

Chapter 10

Prospects and Challenges of Using Lignin for Thermoplastic Materials

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Lignin is a multifunctional biopolymer with high application potential in the synthesis of thermoplastic materials. Industrial and investigational lignins have been incorporated into various commercial polymers, including biobased polymers, to improve their biodegradability, cost, and thermomechanical stability. Lignin is also expected to bring additional benefits to the formulations, such as flame retardancy, UV-protecting ability, and antioxidant and anti-weathering capacity. Strategies focused on lignin size reduction, fractionation, and modification via esterification, etherification, and graft copolymerization, and plasticization and compatibilization have been employed to improve the physicochemical properties of lignin-based thermoplastic materials as promising alternatives to petroleum-based plastics.

Introduction

The high carbon footprint of petroleum-derived plastics, and the dwindling petroleum supplies have brought bioplastics in sharp focus as sustainable alternatives to synthetic plastics (1). However, only 1 % of the 350 million tons of plastic produced annually are sourced from biomass (1, 2). Hence, research and industrial efforts have been urgently directed towards increasing their use for a more sustainable world. Bioplastics is an umbrella term that includes the plastics that are derived from bio-based/renewable sources, as well as those that are biodegradable (1). Examples of the biodegradable bioplastics are polyhydroxyalkanoates (PHAs) and polylactic acid (PLA), which contribute to 12 % and 15 % of the worldwide bioplastics production, respectively (3). There are examples of bioplastics derived from biorenewable platform chemicals, which themselves are non-biodegradable, such as bio-polyethylene (PE). The most readily available biodegradable bioplastics may be derived from biopolymers such as cellulose, chitin, starch, and lignin produced in biological systems (3). However,

in contrast to their availability, their exploitation in the production of plastics is only an emerging field.

Thermoplastic materials are a subset of plastics. These are polymeric materials that can be thermally softened to a flowable state as the macromolecular chains slide past each other, molded into desired shapes, cooled, and then reprocessed by passing through the same cycle while having a limited effect on their inherent properties, allowing for multiple re-use cycles. As a result, desirable properties of thermoplastics include low melt viscosity, good processability, and high thermal and mechanical stability (4). Thus, research efforts are focused on endowing biorenewable thermoplastics, including those produced from biopolymers such as lignin-based thermoplastics, with performances similar to their synthetic counterparts to produce sustainable alternatives.

Lignin is a main structural constituent of lignocellulosic biomass, and the most abundant aromatic polymer on earth. It is readily available as a byproduct of the pulp and paper industry. As of today, approximately 50-70 million tons of lignin are produced worldwide annually (5, 6). Kraft lignin (KL) is the largest source of lignin currently available, which accounts for 85 % of total lignin produced, and approximates 50 million ton/year (7). Kraft lignin is the product of sulfate (kraft) pulping process. Kraft pulping uses an aqueous solution of sodium hydroxide and sodium sulfide to solubilize lignin, and inevitably some hemicelluloses, to produce the so-called black liquor (8, 9). During this process, lignin undergoes degradation and condensation reactions, resulting in its structural modification (10). Conventionally, concentrated black liquor is burnt in the recovery boiler to regenerate chemicals and produce heat and power, whereas acidification of black liquor to recover lignin is rare. LignoBoost is one such patented process, which involves acidifying a portion of the black liquor, followed by filtration, and resuspension of lignin in conjunction with an elaborate washing procedure. It yields a low-ash kraft lignin of high quality (11). A second patented process, LignoForce, includes oxidation of the black liquor to control volatile sulfur-containing compound emissions in the acidification step that follows (12). Organosolv lignins (OSL) are recovered from different organosolv delignification processes conducted mostly on angiosperms. The delignification processes include those using organic solvents, such as the ethanol-based Alcell process (13), and organic acids, such as acetic acid-based acetosolv and formic acid-based formasolv. The Alcell process was commercialized in the 1990s (Repap Enterprise Inc.) and later discontinued. A total of 3,500 tons of Alcell lignin was sold as technical lignin by 2005, and widely used in the studies of lignin valorization, including in the production of thermoplastic materials (14). Soda lignins (e.g. commercially available Protobind) are recovered from spent liquors of soda pulping, which is conducted mainly on herbaceous species (grasses, and agricultural residues; AGR) and thereafter, soda lignins are mostly non-wood lignins (13). Kraft and sulfite pulping processes yield sulfur-containing lignins; KL and lignosulfonates (LS). Sulfur-free pulping processes, such as soda and organosolv produce sulfur-free lignins (Table 1).

Although the majority of the lignin is currently produced during kraft delignification (19), emerging lignocellulosic-based biorefineries are expected to produce large amounts of lignin as a byproduct. Hydrolytic lignin (HL) recovered from autohydrolysis-based pretreatment liquors, (e.g. steam explosion- or hot-water extracted lignin), and lignin recovered as an insoluble residue at the end of enzymatic hydrolysis (enzymatic hydrolysis lignin; EHL) are typical representatives of biorefinery lignins (8). It has been estimated that by 2022, 62 million tons of lignin per year may be generated from the cellulosic biofuel industry in the US alone, with about 60 % more lignin generated than needed to meet internal biorefinery energy needs by its combustion (20). Currently, the majority of lignin is used as a low-cost fuel due to its high heating value of 23.3-25.6 MJ/kg (21). However, the combustion of lignin is a thermodynamically and economically unfavorable

utilization pathway. Hence, alternate commercial uses of lignin that preserve its aromatic structure must be further explored. Lignin is exceptionally valuable for the production of versatile polymeric materials, due to its polyphenolic nature, ease of derivatization and ability to participate in cross-linking reactions, intense UV-absorption and radical quenching capacity, biocompatibility, and antimicrobial properties (22, 23). Valorization of lignin through the production of polymeric materials, including thermoplastics would generate additional revenues for lignocellulosic biorefineries, and would help cellulosic biofuels become more cost-effective and competitive in price with fossil fuels. Moreover, exploiting lignin in polymer form would increase overall sustainability by preserving precious biochemical energy invested by plants into lignin biosynthesis (5, 20, 21, 24).

