

Review article

Recent progress in sulfur-containing technical lignin-based polymer composites

Shritama Mukherjee[✉], Samrat Mukhopadhyay^{*✉}

Department of Textile and Fiber Engineering, Indian Institute of Technology, Hauz Khaz, 110016 New Delhi, India

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Abstract. The aromatic biopolymer lignin, present in lignocellulosic material, can act as an antioxidant and has antimicrobial and UV blocking properties due to the presence of aromatic ring and phenolic hydroxyl groups with aliphatic hydroxyl, carboxyl, methoxy groups. It is produced in huge amounts as a by-product during the delignification process in the paper and pulp industries. Lignin-based polymer composites with advantageous properties can fulfill the growing demand for light-weight polymer composites. Incorporating lignin as reinforcement in polymer composite can make it more environmentally friendly. Among four technical lignin, kraft lignin and liginosulfonate have a unique molecular structure that includes sulfur and can be extracted from black liquor and spent liquor, respectively. Moreover, the negatively charged sulfite groups in liginosulfonate can have an electrostatic attraction to a wide range of positively charged polymers and materials, making it an ideal additive for the adsorbent material. The main intention of this review is to increase the knowledge on the use of cheap and widely available kraft lignin and liginosulfonate as reinforcement in polymer composites and to find the shortcomings to advance further research on the application of technical lignin. The article mainly focuses on advancements in kraft lignin and liginosulfonate polymer composites.

Keywords: biopolymers, lignin fractionation, phenolic hydroxyl group, kraft lignin and liginosulfonate-based composite, polyanion

1. Introduction

The word ‘Lignin’ was first used by a Swiss botanist, A.P. Candolle, in 1813. It is derived from the word ‘lignum’ or wood. It is a highly complex and cross-linked amorphous aromatic heteropolymer. The demand for lightweight polymer composite material has increased dramatically due to its high strength, tailored properties, and wide applications. Along with this, there is also a growing environmental concern for developing suitable polymer composites with renewable, biodegradable biopolymers to reduce the use of non-biodegradable petroleum-based plastics. One promising candidate is lignin, with properties such as antimicrobial, antioxidant, and UV blocking ability due to the presence of aromatic structure.

Lignin is generally present in the cell wall of woody biomass along with cellulose and hemicellulose. Together they are often termed lignocellulosic biomass, which is 30–50% cellulose, 20–35% hemicellulose, and 15–20% lignin [1–5]. Lignin acts as an adhesive that gives lignocellulosic biomass its resistance, rigidity, and structural integrity and protects cell walls from outside stresses [6]. An open network is created by hemicellulose-coated cellulose fibrils, and the empty places are mainly filled with lignin which is described in Figure 1 [7, 8]. It is covalently bonded with hemicellulose by different bonds, such as benzyl ether, γ -ester, and phenyl glycoside bonds [9]. Lignocellulosic biomass is also the main source of lignin which represents nearly 30% of all organic carbon in the biosphere which can be extracted from

*Corresponding author, e-mail: samrat@textile.iitd.ac.in
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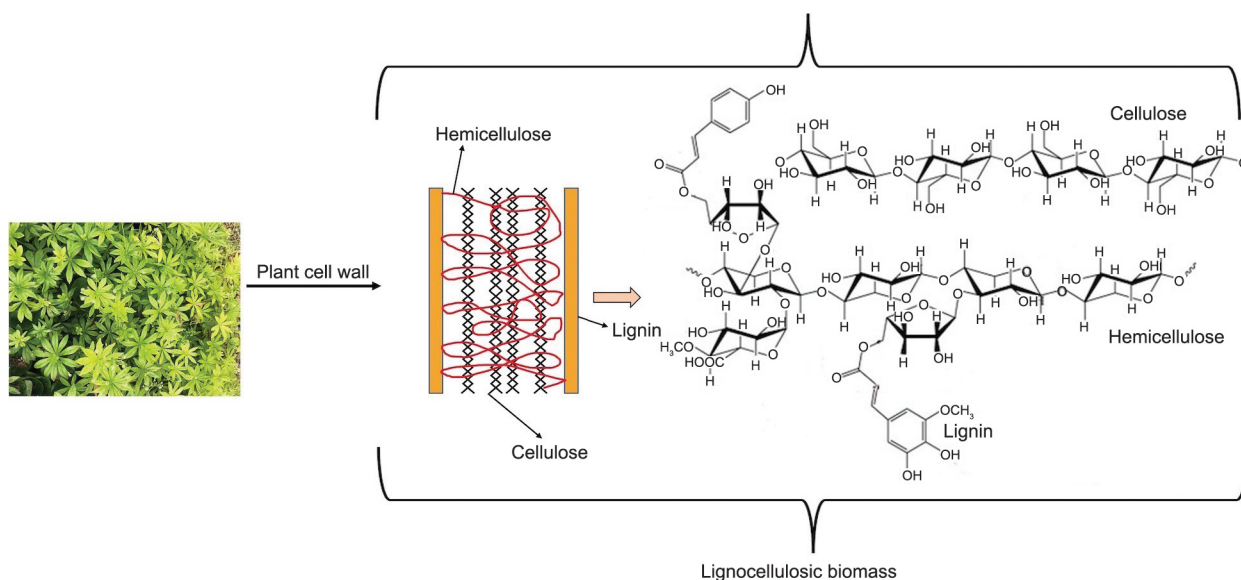


Figure 1. Lignocellulosic biomass and interaction between lignin, hemicellulose and cellulose [7].

the biomass by breaking the bonds between cellulose, lignin, and hemicellulose using strong acids or bases [2].

Lignin consists of three types of phenylpropane monomeric unit, *i.e.*, *p*-coumaryl alcohol (4-hydroxy phenyl (H)), coniferyl alcohol (guaiacyl (G)), and sinapyl alcohol (syringyl (S)) and it is described in Figure 2. In Figure 3, lignin from poplar has been represented with its monomeric unit. G, S, and H units can be bonded by different linkages such as β -aryl

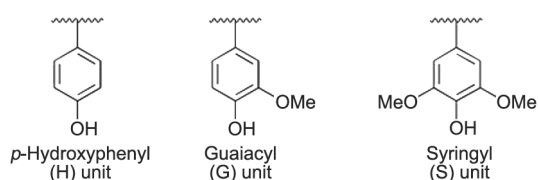


Figure 2. Three types of lignin’s monomeric unit [7].

ether (β -O-4’), phenylcoumaran (β -5), resinol (β - β), *etc.* [10]. It has many functional groups, such as aliphatic hydroxyl, phenolic hydroxyl, methoxy, *etc.* Its structure is highly variable, and the amounts of lignin monomers can vary depending on the origin of the plant and parts of the plant, such as different organs, and tissues. Lignin isolated from different plants has different amounts of monomeric units as well as different linkages and this is displayed in Table 1. Yuan *et al.* [11] isolated lignin from poplar by three different methods, *i.e.*, by the milling process, using cellulolytic enzymes, and by the alkaline process. Lignin isolated by these three methods has different S/G ratios as listed in Table 1. Lignin isolated from bamboo stem and pith contains different amounts of G, S, and H units, as reported by Wen *et al.* [12].

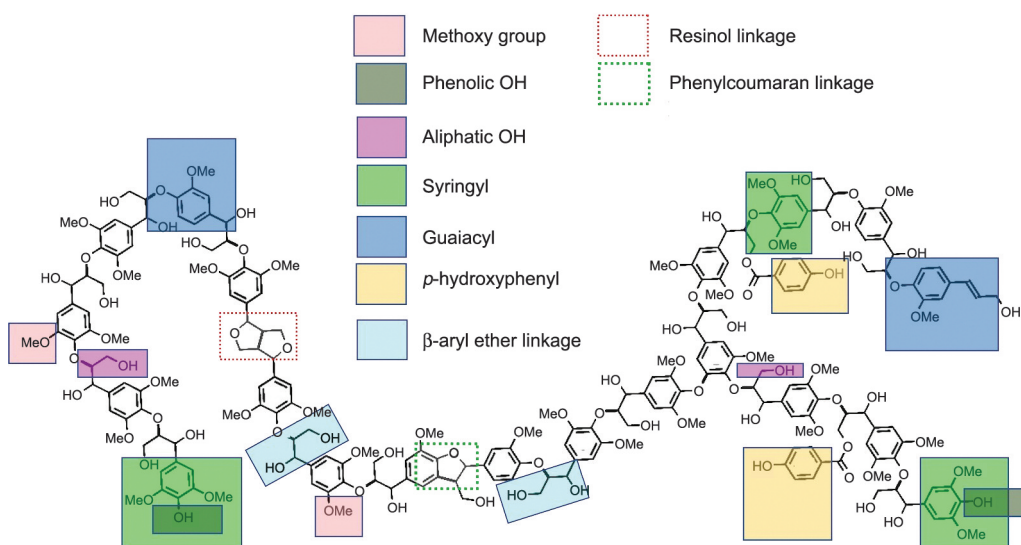


Figure 3. Lignin macromolecular structure from poplar [10]. By permission of Oxford University Press.

Table 1. Compositional analysis of lignin isolated from different plant and different parts of plant by different methods.

Plant species	Parts of the plant	Lignin interunit linkage [%]			<i>p</i> -hydroxyphenyl unit (H) [%]	Guaiacyl unit (G) [%]	Syringyl unit (S) [%]	References	
		(β -O-4') β -aryl ether	(β -5') Phenylcoumarans	(β - β') Resinols					
<i>Cocos nucifera</i>	Coir fiber	82	13	4	4	78	18	[13]	
<i>Corchorus capsularis</i>	Jute fiber	72	4	16	2	33	65	[14]	
<i>Dendrocalamus sinicus</i> (Milled wood lignin from bamboo)	–	79.5	5.6	7.2	9	35	56	[15]	
<i>Miscanthus</i> \times <i>giganteus</i> (Ethanol organosolv lignin)	–	–	–	–	4	52	44	[16]	
<i>Paulownia fortune</i> (milled wood lignin)	–	62	11	12	0	60	40	[17]	
<i>Phyllostachys pubescens</i> (bamboo)	Stem (Milled wood lignin)	–	69.7	6.3	10.5	2	31	67	[12]
	Pith (Milled wood lignin)	–	75	4.7	6	1	21	78	
<i>Quercus suber L.</i> (Oak)	Cork	68	20	4	2	85	13	[18]	
	Phloem	71	13	7	1	58	41		
	Xylem	77	9	8	1	45	55		
<i>Populus tomentosa</i> (Poplar tree)	Milled wood lignin	–	83.2	2.6	12.7	S/G ratio		[11]	
						1.43			
	Cellulolytic enzyme lignin	–	84.5	2.1	12.2	2.29			
	Alkaline lignin		81.1	2.1	16.4	2.83			
<i>E. urophylla</i> \times <i>E. grandis</i> (Eucalyptus) (Milled than enzymatic hydrolysis)	Heartwood	–	62.1	0.2	11.6	3.45		[19]	
	Sapwood	–	62.4	0.4	7.7	2.74			
	Barkwood	–	69.0	1	2.9	2.91			
Softwood kraft lignin (acid precipitation followed by solvent fraction)	Acetone insoluble	–	12.7	2.6	3.5	–		[20]	
	Acetone/hexane soluble 1 (H300)	–	4.4	1.8	2.4	–			
	Acetone/hexane soluble 2 (H500)	–	4.6	1.8	2.9	–			
	Acetone/hexane soluble 3 (H900)	–	2.5	0.90	1.7	–			
	Acetone/hexane soluble 4 (H1500)	–	1.4	0.4	1.6	–			

During pulping process, lignocellulosic biomass is subjected to delignification for the separation of cellulose and hemicellulose. Mainly four methods are used in the industrial pulping process, which are kraft, sulfite, soda, and organosolv. Lignin is produced

as by-product of all these processes. The annual production of lignin from the chemical pulping industry is more than 50 million tons. This lignin can be extracted from pulping effluent by different methods such as using membrane technology, precipitation,

ion exchange membrane, *etc.*, and it is often termed technical lignin.

