <https://doi.org/10.1111/j.1399-3054.2008.01185.x>.
- [18] N.D. Patil, N.R. Tanguy, N. Yan, Lignin Interunit Linkages and Model Compounds, Elsevier Inc., 2016. <https://doi.org/10.1016/B978-0-323-35565-0.00003-5>.
- [19] S. cheranma devi Eswaran, S. Subramaniam, U. Sanyal, R. Rallo, X. Zhang, Molecular structural dataset of lignin macromolecule elucidating experimental structural compositions, *Sci. Data* 9 (2022) 647. <https://doi.org/10.1038/s41597-022-01709-4>.
- [20] R. Katahira, T.J. Elder, G.T. Beckham, A Brief Introduction to Lignin Structure, in: G.T. Beckham (Ed.), *Energy Environ. Ser.*, Royal Society of Chemistry, Cambridge, 2018: pp. 1–20. <https://doi.org/10.1039/9781788010351-00001>.
- [21] D. Feldman, M. Lacasse, L.M. Beznacuk, Lignin-polymer systems and some applications, *Prog. Polym. Sci.* 12 (1986) 271–299. [https://doi.org/10.1016/0079-6700\(86\)90002-X](https://doi.org/10.1016/0079-6700(86)90002-X).
- [22] Q. Liu, L. Luo, L. Zheng, Lignins: Biosynthesis and biological functions in plants, *Int. J. Mol. Sci.* 19 (2018). <https://doi.org/10.3390/ijms19020335>.
- [23] Y. Tobimatsu, M. Schuetz, Lignin polymerization: how do plants manage the chemistry so well?, *Curr. Opin. Biotechnol.* 56 (2019) 75–81. <https://doi.org/10.1016/j.copbio.2018.10.001>.
- [24] J.L. McCarthy, A. Islam, Lignin Chemistry, Technology, and Utilization: A Brief History, in: *Lignin Hist. Biol. Mater. Perspect.*, American Chemical Society, 1999: pp. 2–99. <https://doi.org/10.1021/bk-2000-0742.ch001>.
- [25] E. Novo-Uzal, F. Pomar, L.V. Gómez Ros, J.M. Espiñeira, A. Ros Barceló, Evolutionary History of Lignins, in: L. Jouanin, C. Lapierre (Eds.), *Adv. Bot. Res.*, Academic Press, 2012: pp. 309–350. <https://doi.org/10.1016/B978-0-12-416023-1.00009-4>.
- [26] J.-K. Weng, C. Chapple, The origin and evolution of lignin biosynthesis, *New Phytol.* 187 (2010) 273–285. <https://doi.org/10.1111/j.1469-8137.2010.03327.x>.
- [27] J. Huang, S. Fu, I. Gan, Structure and Characteristics of Lignin, in: J. Huang, S. Fu, L. Gan (Eds.), *Lignin Chem. Appl.*, Elsevier, 2019: pp. 25–50. <https://doi.org/10.1016/B978-0-12-813941-7.00002-3>.
- [28] A.S. Klett, Purification , Fractionation , and Characterization of Lignin from Kraft Black Liquor for Use as a Renewable Biomaterial, Clemson University, 2017.
- [29] A.G. McDonald, L.A. Donaldson, Constituents of Wood, *Encycl. Mater. Sci. Technol.* Second Ed. (2001) 9612–9615. <https://doi.org/10.1016/B0-08-043152-6/01739-3>.
- [30] E. Novaes, M. Kirst, V. Chiang, H. Winter-Sederoff, R. Sederoff, Lignin and biomass: A negative correlation for wood formation and lignin content in trees, *Plant Physiol.* 154 (2010) 555–561. <https://doi.org/10.1104/pp.110.161281>.
- [31] A. Demirbas, Combustion characteristics of different biomass fuels, *Prog. Energy Combust. Sci.* 30 (2004) 219–230. <https://doi.org/10.1016/j.pecs.2003.10.004>.
- [32] D.N.-S. Hon, Chemical modification of lignocellulosic materials, Marcel Dekker, New York :, 1996.
- [33] M. Garedew, F. Lin, B. Song, T.M. DeWinter, J.E. Jackson, C.M. Saffron, C.H. Lam, P.T. Anastas, Greener Routes to Biomass Waste Valorization: Lignin Transformation Through Electrocatalysis for Renewable Chemicals and Fuels Production, *ChemSusChem* 13 (2020) 4214–4237. <https://doi.org/10.1002/cssc.202000987>.
- [34] E. Adler, Lignin chemistry-past, present and future, *Wood Sci. Technol.* 11 (1977) 169–218. <https://doi.org/10.1007/BF00365615>.
- [35] F.S. Chakar, A.J. Ragauskas, Review of current and future softwood kraft lignin process chemistry, *Ind. Crops Prod.* 20 (2004) 131–141. <https://doi.org/10.1016/j.indcrop.2004.04.016>.
- [36] R. Nadányi, A. Ház, A. Lisý, M. Jablonský, I. Šurina, V. Majová, A. Baco, Lignin Modifications, Applications, and Possible Market Prices, *Energies* 15 (2022) 6520.
- [37] S. Constant, H.L.J. Wienk, A.E. Frissen, P.D. Peinder, R. Boelens, D.S. Van Es, R.J.H. Grisel, B.M. Weckhuysen, W.J.J. Huijgen, R.J.A. Gosselink, P.C.A. Bruijnincx, New insights into the structure and composition of technical lignins: a comparative characterisation study, *Green Chem.* 18 (2016) 2651–2665. <https://doi.org/10.1039/C5GC03043A>.

- [38] X. Liu, F.P. Bouxin, J. Fan, V.L. Budarin, C. Hu, J.H. Clark, Recent Advances in the Catalytic Depolymerization of Lignin towards Phenolic Chemicals: A Review, *ChemSusChem* 13 (2020) 4296–4317. <https://doi.org/10.1002/CSSC.202001213>.
- [39] J. Dean, Lignin Analysis, (n.d.). <https://www.researchgate.net/publication/236878736> (accessed June 13, 2022).
- [40] F. Lu, J. Ralph, Derivatization Followed by Reductive Cleavage (DFRC Method), a New Method for Lignin Analysis: Protocol for Analysis of DFRC Monomers, *J. Agric. Food Chem.* 45 (1997) 2590–2592. <https://doi.org/10.1021/JF970258H>.
- [41] R. Rana, S. Nanda, V. Meda, A.K. Dalai, A Review of Lignin Chemistry and its Biorefining Conversion Technologies, *J. Biochem. Eng. Bioprocess Technol.* 1 (2018) 1–14.
- [42] A.K.S. Kameshwar, W. Qin, Recent developments in using advanced sequencing technologies for the genomic studies of lignin and cellulose degrading microorganisms, *Int. J. Biol. Sci.* 12 (2016) 156–171. <https://doi.org/10.7150/ijbs.13537>.
- [43] A. Lisý, A. Ház, R. Nadányi, M. Jablonský, I. Šurina, About Hydrophobicity of Lignin: A Review of Selected Chemical Methods for Lignin Valorisation in Biopolymer Production, *Energies* 15 (2022) 6213.
- [44] A. Blažej, M. Košík, Covalent and supermolecular structure of basic components of plant raw materials: Structure of the cell wall, in: T.J. Kemp, J.F. Kennedy (Eds.), *PHYTOMASS Raw Mater. Chem. Biotechnol.*, VEDA Publishing house of Slovak Academy od Science, Bratislava, 1993: pp. 32–47.
- [45] D. Hu, X.B. Liu, H.Z. She, Z. Gao, R.W. Ruan, D.Q. Wu, Z.L. Yi, The lignin synthesis related genes and lodging resistance of *Fagopyrum esculentum*, *Biol. Plant.* 61 (2017) 138–146. <https://doi.org/10.1007/s10535-016-0685-4>.
- [46] M. Schuetz, A. Benske, R.A. Smith, Y. Watanabe, Y. Tobimatsu, J. Ralph, T. Demura, B. Ellis, A.L. Samuels, M.S. Laboratories, Laccases Direct Lignification in the Discrete Secondary Cell Wall Domains of Protoxylem 1[W][OPEN], *Am Soc Plant Biol* 166 (2014) 798–807. <https://doi.org/10.1104/pp.114.245597>.
- [47] S.C. Tripathi, K.D. Sayre, J.N. Kaul, R.S. Narang, Growth and morphology of spring wheat (*Triticum aestivum L.*) culms and their association with lodging: effects of genotypes, N levels and ethephon, *Field Crops Res.* 84 (2003) 271–290. [https://doi.org/10.1016/S0378-4290\(03\)00095-9](https://doi.org/10.1016/S0378-4290(03)00095-9).
- [48] J.C.M.S. Moura, C.A.V. Bonine, J. de Oliveira Fernandes Viana, M.C. Dornelas, P. Mazzafera, Abiotic and Biotic Stresses and Changes in the Lignin Content and Composition in Plants, *J. Integr. Plant Biol.* 52 (2010) 360–376. <https://doi.org/10.1111/j.1744-7909.2010.00892.x>.
- [49] Y. Tobimatsu, F. Chen, J. Nakashima, L.L. Escamilla-Treviño, L. Jackson, R.A. Dixon, J. Ralph, Coexistence but independent biosynthesis of catechyl and guaiacyl/syringyl lignin polymers in seed coats, *Plant Cell* 25 (2013) 2587–2600. <https://doi.org/10.1105/tpc.113.113142>.
- [50] F. Chen, Y. Tobimatsu, D. Havkin-Frenkel, R.A. Dixon, J. Ralph, A polymer of caffeyl alcohol in plant seeds, *Proc. Natl. Acad. Sci. U. S. A.* 109 (2012) 1772–1777. <https://doi.org/10.1073/pnas.1120992109>.
- [51] F. Chen, Y. Tobimatsu, L. Jackson, J. Nakashima, J. Ralph, R.A. Dixon, Novel seed coat lignins in the Cactaceae: structure, distribution and implications for the evolution of lignin diversity, *Plant J. Cell Mol. Biol.* 73 (2013) 201–211. <https://doi.org/10.1111/tpj.12012>.
- [52] F. Lu, J.M. Marita, C. Lapierre, L. Jouanin, K. Morreel, W. Boerjan, J. Ralph, Sequencing around 5-hydroxyconiferyl alcohol-derived units in caffeic acid O-methyltransferase-deficient poplar lignins, *Plant Physiol.* 153 (2010) 569–579. <https://doi.org/10.1104/pp.110.154278>.
- [53] J. Ralph, C. Lapierre, J.M. Marita, H. Kim, F. Lu, R.D. Hatfield, S. Ralph, C. Chapple, R. Franke, M.R. Hemm, J. Van Doorsselaere, R.R. Sederoff, D.M. O’Malley, J.T. Scott, J.J. MacKay, N. Yahiaoui, A. Boudet, M. Pean, G. Pilate, L. Jouanin, W. Boerjan, Elucidation of new structures in lignins of CAD- and COMT-deficient plants by NMR, *Phytochemistry* 57 (2001) 993–1003. [https://doi.org/10.1016/s0031-9422\(01\)00109-1](https://doi.org/10.1016/s0031-9422(01)00109-1).
- [54] R. Vanholme, J. Ralph, T. Akiyama, F. Lu, J.R. Pazo, H. Kim, J.H. Christensen, B. Van Reusel, V. Storme, R. De Rycke, A. Rohde, K. Morreel, W. Boerjan, Engineering traditional monolignols out of lignin by concomitant up-regulation of F5H1 and down-regulation of COMT in *Arabidopsis*, *Plant J. Cell Mol. Biol.* 64 (2010) 885–897. <https://doi.org/10.1111/j.1365-313X.2010.04353.x>.
- [55] J. Rencoret, M.J. Rosado, H. Kim, V.I. Timokhin, A. Gutiérrez, F. Bausch, T. Rosenau, A. Potthast, J. Ralph, J.C. Del Río, Flavonoids naringenin chalcone, naringenin, dihydrotricin, and tricin are lignin monomers in papyrus, *Plant Physiol.* 188 (2022) 208–219. <https://doi.org/10.1093/plphys/kiab469>.
- [56] L. Lepiniec, I. Debeaujon, J.-M. Routaboul, A. Baudry, L. Pourcel, N. Nesi, M. Caboche, Genetics and biochemistry of seed flavonoids, *Annu. Rev. Plant Biol.* 57 (2006) 405–430. <https://doi.org/10.1146/annurev.arplant.57.032905.105252>.
- [57] R.A. Dixon, D.-Y. Xie, S.B. Sharma, Proanthocyanidins—a final frontier in flavonoid research?, *New Phytol.* 165 (2005) 9–28. <https://doi.org/10.1111/j.1469-8137.2004.01217.x>.