Table 1. Global Production of Technical Lignins

<i>Lignin</i>	<i>Pulping/Recovery method</i>	<i>Main producer</i>	<i>Global Production (t/year)</i>
Indulin	Kraft	Ingevity ^a	265,000 (15)
BioChoice	Kraft/LignoBoost	Domtar, Plymouth, NC	25,000 (16)–27,300 (14)
LignoBoost	Kraft/LignoBoost	Stora Enso, Sunila, Finland	50,000 (14)
LignoForce	Kraft/LignoForce	West Fraser, Canada	10,000 (15)
Lignosulfonates	Sulfite	Borregard	1 million (15, 17)
Protobind 1000	Soda	GreenValue, Granit, Switzerland	5,000–10,000 (17)
CIMV	Organosolv ^b	CIMV, DECHEMA/Fraunhofer, Dedini	3,000 (17)

^a Formerly part of WestRock, (Mead)Westvaco. ^b Acetic acid:formic acid:water (50:30:20)18.

Lignin-Based Thermoplastic Materials

Benefits of Incorporation of Lignin in Thermoplastic Materials

Lignin is a natural thermoplastic material up to certain temperatures, with a relatively high glass transition temperature (*T_g*) as compared to synthetic thermoplastic polymers. In its native form, lignin from hardwoods (HW) has a lower *T_g* (~65–85 °C) than from softwoods (SW) (~90–105 °C), mostly due to the less condensed nature of HW lignins (19). Lignins after isolation are characterized by a higher *T_g*. For example, softwood KL, LignoBoost has been reported to contain different fractions characterized by *T_g*s ranging from 74 °C to 190 °C (25). Hence, a thermoplastic containing lignin is expected to benefit from the relatively superior thermal properties of lignin.

Synthetic polymers are known for their excellent mechanical and chemical stability, as well as processability. However, they exhibit a poor thermal stability and high flammability. Therefore, their use in applications requiring flame-retardant grades such as in electronics, automotive, and aerospace industries is limited. Flame-retardant (FR) agents are used to confer fire-resistant properties with effects strongly dependent on their ability to form char during the thermal degradation. The char coats the polymeric materials and provides a good barrier against heat and oxygen diffusion; thus, reducing the combustion rate of the polymeric materials. Halogenated agents, which are commonly used in this area are toxic and may cause severe health issues. Therefore, alternative FR agents are

being actively sought. In this context, lignin as a polyphenolic compound, which results in high char yields (50–60 % (26)) upon thermal decomposition in an inert atmosphere, presents a strong opportunity to improve the flame retardancy of thermoplastic polymers. Various lignin types have been studied as the next-generation FR agents (26–32). Beneficial effects of lignin on the thermal properties of the thermoplastics include an increase in the T_{max} and the residue/char yield (Table 2) for polymers such as polyamide (PA11), polyethylene terephthalate (PET), low-density polyethylene (LDPE), PLA, polypropylene (PP), and polyhydroxybutyrate (PHB) (31, 33–40).

Table 2. Thermal Properties of Select Polymers and Their Blends with Lignin

Lignin Thermoplastic Material			Pure Polymer Degradation			Lignin Thermoplastic Material Degradation			Atm
Lignin		Polymer							
Type	Content (w/w, %)			T ₅ % (°C)	T _{max} (°C)	Residue (%)	T ₅ % (°C)	T _{max} (°C)	
LS (Um) (33)	20	PA11	396	423	0.7	285	468	13.5	N ₂
KL (Um) (33)						341	435	12.4	N ₂
HL (Um) (34)	5	PET	403	438	14.8	396	439	15.9	N ₂
	20					365	436	19.5	N ₂
	5		396	434	17.9	394	440	19.4	Air
	20					365	431	26.7	Air
KL (Um) (35)	5	LDPE	340 ^a	349	N/A	390 ^a	446	N/A	Air
KL (Dp) (35)	5				N/A	404 ^a	450	N/A	Air
HL (Um) (35)	5				N/A	343 ^a	405	N/A	Air
HL (Dp) (35)	5				N/A	393 ^a	446	N/A	Air
KL (Um) (36)	5	PLA	264	314	7.5	337	367	8.6	N ₂
KL (Ac) (36)	5					325	360	9.5	N ₂
OSL (Um) (36)	5					335	365	9.7	N ₂
OSL (Ac) (36)	5					318	365	7.3	N ₂
SWOSL (Dc) (37)	1		309.7	331.6	9.7	292.2	346.1	5.9	N ₂
	25					270.7	357.1	16.1	N ₂
HWOSL (Dc) (37)	1					309.8	336.3	8.4	N ₂
	25					266.7	339.1	12.5	N ₂

Table 2. (Continued). Thermal Properties of Select Polymers and Their Blends with Lignin

Lignin Thermoplastic Material			Pure Polymer Degradation			Lignin Thermoplastic Material Degradation			Atm
Lignin		Polymer				T ₅ % (°C)	T _{max} (°C)	Residue (%)	
Type	Content (w/w, %)								
Soda (Um) (38)	20	PP	409	450	0.07	319	452	5.7	N ₂
	30					297	453	9.3	N ₂
Soda (Um) ^b (38)	20					308	461	6.13	N ₂
	30					286	461	9.5	N ₂
KL (Um) (39)	5		272	331 ^c	0	280	365 ^c	2.1	Air
	20					251	343 ^c	11	Air
Alkali (Um) ^b (31)	30		324 ^d	418	0	316 ^d	472	12.5	N ₂
Alkali (Gr) ^{b, c} (31)	30					361 ^d	483	21.0	N ₂
Acidolysis (Um) (40)	5	PHB	261	293	0	279	306	0	Air
	15					283	310	3	Air

Um: Unmodified; Dp: Depolymerized; Ac: Acetylated; Dc: Dodecanoated; Gr: Grafted; SWOSL: Softwood organosolv lignin; HWOSL: hardwood organosolv lignin. ^a T_{10} %. ^b With maleated PP compatibilizer (5 % w/w). ^c T_{50} %. ^d Onset of the DTG peak. ^e Lignin by grafting phosphorous-nitrogen.

