

Review Article

Lignin as Green Filler in Polymer Composites: Development Methods, Characteristics, and Potential Applications

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After cellulose, lignin is the most commonly used natural polymer in green biomaterials. Pulp and paper mills and emerging cellulosic biorefineries are the main sources of technical lignin. However, only 2–5% of lignin has been converted into biomaterials. Making lignin-based polymer biocomposites to replace petroleum-based composites has piqued the interest of many researchers worldwide due to the positive environmental impact of traditional composites over time. In composite development, lignin is being used as a filler in commercial polymers to improve biodegradability and possibly lower production costs. As a natural polymer, lignin may have different properties depending on the isolation method and source, affecting polymer-based composites. The application has been affected by the characteristics of lignin and the uniform distribution of lignin in polymers. The review's goal was to provide an overview of technical lignin extraction, properties, and its potential appropriate utilization. It was also planned to revisit the lignin-based composites' preparation procedure as well as their composite characteristics. Solvent casting and extrusion methods are used to fabricate lignin from polymeric matrices such as polypropylene, epoxy, polyvinyl alcohol, polylactic acid, starch, wood fiber, natural rubber, and chitosan. Packaging, biomedical materials, automotive, advanced

biocomposites, flame retardant, and other applications for lignin-based composites has existed. As a result, the technology is still being refined to increase the performance of lignin-based biocomposites in several applications. This review could assist explain lignin's position as a composite additive, which could lead to more efficient processing and application strategies.

1. Introduction

Approximately 50–70 billion tons of lignin are produced per year [1, 2] by the pulp and paper industry and emerging cellulosic biorefineries, with 98% being burned for energy or simply dumped in landfills, posing a major disposal issue [3]. In biomass cell walls, lignin is the most available non-carbohydrate polymer. It has several impressive properties, including good mechanical and physicochemical properties, low weight with antioxidant and antimicrobial properties, diverse possible modifications, and excellent thermal stability. Its biodegradability, environmental friendliness, wide ecological adaptability, and reinforcing ability create it as an excellent alternative for developing novel green materials, including polymer composite materials [3–5]. Many potential applications for lignin can be developed and implemented in industries such as adhesives, biosurfactants, antimicrobial agents in packaging and textiles, antioxidants, adhesives, anticorrosion, carbon fiber or carbon black, cosmetics, reinforcing agents, hydrogel, phenolic resin, flame retardant, polyurethane, foam composite, compatibilizers, and new biomedical materials [6–11]. However, lignin-based composites' product commercialization and manufacturing processes need to investigate because some had not yet been commercialized in the market.

Making a lignin-based polymer composite to replace petroleum-based composites has become of great interest to many researchers worldwide, considering its negative environmental impact in the long term on typical composites. Introducing lignin into commercial polymers can create green composite or eco-friendly composite as lignin contributes to improving the product's biodegradability. For example, the presence of lignin in polypropylene-reinforced kenaf core hybrid polymer nanocomposites increases the thermal stability and fire retardant properties of bionanocomposite. However, there is still a great challenge before obtaining lignin-derived biocomposites comparable to those found in the petroleum industry. The composite properties were influenced by the chemical structure of lignin [12]. Lignin can function as a filler, stabilizer, compatibilizer, and reinforcement in composites with its distinctive chemical structure. Its aromatic and cross-linked functional groups make it suitable for a variety of polymeric matrices with improved wettability, mechanical, and fire-retardant properties [13]. Due to the intricacy of its structure and reactivity, lignin is frequently difficult to combine properly. When used as an extender, lignin can lower the cost of polymer composite production while also improving biodegradability. Lignin contains inter- and intramolecular hydrogen bonds, making it thermoplastic and thermally stable at high temperatures [14]. Adding lignin to polylactic acid (PLA) or polypropylene (PP) has been a hot topic over the last decade [15]. The different characteristics between lignin-containing

hydroxyl groups and polymers such as aliphatic polyester become a challenge to make a uniform distribution for lignin and polymer such as polylactic acid (PLA) mixture [15].

Furthermore, lignin matrix compatibility and homogeneity are big challenges in most research [16]. Besides that, high mineral content in lignin and other impurities can interfere with the uniform mixing of the composite. Lignin has different polarity and immiscibility from nonpolar polymers. It is also not easy to dissolve in common solvents. Therefore, some lignin modification is required to modify the lignin properties, such as acetylation, esterification, methylation, and phenolation [17, 18]. Chemical modifications of lignin such as phenolation and acetylation have become prominent in recent years. Modified lignin can be used as a compatibilizer in bi- or multiphase composites. Esterification is one method of modifying lignin when used as a compatibilizer [16]. Previously, some reviews have been reported in lignin-based biocomposites; however, to the best, our acknowledgment is not in deep discussion especially on the method to prepare lignin as filler incorporated with some matrices. Besides that, this review brings detailed information on the characteristic of lignin-based biocomposites. The goal of this review was to present an overview of the application of lignin as filler in composites including the development methods and composite properties such as thermal, morphological, mechanical, thermal, and other properties.

2. Lignin Structure, Extraction Method, and Its Properties

Lignin contains an aromatic structure with an amorphous macromolecule of repeating phenylpropane units, making it a potential precursor to produce materials, fuels, and chemicals. Lignin is the second major component of wood cell walls (20–30%) that serves to cover structural supports and transport water and nutrients, as cement between wood fibers, as a hardening agent in fibers, and as a barrier against chemical, biological, and enzymatic degradation of cell walls [19]. It is a three-dimensional, irregular, and highly branched phenolic polymer with a highly complex chemical structure and formed through an irregular biosynthetic process. Figure 1(a) presents a lignin structure consisting of basic phenylpropanoid monomers, guaiacyl (G), syringyl (S), and p-hydroxyphenyl (H) units, which are derived from coniferyl, synapyl alcohol, and p-coumaryl precursors, respectively [2, 13]. These macromolecules contain large amounts of C-C and ether-related compounds with the aryl glycerol- β -aryl ether (β -O-4) link predominating so far, followed by the biphenyl (5-5) and phenyl coumarin (β -5) bonds [21, 22]. Species and environment influence the content and composition of lignin. Hardwood lignin consists mainly of G and S units and has traces of H units

[23, 24], while grasses contain G, S, and H units. Hardwoods have more lignin composition variability than softwoods. In contrast, softwood lignin consists mainly of G units, with low levels of H units [25].

The proportions of S, G, and H units were 1:94:5 in spruce lignin, 56:40:4 in beech lignin [26], and 1:1:1 in grass lignin. Even though there is variation in the content contingent on the sources, the typical lignin contents measured by the Klason method are 25–35% in softwoods, 20–25% in hardwoods, and 15–25% in herbaceous plants [27]. Precipitation of lignin begins in the primary wall's middle lamella and the secondary wall's S1 layer. Lignin is also found in S2 and S3 layers [28, 29]. Its composition and structure vary depending on the amount and proportion of functional groups linked to aromatic or aliphatic moieties [2, 30, 31] that affect the reactivity of lignin. The structural schematic of lignin in plants is shown in Figure 1(a), while the linkages of lignin are presented in Figure 1(b).

2.1. The Extraction Method and Its Properties. Many conversion pathways for lignin utilization have been proposed and studied. In some cases, the structure and properties of the extracted lignin (technical lignin) change due to the method of processing lignocellulosic biomass into pulp. In commercial applications such as fillers in composites, technical lignin can be extracted from biomass physically with or without chemical or biochemical treatments. However, controlling the physical properties, reactivity, and chemistry of the lignin surface should be performed [32–34]. Processes with sulfur such as kraft and sulfite pulping are discussed below, as are sulfur-free processes such as alkaline pulping (soda lignin) and solvent pulping (organosolv lignin). Sulfur-free lignin is lignin that has a low macromolecular size upon fractionation. In addition to low molar mass phenols or aromatic compounds, they have other desirable properties. Table 1 presents some key features of lignins related to their utilization with a detailed description of each lignin in the discussion.

2.2. Sulfur Bearing Process

2.2.1. Kraft Processes. Kraft lignin (KL) is produced by kraft pulping with sodium sulfide and sodium hydroxide chemicals. The KL is the world's largest source of technical lignin at around 85% [53]. The β -O-4 linkages between the phenyl propane (C9) units in lignin are cleaved by sulfide at high temperatures up to 170°C [54], lowering the molecular weight of the polymer [34]. KL has a high sulfur content resulting in the formation of aliphatic thiol groups as a result of this mechanism and is hydrophobic [25]. During the pulping process, lignin reacts with chemicals to form fragments that are soluble in water or alkali, according to Dias et al. [55]. The phenylpropane group is also broken, resulting in a phenol-free hydroxyl group, making the lignin hydrophilic.

The process of lignin precipitation completes the lignin separation. LignoBoost is a precipitation and separation process to obtain a pure KL. Acidification with carbon

dioxide precipitates and filters out the lignin. However, compared to previously published methods, an improved washing procedure is used by the recent publication of Solihat et al. [7]; they isolated *Acacia mangium* KL by single step and ethanol fractionated step that successfully recovered KL of ~35 and ~16%, respectively. The single step has higher acid-insoluble lignin (AIL) than the ethanol fractionated step. KL produces a complex mixture of breakdown products ranging in molecular mass from low-molecular-mass phenolic compounds to large macromolecules [37]. Acidification can precipitate most of the KL in black liquor. Lignin with a low molecular mass, on the other hand, is still present in the solution. The output of precipitation is primarily determined by the liquid's final pH. Because no corrosive salts are formed when carbon dioxide is used in technical applications, it is advantageous. However, it is impossible to achieve a pH of less than 8.5. If the liquid is acidified with a strong mineral acid, more lignin can be precipitated. The phenolic and hydroxyl groups of lignin can be separated from the weak acid by carbon dioxide but not the stronger carboxylic acid group [39].

KL can be used in the same applications as lignosulfonates (LS), despite having different inherent properties such as limited solubility. In rubber resins and plastics, KL or modified forms of KL can be used as dispersing agents and additives. These polymers can be used to make adhesives for a variety of products, including laminated boards and plywood. Lignin can also be broken down into chemicals with a low molecular mass [39]. The average molecular weight (Mw) of softwood KL is 3,900. KL has a low molar mass (Mn), ranging between 1,000 and 3,000 g·mol⁻¹ [56]. The molecular weight of KL, on the other hand, can vary depending on the type of wood, analytical method, and isolation technique. Using methanol fractionation, Saito et al. investigated the properties of high molecular weight (HMW) and low molecular weight (LMW) kraft softwood lignin (KSL). HMW of KSL has been fruitfully separated from LMW, which is soluble in methanol and has Mw in the range of 3,000 to 86,600 g·mol⁻¹. HMW of KSL is insoluble in methanol and has Mw in the range of 14,900 to 188,000 g·mol⁻¹ [38].

2.2.2. Sulfite Process. Sulfite lignin is traditionally the most widely used type of pulping process and the most widely available commercial type of lignin. A base of calcium, sodium, magnesium, or ammonium and aqueous sulfur dioxide (SO₂) is used in the pulping process. After sulfite pulping at 140°C with chemicals such as SO₂, Na⁺/Ca⁺/Mg⁺, and NH₄⁺, LS results were obtained [54]. It is made through sulfite pulping, which involves incorporating a sulfonate group into partially hydrolyzed lignin and then converting it into sulfonated groups with various functional groups that give them unique colloidal properties [36] and a high molecular weight than KL [40]. It dissolves in a variety of aqueous solutions with varying pH levels but not in organic solvents such as ethanol or acetone. Because of its low molecular weight, LS is extremely compatible with other polymeric materials. During alkaline cooking at high

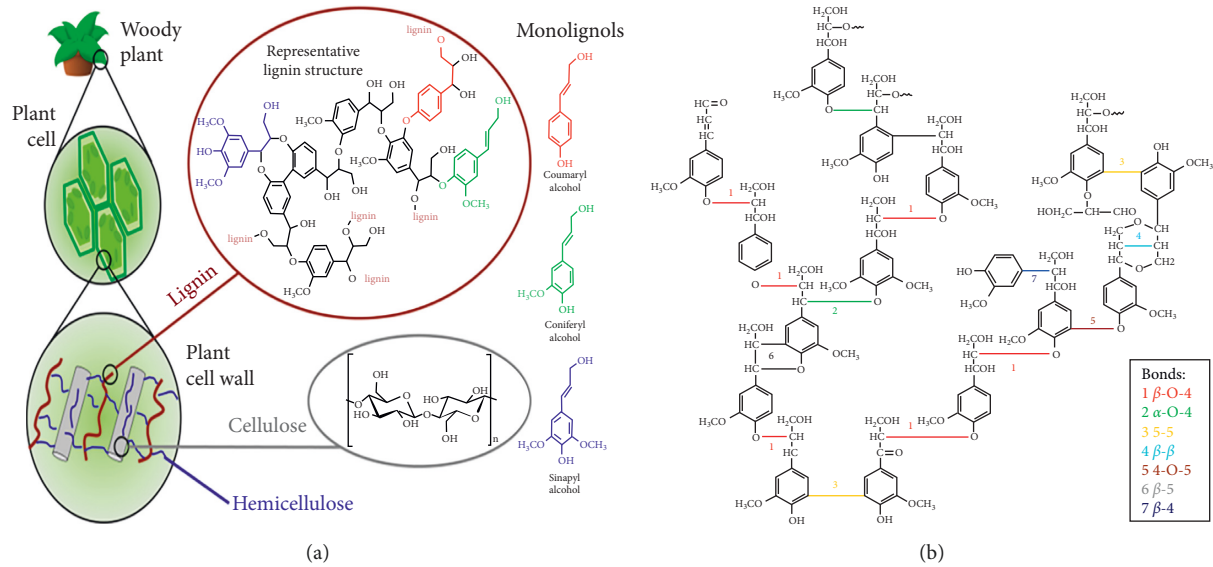


FIGURE 1: (a) The lignin structure and three main lignin precursors [20] (Copyright @ 2017 Science and Education Publishing CC under 4.0) and (b) typical interunit linkages present in softwood lignin [6] (Copyright @ 2018 Springer CC under 4.0).

TABLE 1: Different characteristics of lignins and the appropriate utilization.