- [58] J. Ralph, Hydroxycinnamates in lignification, *Phytochem. Rev.* 9 (2010) 65–83. <https://doi.org/10.1007/s11101-009-9141-9>.
- [59] S. Singh, G. Bashri, A. Singh, S.M. Prasad, Regulation of xenobiotics in higher plants: Signalling and detoxification, in: *Plant Responses Xenobiotics*, Springer Singapore, 2016: pp. 39–56. https://doi.org/10.1007/978-981-10-2860-1_3.
- [60] N.B. Eloy, W. Vooren, W. Lan, M. De Lyra, S. Saleme, I. Cesarino, R. Vanholme, R.A. Smith, G. Goeminne, A. Pallidis, K. Morreel, J. Nicomedes, J. Ralph, W. Boerjan, Silencing CHALCONE SYNTHASE in Maize Impedes the Incorporation of Tricin into Lignin and Increases Lignin Content [OPEN], *Am Soc Plant Biol* 173 (2017) 998–1016. <https://doi.org/10.1104/pp.16.01108>.
- [61] J.J. Stewart, T. Akiyama, C. Chapple, J. Ralph, S.D. Mansfield, The Effects on Lignin Structure of Overexpression of Ferulate 5-Hydroxylase in Hybrid Poplar1, *Plant Physiol.* 150 (2009) 621–635. <https://doi.org/10.1104/pp.109.137059>.
- [62] M. Abhilash, D. Thomas, *Biopolymers for Biocomposites and Chemical Sensor Applications*, Elsevier Inc., 2017. <https://doi.org/10.1016/B978-0-12-809261-3.00015-2>.
- [63] M.M. Campbell, R.R. Sederoff, Variation in lignin content and composition: Mechanisms of control and implications for the genetic improvement of plants, *Plant Physiol.* 110 (1996) 3–13. <https://doi.org/10.1104/pp.110.1.3>.
- [64] M. Lawoko, Unveiling the structure and ultrastructure of lignin carbohydrate complexes in softwoods, *Int. J. Biol. Macromol.* 62 (2013) 705–713. <https://doi.org/10.1016/j.ijbiomac.2013.10.022>.
- [65] M. Lawoko, G. Henriksson, G. Gellerstedt, New Method for Quantitative Preparation of Lignin-Carbohydrate Complex from Unbleached Softwood Kraft Pulp: Lignin-Polysaccharide Networks I in: *Holzforschung* Volume 57 Issue 1 (2003), *Holzforschung* 57 (2003) 69–74.
- [66] D.R. Lobato-Peralta, E. Duque-Brito, H.I. Villafán-Vidales, A. Longoria, P.J. Sebastian, A.K. Cuentas-Gallegos, C.A. Arancibia-Bulnes, P.U. Okoye, A review on trends in lignin extraction and valorization of lignocellulosic biomass for energy applications, *J. Clean. Prod.* 293 (2021). <https://doi.org/10.1016/J.JCLEPRO.2021.126123>.
- [67] C.L. Fitzgerald, M.C. Thies, Continuous recovery of high-purity Kraft lignin from black liquor via simultaneous, liquid-phase acidification and purification, *Ind. Crops Prod.* 184 (2022) 115084. <https://doi.org/10.1016/j.indcrop.2022.115084>.
- [68] L. Dessbesell, M. Paleologou, M. Leitch, R. Pulkki, C. (Charles) Xu, Global lignin supply overview and kraft lignin potential as an alternative for petroleum-based polymers, *Renew. Sustain. Energy Rev.* 123 (2020) 109768. <https://doi.org/10.1016/j.rser.2020.109768>.
- [69] A. Berlin, M. Balakshin, Industrial Lignins: Analysis, Properties, and Applications, *Bioenergy Res. Adv. Appl.* (2014) 315–336. <https://doi.org/10.1016/B978-0-444-59561-4.00018-8>.
- [70] G.L.F. Gellerstedt, E.G. Henriksson, Lignins: Major Sources, Structure and Properties, *Monomers Polym. Compos. Renew. Resour.* (2008) 201–224. <https://doi.org/10.1016/B978-0-08-045316-3.00009-0>.
- [71] A. Kumar, Anushree, J. Kumar, T. Bhaskar, Utilization of lignin: A sustainable and eco-friendly approach, *J. Energy Inst.* 93 (2020) 235–271. <https://doi.org/10.1016/j.joei.2019.03.005>.
- [72] P. Bajpai, Pulping Fundamentals, in: *Biermanns Handb. Pulp Pap.*, Elsevier, 2018: pp. 295–351. <https://doi.org/10.1016/b978-0-12-814240-0.00012-4>.
- [73] CNBM, Comparison of Chemical Pulp, Mechanical Pulp and Chemi-mechanical Pulp, (2018). <https://medium.com/@paperpulpingmachine/comparison-of-chemical-pulp-mechanical-pulp-and-chemi-mechanical-pulp-7b32211e0fdf> (accessed March 21, 2020).
- [74] L.T. Mulyantara, H. Harsono, R. Maryana, G. Jin, A.K. Das, H. Ohi, Properties of thermomechanical pulps derived from sugarcane bagasse and oil palm empty fruit bunches, *Ind. Crops Prod.* 98 (2017) 139–145. <https://doi.org/10.1016/J.INDCROP.2016.11.003>.
- [75] G. Gellerstedt, 3. Mechanical Pulping Chemistry, in: E. Monica, G. Göran, H. Gunnar (Eds.), Vol. 2 *Pulping Chem. Technol.*, De Gruyter, 2009: pp. 35–56.
- [76] M. Ragnar, G. Henriksson, M.E. Lindström, M. Wimby, J. Blechschmidt, S. Heinemann, Pulp, in: *Ullmanns Encycl. Ind. Chem.*, Wiley-VCH Verlag GmbH & Co. KGaA, 2014: pp. 1–92. https://doi.org/10.1002/14356007.A18_545.PUB4.
- [77] J.C. Biermann, Pulping Fundamentals, in: *Handb. Pulping Papermak.* Second Ed., Academic Press, 1996: pp. 55–100. <https://doi.org/10.1016/B978-012097362-0/50007-8>.
- [78] CEPI, Types of Pulping Processes, (n.d.). <http://www.cepi.org/node/22334> (accessed March 21, 2020).
- [79] U. S. Department of Agriculture, *PULP YIELDS FOR VARIOUS PROCESSES AND WOOD SPECIES*, Madison, WIS, 1980.
- [80] L. Viikari, A. Suurnäkki, S. Grönqvist, L. Raaska, A. Ragauskas, Forest Products: Biotechnology in Pulp and Paper Processing, in: *Encycl. Microbiol.*, Elsevier Inc., 2009: pp. 80–94. <https://doi.org/10.1016/B978-012373944-5.00123-1>.