Lignin, as a structural constituent of lignocellulosic biomass evolved to provide strength and rigidity to the cell wall, can improve the mechanical properties of the thermoplastic materials. The Young's modulus for pine lignin (*Pinus radiata*) has been found to be moisture-content and isolation-method dependent, and in the ~3-6 GPa range (41). KL has been reported to have the Young's modulus in a similar range (~3.9 GPa), with the tensile strength of ~23 MPa, and elongation at break of ~0.6 % (42). Alkylated (ethylated methylated) KL has shown a slightly lower Young's modulus at ~1.9 GPa, a higher tensile strength of ~37 MPa, and elongation at break of ~2 %, which were found to be quite similar to the values observed for polystyrene (PS) (43). There are reports where lignin has been employed as a toughening agent in PP formulations (at 5 % lignin), where PP-lignin formulation exhibited an increase in the impact energy and a decrease of 50 % in elongation at break (39). The addition of lignin has been shown to assist β -crystallization of PP, where lignin serves as a β -nucleation agent (39). Additionally, lignin can assist as a plasticizer and compatibilizer in the thermoplastic formulations. It can also improve their performance as a UV absorber and optical modifier, and serve as an alternative for or act synergistically with synthetic antioxidants due to its strong radical quenching capacity (44). This property in concert with its other intrinsic properties, including antimicrobial, antifungal, and cytotoxic activities, and potential to reduce oxygen permeability makes lignin a promising candidate in the production of food and active packaging (45). Lignin is well positioned in the development of strong light-weight materials due to its low density; e.g. Indulin softwood kraft lignin (SWKL) and hardwood organosolv lignin (HWOSL) are characterized by $\rho = 1.3 \text{ gcm}^{-3}$ and $\rho = 1.24 \text{ gcm}^{-3}$, respectively (46–49).

Additional benefits offered by lignin as a component of thermoplastic materials include its low cost (KL; USD 70–1,300 per ton, depending on the application, versus synthetic thermoplastic precursors USD ~1,700 per ton (15)) and smaller carbon footprint, as compared to the petroleum-based alternatives (1, 50). This would also create additional revenue streams for biorefineries and the pulp and paper industries by providing an opportunity for utilization of lignins (4). Furthermore, there are reports of lignin-based thermoplastic materials benefitting from the antibacterial (45), antioxidizing (51, 52), UV-protecting (53, 54), anti-weathering (55), anti-aging (56), and biodegradable (52, 57, 58) properties of lignin.

Challenges in Incorporation of Lignin in Thermoplastic Materials

Despite the proposed advantages, utilization of lignin for value-added applications such as in thermoplastic materials, presents considerable challenges due to the inherently heterogeneous nature of lignin. Lignin structure and properties are dependent on numerous factors, including the species, morphological tissue, and age of the lignocellulosic source from which lignin is isolated. Further complications are caused by the changes that it undergoes by different processing conditions during separation and recovery depending on the isolation process (5).

Due to strong intra- and inter-molecular interactions between the structural units of lignin, it shows immiscibility with a large number of polymers and displays a poor dispersion in the polymer matrix. This is especially true in the case of non-polar, hydrophobic polymers (59). Lignin self-interactions, including hydrogen bonds based on the hydroxyl (OH) groups (primarily free phenolic hydroxyl - PhOH groups), ether oxygens, and carboxylic acid groups, van der Waals attraction forces, and π - π stacking of aromatic rings (60) give rise to a brittle material of globular structure (61). The OH and carboxylic acid groups also make lignin a relatively polar molecule (61, 62), limiting its compatibility with hydrophobic polymers. Lignin's mutual insolubility and incompatibility with the polymers lead to its agglomeration, resulting in two-phase systems with hindered transfer of loads at the interface of the immiscible polymers; hence, a reduced strength (48). However, evidence of lignin's miscibility with various polymers, including polyethylene oxide (PEO) (42), polyvinyl pyrrolidone (PVP) (63, 64), and PET (61) has been driving research and industry efforts toward future applications of these miscible lignin-based thermoplastic blends. In this context, solubility parameters for polymers developed by Hildebrand and Hansen have been instrumental in predicting the miscibility of lignin with the other polymers. Hildebrand is a single solubility parameter, δ , while Hansen describes three separate solubility parameters, each representing different forces that impact miscibility; δ_d , δ_p , and δ_H (65, 66).

The molecular interactions are also responsible for the high T_g of lignin, which is advantageous in terms of thermal stability (67), but results in poor thermal processibility (68). Lignin also shows poor film-forming properties (68, 69). Furthermore, during processing in laboratory or industrial conditions, lignin easily changes color due to the abundance of chromophores formed during the separation/recovery process (70). Dark color has been seen as an obstacle for using technical lignins in polymer applications (71, 72), limiting lignin's suitability for applications where color is not a critical feature (48). Additional challenges associated with lignin as compared to synthetic polymers are its relatively lower molecular weight, higher polydispersity, uncertain reactivity, variable content of free phenolic, hydroxyl, and carboxylic groups, degree of cross-linking, and amount of residual carbohydrates (4, 48). To circumvent these challenges, different strategies have been developed to incorporate lignin in the thermoplastic formulations (Figure 1). Lignin can be mixed/blended with

thermoplastic polymers in specific proportions to produce a material of desired properties and lower cost (73). Various strategies such as lignin size reduction and fractionation to produce more uniform lignin have been explored. Meanwhile, plasticization, compatibilization, and lignin derivatization have been employed to improve its miscibility in thermoplastic blends. Lignin graft copolymers (in both, one and multi-component blends) and elastomers have also been produced as a relatively new approach in producing lignin-based thermoplastic materials.

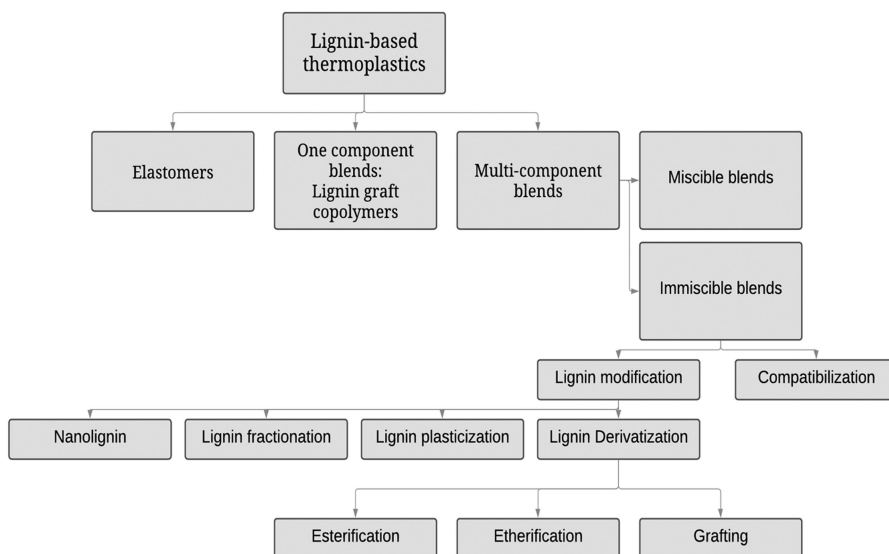


Figure 1. Lignin-thermoplastic materials and major strategies employed in their improvement.