Lignin	Some key lignin characteristics
Kraft lignin (KL)	<ul style="list-style-type: none"> (i) Containing ash of 1–2% and suitable for low-value-added applications [25] (ii) Having a high concentration of condensed structures with strong ether bonds and phenolic hydroxyl groups [35, 36] (iii) Containing the organic matter such as polysaccharides and a few extractive fractions [37] (iv) Molecular weight variability from low to the high molecular weight of 3,000–188,000 g·mol⁻¹ [38] (v) Solubility is limited but can be increased by sulfonation [39] (vi) KL or modified KL can be used as dispersing agents, additives, and thermoset polymers mainly in low molecular weight [39] (vii) KL can produce thermoset polymers when it is condensed with formaldehyde and cross-linked with phenol [39] (viii) KL with higher molecular weight can be used as a thermoplastic mixture or copolymer [38]
Lignosulfonate (LS)	<ul style="list-style-type: none"> (i) High ash content of 4–8% and a high molecular weight than KL [40] (ii) The high molecular weight of 1,000 to 50,000 Da [40] than KL with a polydispersity index (PI) of 4.2–8 [33, 41] (iii) Many impurities (approximately 30% by weight), such as ash or carbohydrates [41] (iv) Required to modify for high compatibility with other polymeric materials [42] (v) Dissolve in a variety of aqueous solutions but not in organic solvents [40] (vi) Good water solubility [40] (vii) Having a variety of functional groups (carboxylate, phenolic, as well as sulfur-containing groups) provide exceptional colloidal properties, dispersants, additives (plasticizers), surfactants, and flocculants [43]
Soda lignin (SL)	<ul style="list-style-type: none"> (i) Sulfur-free and has a higher purity than KL and LS [44] (ii) Suitable for a range of high products (resins, chemical reactants, composites, and antioxidant agents) and natural feed supplements for monogastric animals [45–47] (iii) Commonly derived from soda or soda-anthraquinone pulping of agricultural wastes or perennial crops [44–46] (iv) Soda lignin contains lower phenolic and aliphatic hydroxyl groups [38]
Organosolv lignin (OL)	<ul style="list-style-type: none"> (i) OL has high reactive groups, no sulfur, high purity, and the highest reactivity and is nontoxic [36, 48] (ii) High-quality lignin for higher value-added applications such as chemicals [49] (iii) High solubility in an organic solvent but insoluble in water [50] (iv) The possible application in the adhesive in wood panel production, a monomer in a biopolymer, antioxidant, and pesticide [51] (v) Low content of residual carbohydrates [52]

temperatures, many active lignin groups are destroyed, significantly reducing their activity. Sulfonate groups in aliphatic side chains in LS contain a lot of sulfur. However,

the cations used in the production of pulp and recovery usually contaminate them. LS reactivity is influenced by the cations to some extent. The lowest and highest reactivity was

found in calcium and ammonium-based LS, respectively, while sodium and magnesium-based LS were moderately reactive [57].

Because of the addition of a sulfonate group, these LS typically have extremely high average molecular weights, even higher than KL. The catalytic transformation of LS is more difficult as a result of incorporating these groups [58]. Ethylene bonds are broken; methoxy groups are destructed; and new C–C bonds are formed during the sulfite pulping process.

2.3. Sulfur-Free Process

2.3.1. Organosolv Process. Organosolv lignin (OL) has an advantage over KL in that it lacks sulfur, which reduces the formation of compounds. It also deactivates the catalyst used in the subsequent process by emitting a foul odor. Some solvents used in solvent pulping at temperatures between 150 and 200°C include acid, formic acid, ethanol, methanol, ethylene glycol, and water [49, 54]. To isolate the biomass components, this method employs a combination of aqueous organic solvents including acetone, ethanol, methanol, or organic acids. Distillation allows the cooking liquor to be reused. Because no toxic sulfur chemicals are used in this process, it is eco-friendly. It is also ideal for direct use due to its high purity.

OL are highly hydrophobic in organic solvents [50]. Precipitation is used to remove them from the solvent, which usually involves adjusting various parameters including pH, temperature, and concentration. The most widely used organosolv processes are ethanol/water pulping (e.g., Alcell) and acetic acid pulping (which contains trace amounts of mineral acids) [59]. A new extraction method based on a mixture of acetic acid, water, and formic acid was also established by the CIMV Company (France). According to several published works, the lignin produced is known as bio-lignin, and it is linear and has a low molecular weight [60]. The organosolv process uses acid-catalyzed solvolysis of β -ether bonds in lignin to dissolve them. Acids (for example, H₂SO₄, oxalic acid, HCl, formic acid, and acetic acid) can be added to the reaction mixture or made in situ by deacetylating hemicellulose to release acetic acid [61, 62]. The external acid promotes the acidolysis of β -ether, giving a cellulose pulp with lower lignin content. In contrast, the lignin produced by in situ acid formation is thought to retain a higher number of β -ether bonds present in the original lignin [63, 64].

2.3.2. Soda Process. Soda lignin (SL) is obtained during soda-anthraquinone and soda pulping. Its availability is limited due to the inefficiency of the soda pulping process [44]. In an aqueous alkaline medium with a temperature of 150–170°C, NaOH is used to produce pulp [54]. By lowering the pH of the alkaline solution after delignification, the dissolved SL can be recovered. According to the “cleaner production” standard, soda-oxygen pulping technology is a cleaner pulping process [65, 66]. Remarkably, two-stage acid precipitation of SL at pH 5.5 yields a higher purity and larger

particle size than that obtained at a pH of 3.98. The granite process, which was developed by paper mills for the synthesis of cellulose from perennial crops or agricultural wastes, is a particular approach for lignin deposition in the black liquor of the soda process. Acidification, usually with a mineral acid, lowers the pH of the liquid. Due to the high silica content, which can precipitate lignin, as a result, recovering cooking liquid from nonwood pulp is difficult, and the obtained lignin is of poor quality [46, 67].

To separate lignin from cellulose and hemicellulose, a variety of extraction methods have been reported. The structure and physicochemical characteristics of lignin can be affected by different isolation methods, isolation types, isolation temperature, and raw material sources [68–70]. Physical methods utilizing membranes can be used to catalyze the isolation processes [71]. Membrane technology allows for the separation of black liquor from various lignin fractions of varying molecular weights, which can then be used to make a range of high products (resins, chemical reactants, composites, and antioxidant agents). Lignin can be degraded by enzymatic isolation of lignin, such as using laccase-producing microbes [47]. Chemical isolation is possible using chemicals such as NaOH and KOH. Approximately 75% of the lignin is precipitated as a sodium salt in this step. After that, the lignin is separated using a filtration method. When lignin is hydrolyzed, it leaves behind solid lignin residues as well as a large amount of unhydrolyzed cellulose. Obtaining lignin for use in polyurethane production requires the extraction with NaOH [72–75]. Acid can also be used to isolate lignin [76, 77] such as HCl and H₂SO₄ [6, 7, 78–80] and HPO₃ [81]. Besides that, biological isolation of lignin and combination processes [82], ionic liquids [83, 84], or processed in hydrothermal [85] or supercritical solvents [86] can also be applied. Supercritical pretreatment provides the best environmental performance and economic considering solvents and carbon dioxide recycling [86].

3. Fabrication of Lignin-Based Green Composites

Lignin can be combined with synthetic and natural polymers [16]. In this review, some kinds of polymers that have been incorporated with lignin were discussed. Lignin can be used as filler material, a nucleating agent, compatibilizer, and coupling agent in composites. When used directly, native lignin becomes less reactive and reduces the mechanical strength of copolymer composites [87]; thus, it can be modified before being mixed with polymers to achieve better performance. The different process is possibly affected by the composite properties and the potential applications. The composite properties are strongly influenced by the interfacial interaction between the matrix and reinforcement to maintain stability between phases and the stress transfer process, among others. To improve compatibility, the miscible constituent is not always used, but it can also be modified by surface modification or by adding a compatibilizer agent. Compatibilizer serves to increase the miscibility to form the desired mixture. Lignin shows low miscibility in polymers, causing agglomeration and phase

separation. If adding more lignin, proper homogenization techniques and additives are needed. Lignin tends to agglomerate due to its intermolecular hydrogen bonding, π - π stacking, aromatic groups, and van der Waals interaction between polymer chains [88, 89]. The amount of lignin was added to the polymer so that it can act as a reinforcement is on a 25–40% scale [90]. The homogeneity of lignin in the polymer matrix remains a challenge. Thus, lignin modification is added to achieve the dispersion or compatibility of lignin. The commercial polymers including PP, PVA, and epoxy were discussed, while natural polymers such as PLA, chitosan, starch, rubber, and cellulose have been overviewed. Because of the different characteristics between existing polymers and lignin, some methods for composite preparation have been developed continuously. Table 2 presents the common limitation in the fabrication of lignin with polymer matrices related to possible applications of lignin-based composites.

3.1. Composite Lignin-Polypropylene. Polypropylene (PP) is a thermoplastic that is commonly used as a raw material for various types of products, having the disadvantages of not being able to degrade naturally and having low mechanical properties [91]. One way to address this problem is to mix natural polymers such as lignin to initiate the natural degradation process of PP after its use and to increase its tensile strength, bending strength, or modulus. Furthermore, Dias et al. [92] revealed that the cost to produce KL on an industrial scale was \$70–182/ton, while the PP price was \$1,210/ton [93]. Therefore, adding lignin to PP will be economically beneficial and have a constructive impact on the environment. The process of mixing two or more materials in a composite manufacturing formula needs to consider the suitability and dispersion between the phases of the constituent materials. PP is a synthetic resin formed from the polymerization of propylene, which is a hydrocarbon with a molecular structure of $\text{CH}_2=\text{CHCH}_3$. Through the process of breaking the double bond in the propylene molecule, a polypropylene chain is formed on the backbone of the carbon atom to which the CH_3 group is attached. The arrangement of CH_3 groups on one side of the carbon chain produces isotactic PP, which is the most widely produced type of PP. This molecular structure causes PP to have rigid properties, melting at a fairly high temperature, which is around 170°C, easy to be flexed, water-resistant, inert, and chemically inert (nonpolar) but easily oxidized [94]. The function of lignin as a reinforcement in composites is strongly influenced by the manufacturing process. The use of native and technical lignin in the manufacture of PP-based composites will be described.

Mixing of PP and lignin (pre-hydrolyzed lignin (PL) or OL) with various weight ratios of the materials was carried out using a roll mill for 1 hour, then formed into granules, at a temperature of 200°C. Then a film sheet was obtained by extruding PP/lignin granules with stabilizer 2,6-di-tert-butyl-4-methyl phenol (0.15 mass %) + calcium stearate (0.15 mass %), as a comparison. In general, composite films containing lignin outperformed PP films without lignin in

terms of photodegradation stability. The phenolic group in lignin acts as a stabilizer that can break the polymer chain reaction due to oxidation and radical products. However, the higher the lignin content, the more it encourages radical reactions that can cause oxidative degradation of PP with a hydroperoxide radical mechanism. OL is a more effective initiator of oxidation reactions, compared to PL. Thus, it gives a more significant role in assisting the PP degradation process. The addition of lignin not only can trigger the photo oxide reaction to accelerate the degradation of PP but also stimulates the activity of microorganisms to degrade PP/lignin composites [95]. PP/lignin film composite (4% wt) was produced by processing PP isotactic powder and OL powder in a roll mill for 1 hour, then granulated in a homogenizer at 200°C. Then, film sheets were obtained by extruding PP/lignin granules without the addition of a stabilizer.

Toriz et al. [90] developed an isotactic PP/KL composite with the addition of maleic anhydride-modified PP (MAPP) as a compatibilizer. Isotactic PP with a melting point of 152°C, added with 10–60% KL (5–20 microns in powder form) in a Brabender bowl mixer, with process conditions at 170°C, mixer speed of 120 rpm, for 3–4 min. The resulting compound is ground and then molded by injection molding at a pressure of 600–1,000 psi, a temperature of 170°C. Maldhure et al. [96] developed a PP composite with modified KL from sugarcane bagasse (alkylated lignin and arylated lignin) to improve compatibility and produce a reactive side. The alkylation reaction uses dichloromethane, while the arylation reaction uses chlorobenzene. Mixing PP and modified lignin using Brabender electronic plasticorder (HAAKE AEV 153 mixer, Germany) at 60 rpm, at a temperature of 190°C, for 10 minutes. During mixing, dry nitrogen was added to prevent polymer degradation. The antioxidant properties of modified lignin can increase the stability of the composite to heat. The addition of lignin causes an increase in melt flow index (MFI), indicating that lignin can act as a stabilizer in the PP extrusion process. Dias et al. [92] compared the composite properties of PP and KL from sugarcane bagasse and softwood with 3% MAPP as compatibilizer. Before compounding with a twin-screw extruder, lignin and PP were oven-dried at 80°C for 3 hours. Then PP, MAPP, and lignin were mixed manually. The process in the extruder was carried out at 180°C with a speed of 50 rpm for 5 min. After the extrusion process, lignin behaves as a stiffness-inducing filler in the PP matrix, improving the stiffness and thermal properties of the composite in a synergistic manner. In general, there is no significant difference between the use of sugarcane bagasse KL and softwood KL on the characteristics of PP/KL composites.

In another report, Ahmad Saffian et al. [97] developed a composite as heat and thermal insulator material from PP, 30% KL, and 10% kenaf core fiber with 3% polymeric methylene diphenyl diisocyanate (pMDI) as a compatibilizer. Compounding process with mixer was done at a temperature of 175°C, and finally pMDI was added. The resulting compound was then placed in a mold and pressed on a hot press machine to become a composite board. Hot pressing stage, starting with melting compound for 9 min,

TABLE 2: Description of lignin as filler in lignin-based biocomposites.

Polymer matrices	A common limitation in fabrication	Possible application of lignin-based composites
PLA	The need for compatibilizer	Packaging, food packaging
PVA	The hydrophilic properties of PVA	Packaging, drug delivery system, biomedical, wound healing application, agricultural application
Cellulose	The need for compatibilizer	Seed coating
Starch	The hydrophilic properties of starch	Packaging, food packaging
Epoxy	The need for compatibilizer due to the incompatibility resulted in hydrophilic properties	Coating
Natural rubber	The need for compatibilizer due to the incompatibility resulted in hydrophilic properties	Tire industry, automotive devices
Polypropylene	The need for compatibilizer due to the incompatibility; the reduction in elongation; the susceptibility to microorganism	Automotive devices
Commercial adhesives	Difficulties in particles distribution	Filler in adhesives system

then hot pressing and cold pressing for 3 and 4 min, respectively. The results showed that the PP composite was suitable as a building insulator. However, the composite tensile strength decreased after the addition of lignin or kenaf core fiber into PP. Seydibeyoglu et al. [98] added 10% SL to the PP copolymer, using two types of commercial coupling agents, at a concentration of 0.1%, 0.3%, and 0.5%. The SL was mixed with PP using a twin-screw extruder with a feeding rate of 20%, extruder temperature between 170 and 185°C with a screw speed of 190 rpm. PP/lignin composites as oil absorbers are made using a thermally induced phase separation (TIPS) technique (Figure 2), which is the process of solubilizing a polymer in a high-temperature solvent and then cooling the polymer solution to form a porous structure. PP was dissolved in a decalin and 1-butanol mixture at a temperature of 115°C. Furthermore, lignin was added at 10 and 20% levels. After cooling at 20°C a separate phase (monolith) was formed. After that, it was soaked in acetone and vacuum oven-dried. The absorption of soybean oil and lubricating oil was better in PP monoliths containing 10% lignin than in monoliths containing 20% lignin [99].