- [81] I. Tiseo, Pulp production by world type 2018, Statista, 2021. <https://www.statista.com/statistics/1177461/global-pulp-production-by-type/> (accessed March 4, 2022).
- [82] Confederation of European Paper Industries, Key statistics 2020 - European pulp & paper industry, Confederation of European Paper Industries, Northhamptonshire, UK, 2021. <https://library.cepi.org/> (accessed March 3, 2022).
- [83] T. Aro, P. Fatehi, Production and Application of Lignosulfonates and Sulfonated Lignin, *ChemSusChem* 10 (2017) 1861–1877. <https://doi.org/10.1002/cssc.201700082>.
- [84] M. Jablonský, J. Kočiš, A. Ház, J. Šima, Characterization and comparison by UV spectroscopy of precipitated lignins and commercial lignosulfonates, *Cellul. Chem. Technol.* 49 (2015) 267–274.
- [85] C. Crestini, H. Lange, M. Sette, D.S. Argyropoulos, On the structure of softwood kraft lignin, *Green Chem.* 19 (2017) 4104–4121. <https://doi.org/10.1039/C7GC01812F>.
- [86] P. Bajpai, Overview of Pulp and Papermaking Processes, in: *Environ. Friendly Prod. Pulp Pap.*, John Wiley & Sons, Inc., 2010.
- [87] M.C. Area, NSSC process optimization, part I: Pulping, pulps, and spent liquors, *Tappi J.* (2001). <https://www.researchgate.net/publication/235354087>.
- [88] M.M. Rahman, M.S. Jahan, Y. Ni, Chapter 7 - Pulping and papermaking of jute, in: Z.M.A. Ainun, S.M. Sapuan, R.A. Ilyas (Eds.), *Pulping Papermak. Nonwood Plant Fibers*, Academic Press, 2023: pp. 121–141. <https://doi.org/10.1016/B978-0-323-91625-7.00005-9>.
- [89] M.A. Lambert, H. Wahl, C.E. Bosman, T.M. Louw, L. Auret, J.F. Görgens, The effect of operating conditions on neutral sulphite semi-chemical pulping properties: an industrial pilot plant study, *Cellulose* 31 (2024) 8221–8234. <https://doi.org/10.1007/s10570-024-06091-5>.
- [90] M. Dashtban, A. Gilbert, P. Fatehi, Separation of lignocelluloses from spent liquor of NSSC pulping process via adsorption, *J. Environ. Manage.* 136 (2014) 62–67. <https://doi.org/10.1016/j.jenvman.2014.01.032>.
- [91] X. Zhao, K. Cheng, D. Liu, Organosolv pretreatment of lignocellulosic biomass for enzymatic hydrolysis, *Appl. Microbiol. Biotechnol.* 82 (2009) 815–827. <https://doi.org/10.1007/S00253-009-1883-1>.
- [92] P. Azadi, O.R. Inderwildi, R. Farnood, D.A. King, Liquid fuels, hydrogen and chemicals from lignin: A critical review, *Renew. Sustain. Energy Rev.* 21 (2013) 506–523. <https://doi.org/10.1016/j.rser.2012.12.022>.
- [93] I. Haq, P. Mazumder, A.S. Kalamdhad, Recent advances in removal of lignin from paper industry wastewater and its industrial applications – A review, *Bioresour. Technol.* 312 (2020) 123636. <https://doi.org/10.1016/j.biortech.2020.123636>.
- [94] C.S. Lancefield, I. Panovic, P.J. Deuss, K. Barta, N.J. Westwood, Pre-treatment of lignocellulosic feedstocks using biorenewable alcohols: towards complete biomass valorisation, *Green Chem.* 19 (2017) 202–214. <https://doi.org/10.1039/C6GC02739C>.
- [95] S. Bauer, H. Sorek, V.D. Mitchell, A.B. Ibáñez, D.E. Wemmer, Characterization of Miscanthus giganteus Lignin Isolated by Ethanol Organosolv Process under Reflux Condition, *J. Agric. Food Chem.* 60 (2012) 8203–8212. <https://doi.org/10.1021/jf302409d>.
- [96] N. Smolarski, High-Value Opportunities for Lignin: Unlocking its Potential, Frost & Sullivan, Santa Clara, CA, 2011.
- [97] N. Izaguirre, M. Alberro, X. Erdocia, J. Labidi, Kraft and organosolv lignin-activated carbon composites for supercapacitor electrode materials, *J. Energy Storage* 80 (2024) 110386. <https://doi.org/10.1016/j.est.2023.110386>.
- [98] T.N. Kleinert, Organosolv pulping and recovery process, US3585104A, 1971.
- [99] J. Kautto, M.J. Realff, A.J. Ragauskas, T. Kässi, Economic analysis of an organosolv process for bioethanol production, *Econ. Anal. Organosolv Process Bioethanol Prod.* 9 (2014) 6041–6072. <https://doi.org/10.15376/biores.9.4.6041-6072>.
- [100] O. Yu, K.H. Kim, Lignin to Materials: A Focused Review on Recent Novel Lignin Applications, *Appl. Sci.* 10 (2020) 4626. <https://doi.org/10.3390/app10134626>.
- [101] D. Stewart, Lignin as a base material for materials applications: Chemistry, application and economics, *Ind. Crops Prod.* 27 (2008) 202–207. <https://doi.org/10.1016/j.indcrop.2007.07.008>.
- [102] M.S. Hasan, M.R. Sardar, A.A. Shafin, M.S. Rahman, M. Mahmud, M.M. Hossen, A brief review on applications of lignin, *J Chem Rev* 5 (2023) 56–82.
- [103] L. Kouisni, P. Holt-Hindle, K. Maki, M. Paleologou, THE LIGNOFORCE SYSTEM™: A NEW PROCESS FOR THE PRODUCTION OF HIGH-QUALITY LIGNIN FROM BLACK LIQUOR, 2012.
- [104] L. Kouisni, A. Gagné, K. Maki, P. Holt-Hindle, M. Paleologou, LignoForce System for the Recovery of Lignin from Black Liquor: Feedstock Options, Odor Profile, and Product Characterization, *ACS Sustain. Chem. Eng.* 4 (2016) 5152–5159. <https://doi.org/10.1021/acssuschemeng.6b00907>.
- [105] L. Kouisni, M. Paleologou, Method for separating lignin from black liquor, US8771464B2, 2014.

- [106] A. Salaghi, L. Zhou, P. Saini, F. Kong, M. Konduri, P. Fatehi, Lignin production in plants and pilot and commercial processes, *Biomass Biofuels Biochem. Biodegrad. Polym. Compos. - Process Eng. Commer.* (2021) 551–587. <https://doi.org/10.1016/B978-0-12-821888-4.00002-2>.
- [107] A. Mazar, M. Paleologou, New approach to recycle and valorize the first filtrate of the LignoForce systemTM: Lignin extraction and its use in rigid lignin-based polyurethane foams, *Int. J. Biol. Macromol.* 244 (2023) 125346. <https://doi.org/10.1016/j.ijbiomac.2023.125346>.
- [108] P. Sannigrahi, A.J. Ragauskas, Fundamentals of Biomass Pretreatment by Fractionation, Aqueous Pretreat. Plant Biomass Biol. Chem. Convers. Fuels Chem. (2013) 201–222. <https://doi.org/10.1002/9780470975831.CH10>.
- [109] R.A. Young, R. Kundrot, D.A. Tillman, Pulp and Paper, Encycl. Phys. Sci. Technol. (2003) 249–265. <https://doi.org/10.1016/B0-12-227410-5/00619-0>.
- [110] M. Kienberger, S. Maitz, T. Pichler, P. Demmelmayer, Systematic Review on Isolation Processes for Technical Lignin, *Process.* 2021 Vol 9 Page 804 9 (2021) 804. <https://doi.org/10.3390/PR9050804>.
- [111] W. Zhu, H. Theliander, Precipitation of Lignin from Softwood Black Liquor: An Investigation of the Equilibrium and Molecular Properties of Lignin, *BioResources* 10 (2015) 1696–1714. <https://doi.org/10.15376/BIORES.10.1.1696-1715>.
- [112] P. Tomani, THE LIGNOBOOST PROCESS, *Cellul. Chem. Technol. Cellul. Chem Technol* 44 (2010) 53–58.
- [113] L. Kouisni, P. Holt-Hindle, K. Maki, M. Paleologou, The LignoForce SystemTM: A new process for the production of high-quality lignin from black liquor, *Pulp Pap. Can.* 115 (2014) 18–22.
- [114] J. Kihlman, The sequential liquid-lignin recovery and purification process: Analysis of integration aspects for a kraft pulp mill, *Nord. Pulp Pap. Res. J.* 31 (2016) 573–582. <https://doi.org/10.3183/NPPRJ-2016-31-04-P573-582/MACHINEREADABLECITATION/RIS>.
- [115] R. Alen, P. Patja, E. Sjostrom, Carbon dioxide precipitation of lignin from pine kraft black liquor., *Tappi J.* 62 (1979) 108–110.
- [116] P. Tomani, I. Ab, P. Axegård, N. Berglin, A. Lovell, D. Nordgren, F. Öhman, Integration of lignin removal into a kraft pulp mill and use of lignin as a bio-fuel, (n.d.).
- [117] R.J.A. Gosselink, J.E.G. van Dam, E. de Jong, E.L. Scott, J.P.M. Sanders, J. Li, G. Gellerstedt, Fractionation, analysis, and PCA modeling of properties of four technical lignins for prediction of their application potential in binders, 64 (2010) 193–200. <https://doi.org/10.1515/hf.2010.023>.
- [118] R. Ziesig, P. Tomani, H. Schweinebarth, L. Norberg, Production of a pure lignin product, Part 1: Distribution and removal of inorganics in Eucalyptus globulus kraft lignin, *Tappi J.* 13 (2014) 65–72.
- [119] J. Durruty, On the Local Filtration Properties of LignoBoost Lignin. Studies of the influence of xylan and ionic strength, CHALMERS UNIVERSITY OF TECHNOLOGY, 2017.
- [120] M.A. Hubbe, R. Alén, M. Paleologou, M. Kannangara, J. Kihlman, Lignin recovery from spent alkaline pulping liquors using acidification, membrane separation, and related processing steps: A review, *BioResources* 14 (2019) 2300–2351.
- [121] M. Suhr, G. Klein, I. Kourtzi, M. Rodrigo Gonzalo, G. Giner Santonja, S. Roudier, L. Delgado Sancho, Best Available Techniques (BAT) reference document for the production of pulp, paper and board., Publications Office of the European Union, Luxembourg, 2015. <https://data.europa.eu/doi/10.2791/370629> (accessed March 25, 2025).
- [122] R. Ziesig, P. Tomani, H. Theliander, PRODUCTION OF A PURE LIGNIN PRODUCT PART 2: SEPARATION OF LIGNIN FROM MEMBRANE FILTRATION PERMEATES OF BLACK LIQUOR, 2014.
- [123] A. Jablonskis, A. Arshanitsa, A. Arnautov, G. Telysheva, D. Evtuguin, Evaluation of Ligno BoostTM softwood kraft lignin epoxidation as an approach for its application in cured epoxy resins, *Ind. Crops Prod.* 112 (2018) 225–235. <https://doi.org/10.1016/j.indcrop.2017.12.003>.
- [124] M. Kannangara, M. Marinova, L. Fradette, J. Paris, Lignin recovery by acid precipitation in a kraft mill: An energy perspective, *J-For* 2 (2012) 28–32.
- [125] K. Wells, D. Pors, J. Foan, C. Chan, K. Maki, L. Kouisni, M. Paleologou, CO₂ Impacts of Commercial Scale Lignin Extraction at Hinton Pulp using the LignoForce Process & Lignin Substitution into Petroleum-based Products, 2015.
- [126] M.A. Lake, J.C. Blackburn, Process for recovering lignin, US20110294991A1, 2011.
- [127] G.H. Tomlinson, J.G.H. Tomlinson, Method of treating lignocellulosic material, US2406867A, 1946.
- [128] M.A. Lake, J.C. Blackburn, SLRPTM-AN INNOVATIVE LIGNIN-RECOVERY TECHNOLOGY, *Cellul. Chem. Technol. Cellul. Chem Technol* 48 (2014) 799–804.
- [129] J. Velez, M.C. Thies, Liquid Lignin from the SLRPTM Process: The Effect of Processing Conditions and Black-Liquor Properties, *J. Wood Chem. Technol.* 36 (2016) 27–41. <https://doi.org/10.1080/02773813.2015.1039545>.