At a low price, the most common technical lignin available in the market is lignin isolated from the kraft process (kraft lignin) and lignin isolated from the sulfite process (lignosulfonate), followed by lignin isolated from soda and organosolv process. Differences between kraft, lignosulfonate, soda, and organosolv lignin in molecular weight, sulfur content, and solubility in water and the organic solvent is shown in Table 2. Kraft lignin and lignosulfonates are structurally different from soda and organosolv lignin. Both kraft lignin and lignosulfonate contain sulfur due to using sulfur-containing materials during pulping. As it is listed in Table 2, the amount of sulfur groups in the kraft lignin structure is around 1–3% by weight. This lignin also has a higher amount of aliphatic thiol groups and is primarily hydrophobic [23, 24]. On the other hand, lignosulfonate acts like polyanion due to the presence of negatively charged sulfonate groups (Table 2). For this reason, lignosulfonate can attract different cationic materials by electrostatic interaction. This property is extensively used by researchers to prepare polymer composite with polycation by electrostatic interaction. Lignosulfonates are also water-soluble at a wide range of pH, which is very advantageous for the preparation of hydrogel [25]. Moreover, lignin has antioxidant and antimicrobial properties due to the abundant presence of phenolic groups in its macromolecular structure. It is also highly resistant to biological attacks due to its highly complex structure [1, 3, 26]. Often waste technical lignin is used as fuel, and sulfur present in kraft and lignosulfonate can cause secondary pollution in the form of sulfur dioxide [27, 28]. Thus, kraft lignin and lignosulfonate have been widely used in different polymer composite materials for diverse applications. The main scope of this review is on the use of kraft lignin and lignosulfonate in different polymer composites as reinforcement for different applications. For better understanding, a brief discussion about the extraction of kraft lignin and

lignosulfonate from black liquor and spent liquor, respectively, has also been included in this review.

2. Lignin extraction process

Depending on the amount of lignin production, two kinds of lignin extraction methods exist. The first is analytical scale extraction, and the second is industrial scale extraction [1]. The analytical process is mainly used for small-scale production of lignin to isolate more precise structure or pure form of native lignin. Technical lignin is primarily produced as a by-product in the paper and pulp industry in the delignification process. Strong acids or base and vigorous mechanical treatment are used to separate lignin from carbohydrates which leads to the fragmentation of lignin macromolecules. The soda process, organosolv process, sulfite process, and kraft process are the major industrial processes. These processes are described in Figure 4 with the structure of isolated lignin. The different process used for industrial scale and laboratory scale extraction of lignin from lignocellulosic material has been discussed in recent review articles [1, 29]. However, for better understanding and as the extraction process has a significant effect on the properties of extracted kraft lignin and lignosulfonate, a summary of the extraction of kraft lignin from black liquor and lignosulfonate from spent liquor has been discussed in the next section.

2.1. Kraft lignin

German chemist Carl Ferdinand in Gdansk invented the kraft process for separating lignin from cellulose and hemicellulose. The Kraft extraction process is a widely used method in the paper and pulp industry due to its high yield. This process utilizes sodium hydroxide (NaOH) and sodium sulfide (Na₂S) in a solution with the former in a higher percentage as described in Figure 4. This process is also termed as the sulfate process due to the use of Na₂S. After the final stage, more than 90% of lignin is extracted in the form of black liquor. Black liquor has lignin along with NaOH, Na₂S, and other materials from the wood.

Table 2. Properties of technical lignin [21, 22].

Technical lignin	Molecular weight [kDa]	Sulfur content [wt%/wt%]	Solubility
Kraft lignin	1.5–5.0 (up to 25)	1.0–3.0	Alkali, organic solvent <i>i.e.</i> , dimethylformamide (DMF), pyridine, dimethyl sulfoxide (DMSO)
Lignosulfonate	1.0–50.0 (up to 150)	3.5–8.0	Water
Soda lignin	0.8–3.0 (up to 15)	0	Alkali
Organosolv	0.5–5.0	0	Different organic solvent

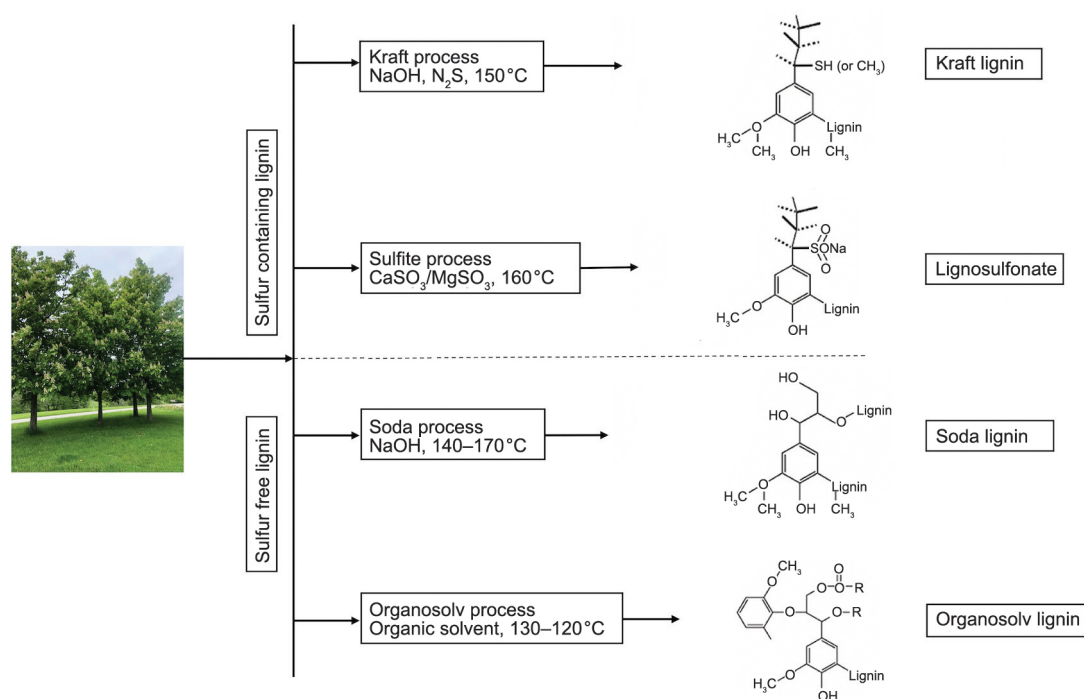


Figure 4. Technical lignin and their structure.

This liquor is highly alkalic, viscous, and black or brown due to its high lignin content [29, 30]. Lignin produced during the kraft process is termed as kraft lignin (KL). Several studies are currently being conducted to develop cost-effective methods for isolating lignin from black liquor. Generally, a cost-effective and more sophisticated method involves a combination of acid precipitation and membrane filtration, such as microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF).

It is predicted that high molecular weight lignin molecules remain in colloidal form in black liquor. During precipitation, lignin self-aggregates due to the instability of its molecular structure. The stability of lignin molecules in an aqueous solution is resulted due to interplay between forces such as van der Waals forces, electrostatic forces, and other hydrophobic forces. According to Rudatin *et al.* [31], the equilibrium of these forces mainly depends on the functional groups present in the lignin molecule, conditions such as pH, temperature, *etc.* of the solution and concentration of lignin in that solution. In black liquor, under alkaline pH, lignin remains as negatively charged due to the dissociation of phenolic and carboxyl groups. Lignin molecules remain associated with sodium as a counter ion. In this stage, negatively charged lignin molecules repel each other due to electrostatic forces, and as a result, these molecules remain stable and dissolve in an aqueous solution. For this reason, KL is soluble in an aqueous solution

at alkaline pH. Lignin molecules become neutral when pH of the black liquor is reduced due to the interaction of hydrogen ions with negatively charged functional groups and the replacement of sodium ions with hydrogen ions (protonation). Consequently, neutral lignin molecules do not repel each other by electrostatic forces and start to attract each other by hydrophobic forces, which results in self-aggregation followed by precipitation. The whole mechanism of KL precipitation is described in Figure 5. At pH value the same or below the pK_a value of phenolic groups (9, 4–10), functional groups of lignin are protonated, which results in further instability of lignin molecules and resulted in precipitation of lignin. Usually, pH value of the solution is kept below pK_a value of lignin. A pH of less than 2 is preferable as it facilitates complete protonation of hydroxyl and carboxyl groups to form sodium-free hydrogen lignite. According to Norgren *et al.* [32], high molecular weight lignin molecule has higher pK_a values than lower molecular weight fraction. Therefore, larger lignin molecules with higher pK_a values are more unstable even in highly alkalic black liquor. This is why self-aggregation and precipitation occur first in the case of larger molecules, followed by smaller lignin molecules [33].

Sulphuric acid, carbon dioxide, or chlorine dioxide is usually used to reduce the pH of the black liquor to 5–7. Subsequently, precipitated lignin is separated by membrane filtration. The molecular weight of KL

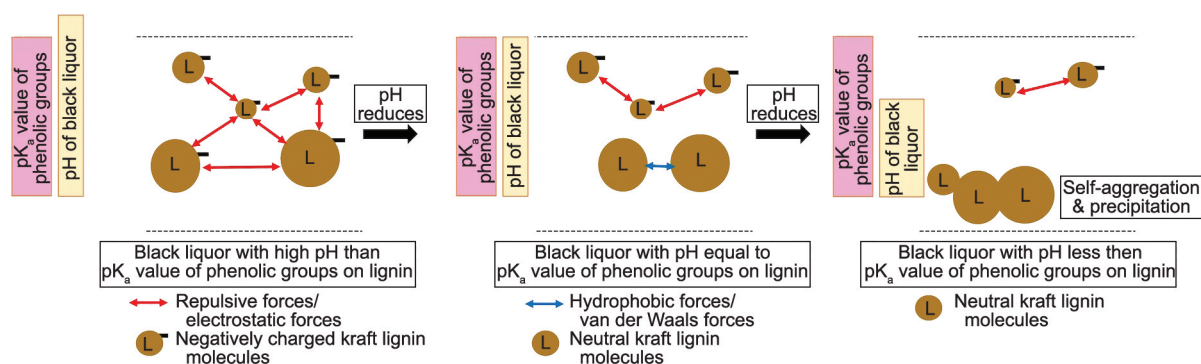


Figure 5. Mechanisms of kraft lignin precipitation from black liquor by acidification.

can vary between 1000 to 3000 Da and can go up to 15 000 Da. Due to lignin molecules' wide molecular weight distribution, flux decline is a significant obstacle for membrane filtration. However, membrane technology is a very energy-efficient and cheap alternative. Between polymeric and ceramic membranes, ceramic ones are reported to be the most efficient for membrane filtration as they can tolerate the high pH of black liquor [34, 35]. Membrane filtration of KL has been reviewed in detail recently by Humpert *et al.* [34]. In addition to these methods, electrochemical methods and liquid-liquid extraction methods have also been used by researchers to isolate lignin from black liquor [33].