Rozman et al. [100] compounded coconut fiber that had been modified with lignin was carried out using a rheomixer at 170°C for 20 min at a speed of 25 rpm. The resulting compound was put into a mold, which was preheated at 170°C for 10 min, then hot-pressed for 10 min, and cold-pressed for 10 min. The amount of lignin used for the modification of coconut fiber varied as much as 0%–20% of the coconut fiber weight. The addition of lignin can increase the flexural strength but decrease the tensile strength of coconut fiber and PP composites, although not as good as using MAPP. This is due to improved compatibility in the interfacial area. Because a large amount of lignin can cause voids and reduce mechanical properties, a small amount of lignin (max 2%) can increase the interfacial adhesion between PP and sawdust [101].

3.2. Composite Lignin-Epoxy Resin. Epoxy is an attractive material because of its wide range of applications, including aircraft components, sports equipment, construction, and many more. Epoxy is a thermoset material that consists of

high degree cross-linking and networking molecules [102]. The chain motion in epoxy is greatly restricted and causes excellent chemical resistance, high electrical insulation, and adequate strength [103]. Epoxy, on the other hand, is unsuitable for many applications due to its low thermal resistance, brittleness, and high viscosity [104]. In commercial applications, epoxy resins are frequently mixed with other materials to change their properties. The use of inorganic fillers such as silica [105], zirconium dioxide (ZrO_2) [106], and iron oxide (Fe_3O_4) [107] into epoxy proved to increase hardness, elastic modulus, toughness, and thermal stability. However, to improve the bio-based content in epoxy nanocomposites, lignin is considered an excellent candidate to substitute inorganic fillers and enhance the sustainability and renewability of the material. The presence of various functional groups such as aliphatic, hydroxyl, methoxy, and carbonyl makes lignin has a significant potential to enhance epoxy's toughness and thermal resistance. It also can enhance the mechanical and adhesive properties [108]. The phenolic backbone in lignin makes high thermal stability and is naturally hydrophobic, which differs from other bio-based materials [109].

The bio-based epoxy resin has been prepared by reacting alkali lignin with epichlorohydrin, resulting in a good mechanical property of bio-based epoxy [111–113]. Figure 3 shows the proposed mechanism of an epoxidation reaction involving epichlorohydrin in alkali with lignin to create lignin-based epoxy resins as a promising alternative for bisphenol A in the production of epoxy resins [110]. Lignin reduces the epoxy network density without significantly affecting tensile strengths and thermal properties [114]. Feldmann constantly investigated the influence of lignin incorporation in bisphenol and epoxy resin [115–117]. Feldmann added 5–20 %wt. lignin to bisphenol A diglycidyl ether (DGEBA). The composite with lignin composition between 10 and 20% displayed a noticeable effect on the adhesive tensile strength. Meanwhile, the adhesive shear strength only improved when received heat curing at 75°C for 4 hours. The excellent dielectric properties of lignin/epoxy composites motivated Kosbar et al. to produce printed wiring boards (PWB) [109]. They added 25–67 %wt. lignin to DGEBA with an amine curing agent. In epoxy resin, lignin

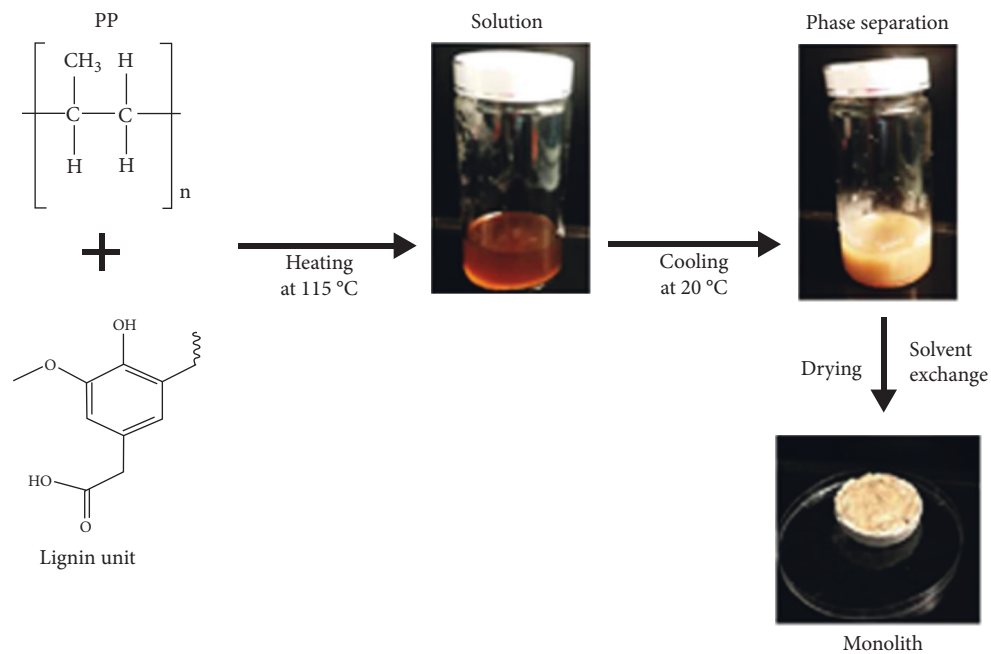


FIGURE 2: A general protocol for using a thermally induced phase separation technique to prepare PP/lignin blend monoliths [99] (Copyright @ 2020 Elsevier under CC BY-NC-ND 4.0).

can be added to 50% w/w [118]. This addition resulted in properties such as glass transition temperature (T_g), decomposition temperature, and dielectric constant being similar to those of FR4 (glass-reinforced epoxy laminate material), a common resin for FWB. The composite shows an excellent property up until around 60% lignin. Higher lignin content reduces properties but can still be used for lower performance PWB.

Mendis et al. functionalized lignin through hydration of lignin-amine solution and the Mannich reaction [119, 120]. The modification of lignin in this work is not well dispersing the lignin in the epoxy causing a small region of agglomerates. In addition, the water in the hydration sample evaporated after degassing. Incorporating functionalized lignin in epoxy was insignificantly affecting the fracture modulus, but a significant reduction was shown in fracture stress. On the other hand, the strong plasticization effect of water lowered the thermomechanical properties of the Mannich high level and Mannich hydration sample. Liu et al. modified alkali lignin with carboxylic acid via hydroxyl group esterification along with anhydride [89]. The functionalized lignin was mixed with epoxy, which had been cured with anhydride. Introducing 1 wt% modified lignin into the epoxy resin improved the critical stress intensity factor (KIC) and required strain energy release rate (GIC). The decreased cross-linking density in epoxy was considered proof of the toughening effect of lignin in epoxy resin.

3.3. Composite Lignin Polylactic Acid. Polylactic acid (PLA) is a bio-based and biodegradable polymer with eco-friendly properties for long-term development, including biodegradability, biocompatibility, and renewable resources [121–123] with solid mechanical properties, and is easy to

prepare [124]. PLA can be synthesized from crops such as wheat, sugar beets, and corn [125, 126]. However, PLA has also limitations related to its high cost. Much research was done on PLA with lignin that can act as filler or reinforcement material with emphasis on the investigation of the lignin composition of PLA, either native or modified lignin. The preparation of lignin/PLA composites can be classified into two methods, that is, solvent casting and melt extrusion [127].

The addition of lignin to PLA in the melt extrusion method increased the value of each parameter, whereas the solvent casting method had the opposite effect. This is because of the involvement of lignin particles, which may impair the structure's flexibility due to the internal plasticizers formed by the linking of benzene and ether rings [128, 129]. Because of the hydrogen bonding between the functional groups in lignin and the carbonyl groups in PLA, the melting temperature of the lignin/PLA composites increased. The lignin/PLA composites made from hardwood lignin had the best mechanical properties before and after weathering [12]. Gordobil et al. used acetylated KL (AKL) in a lignin/PLA composite by extrusion at 200°C at a rate of 75 min⁻¹ with a recirculation time of 10 min [130]. Furthermore, some of the hydroxyl groups in the lignin that were added to the blend had an impact on the stability [130]. This method has previously been used to fill lignin/PLA composites with acetylated alkaline lignin and OL from almond shells [126]. According to the study, acetylated lignin/PLA blends are more compatible than unacetylated lignin/PLA blends. Additionally, acetylated lignin can prevent PLA from dissolving hydrolytically. The better dispersion of lignin in the PLA as a matrix may have resulted in a urethane linkage, which resulted in improved PLA/lignin blend reinforcement [131]. Besides the solvent casting

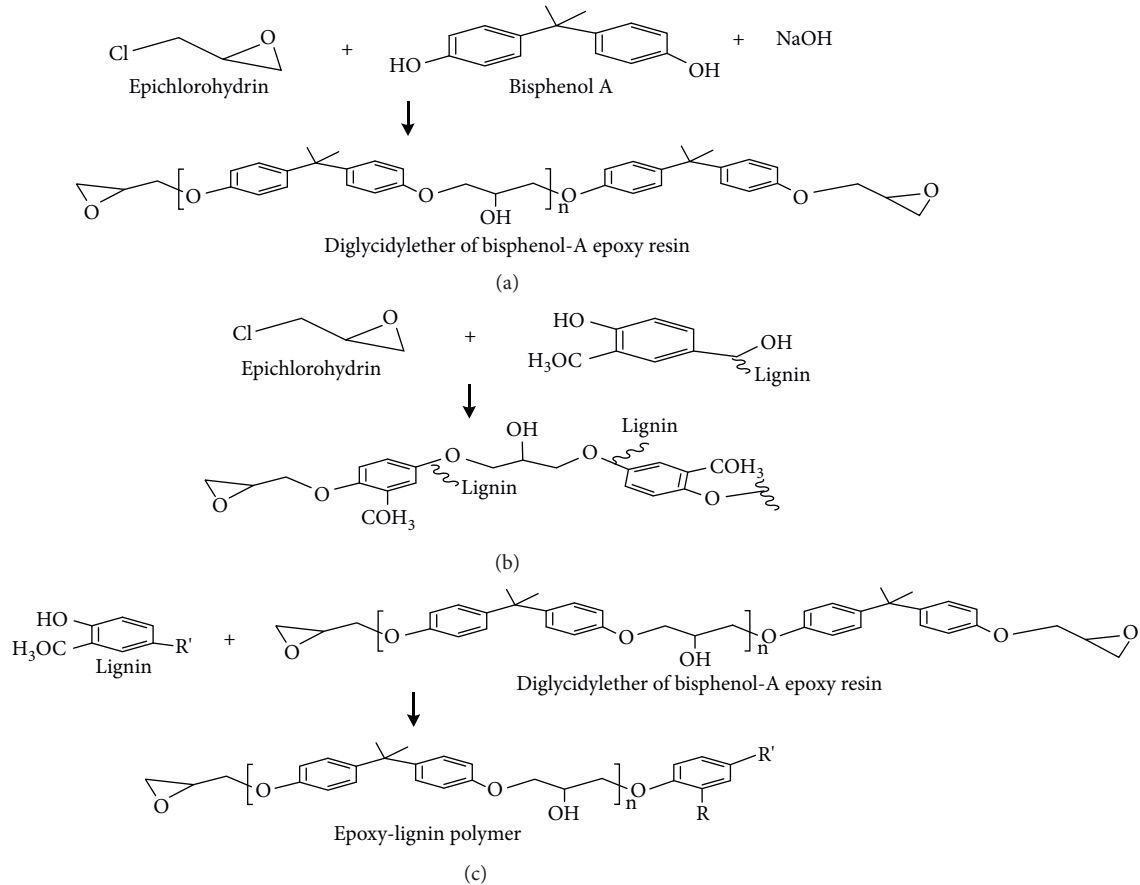


FIGURE 3: Proposed pathway in synthesis of lignin-bisphenol A epoxy resin: (a) bisphenol A-epoxy resins, (b) cross-linking of lignin with epichlorohydrin, and (c) lignin-bisphenol A epoxy resin [110] (Copyright © 2017 Springer-Verlag GmbH, Germany).

method, melt extrusion has been employed as a method to incorporate lignin nanoparticles into PLA. The uniform dispersion of lignin nanoparticles was found at 1% but not in 3% wt causes the aggregation of lignin nanoparticles with PLA [127].

The solvent casting and melt extrusion method resulted in a different surface structure [127]. The extruded film sample had a morphology with a smoother surface due to the equal distribution of lignin in the PLA matrix. Solvent casting produces a sample with a lot of microholes and a less uniform surface. When lignin/PLA composites with KL and AKL were compared to PLA/nonmodified lignin, the PLA interaction with AKL showed a significant difference [130]. Zhu et al. investigated unmodified lignin to be used as an adsorbent in lignin/PLA composites prepared by solvent evaporation-cross-linking. The microstructure and compression strength of the adsorbent are influenced by the lignin/PLA composites ratio [132]. Using a twin-screw extruder, Park et al. looked into adding KL and its plasticized form to a PLA blend with a pMDI as a coupling agent [131]. Adding lignin to composites as a biodegradation agent has also been studied. The addition of KL and its plasticized form to a PLA blend with a coupling agent pMDI was investigated by Park et al. PLA was melted and mixed with a variety of KL concentrations. A high-speed mixer spinning at 3,000 rpm

was used to create the composites. Because of the high friction between the polymer and the rotor, mixing, melting, and homogenization are all possible. According to the findings, lignin may aid in the biodegradation of lignin/PLA composites [133]. It has previously been reported on the effect of using lignin from hardwoods and softwood for lignin/PLA composites to accelerate weathering [12].

As a source of esterified lignin, Vila et al. recovered the liquid phase of organosolv pulping catalyzed with H₂SO₄ from *Pinus pinaster* wood. The extruder was used to blend lignin and esterified OL to PLA in a 30:70 mass ratio [134]. Ye et al. reported the effect of different ratios (5, 10, and 20%) of desulfonation LS or LS particles in lignin/PLA composites (DLS) using a casting method and then drying them at room temperature for 24 hours [135]. Zhang et al. developed PLA composites with lignin-silica hybrid (LSH) as the inflammable flame retardant (IFR). LSH is blended with PLA and ammonium polyphosphate (APP) in a two-roll mixing mill at 180°C for 10 min at a speed of 40 rpm. The samples were then compressed and formed into sheets [136]. Li et al. [137] investigated a Pickering emulsion method for preparing lignin/PLA composites by blending lignin nanoparticle suspension with PLA and dichloromethane solution (DCM). The PLA/lignin films were compression molded at 180°C for 5 min using a 20 MPa pressure. The lignin dispersion was

improved by over 5.0%wt. using this Pickering emulsion method. The performance of PLA composites filled with unpurified, purified, and acetylated OL from corn stover was compared by Gao et al. [138]. When compared to treated lignin, untreated lignin/PLA composites can be used as a filler in PLA composites with comparable or better performance. The use of unpurified lignin as a filler in PLA can lower the cost of purification.