Miscible Blends

A negative free energy of mixing ($\Delta G_m < 0$) is a prerequisite for spontaneous mixing of components to produce a single-phase system. ΔG_m is determined by the enthalpy of mixing (ΔH_m) and the entropy of mixing (ΔS_m) as (73, 74):

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad \text{Eqn. 1}$$

ΔH_m is further related to the Flory-Huggins interaction parameter, χ_{AB} and the Hildebrand solubility parameter (δ) through χ_{AB} as (42):

$$\Delta H_m = \chi_{AB} RT\phi_A\phi_B \quad \text{Eqn. 2}$$

$$\chi_{AB} = \frac{V_r(\delta_A - \delta_B)^2}{RT} \quad \text{Eqn. 3}$$

$$\text{Hence, } \Delta H_m = (\delta_A - \delta_B)^2 \phi_A\phi_B \quad \text{Eqn. 4}$$

where ϕ_A, ϕ_B are volume fractions of the polymeric components, T is the absolute temperature, δ_A and δ_B are the solubility parameters of the components, and V_r is a reference volume taken as 100 cm³ (42). Therefore, ΔH_m is critically dependent on the solubility parameters of the components of the blend and decreases as the difference between these values decreases.

Generally, ΔG_m values of the polymer blends are largely dependent on ΔH_m , and to a lesser extent on ΔS_m , which is quite small for large polymers, and hence, ΔH_m must be negative (73). Consequently, exothermic interactions between the polymeric components result in the formation of miscible single-phase binary blends. Therefore, miscibility of polymers is defined by the ability of two different polymers to create various polymer-polymer interactions such as hydrogen bonding, acid-base interactions (4, 61), and π -electron interactions (75). In this context, the extent of the formation of intermolecular hydrogen bonds that can occur between the components is a critical factor in determining miscibility. The existence of the intramolecular hydrogen bonding within one of the components (lignin is a typical polymer with strong self-interactions built on hydrogen bonds) decreases the accessibility of the functional groups to participate in the intermolecular hydrogen bonding between the two components leading to their immiscibility (76). The relative strength of the intermolecular interactions determines the manner in which the T_g varies with the blend composition (42). Hence, the T_g in miscible polymer blends can be predicted when the blend composition, T_g values of individual components, and the nature of the interactions between the components are known, by the use of different models. Conversely, by measuring T_g of the blends, the level of intermolecular interactions between the components of the blends can be estimated using these models as well. The Lu and Weiss model (Eqn. 5) takes into account the weight fractions, molar masses, densities, and specific heats for estimation of T_g , and contains two interaction parameters, χ (Flory-Huggins), and k (77). Other models such as Kwei (Eqn. 6), Gordon-Taylor (Eqn. 7), Couchman (Eqn. 8) and Fox (Eqn. 9) have been also introduced to predict T_g of the blends (42).

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} + \frac{A w_1 w_2}{(w_1 + k w_2)(w_1 + b w_2)(w_1 + c w_2)^2} \quad \text{Eqn. 5}$$

$$\text{where, } A = -\frac{\chi R(T_{g1} - T_{g2})c}{M_1 \Delta c_{p1}} \text{ and } k = \frac{(\Delta c_{p2} - w_1 \delta c_p^1)}{(\Delta c_{p1} - w_2 \delta c_p^2)}$$

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} + A w_1 w_2 \quad \text{Eqn. 6}$$

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \quad \text{Eqn. 7}$$

$$\ln T_g = \frac{w_1 \Delta c_{p1} \ln T_{g1} + w_2 \Delta c_{p2} \ln T_{g2}}{w_1 \Delta c_{p1} + w_2 \Delta c_{p2}} \quad \text{Eqn. 8}$$

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad \text{Eqn. 9}$$

Thermal analysis (DSC, DMTA) is the most common method used to evaluate miscibility; other methods include microscopy, solid-state NMR, and FT-IR spectroscopy (42, 78). It has been postulated that a single composition-dependent T_g indicates the formation of a homogeneous one-phase miscible blend through intermolecular interactions. Conversely, two T_g s signify a heterogeneous two-phase immiscible blend. In addition, a comparison between melting temperatures of a neat crystalline polymer and of that after blending with an amorphous polymer provides evidence regarding the miscibility of these polymers, i.e. level of their interactions.

Table 3. Hansen Solubility Parameters of Reference Lignins

<i>Lignin</i>	δ_d (MPa ^{1/2}) ^a	δ_p (MPa ^{1/2}) ^a	δ_H (MPa ^{1/2}) ^a
SWKL	16.7 (84)	13.7	11.7
HWKL	16.7 (84)	13.5	11.3
Björkman Spruce Lignin	21.9 (62)	14.1	16.9

^a Hildebrand solubility parameter, δ based on the energy of vaporization relates to Hansen solubility parameters as: $\delta^2 = \delta_d^2 + \delta_p^2 + \delta_H^2$ (66) where, δ_d = Hansen solubility parameter based on dispersion interaction forces; δ_p = Hansen solubility parameter based on dipolar interaction forces; δ_H = Hansen solubility parameter based on hydrogen bond interaction forces.

Table 4. Hansen Solubility Parameters of Thermoplastic Polymers Miscible with Lignin

<i>Polymer</i>	<i>Hansen Solubility Parameters, (MPa^{1/2})</i>			<i>Lignin Type and Content (%)</i>	<i>Type of interaction</i>
	δ_d	δ_p	δ_H		
PEO	17 (85)	10 (85)	5 (85)	HWKL (12.5-87.5 %) (42)	Hydrogen bonds between PhOH from lignin and ether groups in PEO
				HW Alcell (25-95 %) (61)	
PANI	17.4 (86)	8.1 (86)	10.7 (86)	KL (7-36 %) (87)	Hydrogen bonds between imine-nitrogen and OH groups from lignin
PET	18.2 (88)	7.3 (88)	7.9 (88)	HWKL (25-95 %) (61, 67)	π - π interactions between aromatic rings of lignin and PET
PBAT	19.0 (89)	4.8 (89)	9.1 (89)	SWKL Indulin (30 %) (90)	Hydrogen bonds between OH group from lignin and the aromatic ring of PBAT. π - π bonds between the lignin aromatic rings of lignin and PBAT
PHB	16.5 (65)	9.0 (65)	8.6 (65)	AGR Soda Lignin (10-40 %) (91, 92)	Hydrogen bonds between carbonyl groups in PHB and OH groups in lignin
PVP	21.4 (85)	11.6 (85)	21.6 (85)	Grass Alkali Lignin (4-20 %) (63, 64)	Hydrogen bonds between OH groups of lignin and pyridine ring of PVP or VP monomers in P(VP-co-VAc)
P(VP-co-VAc) ^a	20.9 (88)	11.3 (88)	9.7 (88)	Organosolv (68) (20-80 %)	
PA6	17.0 (93)	10.6 (93)	3.4 (93)	AGR Soda Lignin (5-30 %) (94)	Hydrogen bonds between OH groups from lignin and amine groups from PA6 and PA11
PA11	18.2 (93)	9.1 (93)	8.1 (93)	AGR Soda Lignin (12.5-25 %) (95)	

^a P(VP-co-VAc) with at least 30 mol % vinyl pyrrolidone (VP); Hansen solubility parameters are for PVAc homopolymer.