Lignin can be isolated from black liquor by using electrolysis and electrodialysis. In these processes, lignin is precipitated at the anode, and at the cathode, hydrogen is produced. During electrolysis, the anode chamber has the black liquor, and in the cathode chamber, a diluted solution of NaOH is kept. A cation exchange membrane separates the anode chamber and cathode chamber. During the electrolysis, Na^+ ions from black liquor move towards the cathode chamber through a membrane because of the application of the electrical field. In the cathode chamber, these sodium ions react with OH ions formed due to the cathodic reduction of water, subsequently leading to NaOH formation. In the anode chamber, hydrogen ions are formed due to anodic oxidation of water which is resulted in acidic pH. These two reactions led to the formation of acidified black liquor in the anode chamber and NaOH in the cathode chamber as main outlet streams. These hydrogen ions replace the sodium ions present in the lignin molecules, which convert negatively charged lignin molecules into neutral lignin molecules. Then self-aggregation and precipitation of KL occur following the same principle of acid precipitation. Subsequently,

lignin is deposited on the surface of the anode. In this process, platinum and nickel have proven to be good anode materials [36–38]. Haddad *et al.* [37] studied KL precipitation from black liquor by electrodialysis, where charged membranes such as cation exchange and bipolar membranes were used for ion transport. Electrodes only functioned as electrical terminals [37, 39]. In a recent study by Chen *et al.* [40], a microbial biomass recovery cell was used to isolate lignin by electrolysis. Anaerobic sludge acts as the anode that produces H^+ ions [40, 41].

Many researchers used solvent fractionation to separate lignin from black liquor. Alcohol and calcium solution [42], acetone [43], and ethyl acetate [44] are common organic solvents that have been used as an organic solvent for KL fractionation. Ropponen *et al.* [43] reported that a low molecular weight fraction of KL has higher phenolic hydroxyl groups. Moreover, It has a higher amount of S units and has a low glass transition temperature (T_g).

Dominguez-Robels *et al.* [45] used two different concentrations of acetone for KL fractionation. First, KL extracted by acid precipitation was mixed with a 60% aqueous solution of acetone, and insoluble lignin was separated at this stage. The concentration of the solution was subsequently decreased to 40% and the insoluble fraction was isolated. Molecular structure KL, extracted from black liquor by different methods, has various amounts of functional groups which is shown in Table 3. Acetone soluble fraction had the lowest molecular weight with the highest phenolic hydroxyl groups (Table 3).

Wang *et al.* [54] used hexane, diethyl ether, methylene chloride, methanol, and dioxane with increasing hydrogen bonding capacity. It was observed that the average molecular weight of KL increases with the increasing hydrogen bonding capacity of the solvents. A higher molecular weight fraction is reported to have

Table 3. Amounts of aliphatic-OH, phenolic OH, COOH groups, average molecular weight, and T_g of KL, extracted by different methods.

Extraction process		Aliphatic-OH [mmol/g]	Phenolic-OH [mmol/g]	COOH [mmol/g]	M_w [Da]	T_g [°C]	References
Ceramic membrane	Initial: lignoboost lignin	1.97±0.07	4.27±0.04	0.45±0.01	–	–	[46]
	Final: filtered fraction	0.43±0.02	3.8±0.27	1.00±0.08	1600–400		
Ultrafiltration	Fraction 1: >10 kDa	2.62	2.81	0.52	33 500	170	[47]
	Fraction 2:>5 kDa	2.33	2.95	0.49	28 200	159	
	Fraction 3: 5–10 kDa	1.88	3.87	0.49	4 900	140	
	Fraction 4: 1–5 kDa	1.37	3.7	0.35	4 700	94	
	Fraction 5: 0–5 kDa	1.42	3.61	0.46	4 100	82	
	Fraction 6: 0–1 kDa	1.25	4.11	0.38	2 700	70	
LLE (acetone/water)	Fraction SKL (Softwood kraft lignin)	1.72	3.57	0.44	4 130	–	[45]
	Fraction SKL insoluble	1.75	2.10	0.19	11 230	–	
	Fraction SKL precipitation	1.79	4.38	0.42	5 600	–	
	Fraction SKL soluble	1.70	5.91	0.54	2 260	–	
LLE	Initial KL	1.17	2.76	0.28	4 100	–	[48]
	Ethanol 80% insoluble	1.85	3.43	0.33	7 600	–	
	Ethanol 70% precipitate	1.50	2.75	0.20	5 300	–	
	Ethanol 60% precipitate	1.40	2.53	0.23	4 300	–	
	Ethanol 50% precipitate	1.29	2.82	0.29	3 300	–	
	Ethanol 40% precipitate	1.37	3.01	0.37	2 800	–	
	Ethanol 30% precipitate	2.09	2.94	0.40	2 200	–	
	Ethanol 10% soluble	2.22	4.05	0.71	1 500	–	
	Acetone 50% precipitate	1.28	2.62	0.26	6 000	–	
	Acetone 40% precipitate	1.13	2.94	0.32	3 500	–	
	Acetone 30% precipitate	1.06	2.87	0.33	2 700	–	
	Acetone 10% soluble	2.25	4.04	0.63	1 600	–	
	PGME 50% precipitate	1.97	2.33	0.20	6 700	–	
	PGME 40% precipitate	1.86	2.63	0.24	3 900	–	
	PGME 30% precipitate	1.88	2.74	0.29	2 800	–	
PGME 10% soluble	1.89	3.95	0.56	1 700	–		
Solvent fractionation	KL	2.24	4.25	0.42	6 300	153	[49]
	Acetone soluble fraction	1.63	5.76	0.57	3 500	112	
	Acetone insoluble fraction	2.74	3.08	0.35	14 000	173	
Sequential solvent fractionation	SKL	2.07	4.19	–	–	138	[50]
	Acetone soluble	1.59	5.03	–	–	118	
	Acetone insoluble	1.72	3.69	–	–	146	
	Acetone insoluble, methanol soluble	1.96	4.48	–	–	173	
	Acetone insoluble, methanol insoluble	2.08	4.06	–	–	174	
	Methanol soluble	2.08	4.83	–	–	170	
	Methanol insoluble	1.95	3.94	–	–	175	
	Acetone soluble (by dialysis)	1.57	4.69	–	–	112	
	Acetone insoluble, methanol soluble (by dialysis)	1.63	4.08	–	–	131	
Acetone insoluble, methanol insoluble (by dialysis)	2.34	2.87	–	–	169		
Softwood kraft lignin (acid precipitation followed by solvent fraction)	Acetone insoluble	3.00	3.50	0.50	12 200	–	[20]
	Acetone/hexane soluble 1, (H300)	2.40	5.20	0.60	3 300	–	
	Acetone/hexane soluble 2, (H500)	2.10	5.30	0.70	2 000	–	
	Acetone/hexane soluble 3, (H900)	2.00	5.50	0.80	1 300	–	
	Acetone/hexane soluble 4, (H1500)	1.70	5.70	0.60	1 000	–	

Table 3. Continuously.

Extraction process		Aliphatic-OH [mmol/g]	Phenolic-OH [mmol/g]	COOH [mmol/g]	M_w [Da]	T_g [°C]	References
Kraft lignin	Kraft lignin	3.13	3.09	0.14	5410	162	[51]
	5 kDa	4.11	2.97	0.12	7010	–	
	3 kDa trapped	2.43	3.87	0.15	3540	149	
	3 kDa permeate	1.51	4.21	0.16	1890	117	
Lignin	Softwood kraft lignin	3.48	4.61	0.79	–	–	[52]
	Hardwood soda lignin	2.12	4.04	0.97	–	–	
Lignin	Kraft lignin	1.89	3.97	0.46	–	–	[53]
	KL treated with 0.25 pyrrolidine	0.06	1.07	0.40	–	–	
	KL treated with 1.5 pyrrolidine	0.37	3.07	0.62	–	–	

higher branching as well as higher thermal stability. It was also observed that a higher molecular weight fraction has a higher amount of β -aryl ether bond (β -O-4). In another study by Passoni *et al.* [55], tetrahydrofuran, methanol and 2-butanone were used for kraft lignin fractionation. It was observed that the 2-butanone soluble fraction was low molecular weight while the methanol soluble fraction was higher. This can be due to the strong ability of methanol to form a hydrogen bond with longer OH-rich macromolecular lignin molecules than 2-butanone. However, the main challenge of using solvent fractionation is the use of costly and toxic solvents. Jääskeläinen *et al.* [48] used less toxic chemicals such as ethanol, acetone, and propylene glycol monomethyl ether to extract KL. The soluble fraction of KL had the lowest molecular weight and higher phenolic hydroxyl content. This drawback can also be overcome by using ionic liquids. Ionic liquids are organic salts with low melting points ($<100^\circ\text{C}$). Usually, they are liquid at room temperature and consist of anions and cations entirely. Moreover, they are non-flammable, have lower toxicity, and have scalable physicochemical properties. Pu *et al.* [56] reported that KL is soluble in certain ionic liquids, such as [hmim][CF₃SO₃], [mmim][MeSO₄], [bmim][MeSO₄]. However, the solubility of lignin mainly depends on the types of anions present in ionic liquids. For example, anions such as [PF₄][−] and [BF₆][−] negatively affect the solubilization of lignin [56, 57]. The industry mainly uses four methods for the isolation of lignin from black liquor. These methods are WestVaco, LignoForce, LignoBoost, and SLRP [33].

2.2. Lignosulfonates

Lignin produced by the sulfite process is often termed as lignosulfonates. In this pulping process, lignocellulosic biomass reacts with a metallic sulfite, usually

calcium sulfite (CaSO₃) or magnesium sulfite (MgSO₃) and sulfur dioxide (SO₂). The reaction mainly involves a series of reactions, including sulfonation, hydrolysis, and condensation. The introduction of sulfonic groups leads to the formation of relatively soluble lignosulfonates with cations such as Mg, Na, or NH⁴⁺. By forming lignosulfonates, subsequent fragmentation of the lignin molecule occurs through its hydrolysis and dissolution with cellulose. The sulfite process is carried out at pH ranging from 1.5 to 2 at reaction temperatures ranging from 140 to 160 °C [23, 30].

The spent liquor from the sulfite process mainly consists of lignosulfonates (50–80 wt%), and hemicellulose (30 wt%) with different residual pulping chemicals. Lignosulfonates mainly contain two types of ionizing groups, *i.e.*, sulfonates whose pK_a is around 2 and phenolic groups whose pK_a is around 10. For this reason, it is soluble in water over the entire pH range and cannot be precipitated. Techniques such as membrane filtration, liquid-liquid extraction, ion exchange, and amine extraction have been utilized to isolate lignosulfonates from spent liquor [23, 29, 30, 58].