3.4. Lignin-Cellulose-Based Composite. Lignin is an amorphous thermoplastic polymeric substance with a brittle property at high temperatures and a proclivity for not forming a film in solution. Lignin has a high carbon content, has high thermal stability, is biodegradable, has good antioxidant action, and is powerful [42]. Lignin is made up of hydrophilic groups that are surrounded by hydrophobic chains for the most part. The hydrophobic carbohydrate components of cellulose are often incompatible with hydrophobic chains. The most prevalent polymer, cellulose, has an extended linear chain structure made up of (1,4) connected glucopyranosyl-D units that form a single microfibril and polyhydroxy compound that may be joined with other materials via hydroxy hydrogen bonds [42, 139]. The effect of lignin in the drying and dehydration of nanocellulose was investigated by Kim et al. incorporating lignin reduced aggregation, redispersion kinetics, and stability, as well as allowing for reversible restitution during drying and polymer processing [140]. It is important to add ionic liquid using the blending solution technique or by synthesizing the composite membrane with other solutions to mix cellulose and lignin as a composite material.

Some methods have been reported to prepare cellulose-lignin-based composite, such as the solution casting film technique [141], vapor-induced phase separation method [142], regeneration in acetone [143], aqueous suspensions alkaline [144], blending solution [145], bio-membrane amino-modified [146], and nanocomposite coatings [147]. Cellulose, starch, and lignin are combined in an 85:10:5 ratio in a solution of 1-allyl-3-methylimidazolium chloride, and the fibers are constantly agitated at 80°C. The solution is put onto a glass plate, which is then placed in a vacuum oven with evacuated air and a transparent membrane that has been cleaned with flowing water [141]. Separately dissolved cellulose triacetate and lignin esterified nanoparticles were prepared. The two solutions are then mixed and placed onto a glass plate after being swirled for 2 hours at 25°C. The solution was applied for 2 hours at a regulated temperature and humidity, then removed off the film using a water bath, and dried at room temperature [142].

Sadeghifar et al. [143] developed and characterized semitransparent flexible cellulose-lignin UV-light-blocking films using a simple technique. The regeneration of cellulose-lignin films in acetone was used. Unlike simple mixtures of cellulose and lignin, these covalently bound cellulose-lignin films were homogenous. The UV protection of the prepared films was excellent. UV-B protection was 100%, and UV-A protection was above 90% with a cellulose film containing 2% lignin. Cellulose nanofiber (CNC) film

was created by suspending CNC in a NaOH solution, then adding alkali lignin and KL from softwood at a concentration of (1–10 % wt.). A combination of alkaline aqueous suspensions having appropriate NaOH concentrations is used to make CNC/alkali lignin and CNC/softwood KL films [144]. Bionanocomposite was prepared by melt mixing compounding process of unbleached nanocrystalline cellulose-containing 90% lignin with PP and MAPP as matrix and coupling agent and kenaf core as reinforcement. The presence of residual lignin increases the thermal stability and flammability of nanocomposite [148]. Previously, it was confirmed that higher lignin in CNC contributes to the better thermal stability of CNC which give advantage for promoting the development of nanocomposites [149].

As an additional cross-linker, tannic acid and epoxidized KL was developed to introduce epoxy groups into the lignin to yield the bio-renewable waste cellulose paper (Cell). Cell-epoxy lignin membrane was molded at 80°C for 4 hours with a load of 20–30 kN. At 140°C for 1 hour, a similar load was used to mold the Cell-epoxy lignin-tannic acid membrane [146]. New nanocomposite coatings based on CNC and synthetic/fractionated spruce and corn stalk lignin were created without any chemical modification or functionalization (through covalent bonding) of one of the two CNCs and lignin. Nanoparticles increase the weight ratio of the medium and the CNC-specific surface area of the solid film, allowing more lignin molecules to disperse throughout the solid film. The π - π aromatic aggregates dislocate as a result of the increased molecular expansion of these aromatic polymers on the surface of the cellulose nanoparticles, boosting the extinction coefficient and decreasing UV transmittance. At visible wavelengths, the nanocomposite coverings were optically transparent [147].

3.5. Lignin-Polyvinyl Alcohol Composites. PVA is a biodegradable polymer material that has high strength, chemical stability, and abrasion resistance, as well as biocompatibility [150, 151]. PVA is a polar polymer composed of mostly hydroxyl groups in its polymer chain bonds and has solid hydrophilic properties. On the other side, lignin has polar functional groups and has strong hydrogen bonds between molecules. Based on its properties, theoretically, the combination of PVA and lignin has good compatibility in conversion as a composite membrane.

Melt blending was reported for preparing lignin/PVA flame retardant composites. Adding lignin to PVA has proven to be an efficient way to create ecologically friendly and flame-retardant polymer materials, and the use of PVA and lignin will continue to expand [151]. PVA/poly (glycerol sebacate)/lignin composite was reported suitable for tissue engineering [152], while PVA/lignin nanofibers introduced by silver nanoparticles have been used for wound-healing application [153]. A lignin/PVA nanofiber membrane has been created as a separator for lithium-ion batteries using a water-based approach. To create a nonwoven membrane, PVA and lignin were dissolved in water, and the fibers were removed. As a result, the lignin/PVA membrane can be used as a separator in a variety of anodes for LIBs that are safer and faster [154].

The PVA/salt of the lignin sulfonic acid hybrid membrane was used for preparing the cation exchange membrane for the diffusion dialysis process to recover alkali [150]. Before introducing lignin, sulfonic acid, and HCl with tetraethoxy silane (TEOS) as a cross-linker, PVA was diluted in dimethyl sulfoxide (DMSO) to obtain a homogenous solution. To create the membrane, a homogenous slurry was thrown over just a glass plate at 60°C for approximately 1 day. The sustainable copolymer lignin-rubber-PDLA was produced in two steps employing ring-opening polymerization. To create the composite in chloroform, PVA was mixed with alkaline lignin-g-rubber-g-poly (D-lactide; PDLA). Alkaline lignin dissolves in aqueous alkali at room temperature [155].

The film casting method was investigated by Xu et al. [156] for preparing membrane by mixing alkaline lignin and PVA. Introducing lignin into PVA improves the thermal stability, oxygen, and carbon dioxide barrier, and visible light at 600 nm blockage in which the optimum content of alkali lignin was 15% for blending with PVA. This composition is suitable for green packaging materials. A similar technique was also used by Korbag and Mohamed Saleh [157] in which dissolved lignin was dropped into acetic acid and heated for 2 hours at 80°C. After that, PVA was mixed and stirred for 6 hours at 60–70°C before the drop in the Petri dish. The investigation of the chemical structure of PVA/lignin film presented strong intermolecular hydrogen bonds between PVA and lignin. In such studies, the introduction of a coupling agent is required to increase the tensile strength while maintaining the composite's elastic modulus. PVA biocomposite was synthesized by diluting PVA in Millipore water and agitating it with CNC and lignin nanoparticles before adding glutaraldehyde as a cross-linker and sonification. Figure 4 depicts the intermolecular reaction that occurs between CNC, PVA, and lignin nanoparticles.

3.6. Lignin-Starch Composites. Starch is a low-cost, available, biodegradable, renewable, and flexible thermoplastic that makes it considered a composite in packaging, engineering applications, and biomedical materials [14]. However, hydrophilic properties with poor mechanical and permeability characteristics need to improve by adding filler and enhancing agents such as lignin [159, 160]. Lignin has both hydrophilic and hydrophobic groups, making it suitable for organic and inorganic polymers. Starch composite can be prepared by the extrusion process under high temperature and pressure being added plasticizer such as water or glycerol [161]. However, the heterogeneous and nonuniform structure of lignin limited its application in starch film [162]. The lignin of about 3–10% has been utilized as reinforcement in the starch film by mixing the starch solution with lignin solution by casting technique [163–166]. SL has been utilized to improve the characteristics of lignin-corn starch biofilm blends. By solvent casting, the starch was combined with lignin and was heated to 100°C and then was added glycerol, continued by heating and drying [159]. This method was also used to blend corn and cassava starch with SL as a filler

material to prepare biofilm with the addition of glycerol [167].

For the development of starch-lignin composites, fractionalized SL was used. The ultrafine friction grinding process was used for reducing SL size reduction before use as a filler in starch-based biocomposites [161]. The starch/KL foam was prepared by compression molding with no deleterious effect on the density or morphology of the film when 20% lignin was incorporated into the starch. The blending solution approach has been used to create starch-based films and membranes [168]. By introducing corncob, SL (20–40 %wt.), thermal compounding was used to fabricate a thermoplastic starch (TPS)/poly (butylene adipate-co-terephthalate; PBAT) composite. Lignin acts as a reinforcement, improving the composites' compatibility with the TPS and PBAT phases, as well as their hydrophobicity and water repellency [169]. The TPS-lignin film was prepared by extrusion method by a single-screw extruder continuing irradiation with an electron beam accelerator. Introducing lignin (LS/alkali lignin) in the film improves the hydrophobic surface properties without loss in biodegradability. It is affected by the role of lignin for radical cross-coupling reactions to form hydrophobic condensed networks [164].

3.7. Lignin-Chitosan Composites. Chitosan contains high amino and hydroxyl groups, while lignin has high hydroxyl and carboxyl groups. Chitosan-based composite has been considered in food packaging and biomedical materials such as tissue engineering, drug delivery, and biosensors [170]. Chitosan is a biodegradable and biocompatible material extracted from crab shells. It is also appealing because of its antibacterial and antioxidant qualities, but there are several drawbacks to composite utilization, such as high cost, low water resistance, poor surface area, very acidic solutions, antioxidation, poor thermal stability, and low mechanical capabilities [170, 171]. Some materials such as lignin and PVA can be added to the system. The mechanism to combine two polymers is van der Waals' force or hydrogen bonding [172].

The solution casting method was commonly used in lignin-chitosan functional composite preparation [170, 172]. By this method, a chitosan film with the inclusion of micro ramie fiber and lignin has been created [170]. Mixing ternary and a binary film containing PVA-chitosan and lignin nanoparticles have been prepared via solvent casting for packaging application [171]. Modification of solvent casting method in water/ethanol solvent system was also performed by Crouvisier-Urien et al. [173]. Using the solution casting approach, a membrane comprising chitosan and lignin was successfully used to remove hazardous dyes from wastewater effluents, including methylene blue dye, by up to 95%. Membranes can be used up to five times before they need to be replaced [174]. The blending technique of lignin and chitosan has been carried out in the study of Li et al. [42].

Cross-linking between hydroxymethylated lignin and chitosan was reported in the preparation of composites by Shiyani et al. [175]. The other method involved mechanically fibrillating unbleached tree bark after alkaline extraction to produce lignin-containing cellulose nanofibrils (LCNF),

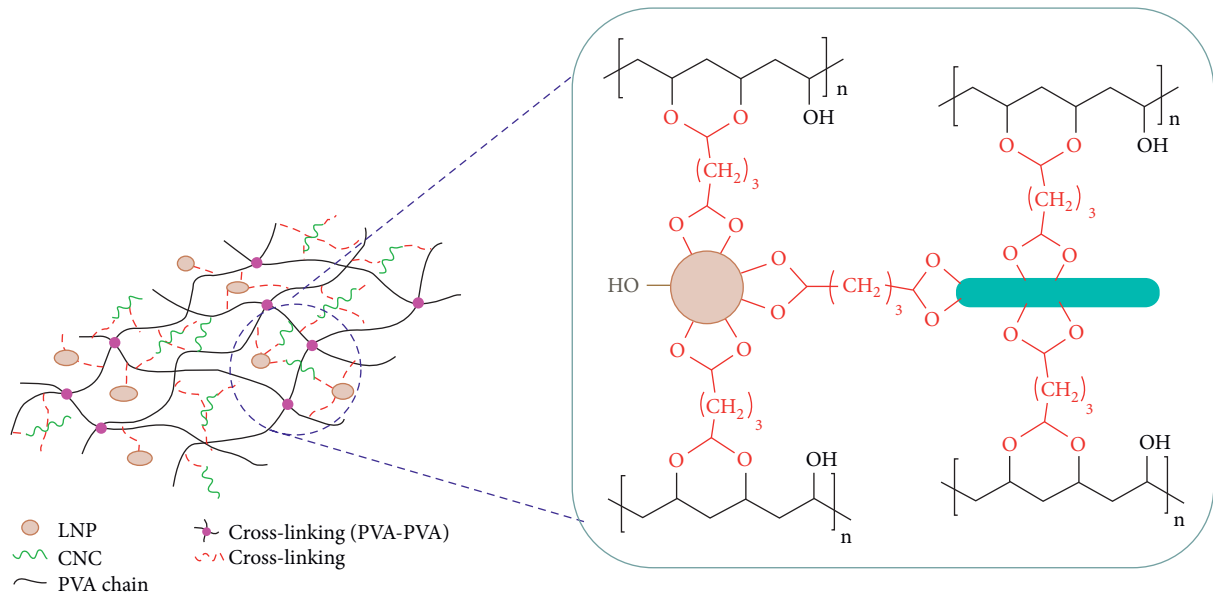


FIGURE 4: The proposed cross-linking reaction of polyvinyl alcohol, cellulose nano cellulose, and lignin nanoparticles uses glutaraldehyde as a cross-linker [158] (Copyright @ 2020 MDPI under CC by 4.0).

which were used as a reinforcement in TPS to create innovative biodegradable composite films. Lou et al. [176] looked into it using a microwave-assisted synthesis of chitosan-acrylamide-lignin terpolymer. Mechanical fibrillation of unbleached tree bark followed by alkaline extraction resulted in the formation of lignin-containing LCNF, which was used as a reinforcement in TPS to create newly biodegradable composite films. Lignin contributes to increase water barrier properties and thermal stability of TPS-LCNF composites [177]. The composite hydrogel containing chitosan and lignin has been prepared for wound dressing in which its mechanical improvement when lignin was introduced [178].

3.8. Lignin-Based Rubber Composite. Silica and carbon black are typical reinforcing materials in rubbers [179, 180] to improve the mechanical and thermal properties of the compounds while lowering the cost and, in some cases, the weight. However, due to pollution concerns and the dark color of carbon black, lignin, which has high availability, annual renewability, and low cost, is being considered as a possible replacement for the carbon black [181, 182]. In rubber composites, natural rubber (NR) is a common matrix [183, 184]. The combination between NR and lignin was a good combination to produce a green composite, especially in the tire industry. The addition of filler to NR alters its character due to a change in the system's polarity level. Furthermore, bio-filler and rubber are incompatible due to the lack of polarity in rubber [185]. Fillers (lignin and silica) can work together to prevent the formation of a filler network. In exchange, silica facilitates the dispersion of lignin in the rubber matrix. Various types of lignin were found in this study, including KL, SL, calcium liginosulfonate, and sulfate

lignin [186–188]. Coupling agents such as maleic anhydride (MA) were grafted onto the polymer backbone to enhance interfacial bonding and mechanical properties.