Lignin has been shown to impact the degree and rate of crystallization, as well as crystal morphology in thermoplastic blends. It has been hypothesized that lignin with low to no miscibility (immiscible) may act as a nucleating agent at lower concentrations, promoting crystallinity in the blend (39, 79). If there are strong interactions (high miscibility) between the components of the blend, lignin may disrupt or interfere with the crystal structure. This could result in decreased crystallinity, altering crystal morphology, and reducing the rate of crystallization (40, 80, 81).

A few polymers are spontaneously miscible with lignin (Table 3), leading to the formation of miscible thermoplastic blends (Table 4). Miscibility results in improved mechanical properties of the blends, as the load transfer in the single-phase systems is not interrupted at the interface between phase-separated components (75, 82). Based on eqn. 1-4, miscibility of components is influenced by their inherent solubility characteristics, generally defined in terms of δ (83) (Tables 3 and 4).

Immiscible Blends

Low compatibility between polymers of dissimilar solubility parameters leads to interfacial tension, poor adhesion, poor dispersion of the minor component in the mixture, and ultimately phase separation. The diameter of the particles (d) of the dispersed phase may be predicted using the following simplified equation:

$$d = \frac{8\alpha\gamma_{AB}f(\eta_{rel})}{\pi\eta_m}\phi \approx \frac{8\alpha\gamma_{AB}}{\pi\eta_m}\phi \quad \text{Eqn. 10}$$

where γ_{AB} is the interfacial tension, $f(\eta_{rel})$ is a function of the relative viscosity of the two components and $f(\eta_{rel}) \rightarrow 1$, α is the coalescence probability or probability that collision between two particles would lead to their fusion, ϕ is the volume fraction of the particles, and η_m is the viscosity of the matrix polymer. Smaller values for d (~5-15nm) indicate miscibility (42). In addition, the interfacial tension can be expressed as a function of the Flory-Huggins interaction parameter, χ_{AB} (Eqn. 3), as defined below:

$$\gamma_{AB} = \frac{bRT\chi_{AB}^2}{V_r} \quad \text{Eqn. 11}$$

where b is the effective length of a monomer unit, V_r is a reference volume taken as 100 cm³, and T is the absolute temperature. Therefore, the diameter of the particles is correlated to the Flory-Huggins interaction parameter as follows:

$$d = k_1 \frac{bRT\chi_{AB}^2}{V_r} \quad \text{Eqn. 12}$$

where $k_1 = 8\alpha/\pi\eta_m$. Hence, greater miscibility is achieved between components that have δ -values closer to each other, which leads to a decrease in the Flory-Huggins interaction parameter, and results in a decrease in the diameter of the particles, d . The difference between solubility parameters ($\Delta\delta$) of two polymers has been suggested as a criteria to predict their miscibility; good miscibility if $\Delta\delta \leq 2 \text{ MPa}^{1/2}$ ($\Delta\delta \leq 1.0 \text{ cal}^{1/2} \text{ cm}^{-3/2}$) (96), partial miscibility if $2 \text{ MPa} < \Delta\delta < 10 \text{ MPa}^{1/2}$, and immiscibility if $\Delta\delta > 10 \text{ MPa}^{1/2}$ (97). This theory is supported by the well-documented reports showing lignin ($\delta = \sim 22 \text{ MPa}^{1/2}$) as largely immiscible with non-polar synthetic polymers such as

polypropylene (PP; $\delta = 16 \text{ MPa}^{1/2}$), polystyrene (PS; $\delta = 18.6 \text{ MPa}^{1/2}$) (65, 71) and LDPE ($\delta = 17.6 \text{ MPa}^{1/2}$) (83). Its immiscibility with biorenewable polymers such as PLA ($\delta = 19.7 \text{ MPa}^{1/2}$) has also been confirmed (71).

Miscibility between lignin and commercial polymers may be influenced by employing different strategies to enhance the quality of lignin-based thermoplastic blends, including the use of plasticizers, compatibilizers, and lignin derivatization.

Compatibilizers

Tailoring lignin structure by derivatization to enhance its miscibility with immiscible polymers further contributes to the cost of producing thermoplastic materials, reducing economic benefits of this approach. Thus, compatibilization is an alternative approach, which may increase the competitiveness of lignin-based thermoplastic blends by increasing the mutual miscibility of lignin with polymers of contrasting solubilities through physical and chemical means (3, 78, 83).

Compatibilizers can be *block or graft polymers*. Their multifunctional structure provides a dual action through chemical bonding and/or formation of hydrogen-bonds, and good blending based on similar solubility at the interface between polymers. They assist blending by decreasing the interfacial tension, promoting adhesion of the components, and reducing the coalescence of polymer particles. Therefore, the dispersion of particles in the polymer matrix is stabilized. In addition, compatibilizers may be *coupling agents*. These are lower-molecular weight compounds such as cross-linking agents and free radical initiators, which promote formation of bonds between polymers during blending; *in situ* compatibilization (98–100).

The lignins used in the production of compatibilized blends include unmodified technical lignins, such as KL (46, 98, 99, 101, 102) and LS (103), and lignin derivatives, such as lignin phthalate (104), maleated lignin (99), and hydroxypropyl lignin (105).