Lignosulfonates have molecular weights ranging from 1000 to 50000 Da. Its molecular weight is higher than the other component of the spent solution, such as hemicellulose and other chemicals. For that reason, membrane filtration is a practical method to separate lignosulfonate from the spent solution. Ultrafiltration (UF) was first employed to separate lignosulfonates which was produced in the calcium bisulfite (Ca(HSO₃)₂) pulping process in 1981 in Norway. The purity of the isolated lignosulfonates was 95% by using polysulfone membrane of molecular weight cut off (MWCO) value of 20000 Da [59]. Polysulfone, cellulose acetate, and fluoropolymer

membrane with MWCO values of 1, 5, 10, 20, 50, and 100 kDa [60], regenerated cellulose NF membrane of 0.5 kDa MWCO value [61], cellulose films [62] were used for extraction of lignosulfonate.

Lignosulfonate is extracted as calcium salt in the commercial lignosulfonate extraction method termed as the ‘Howard method’. In this method, in the first step, adding calcium oxide leads to the precipitation of calcium sulfite present in the spent liquor at pH 8.5, which is then filtered and removed. In the second step, the addition of calcium oxide leads to the formation of calcium lignosulfonates which are solid at pH 12. This can be isolated by filtration and recovery of lignosulfonates in this form; this method can be more than 90% [23, 63]. Another method used for the extraction of lignosulfonates is amine extraction. This method converts lignosulfonates into water-insoluble, lignosulfonic acid-amine adducts using amines such as long chain aliphatic amine, tri-n-hexyl-amine, and poly ethyleneimine. Then water insoluble adducts are extracted by liquid-liquid extraction. However, the main drawbacks of this method are the removal of amines from the solution, the formation of salt (NaCl) during re-extraction as well as the formation of foam, problems regarding emulsion, etc. [64, 65].

Chakrabarty *et al.* [66], used a liquid membrane for the separation of lignosulfonate from spent solution. A liquid membrane is a liquid barrier between two aqueous phases of different compositions, termed as feed phase and strip phase. Components can flow through the liquid membrane by using a diffusional process because of their own concentration gradient. The liquid membrane can be supported or non-supported such as bulk and emulsion liquid membrane. Chakrabarty *et al.* [66] used a bulk liquid membrane of dichloroethane as solvent and trioctylamine (TOA) as a carrier for the separation of lignosulfonate. They also used a supported liquid membrane which is a hydrophobic porous membrane with an organic phase with a carrier phase. One of the important factors affecting the optimal use of a liquid membrane is its stability; the reported stability of the membrane was up to 10 hours. Maximum lignosulfonate recovery was observed in the case of PA 6.6, as a hydrophobic porous membrane at 4% TOA concentration with 0.5 M NaOH as strip [67]. The amount increased significantly when surfactant such as polyethylene glycol was added to the liquid membrane system. The number of optimum lignosulfonates was 85%,

in this case [68]. Sunflower oil was mixed with TOA by Kumar *et al.* [69], for the separation of lignosulfonates by liquid membrane.

In a study by Kontturi and Sundholm, lignosulfonate was extracted using different aliphatic long chain amines-organic solvent systems. Amines used in this process are dodecyl amine, dioctyl amine, and trioctyl amine dissolved in 1-butanol, 1-pentanol, methyl isobutyl ketone, 1,2-dichloroethane, or cyclohexane. Lignosulfonates were extracted according to their molecular weight in this method [70].

3. Kraft lignin-based polymer composite

3.1. Kraft Lignin-based Polymer composites with synthetic polymer matrix

KL was used as reinforcement with polyolefins as a polymer matrix by researchers. Table 4 describes the application of KL as reinforcement in different polymer matrices, chemical modifications of KL for better dispersion, and improvement of properties of end composites. Lignin is a polar polymer with, on average, 1 or 2 hydroxyl groups per monomer as described in Figure 2, and Polyolefins are highly hydrophobic as well as non-polar without any polar groups. So, for better dispersion of lignin in the polymer matrix, alkylation or different types of chemical modifications are required. Chemical modifications are also needed to increase the loading of reinforcements in the polymer matrix. The lower molecular weight fraction of softwood KL has a higher amount of phenolic hydroxy group content, which makes it suitable for such chemical modifications. Aliphatic hydroxyl groups present in lignin was chemically modified by acetylation, esterification *etc.* to reduce its hydrophilicity as it is described in Figures 6 and 7.

Chen *et al.* [71] used alkylated KL for the development of polypropylene-lignin composite. It was reported that with an increase in the amount of alkylated KL in polypropylene, tensile modulus, and strength of the composite decreased. This negative effect can be due to a reduction in crosslink density of the matrix as alkylated KL act as a plasticizer, and this phenomenon can lead to a reduction in matrix integrity. However, an increase in impact strength was observed up to 10% alkylated KL loading in polypropylene which is due to better compatibility of alkylated KL with polypropylene. Acetylation, where phenolic hydroxyl groups of lignin are replaced with acetate groups, can make lignin more compatible with hydrophobic synthetic polymers.

Table 4. Different kraft lignin-based polymer composite.

Types	Polymer type	Chemical modification of KL	Application of KL	Reference
Kraft lignin Polymer composite	Polypropylene	Alkylation, acetylation, Aminolysis, Hybrid with SiO ₂ , hybrid with ZnO	Flame retardant, Improvement of mechanical properties, coupling agent, oil absorption,	[53, 71–90]
	Polyethylene	Methylation Esterification, hybrid with MgO, hybrid with ZnO, lignin reverse micelle	Antioxidant, improvement of thermal stability and mechanical properties, UV protection, antimicrobial,	[49, 51, 91–107]
	Polystyrene	Esterification,	Adsorbent, antioxidant, improvement of mechanical properties,	[108–113]
	PET	Acetylated	Antioxidant, improvement of mechanical properties	[114, 115]
	PVA	–	Adsorbent, antibacterial, antibiofilm, UV protection, antioxidant	[116–119]
	PBAT	Methylation & maleic anhydride grafting with PBAT	Cheap packing material	[120]
	PVC	Hybrid filler with Mg(OH) ₂ , hybrid filler with silica,	Oil rejection, improvement of mechanical properties	[121–123]
	Polyaniline	–	Dopant, adsorbent	[124, 125]
	Starch	–	Improvement of mechanical properties and hydrophobicity, gas separation	[126–128]
	PLA	Acetylation, acidified and methylated,	Improvement of mechanical and water absorption, antioxidant	[129–136]
	CNF	Colloidal lignin particle	UV protection, improvement of mechanical and water absorption, antioxidant	[137, 138]
	MCC	Propargylated	Semitransparent, flexible, UV blocking properties	[139]
	Chitosan	–	Antibacterial, antioxidant, adsorbent, UV protection, improvement of mechanical properties	[140–145]
	PHB	–	Antioxidant, improvement of mechanical properties	[146]
Natural rubber	Hydroxymethylation	Antioxidant, improvement of mechanical properties	[147, 148]	

This chemical modification can also increase thermal stability, which is advantageous for the thermal processing of lignin, such as compression molding. Jeong *et al.* [72] used acetylated softwood KL to develop polypropylene, low-density polyethylene

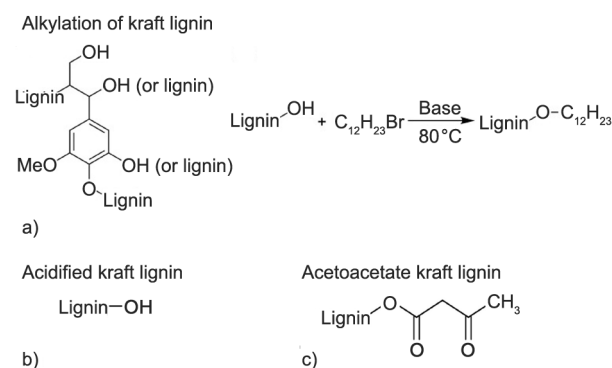


Figure 6. Different chemical modification of kraft lignin for better dispersion in polymer matrix, a) alkylation of kraft lignin, b) acidified kraft lignin, c) acetoacetate kraft lignin [71, 133, 148]. With permission from John Wiley and sons.

(LDPE), polystyrene, and polyethylene terephthalate (PET)-based composite material by melt blending and compression molding. All the composites exhibited a slight increase in the young modulus up to 37% loading of acetylated KL. Improvements in toughness were observed up to a specific loading of KL. With higher percentage of KL loading, resultant composites with all four synthetic polymers showed diminished mechanical properties and became brittle. In the case of esterification, it was reported that with increasing ester carbon chains from C2 to C4, the distribution of KL became more homogenous in the polyethylene matrix. A sharp increase in the Young modulus was observed with increasing loading of KL [94, 99]. Most of the chemical modification of KL was performed to increase hydrophobicity and decrease surface tension. This was done using polymer-surfactant adsorption. Alkenyl succinic acid anhydride or alkyl ketene dimer (AKD) is hydrophobic surface reagent that was used by Atifi *et al.*

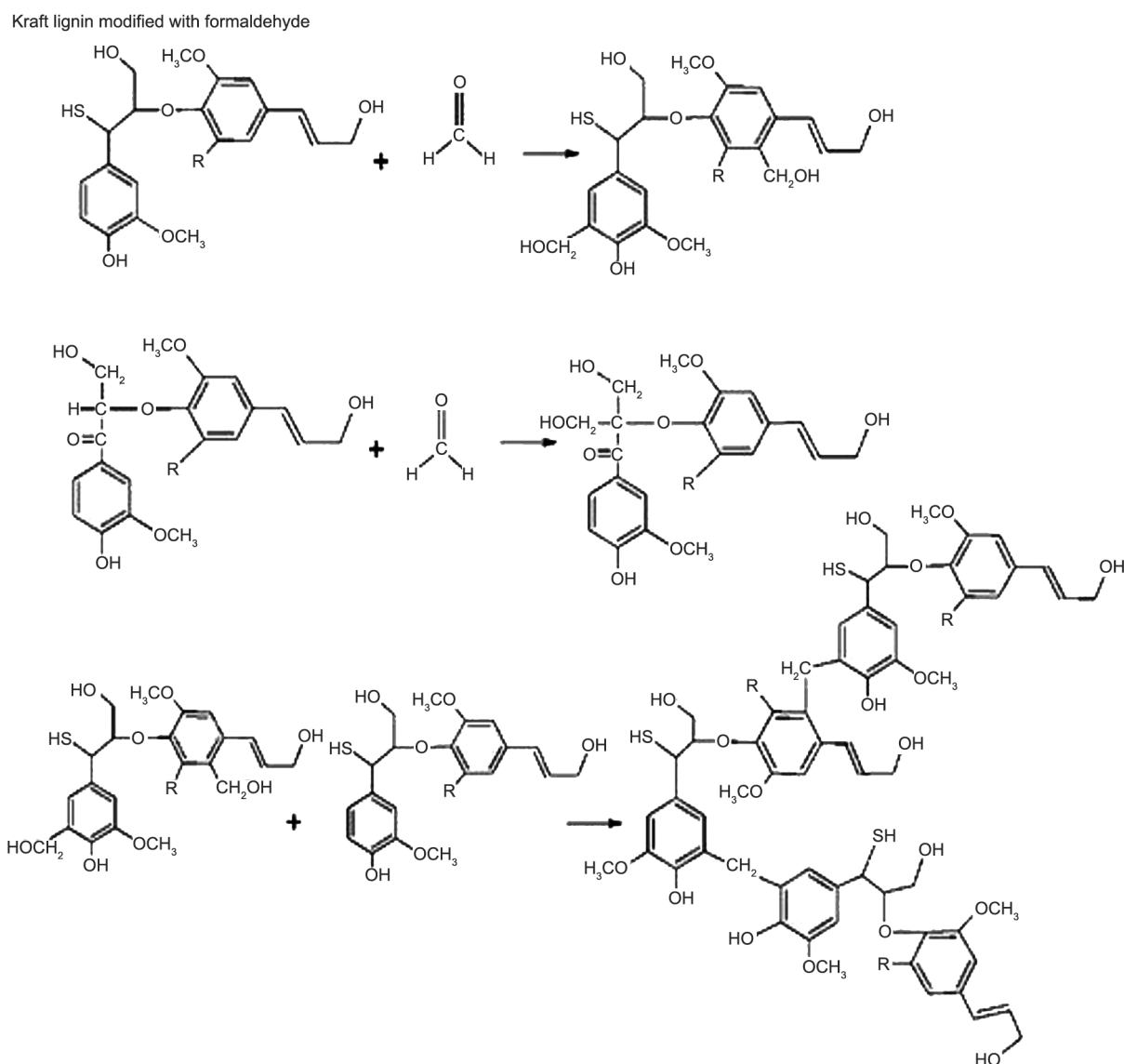


Figure 7. Different chemical modification of kraft lignin by using formaldehyde [148].