- [130] X. Jiang, D. Savithri, X. Du, S. Pawar, H. Jameel, H.M. Chang, X. Zhou, Fractionation and Characterization of Kraft Lignin by Sequential Precipitation with Various Organic Solvents, *ACS Sustain. Chem. Eng.* 5 (2017) 835–842. <https://doi.org/10.1021/ACSSUSCHEMEENG.6B02174>.
- [131] D.S. Bajwa, G. Pourhashem, A.H. Ullah, S.G. Bajwa, A concise review of current lignin production, applications, products and their environment impact, *Ind. Crops Prod.* 139 (2019) 111526.
- [132] N.I. Jeffri, N.F. Mohammad Rawi, M.H. Mohamad Kassim, C.K. Abdullah, Unlocking the potential: Evolving role of technical lignin in diverse applications and overcoming challenges, *Int. J. Biol. Macromol.* 274 (2024) 133506. <https://doi.org/10.1016/j.ijbiomac.2024.133506>.
- [133] M.C. Thies, A.S. Klett, Recovery of Low-Ash and Ultrapure Lignins from Alkaline Liquor By-Product Streams, in: Z. Fang, Jr. Smith Richard L. (Eds.), *Prod. Biofuels Chem. Lignin*, Springer, Singapore, 2016: pp. 55–78. https://doi.org/10.1007/978-981-10-1965-4_3.
- [134] S. Vaz Jr., Extraction Processes, in: S. Vaz Jr. (Ed.), *Lignin Macromol. Compend. Sustain. Technol.*, Springer Nature Switzerland, Cham, 2024: pp. 45–54. https://doi.org/10.1007/978-3-031-75511-8_4.
- [135] C. Fitzgerald, Improving Lignin Recovery From Paper Mill and Biorefinery Waste Streams via Liquid-Phase Splitting, Dissertation, Clemson University, 2023. https://open.clemson.edu/all_dissertations/3257.
- [136] F.E. Brauns, D.A. Brauns, *The Chemistry of Lignin*, Elsevier, 1960. <https://doi.org/10.1016/C2013-0-12026-0>.
- [137] J.J.J. Keilen, F.J. Ball, R.W. Gressang, Method of coagulating colloidal lignates in aqueous dispersions, US2623040A, 1952.
- [138] F.J. Ball, W.G. Vardell, Decantation of lignin, US2997466A, 1961.
- [139] F.J. Ball, W.G. Vardell, Continuous acidulation and coagulation of lignin in black liquor, US3048576A, 1962.
- [140] P. Arthur, J.J.J. Keilen, L.F. Drum, Method of producing lignin from black liquor, US2464828A, 1949.
- [141] S.H. Beis, S. Mukkamala, N. Hill, J. Joseph, C. Baker, B. Jensen, E.A. Stemmler, M.C. Wheeler, B.G. Frederick, A. van Heiningen, A.G. Berg, W.J. DeSisto, Fast pyrolysis of lignins, *BioResources* 5 (2010) 1408–1424. <https://doi.org/10.15376/biores.5.3.1408-1424>.
- [142] W.M. Goldmann, J. Ahola, M. Mikola, J. Tanskanen, Solubility and fractionation of Indulin AT kraft lignin in ethanol-water media, *Sep. Purif. Technol.* 209 (2019) 826–832. <https://doi.org/10.1016/j.seppur.2018.06.054>.
- [143] F.J. Ball, P. Richard, Treatment of kraft black liquor and product, US2976273A, 1961. <https://patents.google.com/patent/US2976273A/en> (accessed May 12, 2025).
- [144] Indulin® AT - Ingevity, (n.d.). <https://www.ingevity.com/products/indulin-at-batteries/> (accessed May 12, 2025).
- [145] M.J. Suota, T.A. da Silva, S.F. Zawadzki, G.L. Sasaki, F.A. Hansel, M. Paleologou, L.P. Ramos, Chemical and structural characterization of hardwood and softwood LignoForce™ lignins, *Ind. Crops Prod.* 173 (2021) 114138. <https://doi.org/10.1016/J.INDCROP.2021.114138>.
- [146] W.G. Glasser, About Making Lignin Great Again—Some Lessons From the Past, *Front. Chem.* 7 (2019). <https://www.frontiersin.org/article/10.3389/fchem.2019.00565> (accessed January 27, 2022).
- [147] C. Gazzurelli, A. Migliori, P.P. Mazzeo, M. Carcelli, S. Pietarinen, G. Leonardi, A. Pandolfi, D. Rogolino, P. Pelagatti, Making Agriculture More Sustainable: An Environmentally Friendly Approach to the Synthesis of Lignin@Cu Pesticides, *ACS Sustain. Chem. Eng.* 8 (2020) 14886–14895. <https://doi.org/10.1021/acssuschemeng.0c04645>.
- [148] S. Mastrolitti, E. Borsella, A. Giuliano, M.T. Petrone, I.D. Bari, R. Gosselink, G. van Erven, E. Annevelink, K.S. Triantafyllidis, H. Stichnothe, Sustainable lignin valorization, *IEA Bioenergy*, 2021. https://www.ieabioenergy.com/wp-content/uploads/2022/01/Sustainable-Lignin-Valorization_rev26-01-2022.pdf.
- [149] R. Nadányi, M. Džuganová, A. Ház, OPTIMIZED LIGNIN RECOVERY FROM BLACK LIQUOR FOR ENHANCED MECHANICAL PROPERTIES OF ACRYLONITRILE BUTADIENE RUBBER COMPOSITES, *Acta Fac. Xylologiae Zvolen* 66 (2024) 51–60.
- [150] A. Moreno, J. Delgado-Lijarcio, J.C. Ronda, M. Galià, G. Lligadas, Monolithic, hybrid and particulate lignin-based hydrogels for sustainable CO₂ capture, *Green Chem.* 27 (2025) 1828–1837. <https://doi.org/10.1039/D4GC05489J>.
- [151] F.H. Blindheim, J. Ruwoldt, The Effect of Sample Preparation Techniques on Lignin Fourier Transform Infrared Spectroscopy, *Polymers* 15 (2023) 2901. <https://doi.org/10.3390/polym15132901>.
- [152] E.S. Esakkimuthu, D. DeVallance, I. Pylypczuk, A. Moreno, M.H. Sipponen, Multifunctional lignin-poly(lactic acid) biocomposites for packaging applications, *Front. Bioeng. Biotechnol.* 10 (2022). <https://doi.org/10.3389/fbioe.2022.1025076>.
- [153] T. Li, S. Takkellapati, The current and emerging sources of technical lignins and their applications, *Biofuels Bioprod. Biorefining Biofpr* 0 (2018) 1–32. <https://doi.org/10.1002/bbb.1913>.

- [154] C.G. Boeriu, D. Bravo, R.J.A. Gosselink, J.E.G. van Dam, Characterisation of structure-dependent functional properties of lignin with infrared spectroscopy, *Ind. Crops Prod.* 20 (2004) 205–218. <https://doi.org/10.1016/j.indcrop.2004.04.022>.
- [155] Z. Hu, Du ,Xueyu, Liu ,Jie, Chang ,Hou-min, H. and Jameel, Structural Characterization of Pine Kraft Lignin: BioChoice Lignin vs Indulin AT, *J. Wood Chem. Technol.* 36 (2016) 432–446. <https://doi.org/10.1080/02773813.2016.1214732>.
- [156] W.M. Goldmann, Ahola, Juha, O. Mankinen, A.M. Kantola, S. Komulainen, V.-V. Telkki, J. Tanskanen, Determination of Phenolic Hydroxyl Groups in Technical Lignins by Ionization Difference Ultraviolet Spectrophotometry ($\Delta\epsilon$ -IDUS method), *Period. Polytech. Chem. Eng.* (2016). <https://doi.org/10.3311/PPch.9269>.
- [157] F.R. Vieira, S. Magina, D.V. Evtuguin, A. Barros-Timmons, Lignin as a Renewable Building Block for Sustainable Polyurethanes, *Materials* 15 (2022) 6182. <https://doi.org/10.3390/ma15176182>.
- [158] P.D. Kouris, D.J.G.P. van Osch, G.J.W. Cremers, M.D. Boot, E.J.M. Hensen, Mild thermolytic solvolysis of technical lignins in polar organic solvents to a crude lignin oil, *Sustain. Energy Fuels* 4 (2020) 6212–6226. <https://doi.org/10.1039/D0SE01016B>.
- [159] S. Sahoo, M.Ö. Seydibeyoğlu, A.K. Mohanty, M. Misra, Characterization of industrial lignins for their utilization in future value added applications, *Biomass Bioenergy* 35 (2011) 4230–4237. <https://doi.org/10.1016/j.biombioe.2011.07.009>.
- [160] J. Sameni, S.A. Jaffer, M. Sain, Thermal and mechanical properties of soda lignin/HDPE blends, *Compos. Part Appl. Sci. Manuf.* 115 (2018) 104–111. <https://doi.org/10.1016/j.compositesa.2018.09.016>.
- [161] PLT Innovations, ProtobindTM 1000 DataSheet, (n.d.). https://www.plt-innovations.com/application/files/8517/0532/7469/DataSheet_PB1000_PLT-I_v2.pdf (accessed May 27, 2025).
- [162] M.V. Alonso, J.J. Rodríguez, M. Oliet, F. Rodríguez, J. García, M.A. Gilarranz, Characterization and structural modification of ammonic lignosulfonate by methylolation, *J. Appl. Polym. Sci.* 82 (2001) 2661–2668. <https://doi.org/10.1002/app.2119>.
- [163] E.S. Wibowo, B.-D. Park, Chemical and Thermal Characteristics of Ion-Exchanged Lignosulfonate, *Molecules* 28 (2023) 2755. <https://doi.org/10.3390/molecules28062755>.
- [164] R.J.A. Gosselink, A. Abächerli, H. Semke, R. Malherbe, P. Käuper, A. Nadif, J.E.G. van Dam, Analytical protocols for characterisation of sulphur-free lignin, *Ind. Crops Prod.* 19 (2004) 271–281. <https://doi.org/10.1016/j.indcrop.2003.10.008>.
- [165] T. Stevanovic, G.K. YOYA, Organosolv process for the extraction of highly pure lignin and products comprising the same, WO2016197233A1, 2016. <https://patents.google.com/patent/WO2016197233A1/en> (accessed May 15, 2025).
- [166] R.H. MCKEE, Recovery of cellulose and lignin, GB560492A, 1944.
- [167] G.H. Tomlinson, G.H. Tomlinson Jr., Improvements in the recovery of lignin from black liquor, GB664811A, 1952.
- [168] J.H. Lora, R. Katzen, M. Cronlund, C.F. Wu, Recovery of lignin, US4764596A, 1988.
- [169] F. Öhman, H. Theliander, P. Tomani, P. Axegard, Method for separating lignin from black liquor, WO2006031175A1, 2006.
- [170] F. Ohman, H. Theliander, P. Tomani, P. Axegard, Method for separating lignin from black liquor, a lignin product, and use of a lignin product for the production of fuels or materials, US9382389B2, 2016.
- [171] F. ALBAN, E.G. Lewis, Y. Fukuda, Methods for lignin extraction, US20240158637A1, 2024.
- [172] C.G. Robertson, N.J. Hardman, Nature of Carbon Black Reinforcement of Rubber: Perspective on the Original Polymer Nanocomposite, *Polymers* 13 (2021) 538. <https://doi.org/10.3390/polym13040538>.
- [173] S. Rebelo, S.M. Shaikh, Hepatic and renal impairment and degenerative changes caused by carbon black nanoparticles in mice: Carbon nanoparticles effect in mice, *Indian J. Exp. Biol. IJEB* 63 (2025) 66–75.
- [174] R. Nirajan, A.K. Thakur, The Toxicological Mechanisms of Environmental Soot (Black Carbon) and Carbon Black: Focus on Oxidative Stress and Inflammatory Pathways, *Front. Immunol.* 8 (2017). <https://doi.org/10.3389/fimmu.2017.00763>.
- [175] M. Dadkhah, M. Messori, A comprehensive overview of conventional and bio-based fillers for rubber formulations sustainability, *Mater. Today Sustain.* 27 (2024) 100886. <https://doi.org/10.1016/j.mtsust.2024.100886>.
- [176] M. Fazeli, S. Mukherjee, H. Baniasadi, R. Abidnejad, M. Mujtaba, J. Lipponen, J. Seppälä, O.J. Rojas, Lignin beyond the *status quo* : recent and emerging composite applications, *Green Chem.* 26 (2024) 593–630. <https://doi.org/10.1039/D3GC03154C>.
- [177] N.A. Mohamad Aini, N. Othman, M.H. Hussin, K. Sahakaro, N. Hayeemasae, Lignin as Alternative Reinforcing Filler in the Rubber Industry: A Review, *Front. Mater.* 6 (2020). <https://doi.org/10.3389/fmats.2019.00329>.