The tensile strength of natural rubber composites improved by about 10% when maleated natural rubber was produced in internal mixing [189–191]. The disadvantages of current techniques are that they take time and are not eco-friendly because they use solvents. Due to the high surface energy of rubber matrices, obtaining a homogeneous distribution of lignin particulates is difficult. As a result, by covalently bonding incompatible polar fillers and nonpolar rubber in rubber composites, MA has the potential to improve interfacial adhesion [192–196]. The interfacial adhesion of the wool fabric and NR latex was improved using sodium liginosulfonate (SLS). SLS plays a role as cementing materials in wool fabric and rubber latex and then was applied in varying amounts to the coarse wool is a woven fabric. SLS treatment improves the density and UV resistance of rubber-based composites. Composites have a broad range of applications, including acoustic panels, mats, and bags [197]. To increase the hydrophobicity of lignin and thus its dispersion in the rubber system, lignin has been modified with silylation. After incorporating 5 %wt. silylated KL into the natural rubber matrix, it can result in a 44.4% improvement in tensile strength. The greater the amount of modified lignin in the filler, the higher the elastic moduli and Payne effect intensity [198]. By mixing KL, OL, and SL into natural rubber composites in a lab-scale two roll mill, better properties were obtained than with soda lignin. The Payne effect was reduced after lignin was added, and their processability, aging resistance, and thermal stability all improved. The filler loading ranged from 5 to 20 phr, with a total hybrid filler content of 50 phr [188].

4. Lignin as Filler in Wood-Based Composite

The main concern is the long harmful effect of formaldehyde emission in the use of traditional formaldehyde resin such as urea-formaldehyde (UF), melamine-formaldehyde (MF), or phenol-formaldehyde (PF) have motivated the researchers to find renewable alternative sources to substitute the adhesive in the wood composite system. Lignin with phenolic structure has been reported prospective as a substitution in wood composite adhesive for creating eco-friendly composites. Despite its complex structure, low reactivity, low solubility, high polydispersity, and strong hydrophobicity, lignin's chemical reactivity is limited, necessitating greater catalyst concentrations and longer heating durations in the manufacture of wood-based composites [33, 132, 199–204]. Chemical modification of lignin, mixing with additional bio-based materials such as starch, tannin, polyethyleneimine, or glyoxal, is a way to improve the performance of lignin-based adhesive [199]. Some different lignin types have been used such as LS, KL, OL, SL, or hydrolysis lignin [18, 201, 205–207] in adhesive applications of plywood, oriented strand board (OSB), fiberboard, particleboard, or structural application.

OL was able to substitute phenol in PF adhesives for particleboard by up to 30% [208]. Magnesium and sodium lignosulfonates (LS) of 30% were introduced in UF adhesive formulation as particleboard that has comparable properties to UF-bonded particleboards [205]. Savov and Antov [209] investigated the use of LS as a medium-density fiberboard adhesive with the optimum content without deterioration the board strength was 35%. Ammonium LS was also used as a bio-based additive in high-density fiberboard in which it was mixed with UF resin at varying levels from 4 to 8% on dry wood fibers mass. The application of up to 6% ammonium LS decreases the mechanical properties of wood fibers impacted by the short press factor while also increasing moisture content [18]. Those studies revealed that LS acts as a formaldehyde scavenger [18, 205] as presented in Figure 5.

In another study, magnesium lignosulfonate was used as fiberboard binder for limited structural application with 15% gluing content based on the dry weight of the fibers [207]. Because of the lower resin reactivity and longer reaction time, lignin can be used to substitute phenol below 50% [201]. Lignin reacted with glyoxal resin and furfuryl alcohol and then was added by variation epoxy resin for particleboard adhesives as reported by Zhang et al. [210]. KL was employed up to 35% in the stein hall process to create starch-based adhesives for use in paperboard. Water resistance and strength of paperboard products are both improved by this addition [211]. KL and SL were also used to substitute lignin-phenol-glyoxal with various weight percentages of 10–50 wt. with which the optimum substitution at 30% [212]. For altering soy flour adhesives, a lignin-based adhesive was made by batch copolymerizing lignin, formaldehyde, and phenol. It was then employed to improve the wet and dry bond strength of plywood adhesives [213]. In the preparation of dry-process fiberboard with modification pressing technique, 10% dilute sulfuric acid hydrolysis lignin (based

on dry fiber) was combined with 2% PF resin. The board possesses physical and mechanical qualities that are comparable to board bonding with 10% PF during a standard hot-pressing cycle [214]. Enzymatic hydrolysis lignin was incorporated with NR latex to prepare bio-adhesive by filler and blending base component method as medium density fiberboard adhesive. Mixing 5 and 10 g lignin into 10 g natural rubber latex provides the highest modulus of elasticity and modulus of rupture value of medium density fiberboard, respectively [215].

5. Characterization of Lignin-Based Greener Composites

5.1. Morphological Analysis of Lignin-Based Composites. A morphological study of lignin-based composites was carried out by analyzing SEM micrographs. Sahoo et al. [216] reported that the SEM micrographs of lignin obtained from Arboform F45 showed the presence of lignin fragments (5–10 μm) and dispersed fibers (20–150 μm). Fibers are connected with varied proportions with flat and uneven textures, suggesting the existence of diverse varieties of fibers in the lignin group. While on the other hand, SEM photographs of the lignin-based poly(butylene succinate) (PBS) composite revealed that the surface morphology of the broken surface of the lignin-PBS composite showed relatively smoother and uniform phases. This could indicate that lignin is more compatible with PBS; this affinity could be explained by the alignment of solubility characteristics and the possibility of polar-polar interaction; the lignin-PBS compliance supports the increased Tg of lignin composites. In the micrograph of the broken layer, deformations and cavities with irregular forms were also visible, indicating a stronger polymer-filler interaction in the polymer matrix. Filament pull-outs having attached polymer matrices are marked by these cavities. In the SEM image of lignin-PBS composites, plucked-out fibers can also be seen precisely. Crushed fibers (short strands) in the lignin encouraged easy fracture deformations via a short fiber pull-out process, which greatly contributed to the composites' poor mechanical characteristics. The size of pulled-out fibers from lignin-PBS composites influences this effect.

Graupner [217] investigates the effects of lignin on the mechanical properties and sustainability of natural fiber-reinforced polymer composites. Lignin plays a critical role as a naturally occurring adhesion stimulant. Furthermore, the hypothesis suggested that lignin promotes matrix-reinforcement adherence in cotton fiber-based biocomposites. Cotton was an excellent choice for this project since it contains no lignin. According to the results of the SEM study, the presence of lignin increased adherence between fiber and resin; lignin also strengthens the interaction between constituent layers of multilayered networks. The unmodified cotton/PLA materials had obvious deformations between constituent layers of multilayered networks; the lignin-treated cotton fiber composites showed few imperfections. Wang et al. [218] studied the morphology of PLA/lignin-containing cellulose nanofibrils (L-CNFs) composites; they analyzed the SEM photographs (Figure 5) and

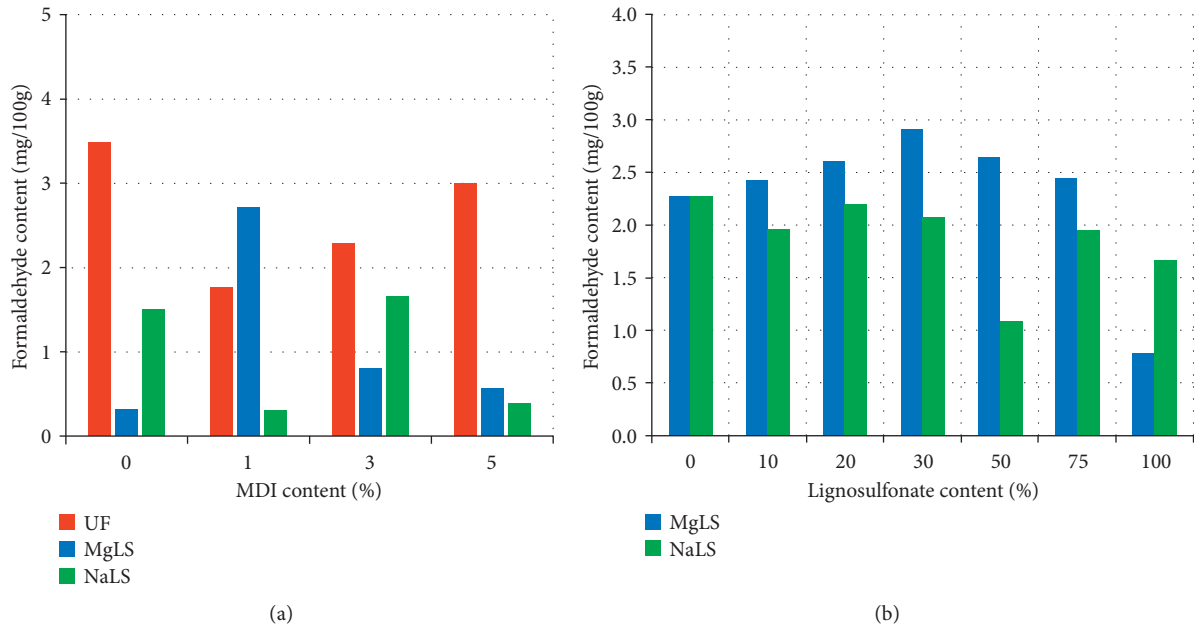


FIGURE 5: (a) Formaldehyde content of board by using magnesium lignosulfonate and sodium lignosulfonate adhesives with a variation of MDI cross-linker and (b) formaldehyde content of board at the variation of lignosulfonate content [205] (Copyright @ 2021 MDPI under CC BY 4.0).

concluded that L-CNFs improve the strength and embrittlement of nano-composites. Furthermore, L-CNFs significantly impact the composite stiffness compared to CNFs. Another study on composite SEM reveals that lignin, organosolv, and LigninBoost lignin can be well distributed in PLA matrix during melt blending in which lignin and PLA have good adhesion [12]. The addition of lignin to PLA seems to have a lousy affinity because it tends to agglomerate with some cracks (Figure 6) displaying poor interfacial compatibility.

Guo et al. [219] analyzed morphology changes that occur due to chemical modification of lignin by reacting lignin with different compounds; they studied how chemically modified lignin causes changes in the morphology of biocomposites. Lignin was modified with acid (Ad), acetoacetate (Act), and butyric (Bt), respectively, and their morphology and compatibility with PLA matrix were examined from SEM micrographs (Figure 7). The particle sizes of modified lignin ranged from 0.5 to 2 μm , although the particle size of Act-lignin was substantially lower than that of other types of modified lignin. The morphology of lignin fibers influenced the degree of anisotropy. All lignin fragments seemed to be fairly spherical, showing that variable levels of lignin aggregation resulted in the formation of diverse microspheres. Simultaneously, the lignin size influenced the surface area per unit volume, leading to strain transmission and composite filler wetness changes, thus altering and controlling the lignin filler's compliance and homogeneity with the polymer composite. Modification of lignin with alkylation has been reported by Maldhure et al. [96] in which the addition of more than 15% alkylated lignin into PP composite causes agglomeration (based on SEM analysis) so that the crystallinity decreases.

Figure 7 depicts the morphological characteristics of PLA/chemically modified lignin biomaterials. The introduction of lignin into the pure PLA increased the irregularity of the composites, leading to a variety of fractions and, as a result, to more regions of vulnerability throughout the composite materials, potentially lowering their tensile strength. Furthermore, chemically modified lignin is evenly diffused and fully integrated into the composite material; the resilience of slightly larger diverse particle sizes is influenced by the degree of permeability and interfacial bonding between PLA and chemically modified lignin [220]. The interface of PLA/lignin biomaterials was noticeably harder and stronger than those of composites without lignin [221]. When Act-lignin was added, a significant characteristic that can be noticed was the presence of distinct phases with recognizable lignin aggregates, whereas in the case of Ad-lignin or Bt-lignin, a considerable number of lignin fragments pierced from the surface, showing poor connectivity among PLA and Ad-lignin or Bt-lignin. Incorporating Act-lignin into the PLA matrix enhances dispersal [218], indicating the greater contact and adherence between PLA and Act-lignin, which establishes a stronger interface region [222]. Due to the increased interfacial contact of matrix filler, PLA/Act-lignin biocomposites demonstrated superior characteristics to other composites. However, a different SEM result was reported Mendis et al. [119] in which the lignin modification cannot disperse well, as shown by the agglomeration of lignin in epoxy (Figure 8).

5.2. Effect of Lignin Concentration on the Morphology of Biocomposites. Hong et al. [223] analyzed the surface morphology of lignin-based biocomposites containing lignin in

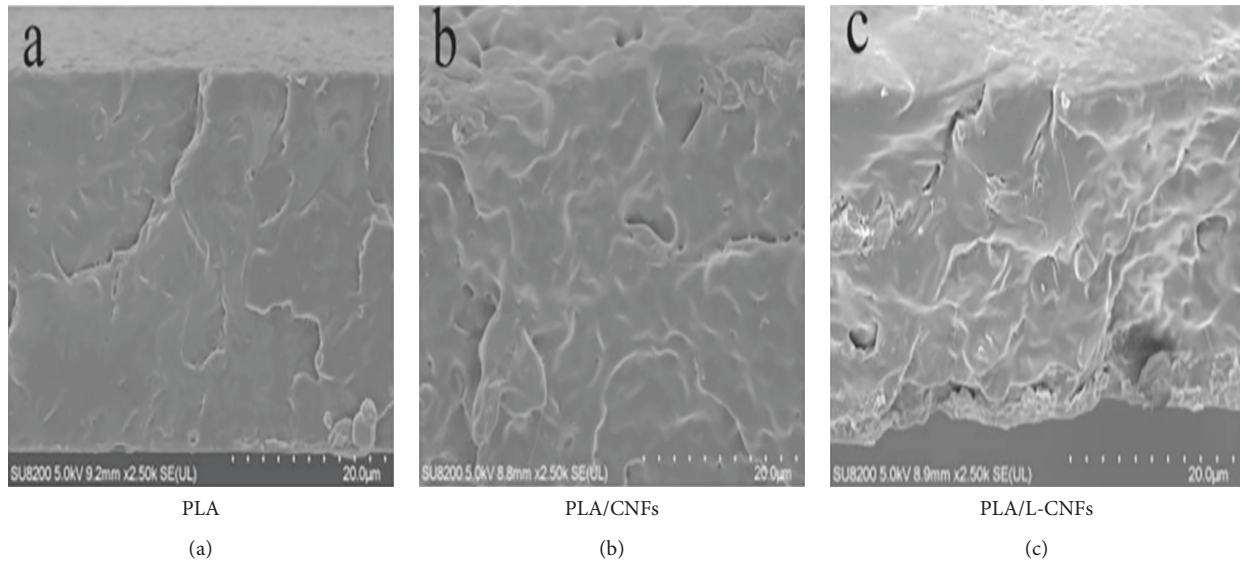


FIGURE 6: SEM photographs of (a) polymer, (b) polymer composite without lignin, and (c) lignin-containing biocomposite [218] (Copyright @ 2018 MDPI under CC BY 4.0).