[149] to modify KL. Other hydrophobic materials such as polyethylene oxide (PEO), polyethylene-block-poly(ethylene glycol) (PE-*b*-PEG), cetrimonium bromide (CTAB), and dodecyl succinic anhydride (DDSA) were also used to modify KL. Treatment of KL with AKD and PE-*b*-PEG showed the best results with the highest hydrophobicity of lignin particles. This resulted in increased young modulus due to better dispersion in the case of AKD-KL/polypropylene and PE-*b*-PEG-KL/polypropylene composite.

Without chemical modification, the incorporation of KL in polyethylene composites resulted in a decrease in mechanical strength [93]. However, it was reported that a low molecular weight fraction of KL, with higher phenolic hydroxyl groups and lower double bonds, had better compatibility with the polyethylene matrix. Better dispersion of KL in polyethylene matrix caused

an increase in young modulus in the case of KL/polyethylene composite [92]. Fractionalization of KL was performed to have different molecular weight fractions with different phenolic hydroxyl group content by Huang *et al.* [51], as described in Figure 8 and listed in Table 3. In Figure 8c, it can be clearly observed that the tensile strength of the composites increased with decreasing molecular weight of KL due to better dispersion of lower molecular weight fraction with a higher amount of phenolic hydroxyl group. Compatibilizer was used to increase the interaction between polyethylene and KL. For better dispersion of KL in KL/polyolefin composites, coupling agents such as poly(styrene-*co*-ethylene-*co*-butylene-*co*-styrene) (SEBS) modified as SEBS-NH₂, maleic anhydride grafted with polyethylene (MAPE) [95], Organic peroxide such as dicumyl

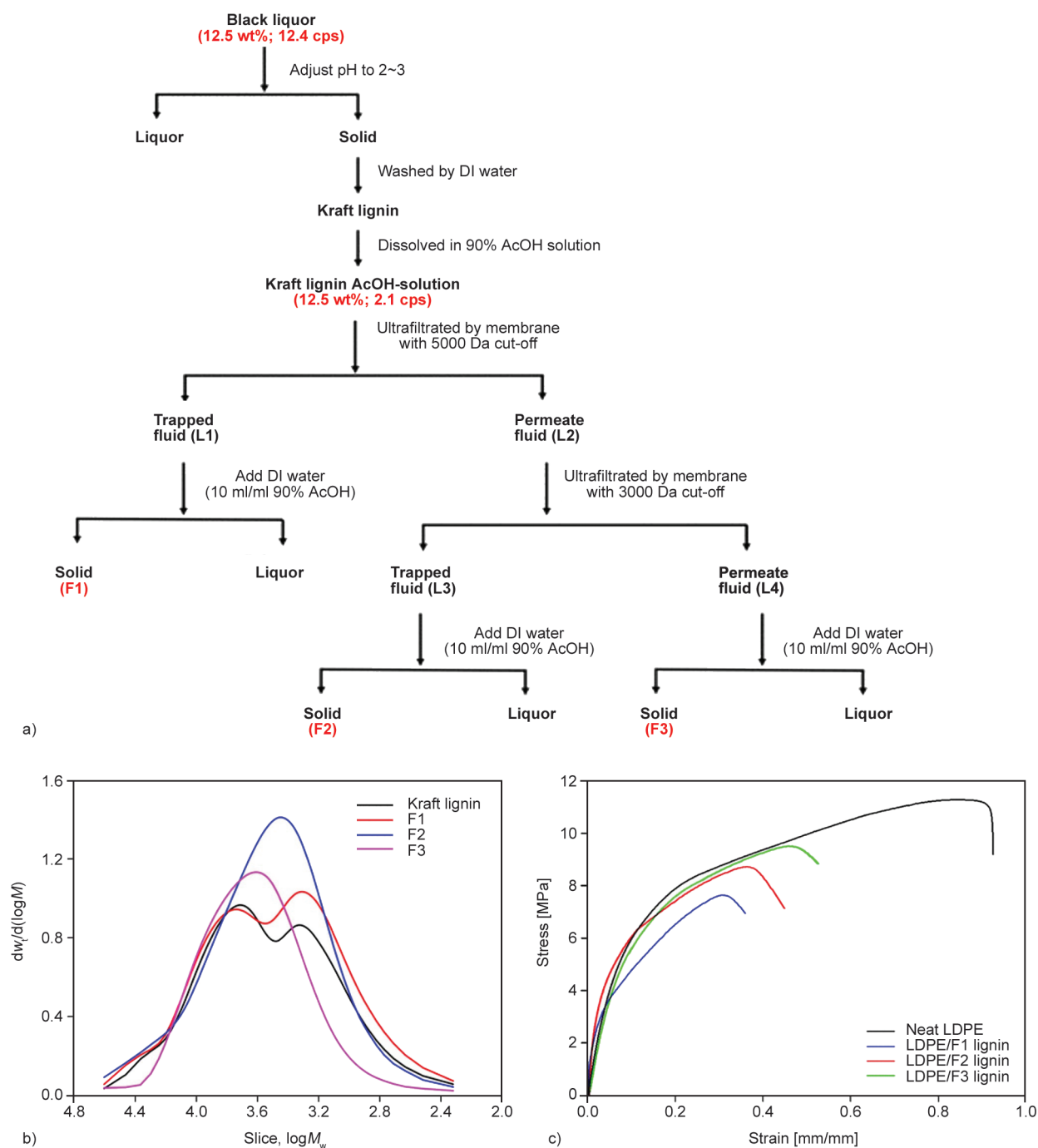


Figure 8. a) Process used for sequential ultrafiltration of KL using membrane with different MWCO, b) Gel permeation chromatography (GPC) chromatograms of KL and fractionated lignin of different molecular weight, c) stress vs. strain curve of LDPE/lignin composites with 20 wt% KL and fractionated lignin [51]. Copyright 2017 American Chemical society.

peroxide (DCP) [51, 89, 92, 93, 98, 150], Polyethylene oxide (PEO) along with boric acid and DCP [52], Silane coupling agent bis (3-triethoxysilyl propyl) tetrasulfide (TESPT) [151], maleated polypropylene in combination with ethylene butyl acrylate glycidyl methacrylate (EBGMA) [90], copper (II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) [152] were used. When SEBS- NH_2 was used as a compatibilizer, a sharp

increase in the young modulus of polyethylene/KL composite was observed. Due to the presence of aromatic molecules in SEBS- NH_2 , the compound is partially miscible in polyethylene matrix and interacts with KL via hydrogen bonding as well as π -stacking forces [95].

Apart from conventional thermal processing techniques, polymerization in the presence of lignin was

also used by researchers to develop lignin-based polymer composites. Modified KL with methacrylic anhydride was used for co-polymerization with styrene and methyl methacrylate to develop a polymer composite of polystyrene and poly(methyl methacrylate) (PMMA) in a study by Goliszek *et al.* [153]. Polymer composites with low levels of modified lignin had slower degradation rates under accelerated aging because of their polymer networks. However, with a concentration of modified lignin above 20 wt%, the polymer composites became more heterogeneous and showed higher degradation in the case of PMMA. The polymer composite of modified lignin and polystyrene showed better resistance toward accelerated aging. Polymerization was used for the preparation of polyethylene/lignin composite by anchoring lignin into vanadium-based Ziegler-Natta catalyst VOCl_3 [105, 109–111]. Industrial process such as solid-state shear pulverization (SSSP) was used by Iyer and Torkelson, and they reported that composites prepared by the SSSP method showed better lignin dispersion in polyolefin matrix than in the conventional melt mixing process. Materials are subjected to extraordinarily large compressive and shear forces during solid state processing, which can be responsible for such better dispersion of lignin [154].

KL was used along with different inorganic oxide fillers, such as MgO , ZnO , SiO_2 , *etc.*, in polymer composites to have different properties, usually for specific application-based properties [155, 156]. Bula *et al.* [96] used MgO -KL for the preparation of polyethylene composite which can have application as packaging material. Although composite film with MgO -lignin showed lower gas and water vapor permeability, this film exhibited excellent UV protection compared to neat LDPE, which can be used as UV screening films. It was reported that hydroxyl groups, double bonds, and aromatic rings present in lignin molecules are mainly responsible for the absorption of UV light [119]. Lignin also has antimicrobial properties. Phenolic hydroxyl groups present in lignin was reported to be primarily responsible for causing damage to the bacterial cell membrane, thereby having antimicrobial properties [119]. For this reason, KL along with ZnO in polyethylene composite [102], and poly(vinyl alcohol) (PVA) PVA/gelatin/KL [118] composite were developed with antimicrobial properties for food packaging applications. Composites with KL was studied for application as adsorbent for metals and other chemicals. Monoliths

were developed from polypropylene and lignin by Alassod *et al.* [87] for thermally induced phase separation techniques for application as oil absorbents. KL-incorporated polystyrene (KL-PS) exhibited better adsorption efficiency for copper ions due to the presence of different functional groups in lignin, which resulted in higher solid surface energy than polystyrene and improved interaction with copper ions [109]. KL/PVA composite was prepared as adsorbents for bisphenol A and erythromycin. The composite was microporous flow permeable material with binding sites of lignin available on the surface. However, during desorption, leakage of lignin along with adsorbed chemicals was reported by Ivanov *et al.* [117].

In a study by Widsten *et al.* [157], KL, acetylated KL and KL were treated with urea and formaldehyde to have higher N_2 , which were then used as a flame retardant in polypropylene composite. KL treated with urea and formaldehyde exhibited similar properties as of pentaerythritol (PER) which is an extensively used flame retardant along with ammonium polyphosphate (APP). The good performance of KL treated with urea and formaldehyde was due to the presence of a higher amount of N_2 , which resulted in the production of poorly burning gases such as ammonia.