Polymeric Compatibilizers in Lignin-Based Thermoplastic Blends

Various copolymers containing two or more constituents have been studied, with maleic anhydride and glycidyl methacrylate grafted (co)polymers as the most commonly attempted; polymer-g-MA and polymer-g-GMA copolymers, respectively (Figure 2). Maleic anhydride grafted PP (PP-g-MA) has been used in the production of PP-lignin blends, by itself and more recently, in concert with ethylene-butyl acrylate-glycidyl methacrylate (EBGMA) (38, 46, 103, 106, 107). The compatibilizing effect of a hyperbranched polymer lubricant (HBPL), synthesized from oleic acid and amino-terminated hyperbranch polymer, has also been studied on PP-lignin blends, and found to be superior to that of a commercial PP-g-MA compatibilizer (107). Other maleic anhydride copolymers, maleic anhydride grafted PE (PE-g-MA) and maleic anhydride grafted styrene-ethylene-butylene copolymer (SEBS-g-MA) have been explored in the production of PE-lignin (104) and PS-lignin blends (101, 102), respectively. Hydroxymethylated wheat straw alkali lignin grafted by flame-retardant elements, phosphorus and nitrogen, has been blended with PP in the presence of PP-g-MA as a compatibilizer, and provided improvements in flame retardancy of PP (Table 2) (31). Similarly, glycidyl methacrylate grafted PE (PE-g-GMA) and PLA (PLA-g-GMA) polymers have been explored in the production of PE-lignin blends (108) and PLA-lignin blends (55, 109), respectively. The PLA-lignin blends in these studies employed a biorefinery lignin produced as a residue from the conversion of giant reed grass (*Arundo donax*) to bioethanol. The grass lignin was transformed to nanosized particles, as an additional strategy to increase its available surface area,

along with the use of PLA-g-GMA as a compatibilizer. The compatibilizing effect of MA- and GMA-based compatibilizers have been reported to take place through the formation of ester (38, 101) and ether (109) bonds with lignin OH groups (Figure 2), and hydrogen bonding between OH groups of lignin and various groups in compatibilizing agents, such as imino groups of HBPL mentioned above (107).

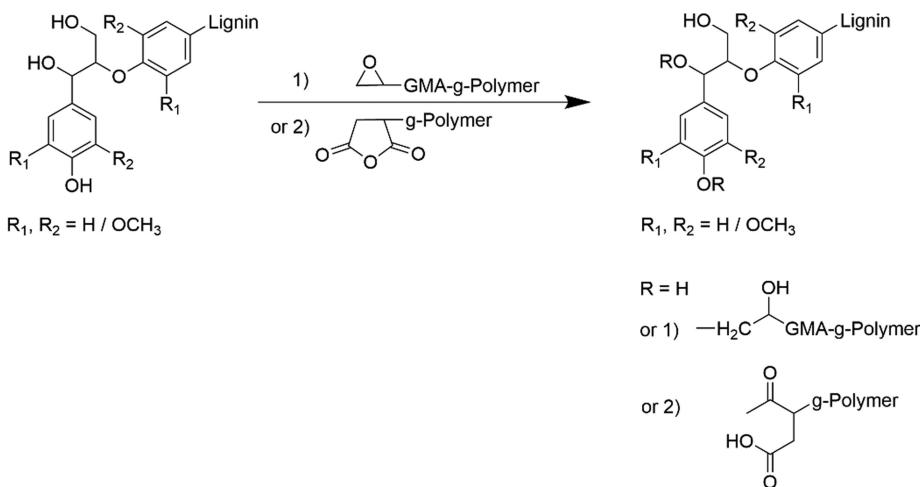


Figure 2. Reactions proposed to occur between lignin and glycidyl methacrylate (1) and maleic acid anhydride (2) copolymers as compatibilizing agents.

Other copolymers that have also been used to improve interactions between lignin and synthetic polymers include ethylene-vinylacetate (EVA) in PE-lignin blends (EVA; 28 % vinyl acetate; 10 % addition) (110) and ethylene acrylic acid copolymer (EAA; 5 % addition), which was added together with a titanate coupling agent (0.5 % addition) to LPDE-, high-density PE- (HDPE-), and PP-lignin blends (72). Lignin-based copolymers have also been suggested for use as compatibilizers. A star-like copolymer between lignin and PS (LPS) was explored for its compatibilizing effect in the production of PS-lignin blends. LPS was synthesized via grafting of NCO-capped PS into hydroxypropyl lignin, (HPL): $PS-NC(=O) + HO-CH(CH_3)-CH_2-O-Lignin \rightarrow PS-NH-C(=O)-O-CH(CH_3)-CH_2-O-Lignin$ (105).

This led to an enhanced compatibility between PS and HPL, documented by SEM indicating an improved anchoring between HPL particles and PS-matrix in the presence of LPS; at 5 and 10 % lignin content (105). In more recent studies on improving PS-lignin blends, random copolymers of styrene and vinyl phenol; PS-ran-4VPh have been investigated. Various levels of 4VPh have been introduced into copolymers to provide a range of concentrations of hydrogen bonding sites through the available PhOH groups. Neutron refractometry results revealed that the 30 % 4VPh copolymer creates the thickest interface layer between lignin and the copolymer indicating the highest degree of interpenetration, i.e. closest interaction. Additionally, the 20 % 4VPh copolymer provides the greatest level of miscibility, i.e. lowest level of phase separation. The compatibilizing effect was reported to be induced by formation of hydrogen bonds through the OH groups of PS-ran-4VPh (82). These studies demonstrated a need for a fine tuning of the level of PhOH groups introduced into PS-ran-4VPh to maximize their accessibility for the hydrogen bond formation with lignin, i.e. minimize steric shielding and formation of hydrogen bonds inside the copolymer (82).

Polymeric methylene diphenyl diisocyanate (PMDI) has also been used for compatibilization of lignin-containing Arboform or liquid wood, (a thermoplastic composite consisting of cellulosic fibers, lignin as a bonding matrix, and additives) with polybutylene succinate (PBS) (111). Inclusion of 1 % PMDI in the composite formulation was reported to enhance the tensile, flexural, and impact strength of the material, along with the heat deflection temperature (111). Arboform composites are fully degradable and recyclable and are applicable in various areas, including automotive interiors, furniture industry, and electronics. Different types of lignin and lignin derivatives can be used as a bonding matrix to create a strong composite material resistant to impact, bending, and compression (106, 112).