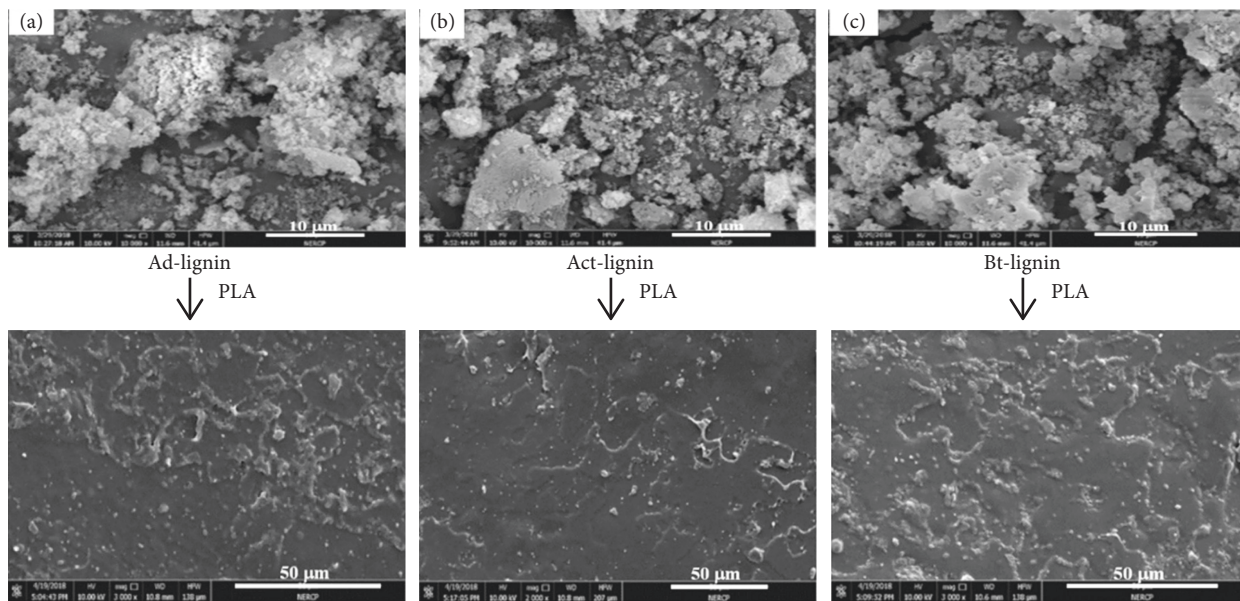


FIGURE 7: SEM images of biocomposites of chemically modified lignin: (a) PLA/Ad-lignin, (b) PLA/act-lignin, and (c) PLA/Bt-lignin [219]. (Copyright @ 2019 MDPI under CC BY 4.0).

different concentrations. They observed that with increased lignin concentration, the surface of the filaments on the 3D printed items grew noticeably rougher and deeper in color. This is owing to the decreased melt strength of the biocomposites. The interface texture of the biocomposite fibers having more than 15% lignin was too rough to bond layer-by-layer, resulting in a large gap. It is due to the diminished melt flow and the lack of adherence between layers. Filler dispersibility and interfacial adherence to the matrix material are important elements in defining the filler-reinforced composite's ultimate physical quality. SEM results demonstrate the influence of lignin on the matrix interface. Furthermore, the findings show that size abnormalities and fiber dispersion

may have a greater impact on the quality and compatibility of biocomposites. In lignin-based composites, water absorption and thickness swelling were reduced [100]. The more lignin added, the rougher the cross-sectional morphological surface became.

The presence of hydroxyl groups in lignin facilitates it to link to PLA, resulting in strong interfacial interaction and enhanced mechanical characteristics [224]. Dias et al. [92] demonstrated that the matrix could survive lignin loading at a low lignin level according to the SEM pictures. The mechanical characteristics of uncompatibilized and compatibilized composites are strikingly comparable; Figure 9 shows the SEM image of softwood KL (SKL) and

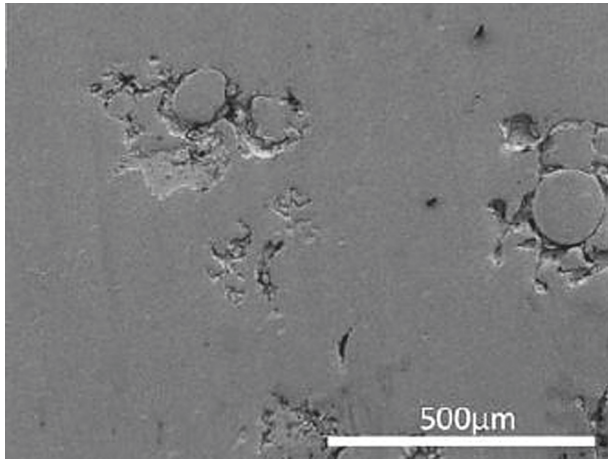


FIGURE 8: SEM figure of the composite sample that was mixed with a hardener in only 5 minutes (IMM) [119] (copy with permission from Wiley).

polypropylene grafted with maleic anhydride (MAPP) composite of SKL.

The SEM micrograph demonstrated that the integration of lignin caused an irregular and hard interface. Lignin aggregation was most likely driven by the increased density of hydroxyl groups with increased lignin content. The image of the lignin-loaded composites with MAPP, on the other hand, shows a more homogenous dispersion of lignin particles. Increased lignin concentration raises the plasticizing effect; thus, it causes chemical alteration, suggesting that interchain interactions alter the physical characteristics of the composite. The rough surface was observed in all lignin-containing biocomposites with varied lignin concentrations. Microspheres and many aggregates scattered on the interface of lignin blends indicate the presence of lignin. Lignin blends have a finer interface because the dispersion size of the lignin is decreased. While the morphological analysis of polystyrene/lignin composites with compatibilizer addition revealed that adding lignin made the cracked surface of the composites seem rougher [225]. Another study reported that incorporating lignin into chitosan until 20% resulted in substantial changes in the chitosan composite morphology. The more porous and textured composite surface was presented, and an increase of pores occurred with an increase in lignin content resulting in a more pronounced [9]. Previously, Chen et al. [172] reported the good dispersion of lignin (until 20% wt.) into chitosan confirmed by SEM analysis contributed by the strong interfacial interaction. When compared to composites containing citric acid (caLNP) and acetylated lignin (aLNP), the PLA composite with 1%wt. unmodified lignin showed higher particle aggregation. Furthermore, no evident effect of lignin chemical alteration was seen in composites with a filler content of 3% wt. [226].

5.3. Effect of Temperature on the Morphology of Biocomposites. The influence of temperature on the morphology of lignin-based biocomposites was investigated by Tanase-Opedal

et al. [227]. Experiments and surface morphology (Figure 10) proved that 215°C temperature was the best for the applications of lignin-based biocomposites in the printing area because this temperature may boost interlayer adhesion and mechanical strength. SEM images of the lignin-based biocomposites at 205°C showed distinctly marked imprinted fibers, suggesting poor interlayer adherence and limited mechanical characteristics. On the other hand, raising the temperature to 230°C resulted in a drop in mechanical performance. This might be due to the degradation of carbohydrates into gaseous products present in the lignin fraction, thus generating microstructures inside the biocomposites.

Rahman et al. [228] reported that the lignin-based biocomposite's surface has fracture toughness characteristics. All lignin compositions in the polymer matrix had a decent dispersal of lignin fibers. This is most likely due to strong lignin particle adherence to the polymeric matrix. Furthermore, adherence improved for materials produced at higher temperatures. Figure 10 showed that the synthesis of the lignin-based biocomposite, poly-L-lactic acid (PLLA) at higher temperatures increased the tensile strength and roughness of the surface.

5.4. Effect of Catalyst on the Morphology of Biocomposites.

The catalyst has no discernible influence on the morphology of the composites. Moreover, water absorption tests on biocomposites in the presence of an aqueous medium might provide useful information regarding the influence of the catalyst on structural strength. In the preparation of PP/lignin composite using a melt mixer, MA-modified lignin was well dispersed in PP up to 25%, while dichloromethane-modified lignin was only up to 15% based on morphological analysis [96]. Yu et al. [229] investigated the catalytic effects of nickel (cobalt or zinc) acetate on the properties of PP-based lignin composites (PP/N-lignin); (Ni(Ac)₂) catalytically destroyed PP/N-lignin while significantly increasing char by-products. Ni (0) and NiO also increase carbonization via the catalytic activity of the composite material and seem to be principally accountable for the PP/N-lignin system's improved physical and chemical properties. SEM photos of PP/N-lignin showed several large cracks, while PP/N lignin-containing nickel has no cracks with a relatively smoother surface (Figure 11).

5.5. The Effect of Particle Size on the Compatibility of Lignin with the Matrix.

The reduction of particle size of lignin in the nanoscale with an ultragrinding process contributes to improving the compatibility between lignin and starch in this composite preparation based on microscopic analysis and membrane filtration [161]. Before extrusion with PLA, caLNP and aLNP lignins were improved dispersion, minimized aggregate size, and improved performance quality. The size of lignin aggregates in the PLA matrix is determined by the compatibility of lignin and PLA, and it decreases as phase compatibility improves [226].

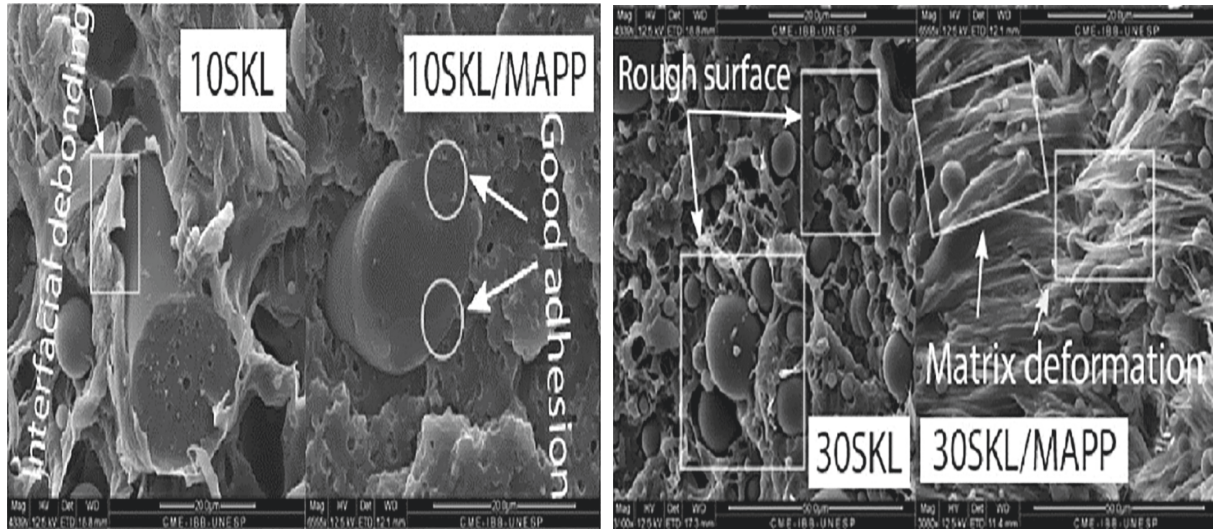


FIGURE 9: SEM photographs of lignin and lignin-based biocomposites containing different concentrations of lignin [92] (Copyright @ 2018 John Wiley & Sons).

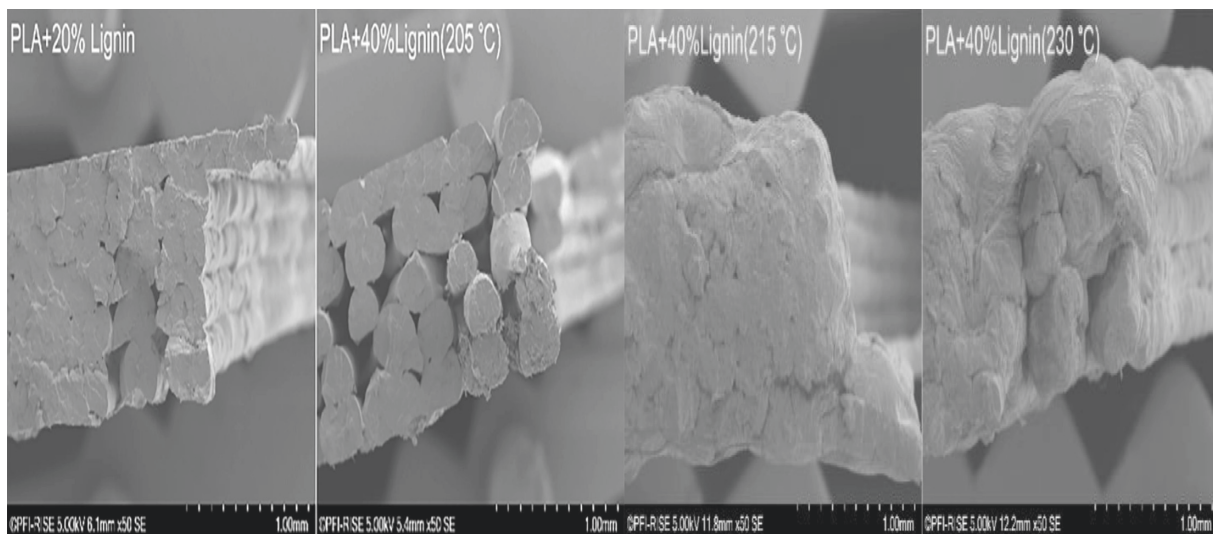


FIGURE 10: SEM images of lignin-based biocomposites at different temperatures [227] (Copyright @ 2019 MDPI under CC BY 4.0).

6. X-Ray Diffraction (XRD) Analysis of Lignin-Based Composites

The crystallinity of lignin-based composites was measured by using the XRD technique. The crystallinity of the composite was determined by dividing the total amount of sample material by the amount of crystalline cellulose. With the addition of lignin to cellulose, XRD peak intensities were dropped, which presents that the addition of lignin should decrease the crystallinity of cellulose, the cellulose crystallinity of lignin was still over 54% [230]. The addition of alkylated lignin (up to 15%) into PP increases the crystallinity compared to PP [96]. However, the addition of more than 15% alkylated lignin causes agglomeration (based on SEM analysis), so the crystallinity decreases [96]. Meanwhile, the addition of arylated lignin into PP decreased the

crystallinity, indicating that arylated lignin was not compatible with PP.

Jiang et al. [187] explored the influence of lignin addition on cellulose crystallinity to fabricate lignin-cellulose biocomposites. After introducing lignin and hot-pressing, the crystallinity of cellulose was preserved. Figure 12(a) shows XRD patterns, which reveal no differences between cellulose sheets and lignin-cellulose composites. The moderate alkali swelling and hot-pressing procedures did not damage the crystalline structure of cellulose, as shown by the diffraction pattern corresponding to the (110), (020), and (040) planes of the cellulose.