Antioxidant properties of KL were reported in polyethylene at a very low concentration, below 2 wt%, due to the presence of phenolic groups in lignin [85]. Moreover, commercial antioxidant was reported to have a higher leaching rate than lignin due to the highly crosslinked structure of lignin, which inhibits its solubilization and consequently reduces its diffusion in the polymer matrix [158]. The thermal antioxidant property of lignin was reported to be dependent on the total content of phenolic and aliphatic hydroxyl groups [159]. The lower amount of phenolic hydroxyl group can reduce the overall anti-oxidative property of lignin. The study by Sedeghifar *et al.* [49] demonstrated that higher phenolic hydroxyl content of the acetone soluble fraction of KL resulted in 55% better anti-oxidant activity. In a study by Ye *et al.* [53], acetylated lignin was subjected to selective aminolysis to have a higher number of phenolic hydroxyl groups with higher numbers of aliphatic hydroxyl groups blocked (Table 3). Polypropylene/KL and polypropylene/modified KL both showed an increase in oxidative thermal stability of the polymer. It is predicted that phenolic hydroxyl groups of

untreated and modified KL capture the radicals generated from the tertiary proton in the polypropylene macromolecular chain. However, superior mechanical properties were observed in the case of polypropylene/modified KL due to better dispersion as blocking of aliphatic hydroxyl groups made modified KL more hydrophobic. So, modified KL was more compatible with polypropylene structure than untreated KL. Subsequently, it was concluded that in the case of thermooxidative stability, the main factor is the number of phenolic hydroxyl groups present in the lignin molecule, not the degree of dispersion of lignin in the polymer matrix. So, selective aminolysis of acetylated KL was concluded to be a better option for having improved mechanical properties, better dispersion in polymer matrix due to the presence of a lower number of aliphatic hydroxyl groups, and improved thermal oxidative stability due to the presence of a higher number of phenolic hydroxyl groups. Similarly, butylated KL using *n*-butyric anhydride in polypropylene could also be advantageous [84]. Moreover, KL can reduce the harmful effects of radiation on the mechanical and thermal properties of the polymer as reported by Sugano-Segura *et al.* [78].

Lignin can also be used as a coupling agent in hybrid polymer composite to increase adhesion between second reinforcements and polymer matrix [79]. Luo *et al.* [80] used different concentrations of KL as a natural compatibilizer in wood flour/polypropylene composite. In the case of lower concentration of KL (0.5 and 1.0 wt%) in wood flour/polypropylene composite, reduced water absorption and improved mechanical properties were observed. However, in the case of a higher concentration, an increase in water absorption and a decrease in mechanical properties were reported. Superior properties in the case of lower concentration were due to better interfacial adhesion between wood flour and polypropylene in the presence of 0.5 and 1.0 wt% KL. Similarly, esterified KL was used as a coupling agent in a bark/ polyethylene composite [103]. Due to lignin's aromatic structure, it is compatible with carbon fiber and alkylation; on the other hand, it can increase the compatibility of lignin with polypropylene. For this reason, Sakai *et al.* [88] used alkylated lignin as a compatibilizing agent in polypropylene/carbon fiber composite. Moreover, another important aspect of this study is the use of ionic liquid 1-ethyl-3-methylimidazolium acetate or [Emim][OAc] for alkylation treatment.

3.2. Kraft lignin-based polymer composites with natural polymer matrix

Lignin was used as reinforcements in bio-polymer composite using starch, cellulose, natural rubber, chitosan, poly lactic acid (PLA), collagen, *etc.*, as polymer matrix (Table 4).

Starch, another abundant biopolymer like lignin, was used extensively by the researcher to develop polymer composite with superior thermal and mechanical properties. In a study by de Freitas *et al.* [126], the incorporation of KL made the composite film more hydrophobic, more thermally stable than native starch and with superior mechanical properties. The developed composite with 4% KL was able to adsorb methyl orange due to the presence of different functional groups in lignin. Zhao *et al.* [127] reported that a lower molecular weight fraction of lignin was a more suitable candidate for improving the mechanical properties of starch composite films than a higher molecular weight fraction with lower G + S unit content.

Farooq *et al.* [137] prepared cellulose nanofibril (CNF) nanocomposite with KL as colloidal lignin particles (CLPs) which are easily dispersed in aqueous media. The authors used an easy and simple method to prepare lignin nanoparticles by dissolving KL into an aqueous solution of acetone. This method can be used for the preparation of lignin nanoparticle-reinforced polymer composites. The prepared composite film with 10% CLP exhibited almost double toughness as the film of only CNF. The authors concluded that at 10% concentration, CLP acted as ball bearing lubricating agent, which could transfer stress and enhance the toughness of the composite film. Moreover, the prepared film had antioxidant, and UV-blocking properties with reduced water sorption. The interaction between CNF and CLP is mainly by hydrogen bonding and electrostatic interaction.

The polymer composite of KL with polylactic acid or PLA is extensively studied by researchers. In recent years, numerous works have been done to develop efficient PLA/KL polymer composite, mainly for food packaging applications and as 3D printing material. Without any chemical modification and coupling agent, PLA/KL composite has shown poor mechanical as well as thermal properties due to poor dispersion of filler in the polymer matrix [160–162]. In work by Kim *et al.* [131], hydrophilic hydroxyl groups of KL were acetylated to improve the compatibility of

lignin. The prepared composite film had UV protection. Both tensile strength and elongation were improved with the addition of modified KL with young modulus remaining unchanged. Other modifications of KL such as grafting of two bio-based monomer lauryl methacrylate (LMA) and tetrahydrofurfuryl methacrylate (THFMA) with KL by free radical polymerization [132], modification to have acetoacetate functional group [133] were also explored to increase the compatibility with PLA. Compatibilizer such as polymeric diphenylmethane diisocyanate (PMDI) [130] was also used to increase the dispersion of lignin in the PLA matrix.

KL was also used as reinforcement in natural rubber or NR. It is reported that the thiol group present in KL can interact with unsaturated chains of the polymer matrix by forming carbon-sulfur covalent bonds, which is subsequently resulted in stronger filler-polymer interaction [163]. However, due to aggregation formation by lignin molecule, contact surface between filler and polymer matrix can be reduced, which leads to poor dispersion. Datta and Parcheta used glycerolysate and naphthenic oil as plasticizing agents for KL/natural rubber composite to have better dispersion of the filler [147, 164]. In work by Aini *et al.* [148], KL was hydroxymethylated for better dispersion in the rubber matrix. Often carbon black was used along with lignin for better dispersion due to the synergistic reinforcing effect. In this study, better crosslinking between hydroxymethylated KL and rubber matrix was observed.

Hybrid polymer composite is a class of polymer composite where two or more reinforcements are used to improve the original properties of the polymer matrix or to introduce new properties. Such hybrid polymer biocomposite was prepared by using starch as polymer matrix and cellulose nano fiber or CNF and KL as reinforcements. The prepared composite was used as a gas separation membrane, and the incorporation of lignin in the composite films improved gas selectivity as well as mechanical properties [128]. In another study, where 2-hydroxyethyl cellulose and KL were used in gellan gum as a polymer matrix, lignin improved the hydrophobicity of the composite film, gave protection under UV, and acted as an antioxidant [165]. Hydroxypropyl methylcellulose (HPMC)/KL/chitosan composite film with the antimicrobial and antioxidant composite film was also prepared [140].

da Rosa *et al.* [135] used KL powder in sludge fiber waste/ PLA composite as a coupling agent. It was reported that incorporation of KL, resulted in improved compatibility between fiber and PLA, which is observed as improved mechanical properties, improved thermal stability as well as reduced water absorption. Reduced water absorption can be due to favorable interaction between aromatic functional groups of lignin with cellulosic fiber. KL was also used as a compatibilizer in PLA/reduced graphene oxide (rGO), where lignin promoted homogenous dispersion by creating weak interaction with PLA and rGO [166].

The composite film of carrageenan/KL had improved mechanical strength and antimicrobial properties. Moreover, lignin made the film more thermally stable due to antioxidant properties and gave protection under UV. Improved hydrophobicity as well as lower water vapor permeability (WVP) was also observed [167]. Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is a biopolymer produced by different bacteria. Native PHBV has poor thermooxidative stability and lower gas permeability. However, PHBV/KL biopolymer composite exhibited improved thermooxidative stability and gas permeability [168]. However, it was also reported that unmodified lignin was found to be poorly miscible in PHBV polymer matrix and can have a limited effect on the resultant composite's properties due to phase separation and non-interaction between two biopolymers. Luo *et al.* [169] used compatibilization by free radical grafting during extrusion of KL and PHBV by using dicumyl peroxide (DCP). The main aim of using compatibilization during melt blending was to have continuous interphase, which can subsequently result in better dispersion of KL in PHBV. Poly(3-hydroxybutyrate) (PHB) is a similar kind of biopolymer to PHBV and is produced by different bacteria. Improved thermal stability, as well as improved mechanical properties, were observed due to strong interfacial interaction between lignin and PHB via hydrogen bond in the case of PHB/KL composite film. It was also reported that pickering emulsion technique could be useful for having uniform dispersion of lignin particles in PHB polymer matrix [146]. Chitosan was also used for preparing polymer composite. In a recent work by Izaguirre *et al.* [141], sequentially solvent extracted KL was used for preparing polymer composite with chitosan. Polymer

composite with lignin fraction obtained from ethanol fraction exhibited improved mechanical strength as well as UV blocking properties. Masilompane *et al.* [143] prepared a nanocomposite from chitosan, KL and TiO₂ for adsorbent of synthetic dyes by electrostatic interaction. Nanocomposites was in powder form, which resulted in higher adsorption due to a larger surface area with more active sites. Duan *et al.* [145] used ionic liquid 1-butyl-3-methylimidazolium acetate and γ -valerolactone for the preparation of composite film with chitin and KL. The prepared film was studied as an adsorbent for heavy metal ions. Moreover, film showed excellent stability and flexibility in the aqueous solution, making it more suitable for wastewater treatment.

4. Lignosulfonate-based polymer composite

Lignosulfonate salt can be made of calcium, sodium, magnesium, and ammonium, depending on the type of base or metallic sulfite used during the pulping process. With many advantageous structural and chemical properties, it is also very cheap form of lignin that can have useful applications in polymer composites. In this section, different studies exploring the use of lignosulfonates as filler in polymer composites are discussed in detail.

4.1. Lignosulphonate-based synthetic polymer composite

Lignosulfonates, like KL, are also immiscible in non-polar polyolefins, such as polyethylene and polypropylene. Due to weak interaction between non-polar polymer and lignin molecules, the latter tend to interact with each other, forming aggregation followed by very poor dispersion. Miscibility can be improved either by chemical modifications or by using a coupling agent. Table 5 shows the use of lignosulfonate in different polymer composites, improvement of the properties after inclusion of

lignosulfonate, and application of resultant polymer composites.