- [178] J.J. Keilen, A. Pollak, Lignin for Reinforcing Rubber, *Rubber Chem. Technol.* 20 (1947) 1099–1108. <https://doi.org/10.5254/1.3543321>.
- [179] P. Arthur, Lignin reinforced rubber and method of making same, US2676931A, 1954.
- [180] T.R. Griffith, D.W. MacGregor, Aids in Vulcanization of Lignin–Natural Rubber Coprecipitates, *Ind. Eng. Chem.* 45 (1953) 380–386. <https://doi.org/10.1021/ie50518a039>.
- [181] D. Barana, S.D. Ali, A. Salanti, M. Orlandi, L. Castellani, T. Hanel, L. Zoia, Influence of Lignin Features on Thermal Stability and Mechanical Properties of Natural Rubber Compounds, *ACS Sustain. Chem. Eng.* 4 (2016) 5258–5267. <https://doi.org/10.1021/acssuschemeng.6b00774>.
- [182] N.A. Mohamad Aini, N. Othman, M.H. Hussin, K. Sahakaro, N. Hayeemasae, Lignin as Alternative Reinforcing Filler in the Rubber Industry: A Review, *Front. Mater.* 6 (2020). <https://doi.org/10.3389/fmats.2019.00329>.
- [183] Å. Henrik-Klemens, F. Caputo, R. Ghaffari, G. Westman, U. Edlund, L. Olsson, A. Larsson, The glass transition temperature of isolated native, residual, and technical lignin, *Holzforschung* 78 (2024) 216–230. <https://doi.org/10.1515/hf-2023-0111>.
- [184] S. Sen, S. Patil, D.S. Argyropoulos, Thermal properties of lignin in copolymers, blends, and composites: a review, *Green Chem.* 17 (2015) 4862–4887. <https://doi.org/10.1039/C5GC01066G>.
- [185] J.E. Mark, B. Erman, M. Roland, *The Science and Technology of Rubber*, Academic Press, 2013.
- [186] A. Bova, Stretching the applications of biomass: Development of lignin based thermoplastic elastomers and composite materials, *Dr. Diss.* (2021). https://trace.tennessee.edu/utk_graddiss/6634.
- [187] J. Koskinen, N. Kemppainen, E. Sarlin, Lignin dispersion in polybutadiene rubber (BR) with different mixing parameters, *Prog. Rubber Plast. Recycl. Technol.* (2024) 14777606241281619. <https://doi.org/10.1177/14777606241281619>.
- [188] S. Hait, D. De, P. Ghosh, J. Chanda, R. Mukhopadhyay, S. Dasgupta, A. Sallat, M. Al Aiti, K.W. Stöckelhuber, S. Wießner, G. Heinrich, A. Das, Understanding the Coupling Effect between Lignin and Polybutadiene Elastomer, *J. Compos. Sci.* 5 (2021) 154. <https://doi.org/10.3390/jcs5060154>.
- [189] S. Hait, D. De, A.K. Ghosh, M. Al Aiti, P. Ghosh, J. Chanda, R. Mukhopadhyay, S. Dasgupta, S. Wießner, G. Heinrich, A. Das, Treasuring waste lignin as superior reinforcing filler in high *cis*-polybutadiene rubber: A direct comparative study with standard reinforcing silica and carbon black, *J. Clean. Prod.* 299 (2021) 126841. <https://doi.org/10.1016/j.jclepro.2021.126841>.
- [190] C.D. Tran, J. Chen, J.K. Keum, A.K. Naskar, A New Class of Renewable Thermoplastics with Extraordinary Performance from Nanostructured Lignin-Elastomers, *Adv. Funct. Mater.* 26 (2016) 2677–2685. <https://doi.org/10.1002/adfm.201504990>.
- [191] Z. Wu, X. Lin, J. Teng, M. Li, J. Song, C. Huang, R. Wang, H. Ying, L. Zhang, C. Zhu, Recent Advances of Lignin Functionalization for High-Performance and Advanced Functional Rubber Composites, *Biomacromolecules* 24 (2023) 4553–4567. <https://doi.org/10.1021/acs.biomac.3c00606>.
- [192] Z. Kramárová, P. Alexy, I. Chodák, E. Špirk, I. Hudec, B. Košíková, A. Gregorová, P. Šuri, J. Feranc, P. Bugaj, M. Ďuračka, Biopolymers as fillers for rubber blends, *Polym. Adv. Technol.* 18 (2007) 135–140. <https://doi.org/10.1002/pat.803>.
- [193] T. Bova, C.D. Tran, M.Y. Balakshin, J. Chen, E.A. Capanema, A.K. Naskar, An approach towards tailoring interfacial structures and properties of multiphase renewable thermoplastics from lignin–nitrile rubber, *Green Chem.* 18 (2016) 5423–5437. <https://doi.org/10.1039/C6GC01067A>.
- [194] M. Laleg, N. Jemaa, W.W.A. DAJANI, Y. ZHANG, M. Paleologou, Meltable lignin compositions, method for producing them and their uses, US20210040273A1, 2021.
- [195] G. Wypych, *Handbook of Plasticizers*, ChemTec Publishing, 2004.
- [196] J. Bouajila, P. Dole, C. Joly, A. Limare, Some laws of a lignin plasticization, *J. Appl. Polym. Sci.* 102 (2006) 1445–1451. <https://doi.org/10.1002/app.24299>.
- [197] J. Kruželák, M. Džuganová, A. Kvasničáková, J. Preťo, J. Hronkovič, I. Hudec, Influence of Plasticizers on Cross-Linking Process, Morphology, and Properties of Lignosulfonate-Filled Rubber Compounds, *Polymers* 17 (2025) 393. <https://doi.org/10.3390/polym17030393>.
- [198] J. Brandrup, E.H. Immergut, E.A. Grulke, eds., *Polymer handbook*, 4th ed, Wiley, New York, 1999.
- [199] D. Kun, B. Pukánszky, Polymer/lignin blends: Interactions, properties, applications, *Eur. Polym. J.* 93 (2017) 618–641. <https://doi.org/10.1016/j.eurpolymj.2017.04.035>.
- [200] J. Kruželák, K. Hložeková, A. Kvasničáková, M. Džuganová, I. Chodák, I. Hudec, Application of Plasticizer Glycerol in Lignosulfonate-Filled Rubber Compounds Based on SBR and NBR, *Materials* 16 (2023) 635. <https://doi.org/10.3390/ma16020635>.
- [201] P. ALEXY, J. FERANC, Z. KRAMAROVA, M. HAJSOVA, M. DURACKA, D. MOSKOVA, I. CHODAK, S. ILISCH, Application of Lignins in Rubber Compounds, *Appl. Lignins Rubber Compd.* 61 (2008) 26–32.