Coupling Agents as Compatibilizers in Lignin-Based Thermoplastic Blends

Studies have been performed to explore benefits of radical coupling reactions in increasing compatibility between lignin and polymers. For example, in efforts to improve PLA-lignin blending, lignin was exposed to electron-beam irradiation (EBI; 30-90 kGy) prior to blending with PLA in reactive extrusion in the presence of triallyl isocyanurate (TAIC, 3 %) as a cross-linking agent. Peroxy and poly-conjugated radicals in lignin formed during EBI are proposed to generate radical sites in TAIC; $\cdot\text{CH}_2\text{-CH-CH}_2\text{-N-}$ and $\cdot\text{CH}(\text{CH}_2)\text{-CH}_2\text{-N-}$, and in PLA; $\text{R-C(=O)-O}\cdot$ and $\cdot\text{CH}(\text{CH}_3)\text{-C(=O)-O}$. The TAIC and PLA couple creating a PLA-TAIC-lignin cross-linked structure. The formation of this three-component structure, which serves as a compatibilizer at the interface between lignin and PLA was confirmed by FT-IR studies of blends. These studies included optimization of the EBI dosage to suppress lignin-self cross-linking as an excessive formation of lignin free radicals may cause this undesirable effect at greater irradiation levels (60-90 kGy) (98).

Effect of Compatibilizers on Polymer Properties

The effect of compatibilizers is evaluated by measuring T_g of the blends made with and without compatibilizers. For this purpose, DSC (98, 102, 109) and DMTA (38, 102, 103, 107) are commonly used methods. The increase in T_g of blends with compatibilizers has been attributed to the formation of lignin-compatibilizer-matrix cross-linked structure, which restricts the motion of the matrix chains as in the case of using HBPL as a compatibilizer in lignin-PS blends (107). Increase in T_g was also noticed for PLA-lignin blends produced in the presence of TAIC as a cross-linking agent with lignin exposed to EBI prior to blending. Processing the data through the Gordon-Taylor equation (Eqn. 7) to estimate the quality of lignin-PLA interactions revealed that the negative values of the k interaction parameter determined for PLA-lignin blends (lignin content 5 and 20 %) increased to positive values for the blends made from EB-irradiated lignin (30 kGy) in the presence of TAIC (3 phr). This clearly indicates a compatibilizing effect from the combination of EBI of lignin and TAIC (98). In addition, it was shown that the elongation at break and impact strength increased even compared to those measured for the neat polymer with increases of ~21 % and ~9 %, respectively. These results highlighted the importance of the EBI of lignin as without EBI of lignin these properties increased for 125 % and 630 %, respectively, but the properties of the neat PLA were not restored (98).

Compatibilization has been observed to improve tensile strength, impact strength, and elongation at break. In studies of LDPE-lignin blends (30 % lignin) reported earlier, the addition of EVA was found to produce a two-fold increase in tensile strength and a thirteen-fold increase in elongation at break demonstrating a strong compatibilizing effect of EVA (110). The improvement

in the mechanical properties was also reported for lignin phthalate-LDPE (40 % lignin) blends compatibilized with LDPE-g-MA. In studies of PP-lignin blends, the impact strength of blends increased by 52.3 % with the addition of HBPL and for 33.6 % with the addition of PP-g-MA compatibilizer (3-5 % addition level) showing superior effects of HBPL (107). In studies of PLA-lignin blends which have explored the use of nanosized lignin (1 % lignin content) and PLA-g-GMA as compatibilizers, mechanical properties were similar to those measured for PLA. The elongation at break increased more than five times compared to that of both PLA and PLA-g-GMA in the formulation containing PLA-g-GMA and lignin (99:1) (55). Use of SEBS-g-MA in compatibilization of PS-lignin blends with 60 % of lignin improved tensile modulus (increase of 1.8 %), tensile strength (increase of 21 %) and elongation at break (increase of 33 %), but did not restore the properties of the neat PS polymer (101).

The effects of compatibilizing agents have also been evaluated for the quality of dispersion of lignin through morphological studies conducted by particle size analysis using microscopy (101, 102) and SEM (38, 55, 98, 99, 103–108). They have provided evidence that the addition of effective compatibilizers leads to improvements in the appearance of blends, which convert from heterogeneous ruptured structures to smoother more continuous surfaces with reduced number of cavities indicating better networking between dispersed particles and the matrix, better dispersion of the particles, and improved interfacial adhesion. The particle size of lignin decreases during processing of blends and it is reduced compared to the initial size even in the blends produced without compatibilizers. However, the addition of compatibilizers facilitates stress transfer from the matrix to the particles, and interferes with fusion of the particles during collision; thus producing smaller particles. Morphological studies have proved instrumental in selecting effective compatibilizers and adjusting their concentration in lignin-based thermoplastic blends.

Compatibilization is a simple strategy to circumvent the challenges posed by lignin's immiscibility with common polymers for the synthesis of thermoplastic blends. The multifunctional structure of compatibilizing agents facilitates the interactions between lignin and the immiscible polymers at the interface improving their mutual miscibility and providing benefits to blends properties, including mechanical properties.

Nanolignin

Thermoplastic materials where lignin plays a role of a filler has long been investigated (22). However, challenges such as large particle size and limited dispersion in the matrix hinder implementation of these materials. Reduction of lignin particle size with an associated increase in specific surface area is one of the emerging and relatively simple methods in this area. Ultrasonication followed by freezing at -196 °C and then freeze-drying has been shown to produce lignin sheet-like particles with thickness of ~200 nm. With 2 % addition of these sheet-like particles in PP, improvements in mechanical properties and decrease in UV-induced and thermo-oxidative degradation was observed. An increase in elongation at break compared to the neat PP (95.5 % versus 54.0 %) with comparable yield stress and elastic modulus, clearly demonstrates benefits of freeze-drying (113). However, freezing at such low temperatures is an energy-consuming method (estimated four-to-ten times higher energy consumption than in hot-air drying), and alternative methods to reduce the size of lignin particles to produce nanosized-lignin have been explored. Some recent attempts include methods such as ultrasonication only, acidolysis, and homogenization (109, 114–116). Nanolignin has shown to promote strong interfacial bonding with the matrix (109, 114);

thus, improving the mechanical properties, thermal stability, and barrier properties of the composite (115).

Nanolignin was prepared by ultrasonication of KL (Indulin) and remained suspended in water even after five months. The increased polarity in nanolignin was attributed to the chemical modification during sonication; mostly oxidation, as observed via FT-IR. Polyurethane- (PU)-KL and PU-nanolignin composites (lignin content 5–20 % in both cases) were fabricated, where the former showed large agglomerates, while an even dispersion was seen in the latter. Improvements in tensile strength and Young's modulus, but a compromised elongation at break were observed with PU-nanolignin. However only a slight improvement in thermal stability was observed (114). Similar results regarding thermal stability, tensile strength, Young's modulus, and elongation at break were obtained from PU-nanolignin (1–7 %), where the nanolignin was prepared by acidolysis (hydrochloric, sulfuric, and phosphoric acids) of biorefinery corn stover lignin. However, this composite also exhibited a significant improvement in hydrophobicity and resistance to UV-light, as well as demonstrating a frequency-dependent behavior for electrical conductivity (116).