Iglesias Montes et al. [231] reported that XRD spectrum of lignin nanomaterials (LNMs) consists of wide peak which revealed that LNMs formed a three-dimensional nanocomposite lacking an organized and consistent

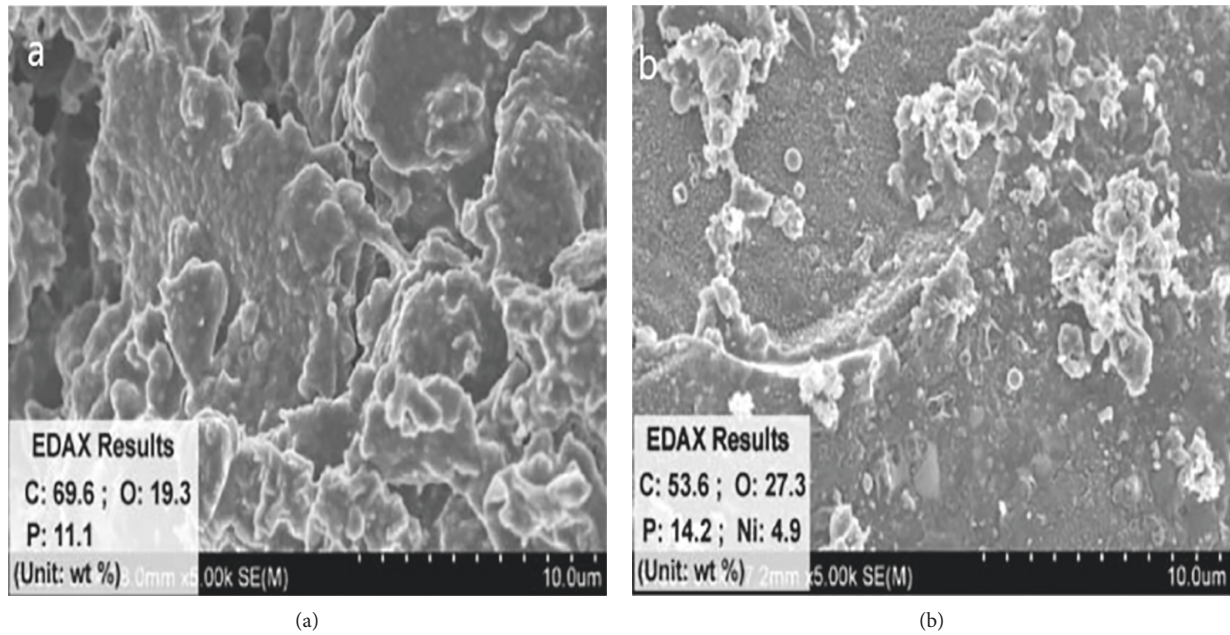


FIGURE 11: SEM images of char residue: (a) polypropylene-based 20% PN lignin composites and (b) polypropylene-based 20 PN-lignin-Ni composites (reprinted with permission from reference [229]; Copyright @ 2012 American Chemical Society).

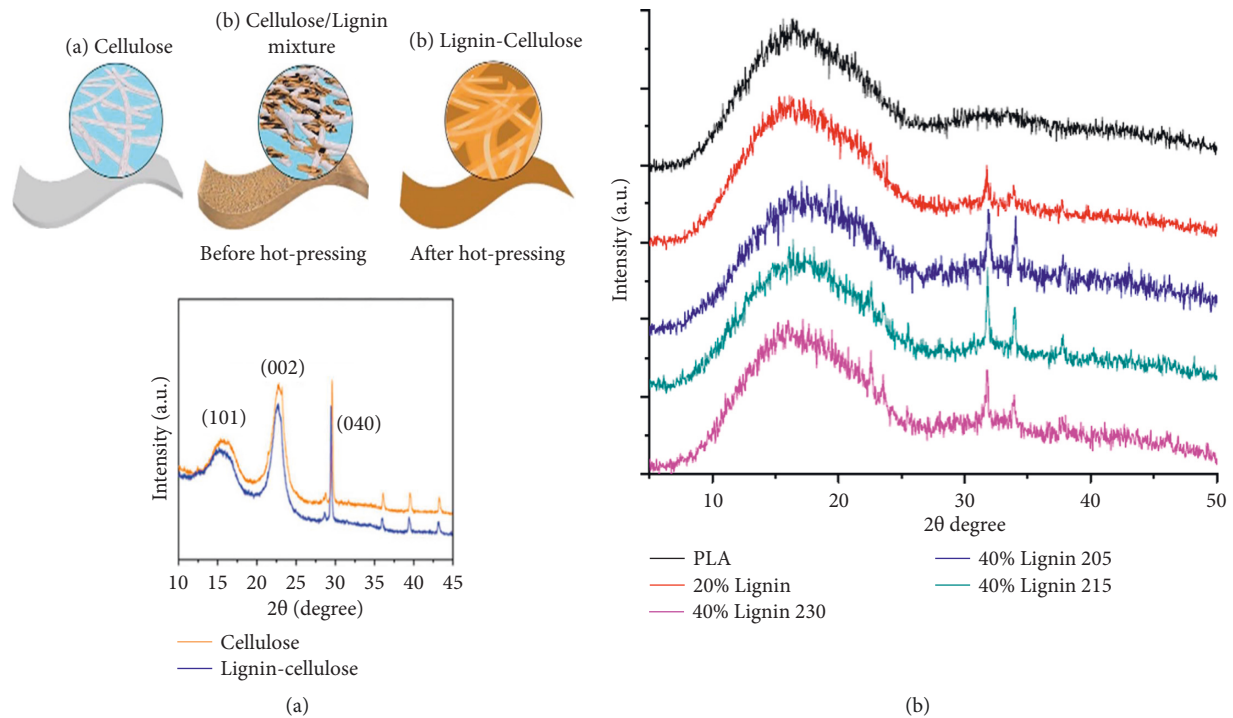


FIGURE 12: (a) Diagrammatic illustration of the crystal phase of lignin-cellulose composite [187] (Copyright @ 2015 Wiley periodicals) and (b) XRD pattern for lignin-based biocomposite [227] (Copyright @ 2019 MDPI under CC BY 4.0).

supramolecular structures, suggesting that the LNMs were only partly crystalline. Crystallization was not produced by the addition of lignin in the case of PLA monolayers; as no extra peaks formed in the XRD spectrum, also there was no noticeable alteration in the crystalline phase as a result of the

addition of lignin and cellulose as binding agents in the XRD patterns of PLA bilayers. Tanase-Opedal et al. [227] reported that when the lignin was added to the matrix, X-ray examination indicated a change in the crystalline phase (Figure 12(b)). PLA has a broad peak due to its

microcrystalline structure. XRD Peaks of lignin biomaterials suggested that PLA crystallization had increased due to lignin's role as the nucleation site.

XRD studies of rubber composites revealed the strain-induced crystallization of epoxidized natural rubber (EDR), demonstrating the basic lignin reinforcing effect on EDR (Figure 13). EDR particles might act as additional connectivity cross-links, strain enhancers, and filler materials to a certain level. As a result, when compared with other synthetic rubbers, the clean EDR outperformed them. The diffraction patterns of EDR crystallites steadily decreased with rising lignin concentrations, showing that lignin prevented EDR crystallization caused by strain. There was no strain-induced crystallization in the rubber composites containing a higher lignin concentration. We could conclude from the XRD results that the rubber composites' reinforcing came mostly from lignin instead of particles of EDR [187].

Rosova et al. [9] studied the crystalline structure of biologically active chitosan-based composites with varying quantities of lignin as reinforcement material. Figure 13(b) depicts the wide-angle X-ray diffraction patterns of chitosan and composite materials with various levels of lignin. The existence of peak positions at $2\Theta = 10.5^\circ$ and 15.3° supports the presence of anhydrous type and hydrated chitosan in the sheets [232]. The addition of lignin to chitosan caused the sheets to be amorphized. Furthermore, when comparing composites to the pure chitosan, the peaks at $2\Theta = 10.5^\circ$ were more prominent, whereas the peaks at $2\Theta = 15.3^\circ$ were relatively weak. With the introduction of lignin, the content of the hydrated type increases while the amount of the anhydrous type decreases.

7. Thermal and Mechanical Properties

The phenolic backbone and aromatic structure in the lignin chemical structure have been well known to contribute to its thermal stability [233, 234]. The phenolic backbone itself degrades at around 200 and 450°C ; meanwhile, the aromatic structure decomposes between 400 and 600°C [235]. The addition of modified KL into PVA resulted in a slight thermal degradation improvement of the resulting composite film [236]. The increment of the thermal degradation temperature is in line with the lignin content. For example, 5 %wt. lignin contents increase the decomposition temperature ($T_{\text{decomposition}}$) by 2°C , while the addition of 25 %wt. increases the $T_{\text{decomposition}}$ by 15°C . In addition, the presence of lignin in PVA broadens the thermal degradation peak of the composites. In another, Canneti and Bertini introduced lignin to polyethylene terephthalate (PET), and it was observed that lignin strongly influences the composites' thermal stability. However, high lignin loading resulted in a decrease in $T_{\text{decomposition}}$ [237].

The thermal properties of lignin/PLA composites were influenced by the preparation method [238]. According to Gordobil et al. [130], adding KL and acetylated KL (AKL) to PLA greatly boosted its thermal stability but did not support PLA crystallization (Table 3). The incorporation of lignin 0.5

and 5% were increased during the initial degradation (T_{onset}) and $T_{\text{decomposition}}$ up to 70°C . The composite with KL has higher thermal stability than the composite with the acetylated sample. After lignin was added, the amount of char residue was reduced. On the other hand, Sahoo et al. discovered that when lignin was added to the composites, the char residue increased [239].

The incorporation of lignin into polymers appears to have an insignificant effect on the thermal transition temperature, T_g , and the melting temperature (T_m) [240]. The addition of lignin to PLA has displayed no significant change in T_g [130]. A similar study on introducing lignin into PLA reported that the thermal degradation property of composites has not changed significantly with this treatment [241]. Meanwhile, T_g was slightly increased after adding polybutylene succinate (PBS) [216]. Lignin addition has contributed substantially to the T_g and degradation temperature of chitosan [172]. When compared to LS in PLA composites, the addition of DLS improved compatibility and thermal stability ($T_5\%$ and T_{max}) [135]. In another study, Li and his groups [242] reported that the introduction of lignin increased the decomposition temperature but decreased the mechanical properties of lignin/PLA composites. Thermal properties analysis of alkylated lignin produced a composite that was more stable to heat than arylated lignin because it was more miscible in the PP matrix [96]. The melting point of the PP + alkylated lignin compound was lower than the PP + arylated lignin compound, indicating that alkylated lignin is more compatible with PP, compared to arylated lignin. After the addition of kenaf core fibers and lignin, the maximum degradation temperature of PP composites increased. According to the thermal conductivity analysis, the addition of kenaf core fiber and lignin did not affect the conductivity of the PP composite. In comparison to other PP composites, PP/L/KCF composites had a higher thermal diffusivity and a lower volumetric specific heat [97]. TGA analysis of PP/lignin blend monoliths showed that the addition of lignin caused T_{onset} to shift to a lower temperature, increasing the degradation temperature and the number of char residues, indicating that PP/lignin composites had better heat stability than PP [99].

The modification of lignin and the interaction between lignin and the functional group in the polymer matrix were suggested to be responsible for these variance results [240]. In some reports, the lignin composition in composites influences the viscoelastic properties of the polymer. The cross-linking ability of lignin is accountable for the rise in the stiffness of the composite. In a study, lignin increased the storage modulus of PP/lignin composites with MAPP as the compatibilizer between the two [92]. The loss modulus and storage modulus were increased in line with the lignin content, indicating the successful cross-linking of lignin by polymer molecules. Besides that, the addition of lignin as much as 30% of the total weight decreased the tensile strength and (unnotched Izod) impact strength of PP/lignin composites but increased the flexural strength, Young's modulus, and flexural modulus. The addition of MAPP, as much as 6.67% by weight of lignin, increased the flexural strength and tensile strength [90]. Meanwhile, adding lignin to polystyrene increases its storage

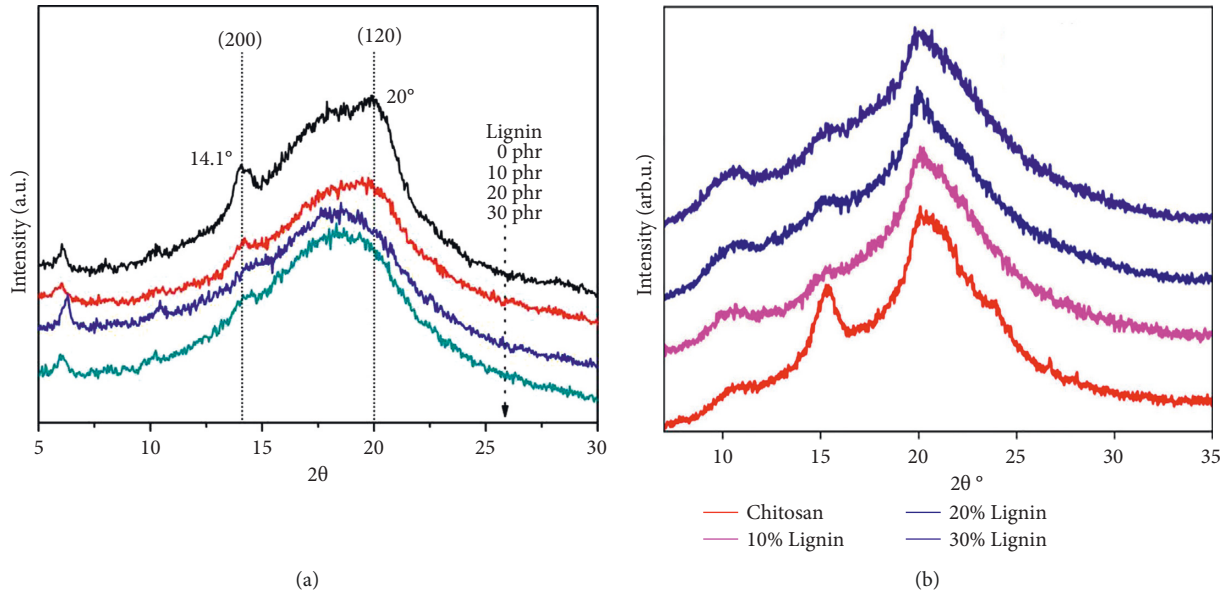


FIGURE 13: (a) XRD analysis of lignin-based rubber composite [187] (Copyright @ 2015 Wiley periodicals) and (b) wide-angle X-ray diffraction patterns of chitosan and composite materials with varying levels of lignin [9] (Copyright @ 2021 MDPI under CC BY 4.0).

modulus from 1.24 to 2.25 GPa [225]. Stewart [118] found that lignin provides high impact toughness and stability in epoxy resins when compared to lignin-free phenol epoxy resins. The addition of 10% KL to PP decreased the impact strength (−11.11%), flexural strength (−15.50%), tensile strength (−27.42%), and tensile modulus (−33.63%) of PP/lignin composites compared to PP. The addition of MAPP as much as 3% can improve the impact strength, flexural strength, and tensile modulus of the PP/KL composite. Even the addition of 30% KL along with 3% MAPP was able to increase the tensile strength of PP/Lignin composites (40.37 MPa) compared to PP (36.19 MPa) [96]. After incorporating SL or kenaf core fiber into PP, the composite's tensile strength decreased. Tensile strength of PP composites decreased when lignin or kenaf core fibers were added. Mechanical properties of pure PP and PP/L/KCF composites, on the other hand, were not significantly different [97].