- [202] M. Džuganová, R. Stoček, M. Pöschl, J. Kruželák, A. Kvasničáková, J. Hronkovič, J. Prešo, Strategy for reducing rubber wear emissions: The prospect of using calcium lignosulfonate, *Express Polym. Lett.* 18 (2024) 1277–1290. <https://doi.org/10.3144/expresspolymlett.2024.95>.
- [203] J. Datta, P. Parcheta, J. Surówka, Softwood-lignin/natural rubber composites containing novel plasticizing agent: Preparation and characterization, *Ind. Crops Prod.* 95 (2017) 675–685. <https://doi.org/10.1016/j.indcrop.2016.11.036>.
- [204] J. Datta, P. Parcheta, A comparative study on selective properties of Kraft lignin–natural rubber composites containing different plasticizers, *Iran. Polym. J.* 26 (2017) 453–466. <https://doi.org/10.1007/s13726-017-0534-0>.
- [205] K. Bahl, N. Swanson, C. Pugh, S.C. Jana, Polybutadiene-g-poly(pentafluorostyrene) as a coupling agent for lignin-filled rubber compounds, *Polymer* 55 (2014) 6754–6763. <https://doi.org/10.1016/j.polymer.2014.11.008>.
- [206] Y. Ikeda, T. Phakkeeree, P. Junkong, H. Yokohama, P. Phinyocheep, R. Kitano, A. Kato, Reinforcing biofiller “Lignin” for high performance green natural rubber nanocomposites, *RSC Adv.* 7 (2017) 5222–5231. <https://doi.org/10.1039/C6RA26359C>.
- [207] A. Adibi, D. Jubinville, G. Chen, T.H. Mekonnen, In-situ surface grafting of lignin onto an epoxidized natural rubber matrix: A masterbatch filler for reinforcing rubber composites, *React. Funct. Polym.* 197 (2024) 105856. <https://doi.org/10.1016/j.reactfunctpolym.2024.105856>.
- [208] C. Jiang, H. He, X. Yao, P. Yu, L. Zhou, D. Jia, In situ dispersion and compatibilization of lignin/epoxidized natural rubber composites: reactivity, morphology and property, *J. Appl. Polym. Sci.* 132 (2015). <https://doi.org/10.1002/app.42044>.
- [209] C. Jiang, H. He, X. Yao, P. Yu, L. Zhou, D. Jia, Self-crosslinkable lignin/epoxidized natural rubber composites, *J. Appl. Polym. Sci.* 131 (2014). <https://doi.org/10.1002/app.41166>.
- [210] K. Hložeková, J. Kruželák, M. Džuganová, I. Hudec, Properties of Rubber Blends Filled with Calcium Lignosulfonate, *Macromol. Symp.* 404 (2022) 2100335. <https://doi.org/10.1002/masy.202100335>.
- [211] J. Kruželák, M. Džuganová, K. Hložeková, A. Kvasničáková, A. Ház, R. Nadányi, H. Krump, I. Hudec, Sulfur and peroxide curing of NBR based rubber compounds filled with kraft lignin and calcium lignosulfonate, *J. Appl. Polym. Sci.* 141 (2024) e55593. <https://doi.org/10.1002/app.55593>.
- [212] H. Wang, W. Liu, J. Huang, D. Yang, X. Qiu, Bioinspired Engineering towards Tailoring Advanced Lignin/Rubber Elastomers, *Polymers* 10 (2018) 1033. <https://doi.org/10.3390/polym10091033>.
- [213] H. KYSELÁ, ALEXY. Výroba a spracovanie kaučukov a gumen. 1. vyd. Bratislava: Nakladateľstvo STU, 2010, 269 s, (n.d.).
- [214] K. Bahl, T. Miyoshi, S.C. Jana, Hybrid fillers of lignin and carbon black for lowering of viscoelastic loss in rubber compounds, *Polymer* 55 (2014) 3825–3835. <https://doi.org/10.1016/j.polymer.2014.06.061>.
- [215] K. Bahl, Towards development of lignin reinforced elastomeric compounds with reduced energy dissipation, Ph.D., The University of Akron, 2014. <https://www.proquest.com/docview/1645957221/abstract/1C4CC3F8FDA44A46PQ/1> (accessed May 12, 2025).
- [216] R. Liu, J. Li, T. Lu, X. Han, Z. Yan, S. Zhao, H. Wang, Comparative study on the synergistic reinforcement of lignin between carbon black/lignin and silica/lignin hybrid filled natural rubber composites, *Ind. Crops Prod.* 187 (2022) 115378. <https://doi.org/10.1016/j.indcrop.2022.115378>.
- [217] J. Kubáčková, Gumárenské zmesi s prírodnými plnivami, Slovak University of Technology in Bratislava, 2014.
- [218] G. Wypych, *Handbook of Antioxidants*, Elsevier, 2025.
- [219] B. Košíková, A. Gregorová, A. Osvald, J. Krajčovičová, Role of lignin filler in stabilization of natural rubber-based composites, *J. Appl. Polym. Sci.* 103 (2007) 1226–1231. <https://doi.org/10.1002/app.24530>.
- [220] U.E.N.C. for E. Assessment, Study on use of lignin as an antioxidant in SBR based tire tread compound, (2009). https://hero.epa.gov/hero/index.cfm/reference/details/reference_id/9108277 (accessed May 12, 2025).
- [221] J. Kubáčková, J. Feranc, I. Hudec, Š. Šutý, J. Annus, Antioxidant properties of lignin in rubber blends, (2013).
- [222] R.C. Tomazi, N.B. Guerra, M. Giovanel, S. Moresco, J. da Silva Crespo, Evaluation of vulcanization systems in natural rubber elastomeric tire sidewall compositions with lignin as a stabilizing agent, *Polym. Bull.* 80 (2023) 8977–8994. <https://doi.org/10.1007/s00289-022-04485-8>.
- [223] J.L. Espinoza-Acosta, P.I. Torres-Chávez, B. Ramírez-Wong, C.M. López-Saiz, B. Montaño-Leyva, Antioxidant, antimicrobial, and antimutagenic properties of technical lignins and their applications, *BioResources* 11 (2016) 5452–5481. https://doi.org/10.15376/biores.11.2.Espinoza_Acosta.
- [224] T.J. Gutiérrez, *Reactive and Functional Polymers Volume One: Biopolymers, Polyesters, Polyurethanes, Resins and Silicones*, Springer Nature, 2020.

- [225] N.A. Mohamad Aini, N. Othman, M.H. Hussin, K. Sahakaro, N. Hayeemasae, Effect of hybrid carbon black/lignin on rheological, mechanical and thermal stability properties of NR/BR composites, *Plast. Rubber Compos.* 51 (2022) 293–305. <https://doi.org/10.1080/14658011.2021.1981718>.
- [226] H.D.A. Gunasekara, S.M. Egodage, Study on use of Lignin Based Antioxidant in a Solid Tire Tread Compound, (n.d.).
- [227] N. Kanbargi, D. Hoskins, S. Gupta, Z. Yu, Y. Shin, Y. Qiao, D.R. Merkel, C.C. Bowland, N. Labbé, K.L. Simmons, A.K. Naskar, A renewable lignin-based thermoplastic adhesive for steel joining, *Eur. Polym. J.* 189 (2023) 111981. <https://doi.org/10.1016/j.eurpolymj.2023.111981>.
- [228] Z. Yu, N. Kanbargi, S. Gupta, Y. Shin, Y. Qiao, C.C. Bowland, D.R. Merkel, K.L. Simmons, A.K. Naskar, Acrylonitrile-butadiene-lignin thermoplastic rubber adhesive for enhanced metal-to-metal joining, *Polym. Compos.* 45 (2024) 7178–7190. <https://doi.org/10.1002/pc.28258>.
- [229] A.F. Halasa, J.J.A. Verthe, A. Lechtenboehmer, EP2433813 Wire coat compositions for rubber articles, EP2433813, 2012.
- [230] WIPO - World Intellectual Property Organization, (n.d.). <https://www.wipo.int/portal/en/> (accessed May 19, 2025).
- [231] S.P. Boutsicaris, Lignin reinforced synthetic rubber, US4477612A, 1984.
- [232] C. Veas, E.L. Hotaling, Lignin in tire components, US20110073229A1, 2011.
- [233] K. FUJIKURA, Rubber composition for tire, method of preparing the same, and pneumatic tire, US20130197132A1, 2013.
- [234] N.R. Washburn, H. Chung, Lignin-containing polymers and compositions including lignin-containing polymers, US9914870B2, 2018.
- [235] T. Murai, H. Nakagawa, M. Matsumoto, Lignin derivative, lignin resin composition, rubber composition, and molding material, US10138377B2, 2018.
- [236] Q. XUEQING, L. WEIFENG, W. HAIXU, H. JINHAO, Y. DONGJIE, L. HONGMING, Lignin-reinforced NBR/PVC elastomer and preparation method thereof, CN109608713, 2020.
- [237] Q. XUEQING, L. WEIFENG, W. HAIXU, H. JINHAO, Y. DONGJIE, L. HONGMING, Lignin/nitrile butadiene rubber composite and preparation method thereof, CN107383475, 2019.
- [238] L. WEIFENG, Q. XUEQING, M. JIE, H. JINHAO, W. HAIXU, Lignin/EPDM (ethylene propylene diene monomer) rubber composite and preparation method thereof, CN107337857, 2019. https://patentscope.wipo.int/search/en/detail.jsf?docId=CN207656338&_cid=P21-MAQM1X-78927-1 (accessed May 16, 2025).
- [239] S. PAN, X. XIMING, W. LEILEI, L. JING, Q. XUNCHANG, L. CUIYUN, Nitrile rubber/lignin composition, nitrile rubber/lignin composite material, and preparation method and application thereof, CN111423637, 2020.
- [240] Z. CHENJIE, Y. HANJIE, L. MING, O. PINGKAI, S. JIANNONG, X. XINJIAN, Z. WEI, S. TAO, Application of lignin in preparation of radial tires, CN111748133, 2020.
- [241] T. Manabe, S. Nishihata, Y. Kato, Rubber/Fiber Adhesion Treating Agent and Synthetic Fiber Cord for Rubber Reinforcement Using Same, WO2023095655, 2023.
- [242] A. OJALA, N. KEMPPAINEN, EP4434765 A PNEUMATIC TYRE COMPRISING RECOVERED FILLER, EP4434765, 2024.
- [243] L. QIANG, W. DONGLIN, L. WEI, CN118725423 High-wear-resistance conveyor belt cover rubber and preparation method thereof, CN118725423, 2024.
- [244] L. TADIELLO, L. GIANNINI, S. GUERRA, TIRES FOR VEHICLE WHEELS, US20250033411, 2025.
- [245] L. Dehne, C. Vila Babarro, B. Saake, K.U. Schwarz, Influence of lignin source and esterification on properties of lignin-polyethylene blends, *Ind. Crops Prod.* 86 (2016) 320–328. <https://doi.org/10.1016/j.indcrop.2016.04.005>.
- [246] J. Sternberg, O. Sequerth, S. Pilla, Green chemistry design in polymers derived from lignin: review and perspective, *Prog. Polym. Sci.* 113 (2021) 101344. <https://doi.org/10.1016/j.progpolymsci.2020.101344>.
- [247] C. Wang, S.S. Kelley, R.A. Venditti, Lignin-Based Thermoplastic Materials, *ChemSusChem* 9 (2016) 770–783. <https://doi.org/10.1002/cssc.201501531>.
- [248] V. Romhányi, D. Kun, B. Pukánszky, Correlations among Miscibility, Structure, and Properties in Thermoplastic Polymer/Lignin Blends, *ACS Sustain. Chem. Eng.* 6 (2018) 14323–14331. <https://doi.org/10.1021/acssuschemeng.8b02989>.
- [249] Y. Byun, Y. Zhang, X. Geng, Chapter 5 - Plasticization and Polymer Morphology, in: J.H. Han (Ed.), *Innov. Food Packag.* Second Ed., Academic Press, San Diego, 2014: pp. 87–108. <https://doi.org/10.1016/B978-0-12-394601-0.00005-9>.
- [250] M. Kutz, *Applied Plastics Engineering Handbook: Processing, Sustainability, Materials, and Applications*, Elsevier, 2023.
- [251] H. Chung, N.R. Washburn, Chemistry of lignin-based materials, *Green Mater.* 1 (2013) 137–160. <https://doi.org/10.1680/gmat.12.00009>.