Lignosulfonate was chemically modified by using hydrotalcite or layered double hydroxide (LDH) for incorporation into polypropylene. Layered double hydroxide, is a well-known flame retardant that is used widely with other polymers. However, due to its hydrophilic nature, LDH is poorly dispersed in a non-polar polymer such as polypropylene, resulting in poor flame retardant properties. LDH has positively charged layers that can be used for modification with negatively charged organic molecules by surface adsorption and anion exchange. Lignosulfonates are polyanions and Wu *et al.* [173] prepared LDH-lignosulfonate for incorporation in polymer composites with polypropylene. The addition of lignosulfonates in LDH resulted in increased hydrophobicity and subsequently improved dispersion in the polypropylene matrix. Due to better dispersion, and synergistic flame retardancy between LDH and lignosulfonate, the prepared composite with LDH-LS (lignosulfonate) exhibited minimum heat release rate, total heat release, and total smoke production. LDH and lignosulfonate form a continuous and higher amount of char residues due to the uniform dispersion of filler in the polymer matrix. Hydrophilic and water-soluble lignosulfonate is a polyanionic molecule. It can adsorb heavy metal ions in water, dyes and alcohols, and this property is advantageous for use as a nanofiltration membrane. Moreover, abundant carboxyl and hydroxyl groups present in lignin molecules are also useful as adsorption sites. Polyethyleneimine (PEI)/lignosulfonate thin film was prepared on polysulfone ultrafiltration membrane by the layer-by-layer assembly and crosslinking technology where PEI was polycation. The prepared membrane had amino and hydroxyl groups on the surface and showed improved adsorption efficiency towards heavy metal ions [202].

Table 5. Different lignosulfonate-based polymer composite.

Lignosulfonates	Types	Polymers	Application of lignosulfonates	References
	Polymer composite	Polypropylene	Flame retardant, antioxidant, improvement of mechanical properties	[170–173]
	PVA	Lowering of melting point, improvement of mechanical properties, antioxidant	[174–176, 205]	
	PANI	Dopant, adsorbent	[177–181]	
	Polypyrrole	Dopant, adsorbent	[182, 183]	
	PEDOT	Dopant	[184, 185]	
	PLA	UV protection, antioxidant, improvement of mechanical properties	[160, 186–189]	
	Chitosan	Adsorbent, antimicrobial, improvement of mechanical properties, antioxidant, antibiofilm	[190–201]	

Szabó *et al.* [203] used different polymer matrices to understand which polymer is best suited for uniform dispersion of lignosulfonates without any chemical modification or incorporation of a coupling agent. They used polypropylene and aromatic polymers such as polystyrene, polycarbonate and glycol-modified poly(ethylene terephthalate) (PET). Lignin molecules mainly interact with other polymers via hydrogen bond and aromatic π electron interaction, as reported in previous studies. Therefore, all three aromatic polymers showed better interaction with lignosulfonate via π interaction than the polypropylene/lignosulfonate composite. However, the interaction between lignosulfonate and polystyrene was weaker among the three as the aromatic ring in polystyrene does not have any functional groups, and interaction is only via π interaction. In glycol-modified PET, the aromatic ring has two carbonyl groups which can form hydrogen bonds with different functional groups present in lignosulfonates and this, combined with π interaction, lignosulfonate/glycol modified PET exhibited strong interaction. From this study, it can be concluded that polymers with aromatic rings and different functional groups in the repeating unit was found to be a more suitable choice of polymers for the preparation of polymer composites with lignosulfonate. Better dispersion of lignosulfonate was also observed in another aromatic polymer (PBAT) polybutylene adipate terephthalate. However, lignosulfonate used in this study was modified by maleic anhydride. π interaction and chemical modifications can be resulted in better miscibility [204].

Polyaniline (PANI) is also an aromatic polymer that was used with lignosulfonate for the preparation of composite with a different range of applications. Lignosulfonate is rich in phenylpropane groups with hydrophilic sulfonic groups and electroactive methoxy phenol groups. These phenols groups can be converted to quinone/hydroquinone groups which make lignosulfonate a quinone-based redox polymer undergoing fast proton-coupled reversible redox transitions over a wide pH range. Moreover, these quinone groups can further be utilized for electrochemical energy storage. Being polyanionic and water soluble, lignosulfonate has become a popular, cost-effective and environmentally friendly polyanionic dopant that is added to increase electrical conductivity of conducting polymers. However, lignin molecules are electronically insulating. Therefore, for the successful use of the quinone group converted

from phenol groups in lignin as energy storage, it is required to choose a polymer material of good electronic and ionic conductivity [180]. Rebis and Milczarek prepared a composite with lignosulfonate using three different conducting polymers *i.e.*, PANI, polypyrrole and poly(3,4-ethylene dioxythiophene) (PEDOT). It was observed that methoxy phenol groups of lignosulfonates were converted to quinones during the preparation of PANI/lignosulfonate and PEDOT/lignosulfonate composite. However, in the case of polypyrrole/lignosulfonate, methoxy phenol groups remained in their native form and were converted to quinone by post-polymerization oxidation. All three composites showed improved redox electroactivity and increased charge storage. Moreover, PANI/lignosulfonate exhibited optimal electroactivity in pH 7 to 9. This is a usual characteristic of PANI polymerized in the presence of polyanionic structures; in this case, the polyanion is lignosulfonate [180]. To improve electrical conductivity, Qian *et al.* [185] prepared PEDOT/lignosulfonate composite by emulsion polymerization and then prepared composite was again subjected to pickering emulsion polymerization using 3,4-ethylenedioxythiophene (EDOT) monomer. It was reported that the final composite was much more conductive than the initial materials due to the high content of PEDOT in the core structure. Xu *et al.* [177] used $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as an oxidizing agent for the preparation of PANI/ lignosulfonate and phenol groups were converted to quinone by oxidation during polymerization. Zhang *et al.* [179] used laccase, a lignin-degrading enzyme for polymerization of PANI-Emeraldine salt (PANI-ES)/lignosulfonate composite, using atmospheric oxygen as an oxidizing agent. The prepared composite can be used on the surface of the cotton fabric to make it electrically conductive. PANI/lignosulfonate composite was also used as expanders in a lead-acid battery. Expanders are usually used to reduce the degree of compaction within negative plates and to provide more ionically transport channels within plates during the charge/discharge process. Although lignosulfonates are mainly used as expanders for their 3D structure, it is electrically insulating, and this limits their application in the battery. However, PANI/lignosulfonate composite exhibited more advantageous properties than lignosulfonate due to the optimal combination of electronically conductive PANI and ionically conductive lignosulfonate with 3D structure. Moreover, this composite

made the battery's lifecycle longer as reported in this study [181]. PANI/lignosulfonate [178], Polypyrrole/lignosulfonate [183] composite were used as adsorbents for textile dyes and heavy metals via electrostatic interaction, hydrogen bond and intermolecular interaction. Lignosulfonate was used to improve the bonding strength of polypyrrole/cellulose fiber composite. Incorporation of lignosulfonate improved the bonding strength due to formation of more hydrogen bonds. However, the electrical conductivity of the prepared composite was reduced due to the non-conducting properties of lignosulfonate [182]. PVA is widely used in the food packaging industry for its water soluble, low cost, and excellent gas barrier properties. Thermal processing, such as extrusion, compression molding *etc.*, are industrial processing techniques used for thermoplastics. Due to the presence of strong inter- and intermolecular hydrogen bonding, PVA has a very narrow thermal processing window which makes thermal processing of this polymer challenging. Usually, the plasticizer is incorporated to lower its melting point, which can have a negative effect on the application as food packaging materials, as plasticizers are often toxic in nature. Lignin molecules are safe and reported to have lower cytotoxicity. Ye *et al.* [175] prepared a polymer composite with calcium lignosulfonate/PVA. Polymer composite exhibited a reduction of the melting temperature from 226.1 to 212.8 °C with increasing loading of lignosulfonates. In PVA, this reduction of melting temperature is caused by disruption of the crystalline region due to strong interactions between lignosulfonates and the polymer [175]. Moreover, improved mechanical properties were also observed in the case of polymer composites with increasing loading of lignosulfonates. Lignosulfonates, like PVA, are water soluble, which is advantageous for the preparation of polymer composite by a simple solvent casting method [175, 176]. To improve interaction between PVA and lignosulfonates, the latter was grafted with acrylic acid. The grafted lignosulfonate had better interaction with PVA via hydrogen bonding than unmodified lignosulfonate. A reduced melting temperature of 214 °C was observed with only 35% of grafted lignosulfonates when similar reduction was observed with 60% unmodified lignosulfonate. Moreover, improved mechanical strength and thermal stability were observed in acrylic acid grafted lignosulfonate/PVA composite [174].

Lignosulfonate was used as a compatibilizer. In a study by Wang *et al.* [206], jute fibers were coated with sodium lignosulfonate, which interacted with fiber via hydrogen bond and dipole bond. Improved mechanical properties were observed in the case of jute fiber coated with lignosulfonate/polypropylene composite than jute fiber/polypropylene composite due to increased interfacial binding between filler and polymer matrix. Methacrylated lignosulfonate was used as a compatibilizer in the flax fiber/polyester matrix. Flax fibers were treated with methacrylated lignosulfonate and this treatment enhanced the interaction between fiber and the polymer matrix [207].

4.2. Lignosulphonate-based natural polymer composite

Different natural polymers were used with lignosulfonate for the preparation of bio-composite. Chitosan, PLA, and CNF have extensively studied polymers. Unlike KL, very limited work has been performed on starch/lignosulfonate composite (Table 5) [208].

A composite film was prepared from α -cellulose/ZnCl₂/CaCl₂ along with lignosulfonate by crosslinking via intermolecular hydrogen bond and using succinic anhydride and triethanolamine as linkage bridge. The prepared film had improved mechanical strength, hydrophobicity, antibacterial properties, thermal stability as well as UV blocking properties [209]. A similar composite film was prepared from carboxylated cellulose nanofiber (CNF) and lignosulfonate. The prepared film showed elastic properties due to the uniform dispersion of CNF resulting from electrostatic repulsion by lignosulfonates [138]. Moreover, CNF/lignosulfonate/CaCl₂ film exhibited flame retardancy and high electrical resistance [210]. Sodium ion of lignosulfonate was modified by using ionic liquid tris-[2-(2-methoxy ethoxy)ethyl]amine (TrisEG). Modified lignosulfonate with ethylene glycol functionality was used as a dispersant for cellulose/gluten composites. The prepared composite had improved mechanical strength than the composite containing unmodified lignosulfonate [211]. Bacterial cellulose (BC) is a nano form of cellulose. Lignosulfonate/BC membrane has been prepared for application ion exchange membrane in a fuel cell with improved thermal stability and mechanical properties [212].