Despite being known for its antioxidant properties and thermal stability; lignin is also famous for its negative effect on the mechanical properties of the corresponding polymer. For instance, lignin and carbon black filler mixture in styrene-butadiene rubber (SBR) matrix has a lower tensile strength than the composite with only carbon black filler [243]. The lignin increases tensile modulus and thermal stability while lowering the tensile strength and strain. Because a high ash content in lignin as a filler can reduce the mechanical properties and thermal stability of lignin/PLA composites, inorganic ash in lignin cannot be overlooked [15]. PLA composites using a combination of LSH and APP have significantly improved thermal stability [136]. The introduction of lignin into cellulose and chitosan polymers upgraded the mechanical characteristics, for example, tensile strength, storage modulus, and water vapor permeability due to some functionalities [244]. It can be affected by the strong interaction and good dispersion of lignin and chitosan [172].

TABLE 3: Thermal degradation properties of PLA and lignin [130].

Samples	Consent (°C)	$T_{\text{decomposition}}$ (°C)	Char residue (%)
PLA	269	314	6.5
PLA + 0.5% KL	340	365	0.5
PLA + 5% KL	337	367	2.1
PLA + 0.5% AKL	328	364	0.2
PLA + 5% AKL	323	366	1.4

The strong molecular interaction, large particle size, and polarity of lignin are considered responsible for its limited use as a filler [4, 245]. Thus, extensive research is being made to improve the compatibility of lignin with the polymer matrix to improve the mechanical properties of the polymer/composite. Some of the efforts are adding a compatibilizer [246, 247], reducing the particle size [248–253], and changing the polarity. Compatibilizer was added to increase the interfacial adhesion between lignin and polymer. In a report, a linear triblock copolymer based on ethylene, styrene, and butylene (SEBS) was introduced to the polystyrene/lignin composite to boost the interaction between polystyrene and lignin [246]. The flexural modulus and tensile modulus were enhanced significantly as evidence of the improvement of the lignin/PS interfacial adhesion. In another study, maleic anhydride graft-PBAT was added to enhance the tensile properties of polybutylene-adipate-co-terephthalate/lignin composite (P/L) [247]. The improvement in tensile strength and elongation at break were noticed in the sample with compatibilizer compared to the P/L composite. However, the tensile properties are still considered lower than the neat polymer.

Sahoo et al. prepared the polybutylene succinate (PBS) and lignin composite using melt mixing [239]. The addition

of lignin reduced the elongation at break, increased Young's modulus, and removed the stress softening in PBS. The 30 and 50 %wt. loading of lignin decreased the tensile strength of the composite; meanwhile, the loading of 65 %wt. increased the tensile strength. pMDI was added as a compatibilizer in a composite with 50 wt%. lignin. Only the sample with 1 %wt. of pMDI showed an increase in tensile strength; meanwhile, the addition of 2 %wt. resulted in the opposite. The addition of 10% lignin decreased elongation (43–17%) and increased Young's modulus (583 to 744 MPa) but did not significantly affect tensile strength. The addition of a 0.3% coupling agent in a mixture of PP and lignin improved elongation and had no significant effect on the values of Young's modulus and tensile strength [98]. Toriz et al. [90] added 10–60% lignin in PP and compared it with mica and talc (mineral filler) as fillers in PP. The addition of lignin causes a decrease in tensile strength, flexural strength, and impact strength. However, the addition of mica in the mixture of PP and lignin was able to increase the tensile strength because the distribution and interaction of lignin and PP became better in the presence of mica. The addition of 30% eucalyptus lignin increased the tensile strength and flexural strength because there was an increase in the interaction between PP and eucalyptus fibers [254]. The addition of lignin to PP increased the torsion modulus and flexural while decreasing tensile properties, according to Thakur et al. [4]. Dias et al. [55] stated that the addition of 30% lignin with 3% MAPP increased the flexural strength of PP composites.

The large particle size of lignin is one of the significant challenges to developing lignin as a filler. Various attempts have been made to reduce lignin particle sizes, such as ball milling [248–250], acidification [251], and hybrid filler [243]. Ball milling is considered an environmentally friendly, facile, and low-cost technique compared to other techniques [252]. The ball milling incites the impact energy of the rotating grinding medium to break down solid particles. However, the chances of contamination and lignin with irregular shape and size have resulted in the poor compatibility between lignin and polymer matrix [255]. The reduction of lignin particle size through ball milling was noticed to increase only Young's modulus and reduce other properties such as elongation at break and tensile strength in PP/lignin composite [249]. While ball milling is aimed to break down the particle size physically, acidification is aimed to reduce it chemically. Acidification is conducted during the lignification of black liquor and followed by washing with sulfuric acid and water [249]. Some reports mixed lignin with other types of filler such as carbon black [243], silica [256], ZnO [257], and magnesium oxide (MgO) [258] to enhance the properties of each precursor. Bula et al. investigated the effect of silica/lignin hybrid material as polypropylene filler [256]. Only low concentration (<5 %wt.) of the hybrid filler displayed improvements in elongation at break and notched impact strength. On the other hand, the high loading of the hybrid filler resulted in insignificant improvement in those properties.

Modification of lignin with various methods, including surface grafting [259], hydroxymethylation [260],

epoxidation [113], alkylation [96, 261], esterification [134, 262–264], carboxymethylation [265], arylation [96], esterification [134], and sulfonation [43], were used to enhance the compatibility between lignin and polymer matrix. Besides that, the reduction of lignin size in nanoparticles increases 40% of the tensile strength of starch-lignin composites than that of starch composites with higher thermal stability [161]. The lignin modification successfully prevented the reduction of cross-linking rate and thus reinforced the impact and adhesion strength. Meanwhile, when esterified lignin was incorporated in low-density polyethylene (LDPE), the mechanical properties of the composite were similar to the neat polymer [262]. Lee et al. [266] used PP-esterified lignin as a compatibilizer in PLA/coffee grounds composites. The lignin increases stability to heat, while PP increases flexural. The lignin increases the miscibility between PP and PLA, while PP reduces the phase separation between PLA and lignin. In general, the addition of alkylated lignin has a better effect on the mechanical properties of the composite than the addition of arylated lignin. This is indicated by an increase in Young's modulus and elongation, with less decrease in impact strength and tensile strength [96]. Modification of lignin with esterification agents such as butyric anhydride and then blending with PLA resulted in higher Young's modulus and elongation at break than PLA itself [134]. The mechanical properties of lignin/PLA composites have been improved by some esterified lignins [88, 267]. Even though the mechanical properties of neat LDPE did not improve, the lignin's negative effect could be reduced. Despite all efforts to improve lignin's ability to reinforce the mechanical properties of polymers, it appears that more research is needed to improve the lignin compatibility and polymer matrix, such as by adding a compatibilizer.

8. Other Properties

Lignin can function as a free radical scavenger that can prevent oxidation reactions. Stabilizers are compounds that play a role in preventing polymer decomposition due to oxidation reactions with an increase in temperature or light radiation, by suppressing the action of free radicals or preventing the formation of free radicals. Lignin acts as a UV barrier because it blocks UV transmission. The addition of lignin in PP is to accelerate the photooxidation reaction so that PP is more easily decomposed after use. Lignin can act as a stabilizer or initiator of PP degradation, depending on the type and amount of lignin added to PP [268]. Peng et al. [269] investigated the addition of lignin in a mixture of cellulose and PP to produce a composite with a smoother surface, suppressing the decrease in flexural strength and resistance to heat, after weathering treatment. This proves that lignin can act as an antioxidant and stabilizer. Gadioli et al. [254] added eucalyptus lignin in the PP extrusion process, resulting in a composite with mechanical properties and resistance to UV for 200 hours (preventing elongation loss). The addition of 30% eucalyptus lignin increased the tensile strength and flexural strength because there was an increase in the interaction between PP and eucalyptus fibers



FIGURE 14: Potential application of lignin-based composites.

[254]. The UV transmission of the starch-fractionated SL composite shows promise as an ultraviolet barrier for packaging applications [161]. A similar investigation on the improvement of UV protection of starch-lignin films has been reported previously [162, 165]. Lignin is primarily used as an additive at very low concentrations below 5% because lignin-based materials exhibit high antioxidant and anti-UV properties. These properties were contributed by belonging to the amount of oxygen and the phenolic group as functional groups in lignin [270, 271]. These properties have prospected lignin in wound dressings or anti-inflammatory biomaterial [272].

9. Potential Application Lignin-Based Composites

Lignin has a high potential available biopolymer that can be converted into various bioproducts. The main utilization of lignin is for low-grade fuel by burning that can cause wastage of resources and environmental pollution [273]. Only a limited quantity of lignin has been valorized into biomaterials and renewable chemicals [274, 275]. To promote lignin valorization, some researchers develop advanced technology in this area. Lignin-based composites are biomaterials that utilize lignin for incorporation with typical polymers. As presented in an earlier discussion about the method for lignin-based composite preparation, thus, this section presents some possible applications of lignin-based composites in diverse applications. The properties of the lignin-based composite were influenced by the method for preparation besides polymer constituents. Some functional groups of lignin including methoxyl, hydroxyl, carbonyl, and carboxyl groups [274] become active points in the

fabrication process of lignin-based composites. Lignin offers excellent properties such as high carbon content, high thermal stability, biodegradability, antioxidant activity, and rigidity [276] that can be utilized in composites. The potential representative application of lignin in a composite system is depicted in Figure 14, while some effect of introducing lignin in the biocomposites has been summarized in Table 4.

10. Challenges and Future Perspective

Lignin has proven interesting for conversion into renewable biomaterials and chemicals as the second most abundant biopolymer after cellulose. The technique of extracting lignin from biomass has changed the characteristics of lignin. In comparison to OL and SL, KL and LS have a higher ash concentration and lesser purity. The properties of lignin should be examined for acceptable uses, with KL being appropriate for low value-added applications and OL being appropriate for higher value-added applications. In light of environmental concerns, particularly biodegradability issues, lignin becomes more appealing to combine with other polymers in biocomposite systems, including synthetic and natural polymers. The inclusion of lignin into synthetic polymers such as epoxy and PP was covered in this paper, as well as natural polymers such as PVA, PLA, cellulose, starch, NR, and chitosan. Solvent casting and extrusion processes are the two methods utilized to combine lignin in both polymers, with compatibility being the most important factor in the final composite. For better lignin dispersion into polymers, it has been recognized that the differences

TABLE 4: The lignin introduction and its utilization.

Utilization	Remarks
Particleboard (advanced composite)	The addition of lignin into the particleboard can increase hydrophobicity, reduce thickness swelling and water absorption, and increase the density of particleboard [277].
Rubber (reinforcing agents)	The lignin can improve mechanical properties, tensile strength, and thermal stability in rubber [245, 278].
Filler in adhesives	Lignin is the initiator of cross-linking and condensation reactions, increasing the adhesive's polarity and increasing the penetration of the wood veneer [279].
Anticorrosion	Lignin can form self-cross-linking in the coating process, thermal stability, and hydrophobic properties increase after using silanized fraction lignin [280].
Antimicrobial agents in packaging	Adding lignin to food packaging materials can increase antimicrobial against Gram-positive and Gram-negative bacteria [281].
Carbon fiber or carbon black	Adding lignin to the carbon fiber can increase the spinning performance. High and stable mechanical properties of carbon fiber at the lowest lignin composition [282].
UV blocker	Lignin nanoparticles have higher antioxidants and higher efficiency in protection against <i>Escherichia coli</i> and as a good UV protector [283].
Flame retardants	The addition of lignin to the refractory material can improve good thermal stability, increase the residual char, and has excellent coating properties when applied to films [284].
Hydrogel	The addition of lignin into the hydrogel can increase the swelling of the hydrogel. Also, it can be applied as a colorant pollutant remover of soil and seed cultivation [285].
Phenolic resin	Resin from depolymerization alkali lignin phenol-formaldehyde (DAPLF) has higher bonding properties, lower emission, and a faster curing rate [276].
Polyurethane	The addition of lignin into polyurethane as a coating causes cross-linking reactions to increase thermal stability, moderate hydrophobicity in polyurethane coating, and mechanical properties [286].
Lignin-based foam	Incorporating lignin in wood-polyurethane composite foams can increase the density and improve mechanical properties. In addition, it can improve thermal properties as indicated by increasing the mass of charcoal residue, as well as decreasing foam reactivity [287].
Biomedical materials	The application of lignin in wound dressing hydrogels can accelerate wound healing and increase elasticity strength, protein absorption capacity, and the ability to regulate the wound environment in hydrogels [178].

in basic properties between them must be addressed. Lignin can act as a filler, reinforcing, and nucleating ingredient in biocomposite systems. To improve the compatibility of lignin with polymers, the coupling agent and compatibilizer can be added to lignin-based composites. The low reactivity of lignin, which can be improved by modifying it before adding it to polymers, has limited its usage in combining it with other polymers. The process conditions, amount of lignin, and other chemicals used in biocomposite fabrication remain a problem when it comes to achieving the best composite properties. To broaden the applicability of lignin-based composites in the market, a new optimization strategy is required.

11. Concluding Remarks

To improve biodegradability, lignin can be added to polymeric matrices to form lignin-based composites. However, the compatibility of the biocomposite system is influenced by the differences in characteristics between lignin and conventional polymers. In the preparation of lignin-based composites, solvent casting and extrusion are two popular processes. However, variable levels of lignin, lignin-to-polymer ratios, and operational conditions are influenced by the type of polymer that interacts with lignin, as well as other considerations. To improve biocompatibility between two polymers, additional chemicals such as coupling agents and compatibilizers can be added to the process. The morphological qualities, mechanical-thermal properties, and other aspects of lignin-based

biocomposites have all been explored. The influence of lignin on the characteristics of composites varies according to the studies studied. The introduction of lignin contributes to increasing the thermal stability of composites, but it is influenced by the preparation method. The 3D printing, advanced composites, reinforcing filler in natural rubber, filler in adhesives, anti-corrosion, antimicrobial agent in packaging and textile, flame retardant, carbon fiber, UV blocker, biomedical materials, polyurethane, lignin-based foam, and phenolic resin are just a few of the applications for lignin-based composites. As a result, the preparation technique, which includes the amount of lignin or other additives in the lignin-based system, is still being developed to improve the performance of lignin-based biocomposites for a variety of applications.

Data Availability

The data presented in this study are available on request from the corresponding authors.

Consent

Not applicable.

Disclosure

This study is part of Muhammad Rasyidur Ridho's master's thesis at IPB University.

Conflicts of Interest

The authors declare that there are no conflicts of interest.

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