- [252] A. Duval, M. Lawoko, A review on lignin-based polymeric, micro- and nano-structured materials, *React. Funct. Polym.* 85 (2014) 78–96. <https://doi.org/10.1016/j.reactfunctpolym.2014.09.017>.
- [253] S. Laurichesse, L. Avérous, Chemical modification of lignins: Towards biobased polymers, *Prog. Polym. Sci.* 39 (2014) 1266–1290. <https://doi.org/10.1016/j.progpolymsci.2013.11.004>.
- [254] D. Feldman, Lignin and Its Polyblends — A Review, in: T.Q. Hu (Ed.), *Chem. Modif. Prop. Usage Lignin*, Springer US, Boston, MA, 2002: pp. 81–99. https://doi.org/10.1007/978-1-4615-0643-0_5.
- [255] O. Faruk, M. Sain, Lignin in Polymer Composites, William Andrew, 2015.
- [256] K. Levon, J. Huhtala, B. Malm, J.J. Lindberg, Improvement of the thermal stabilization of polyethylene with lignosulphonate, *Polymer* 28 (1987) 745–750. [https://doi.org/10.1016/0032-3861\(87\)90223-0](https://doi.org/10.1016/0032-3861(87)90223-0).
- [257] P. Alexy, B. Košíková, G. Podstránska, The effect of blending lignin with polyethylene and polypropylene on physical properties, *Polymer* 41 (2000) 4901–4908. [https://doi.org/10.1016/S0032-3861\(99\)00714-4](https://doi.org/10.1016/S0032-3861(99)00714-4).
- [258] B. Košíková, M. Kacurakova, V. Demianova, Photooxidation of the composite lignin/polypolypropylene films, *Chem Pap* 47 (1993) 132–136.
- [259] M. Mikulášová, B. Košíková, P. Alexy, F. Kačík, E. Urgelová, Effect of blending lignin biopolymer on the biodegradability of polyolefin plastics, *World J. Microbiol. Biotechnol.* 17 (2001) 601–607. <https://doi.org/10.1023/A:1012415023385>.
- [260] M. Ghozali, W.K. Restu, I. Juliana, Y. Meliana, E. Triwulandari, Chapter 9 - Effect of lignin on bio-based/oil-based polymer blends, in: D. Puglia, C. Santulli, F. Sarasini (Eds.), *Micro Nanolignin Aqueous Dispers. Polym.*, Elsevier, 2022: pp. 251–291. <https://doi.org/10.1016/B978-0-12-823702-1.00009-8>.
- [261] P. Alexy, B. Košíková, G. Crkonová, A. Gregorová, P. Martiš, Modification of lignin–polyethylene blends with high lignin content using ethylene–vinylacetate copolymer as modifier, *J. Appl. Polym. Sci.* 94 (2004) 1855–1860. <https://doi.org/10.1002/app.20716>.
- [262] M. Parit, Z. Jiang, Towards lignin derived thermoplastic polymers, *Int. J. Biol. Macromol.* 165 (2020) 3180–3197. <https://doi.org/10.1016/j.ijbiomac.2020.09.173>.
- [263] J. Li, Y. He, Y. Inoue, Thermal and mechanical properties of biodegradable blends of poly(L-lactic acid) and lignin, *Polym. Int.* 52 (2003) 949–955. <https://doi.org/10.1002/pi.1137>.
- [264] S. Baumberger, C. Lapierre, B. Monties, D. Lourdin, P. Colonna, Preparation and properties of thermally moulded and cast lignosulfonates-starch blends, *Ind. Crops Prod.* 6 (1997) 253–258. [https://doi.org/10.1016/S0926-6690\(97\)00015-0](https://doi.org/10.1016/S0926-6690(97)00015-0).
- [265] Y. Teramoto, S.-H. Lee, T. Endo, Phase Structure and Mechanical Property of Blends of Organosolv Lignin Alkyl Esters with Poly(ϵ -caprolactone), *Polym. J.* 41 (2009) 219–227. <https://doi.org/10.1295/polymj.PJ2008301>.
- [266] L. Dehne, C. Vila, B. Saake, K.U. Schwarz, Esterification of Kraft lignin as a method to improve structural and mechanical properties of lignin-polyethylene blends, *J. Appl. Polym. Sci.* 134 (2017). <https://doi.org/10.1002/app.44582>.
- [267] K. Komisarz, T.M. Majka, K. Pielichowski, Chemical and Physical Modification of Lignin for Green Polymeric Composite Materials, *Materials* 16 (2023) 16. <https://doi.org/10.3390/ma16010016>.
- [268] R.R.N. Sailaja, M.V. Deepthi, Mechanical and thermal properties of compatibilized composites of polyethylene and esterified lignin, *Mater. Des.* 31 (2010) 4369–4379. <https://doi.org/10.1016/j.matdes.2010.03.046>.
- [269] P.R.S. Bittencourt, E.A.G. Pineda, A.A.W. Hechenleitner, Kraft lignin/PVA blends studied by thermal analysis and FTIR spectroscopy, in: Proc. 5th Int. Symp. Nat. Polym. Compos. 8th Braz. Symp. Chem. Lignins Wood Compon., Águas de Lindóia, 2004.
- [270] S. Kubo, J.F. Kadla, The Formation of Strong Intermolecular Interactions in Immiscible Blends of Poly(vinyl alcohol) (PVA) and Lignin, *Biomacromolecules* 4 (2003) 561–567. <https://doi.org/10.1021/bm025727p>.
- [271] R. Ratnawati, R. Wulandari, A. Kumoro, H. Hadiyanto, Response surface methodology for formulating PVA/starch/lignin biodegradable plastic. *Emerging Science Journal*, 6 (2), 238-255. doi: 10.28991/ESJ-2022-06-02-03, 2022.
- [272] L. Lazzari, E. Domingos, L. Silva, A. Kuznetsov, W. Romão, J. Araujo, Kraft lignin and polyethylene terephthalate blends: effect on thermal and mechanical properties, *Polímeros* 29 (2020) e2019055. <https://doi.org/10.1590/0104-1428.06618>.
- [273] J. Minet, A. Cayla, C. Campagne, Lignin as Sustainable Antimicrobial Fillers to Develop PET Multifilaments by Melting Process, in: A. Sand, E. Zaki (Eds.), *Org. Polym.*, IntechOpen, Rijeka, 2019. <https://doi.org/10.5772/intechopen.86634>.
- [274] J.F. Kadla, S. Kubo, Lignin-based polymer blends: analysis of intermolecular interactions in lignin–synthetic polymer blends, *Compos. Part Appl. Sci. Manuf.* 35 (2004) 395–400. <https://doi.org/10.1016/j.compositesa.2003.09.019>.

- [275] Q. Yu, A. Bahi, F. Ko, Influence of Poly(ethylene oxide) (PEO) Percent and Lignin Type on the Properties of Lignin/PEO Blend Filament, *Macromol. Mater. Eng.* 300 (2015) 1023–1032. <https://doi.org/10.1002/mame.201500045>.
- [276] L.-S. Ebers, R. Auvergne, B. Boutevin, M.-P. Laborie, Impact of PEO structure and formulation on the properties of a Lignin/PEO blend, *Ind. Crops Prod.* 143 (2020) 111883. <https://doi.org/10.1016/j.indcrop.2019.111883>.
- [277] M. Reza Barzegari, A. Alemdar, Y. Zhang, D. Rodrigue, Mechanical and rheological behavior of highly filled polystyrene with lignin, *Polym. Compos.* 33 (2012) 353–361. <https://doi.org/10.1002/pc.22154>.
- [278] M.R. Barzegari, A. Alemdar, Y. Zhang, D. Rodrigue, Thermal Analysis of Highly Filled Composites of Polystyrene with Lignin, *Polym. Compos.* 21 (2013) 357–366. <https://doi.org/10.1177/096739111302100604>.
- [279] N. Ghavidel, P. Fatehi, Synergistic effect of lignin incorporation into polystyrene for producing sustainable superadsorbent, *RSC Adv.* 9 (2019) 17639–17652. <https://doi.org/10.1039/C9RA02526J>.
- [280] M. Culebras, A. Beaucamp, Y. Wang, M.M. Clauss, E. Frank, M.N. Collins, Biobased Structurally Compatible Polymer Blends Based on Lignin and Thermoplastic Elastomer Polyurethane as Carbon Fiber Precursors, *ACS Sustain. Chem. Eng.* 6 (2018) 8816–8825. <https://doi.org/10.1021/acssuschemeng.8b01170>.
- [281] H. Hatakeyama, T. Hatakeyama, Environmentally Compatible Hybrid-Type Polyurethane Foams Containing Saccharide and Lignin Components, *Macromol. Symp.* 224 (2005) 219–226. <https://doi.org/10.1002/masy.200550619>.
- [282] S. Kalami, M. Arefmanesh, E. Master, M. Nejad, Replacing 100% of phenol in phenolic adhesive formulations with lignin, *J. Appl. Polym. Sci.* 134 (2017) 45124. <https://doi.org/10.1002/app.45124>.
- [283] Y. Ren, J. Xie, X. He, R. Shi, C. Liu, Preparation of Lignin-Based High-Ortho Thermoplastic Phenolic Resins and Fibers, *Molecules* 26 (2021) 3993. <https://doi.org/10.3390/molecules26133993>.
- [284] X. Lu, X. Gu, A review on lignin-based epoxy resins: Lignin effects on their synthesis and properties, *Int. J. Biol. Macromol.* 229 (2023) 778–790. <https://doi.org/10.1016/j.ijbiomac.2022.12.322>.
- [285] S. Nikafshar, J. Wang, K. Dunne, P. Sangthonganotai, M. Nejad, Choosing the Right Lignin to Fully Replace Bisphenol A in Epoxy Resin Formulation, *ChemSusChem* 14 (2021) 1184–1195. <https://doi.org/10.1002/cssc.202002729>.
- [286] S. Zhao, M.M. Abu-Omar, Materials Based on Technical Bulk Lignin, *ACS Sustain. Chem. Eng.* 9 (2021) 1477–1493. <https://doi.org/10.1021/acssuschemeng.0c0882>.
- [287] C. Gioia, G. Lo Re, M. Lawoko, L. Berglund, Tunable Thermosetting Epoxies Based on Fractionated and Well-Characterized Lignins, *J. Am. Chem. Soc.* 140 (2018) 4054–4061. <https://doi.org/10.1021/jacs.7b13620>.
- [288] X. Lu, X. Gu, Fabrication of a bi-hydroxyl-bi-DOPO compound with excellent quenching and charring capacities for lignin-based epoxy resin, *Int. J. Biol. Macromol.* 205 (2022) 539–552. <https://doi.org/10.1016/j.ijbiomac.2022.02.103>.
- [289] C. Gioia, M. Colonna, A. Tagami, L. Medina, O. Sevastyanova, L.A. Berglund, M. Lawoko, Lignin-Based Epoxy Resins: Unravelling the Relationship between Structure and Material Properties, *Biomacromolecules* 21 (2020) 1920–1928. <https://doi.org/10.1021/acs.biomac.0c00057>.
- [290] B. Xue, R. Tang, D. Xue, Y. Guan, Y. Sun, W. Zhao, J. Tan, X. Li, Sustainable alternative for bisphenol A epoxy resin high-performance and recyclable lignin-based epoxy vitrimers, *Ind. Crops Prod.* 168 (2021) 113583. <https://doi.org/10.1016/j.indcrop.2021.113583>.
- [291] A. Jablonskis, A. Arshantsa, A. Arnaudov, G. Telysheva, D. Evtuguin, Evaluation of Ligno Boost™ softwood kraft lignin epoxidation as an approach for its application in cured epoxy resins, *Ind. Crops Prod.* 112 (2018) 225–235. <https://doi.org/10.1016/j.indcrop.2017.12.003>.
- [292] P. Menčík, R. Přikryl, I. Stehnová, V. Melčová, S. Kontárová, S. Figalla, P. Alexy, J. Bočkaj, Effect of Selected Commercial Plasticizers on Mechanical, Thermal, and Morphological Properties of Poly(3-hydroxybutyrate)/Poly(lactic acid)/Plasticizer Biodegradable Blends for Three-Dimensional (3D) Print, *Materials* 11 (2018) 1893. <https://doi.org/10.3390/ma11101893>.
- [293] M. Mariana, T. Alfatah, A.K. H.p.s., E.B. Yahya, N.G. Olaiya, A. Nuryawan, E.M. Mistar, C.K. Abdullah, S.N. Abdulmadjid, H. Ismail, A current advancement on the role of lignin as sustainable reinforcement material in biopolymeric blends, *J. Mater. Res. Technol.* 15 (2021) 2287–2316. <https://doi.org/10.1016/j.jmrt.2021.08.139>.
- [294] P. Mousavioun, G.A. George, W.O.S. Doherty, Environmental degradation of lignin/poly(hydroxybutyrate) blends, *Polym. Degrad. Stab.* 97 (2012) 1114–1122. <https://doi.org/10.1016/j.polymdegradstab.2012.04.004>.
- [295] I. Korbag, S. and Mohamed Saleh, Studies on mechanical and biodegradability properties of PVA/lignin blend films, *Int. J. Environ. Stud.* 73 (2016) 18–24. <https://doi.org/10.1080/00207233.2015.1082249>.