Chitosan is a natural biopolymer with high content of hydrophilic hydroxyl and amino functional groups

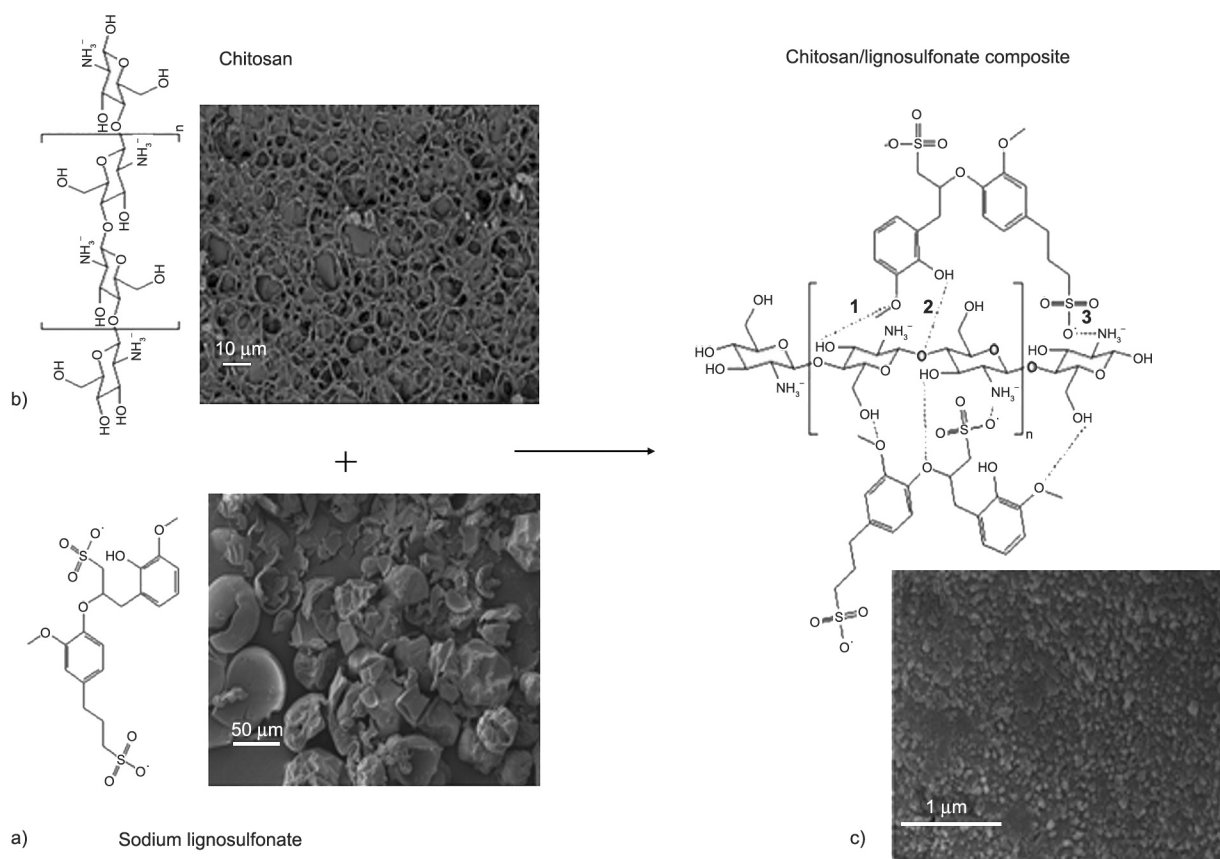


Figure 9. a) Chitosan, b) sodium lignosulfonate, c) chitosan/lignosulfonate composite and SEM image [201]. Copyright 2019 American chemical society.

i.e. primary, secondary, and acetylamino groups [198]. Chitosan with a positively charged amino group can be crosslinked with lignosulfonate with a negatively charged sulfonate group, as described in Figure 9. For their effective and strong interaction, the chitosan/lignosulfonate composite is extensively studied by the researcher. Gu *et al.* [201] prepared chitosan/lignosulfonate composite in powder form for adsorption of textile dyes. Two polymers interact with each other by electrostatic interaction between the amino group and the sulfonate group. Moreover, a weak hydrogen bond has also been formed between the hydroxyl group of chitosan and the methoxy group of lignosulfonates. Phenolic hydroxyl group also can interact with β -1,4-glycosidic oxygen of chitosan. The composite has strong adsorption efficiency towards congo red, rhodamine B and Cr (VI). Adsorption was due to electrostatic interaction between cations and anions of the composite and respected materials. Due to effective electrostatic and chemical adsorption, chitosan/lignosulfonate composite was also used for adsorption of other heavy metals like Pb (II) [194, 199], Cu (II), Co (II) [200], Hg (II) [198], methylene blue [197].

Often, other materials are also incorporated into the composite to enhance their effective adsorption of specific toxic chemicals. One such element is graphene oxide (GO). Chitosan treated with Fe_3O_4 was used in this study to give the composite magnetic properties, which can be used for the collection of adsorbents, after use, by using a magnet. Moreover, other than electrostatic interaction and weak hydrogen bonding, π - π stacking interaction can be involved during the adsorption process, as it was reported in this study [197]. In another study, Zhang *et al.* [194] prepared chitosan/lignosulfonate composite by free radical polymerization in the presence of *N,N*-methylene bisacrylamide and potassium persulfate. The prepared composite had 3D structural network and good mechanical strength due to which the adsorbent can be reused repeatedly after adsorption of Pb (II) ions followed by desorption at lower pH. Chitosan/lignosulfonate composite was prepared as a nanosphere with antimicrobial properties [193]. The antibacterial property of the composite was used to protect carbon steel from different sulfate-reducing bacteria-induced corrosion by Rasheed *et al.* [192]. Authors concluded that chitosan/lignosulfonate could

be used commercially in oil and gas industry pipelines to prevent microbial-induced corrosion [191]. Chitosan/lignosulfonate was used as flame retardants on cotton fabric. Due to the presence of the amino group, a higher amount of non-combustible product has been formed, which resulted in good flame retardancy properties of chitosan/lignosulfonate [190].

Like KL, lignosulfonate is also a suitable choice for preparing polymer composite material with PLA for different applications, mainly for the food packaging industry. Different properties of PLA were enhanced by the addition of lignosulfonate. The incorporation of lignosulfonate has improved antioxidant properties, UV light adsorption capacities of the prepared composite. However, the sulfonic group present in lignosulfonate is highly hydrophilic, due to which PLA/lignosulfonate usually has increased water absorption and accelerated biodegradation. To make PLA/lignosulfonate composite more hydrophobic, Ye *et al.* [186] subjected lignosulfonate to desulfonation to reduce hydrophilic group content. PLA/desulfonated lignosulfonate showed improved thermal stability than PLA/lignosulfonate, which can be due to better compatibility between PLA and desulfonated lignosulfonate. However, mechanical properties and UV absorption properties of both types of composites remained almost similar. PLA has dielectric properties and can be used as an electrically insulating material for different purposes. For better interaction and dispersion, lignosulfonate was modified with oleic acid, lactic acid, butyric acid and butyrolactone by radio frequency cold plasma method. PLA/modified lignosulfonate exhibited improved dielectric properties, mechanical strength, and hydrophilicity. Chemical modification improved the dispersion of filler in the PLA matrix [187]. PLA also has poor fire retardancy properties. For that purpose, Tawiah *et al.* [188] prepared azo-boron coupled with 4,4'-sulfonoyldiphenol-(((1E,1'E)-(sulfonyl-bis(6-hydroxy-3,1-phenylene))bis(diazene-2,1-diyl))bis(3,1-phenylene)) diboronic acid (SBDA). Composite material was prepared from PLA with SBDA and calcium lignosulfonate to reduce fire retardancy of PLA. PLA with 10 wt% lignosulfonate and 5 wt% SBDA exhibited improved fire retardancy as well as a lowered melting point for easier thermal processing. It was reported that the presence of the boron-hydroxyl group along with calcium lignosulfonate had produced an increasing amount of glassy carbonaceous char during combustion, which was mainly responsible

for increasing fire retardancy. PLA/lignosulfonate also exhibited antimicrobial and improved biodegradability than pure PLA films [189]. Mimini *et al.* [160] prepared PLA composite with KL, organosolv lignin and lignosulfonate to understand the effects of different types of lignin on composite's properties. It was reported that PLA/lignosulfonate exhibited lower melting point and higher mechanical strength than PLA/KL and PLA/organosolv lignin. Moreover, PLA/lignosulfonate is a better choice for the application of 3D printing. This advantageous effect of lignosulfonate over KL and organosolv lignin is mainly due to the presence of sulfonic groups, which give the lignin molecule net negative charge along with high surface activity, stabilizing and dispersing properties [160].

Lignosulfonate/polypropylene composite was used as a compatibilizer for PLA/coffee grounds composite. The amount of polypropylene and lignosulfonate has been 9 and 2–5%, respectively. Better mechanical properties, as well as better thermal stability, were observed in case of PLA/coffee ground composite with lignosulfonate and polypropylene than PLA/coffee ground/polypropylene and PLA/coffee ground/lignosulfonate due to the synergistic effect of lignosulfonate/polypropylene as compatibilizer [213]. The incorporation of ammonium lignosulfonate has as compatibilizer enhanced mechanical properties and improved internal bonding between PLA and wood fiber. However, due to higher hydrophilicity, the prepared composite had higher hydrophilicity and water swelling properties [214].

5. Conclusions and perspective

In this review, recent progress and challenges regarding the extraction of kraft lignin and lignosulfonates from black liquor and spent liquor, respectively, were discussed in detail. Recent progress in polymer composite with KL and lignosulfonate with synthetic and natural polymers are summarized. The final properties of the composites, as well as their different application, were also discussed. The review outlines various chemical modifications and extraction methods of KL and lignosulfonate and suggests recommendations for modification strategies in polymer matrices to enhance dispersion and compatibility. Based on the review, some of the areas worth exploring are detailed below:

- KL is more hydrophobic in nature and more compatible with polyolefin, such as polypropylene,

polyethylene, *etc.* than lignosulfonate. Chemical modifications such as esterification, alkylation, acetylation of KL, and addition of coupling agents are advantageous for better dispersion in a polyolefin matrix. The fractionation of KL by organic solvent to have a lower molecular weight fraction with high amounts of phenolic hydroxyl groups also improves its compatibility with polyolefins. The biodegradability of the polyolefin/KL composite needs to be explored to understand whether KL affects polyolefin biodegradability.

- Aromatic polymers such as PET, PS, and PANI are more compatible with KL and lignosulfonate than polyethylene, polypropylene, *etc.* Lignin can interact with aromatic polymers via π - π interaction, which is resulted in better dispersion of lignin in a polymer matrix. Moreover, aromatic polymers with functional groups such as phenolic hydroxyl group are the most suitable choice of polymer matrix for lignin-based polymer composites. Polymers can also be modified for better dispersion of lignin. This field merits further study.
- In the case of polyolefins, several studies report an increase in young's modulus with the addition of KL. Hence, kraft lignin can be further explored as a component in composite materials where a high modulus is desired.
- Colloidal lignin particle (CLP) has a very strong positive effect on thermal oxidative stability, mechanical properties, and on UV protection. However, CLP is only used with CNF for the preparation of polymer composites. To gain a deeper understanding of their effects, it is crucial to understand how they interact with different polymers.
- Lignosulfonate is a unique form of lignin molecule with a net negative charge and affinity towards different chemicals from aqueous solution by electrostatic interaction and hydrogen bonding. Lignosulfonate is soluble in water in a wide range of pH. For this reason, lignosulfonate has been studied extensively as a component for the preparation of many effective adsorbents. The availability and low price of lignosulfonate make it a feasible candidate for industrial use in water treatment.
- Lignosulfonate is also successfully used for doping electrically conductive material. In applications, these materials may effectively increase the

electrical conductivity of electrically conducting materials and energy storage.

- Many researchers have reported the amphiphilic nature of lignosulfonate, which can be used as a coupling agent or compatibilizer in hybrid composite to improve the interaction between filler and polymer. This area, however, is hardly explored by researchers. More insight is needed to explore the full potential of lignosulfonate as a coupling agent.

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