- [296] C. Mu, L. Xue, J. Zhu, M. Jiang, Z. Zhou, Mechanical and thermal properties of toughened poly (L-lactic) acid and lignin blends, *BioResources* 9 (2014) 5557–5566.
- [297] J.A. Diaz-Baca, P. Fatehi, Production and characterization of starch-lignin based materials: A review, *Biotechnol. Adv.* 70 (2024) 108281. <https://doi.org/10.1016/j.biotechadv.2023.108281>.
- [298] K. Kaewtatip, J. Thongmee, Effect of kraft lignin and esterified lignin on the properties of thermoplastic starch, *Mater. Des.* 49 (2013) 701–704. <https://doi.org/10.1016/j.matdes.2013.02.010>.
- [299] Chemistry of lignin-based materials, (n.d.). <https://doi.org/10.1680/gmat.12.00009>.
- [300] A. de S. M. de Freitas, J.S. Rodrigues, C.C. Maciel, A.A.F. Pires, A.P. Lemes, M. Ferreira, V.R. Botaro, Improvements in thermal and mechanical properties of composites based on thermoplastic starch and Kraft Lignin, *Int. J. Biol. Macromol.* 184 (2021) 863–873. <https://doi.org/10.1016/j.ijbiomac.2021.06.153>.
- [301] P. Mousavioun, P.J. Halley, W.O.S. Doherty, Thermophysical properties and rheology of PHB/lignin blends, *Ind. Crops Prod.* 50 (2013) 270–275. <https://doi.org/10.1016/j.indcrop.2013.07.026>.
- [302] A.P. Lemes, M.A. Soto-Oviedo, W.R. Waldman, L.H. Innocentini-Mei, N. Durán, Effect of Lignosulfonate on the Thermal and Morphological Behavior of Poly(3-hydroxybutyrate-co-3-hydroxyvalerate), *J. Polym. Environ.* 18 (2010) 250–259. <https://doi.org/10.1007/s10924-010-0170-7>.
- [303] H. BENGS, G. BOEHM, STARCH-BASED THERMOPLASTIC MIXTURE FOR PRODUCING BIODEGRADABLE SHAPED BODIES, EP0994917, 2000.
- [304] D. Mingwei, Y. Quanfu, Lignin-epoxy resin composite material and preparation method thereof, CN102585531, 2012.
- [305] N. Cao, K. Oden, BLENDING LIGNIN WITH THERMOPLASTICS AND A COUPLING AGENT OR COMPATIBILIZER, US20140121307, 2014.
- [306] J. ERDMANN, J. GANSTER, G. ENGELMANN, THERMOPLASTIC POLYMER COMPOUNDS WITH LOW-MOLECULAR-WEIGHT LIGNINS, A METHOD FOR PRODUCING SAME, MOULDINGS AND USES, EP2954008, 2015.
- [307] J.V. Olsson, Y.-L. Chung, R. Jingxian Li, R. Waymouth, E. Sattely, S. Billington, C.W. Frank, Lignin poly(lactic acid) copolymers, US20140080992, 2017.
- [308] S. XIAODAN, J. XIUMEI, S. WEI, Lignin/PVC film and preparation method thereof, CN108948559, 2018.
- [309] W. YUNXUAN, W. NINGNING, C. CHENYAO, H. ZHIGANG, S. XINYU, T. BIN, Biodegradable color masterbatch taking lignin as pigment as well as preparation method and application thereof, CN108976737, 2018.
- [310] Q. XUEQING, L. WEIFENG, H. JINHAO, W. SHENGYU, L. HONGMING, Q. YONG, Lignin/polyolefin thermoplastic elastomer composite and preparation method thereof, CN107474374, 2017.
- [311] J. Obielodan, Wu, Polyactic Acid and Lignin Composite Thermoplastic for 3D Printing, US20210171764, 2021.
- [312] C. CARRICK, J. VERENDEL, M. RUDA, T. ROULIN, COMPOSITION COMPRISING POLYESTER AND MODIFIED SOFTWOOD LIGNIN, SE2030181, 2021.
- [313] Z. YAQIONG, C. JIAWEI, W. ZHONGKAI, W. MANG, X. MINGXIN, K. WEIMING, Lignin-containing bio-based composite material and preparation method thereof, CN111718591, 2020.
- [314] W. DAWEI, L. YIXIN, T. PEI, J. YANG, W. JIANGYU, Z. XIAOPING, W. PIYE, Calcium lignosulphonate thermoplastic elastomer modified polylactic acid material and preparation method thereof, CN115477835, 2022.
- [315] T. Torrezan, J.A. Marcondes Agnelli, S.H. Prado Bettini, BIODEGRADABLE AND/OR COMPOSTABLE THERMOPLASTIC COMPOSITION COMPRISING LIGNIN, USE OF SAID COMPOSITION AND PRODUCT COMPRISING SAME, US20220025183, 2022.
- [316] K. Kurple, N. Kurple, M. Kerman, Lignin hybrid polymers obtained from the reaction of lignin and compatible polymer precursors, and starting compositions for forming lignin hybrid polymers, US20200140624, 2020.
- [317] Y. TONGQI, W. HAOHUI, S. RUNCANG, Y. SHIXIN, Z. SIJIE, X. SHAOJUN, Z. CHENJIE, Lignin/starch/PBAT composite film material and preparation method and application thereof, CN115819814, 2023.
- [318] C.D. Webb, W.M. Sanford, A.A. McCall, Acrylonitrile butadiene styrene copolymer/lignin blends, US20200131359, 2020.
- [319] J.R. Austin, Antioxidant stabilizer in polymers, US20200270418, 2024.
- [320] M. COLLINS, M.C. RUBIO, COMPOSITE PACKAGING MATERIAL, US20250001744, 2025.
- [321] M. Borg, J. Verendel, Lignin-Containing Composites, WO2025048695, 2025.

Figure1

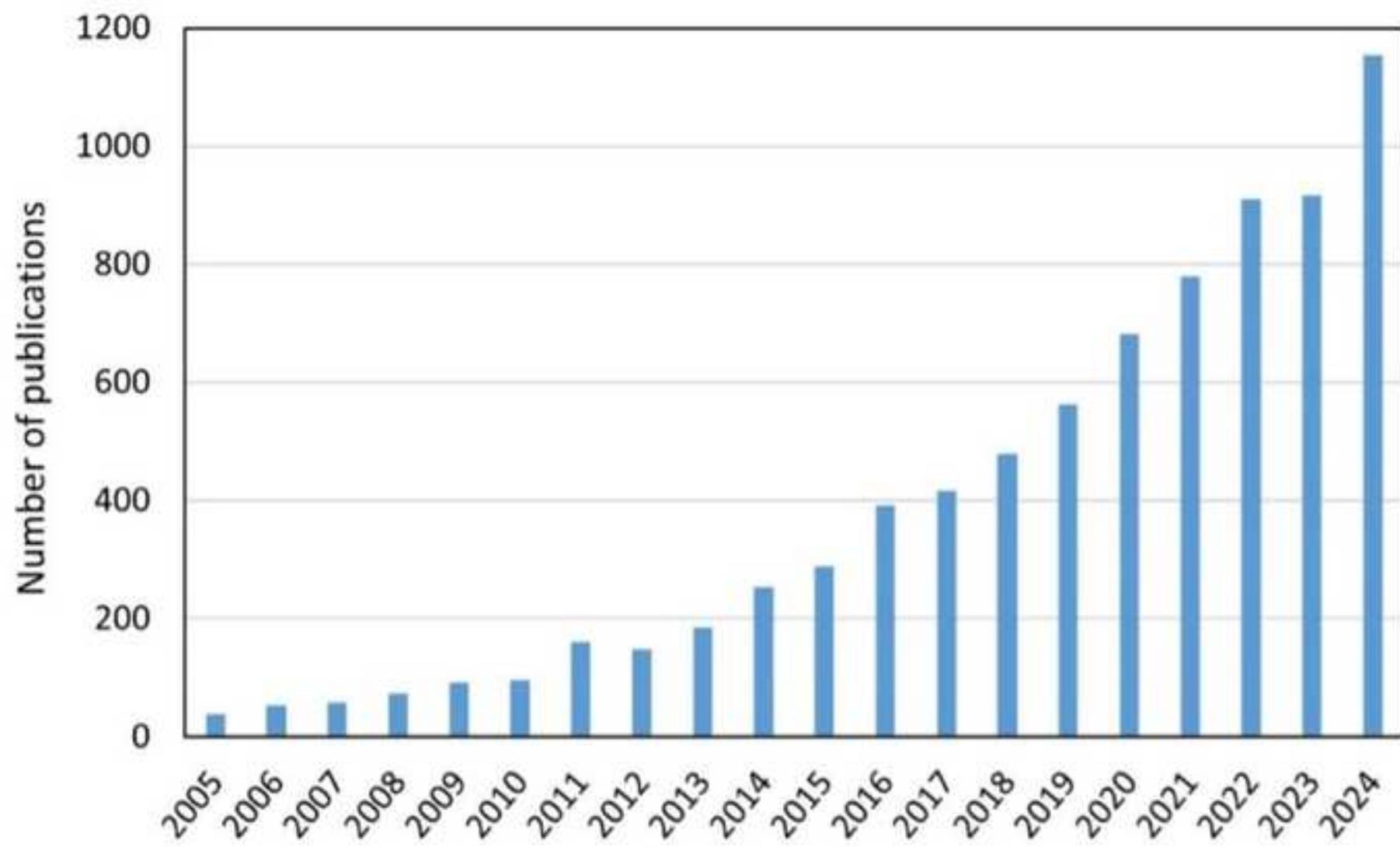
[Click here to access/download;Figure;Fig1.jpg](#)

Figure2

Click here to access/download;Figure;Fig2.png