Lignin nanoparticles were produced by hydrochloric acidolysis and incorporated into PLA in varying amounts of 1–3 % by either extrusion or solvent casting. Incorporating lignin had little to no effect on the T_g , and only a slight improvement in thermal stability was observed. For extruded polymers, 1 % lignin-PLA blends showed better tensile strength than pure PLA, and 3 % lignin-PLA blends. However, adding lignin decreased tensile strength for solvent-cast polymers. Elongation at break of a 3 % lignin-PLA extruded blend was radically higher than of all the other polymers, which is noteworthy. This may have been due to the flexibility of the lignin structure, which enabled it to act as a plasticizer. Overall, extruded blends demonstrated better mechanical properties than solvent-cast. This was attributed to the uneven distribution of lignin in the PLA matrix for solvent-cast polymers (117). The effect of nanolignin on the crystallinity of lignin-PLA blends has also been studied. Blending of PLA with underivatized lignin nanoparticles resulted in more than a two-fold increase in crystallinity at 5 % lignin content, with crystallinity continuing to increase at 10 % lignin content (79). While the small particle size and a more even distribution of lignin aided in increasing crystallinity, the immiscibility of underivatized lignin in PLA allowed lignin to act as a potent nucleating agent, as mentioned in the earlier section on miscibility.

Nanolignin prepared by acidolysis was used in the production of various thermoplastic blends with PLA and PLA-g-GMA by extrusion, employing a masterbatch approach (1 % lignin in all blends). Nanolignin in combination with the proposed masterbatch approach and with the assistance of PLA-g-GMA as a compatibilizer produced blends with tailored mechanical, optical, and thermal properties (55).

SWKL was homogenized (15,000 rpm for 1–4 h) to yield nanolignin (115). This homogenization method did not result in noticeable chemical changes in the lignin, as no cleavage of β -aryl ether bonds was recorded, and the aliphatic, phenolic and carboxylic OH content remained the same. The nanolignin did not exhibit change in molecular weight distribution either. Solvent-cast polyvinyl acetate (PVA)-SWKL and PVA-nanolignin films were produced. The PVA-nanolignin films demonstrated superior thermal stability compared to PVA-SWKL films. The SEM revealed an even distribution of nanolignin in the PVA matrix, whereas agglomerates were present with SWKL.

Although some work on nanolignin has been done, there are several opportunities that are yet to be explored. The studies so far are promising, and show that nanolignin has the ability to improve properties and performance of the thermoplastic materials.

Solvent Fractionation of Lignin

Fractionation of lignin using single or sequential organic solvents is another approach in modifying lignin by its partition into homogenous fragments with distinct physicochemical properties, depending on their differential solubilities in the solvent(s) (118). Thus, fractionation offers an opportunity to influence miscibility/compatibility of lignin with thermoplastic polymers by tailoring its molecular weight and functional group profile, especially the PhOH and aliphatic OH group content, which is responsible for lignin's extensive internal hydrogen bonding (119–129). Higher molecular weight (HMW)-fractions have been found to induce higher thermostability owing to their relatively rigid structure and higher T_g (128). Furthermore, HMW-fractions contain a relatively lower amount of PhOH groups than lower molecular weight (LMW)-fractions because of the differential partitioning of PhOH groups in organic solvents (119, 121–124, 126, 129). Therefore, HMW-fractions can be advantageous in thermoplastic formulations as they are expected to avoid issues related to excessive cross-linking and incompatibility with hydrophobic polymers and solvents (24). On the other hand, LMW-fractions can be good plasticizers in thermoplastics due to their relatively lower T_g and flexible structure (130, 131). For example, an LMW-fraction obtained from sequential fractionation of softwood soda lignin using isopropanol/ethanol (4:1 v/v) and methanol was found to result in better dispersion of lignin in lignin-polyvinyl chloride (PVC) blends (2.5–10 % lignin), a faster plasticization effect as compared to the HMW-fraction (131). This blend also showed a higher tensile strength as compared to the HMW-fraction-PVC blend and the pristine lignin-PVC blend. Similar plasticizing effect was also observed for lignin-PE blends (5–25 % lignin), containing LMW-fractions of SWKL fractionated with acetone (130). LMW-fractions have also been reported to result in improved compatibility between lignin and synthetic polymers, and hence in improved blend morphology (59). Fractionation has additionally been used in concert with lignin graft copolymerization, as described in subsequent sections (24, 132).

Plasticizers

Plasticizers are used to modify polymers to improve their processability, as they are able to interrupt the internal bonds and associations originally present in the polymers. As the interactions between the polymer chains weaken, and the chains are spaced apart, their free volume and mobility increase, leading to a decrease in T_g and improved thermal processability. The melt viscosity and elastic modulus also decrease (4). Numerous agents have been explored for lignin plasticization, including polyethers, esters of various organic acids, lignin-like aromatic compounds, and commercial polymer plasticizers (3, 133–137). The plasticization effect increases with the concentration of plasticizers, as estimated by the decrease in T_g of lignin in their presence (Table 5).

Sakata and Senju (1975) performed a thorough initial study of more than 30 organic plasticizers, including phthalates, organophosphates, and aliphatic acid esters on their effects on two types of lignin; thiolignin (SWKL; $T_g = 174\text{ }^{\circ}\text{C}$) and dioxane lignin (laboratory isolated lignin; $T_g = 138\text{ }^{\circ}\text{C}$) (138). Plasticizers were characterized by different δ -values, ranging from 15.4 to 26.2 $\text{MPa}^{1/2}$, and with low hydrogen-bonding capacity (mainly esters). The δ -value of lignin was assumed to be 22.5 $\text{MPa}^{1/2}$ based on the results of lignin solubility studies by Schuerch (139); this value was also close to later estimates for softwood lignin (78) (24 MPa)^{1/2}. It was shown that agents with solubility lower than 18.4 $\text{MPa}^{1/2}$ were not able to decrease the T_g of lignin to any extent. As expected, the

plasticization effect increased with greater compatibility between lignin and plasticizer, i.e. with the decrease in difference between the δ -values of lignin and plasticizer; $\Delta\delta$. Later reports have supported these results and established that a polymer and a plasticizer are compatible, if $\Delta\delta < 3.1 \text{ MPa}^{1/2}$ for the pair. Furthermore, a linear decrease in the T_g of lignin was noticed with the increase in plasticizer concentration up to 20 %. A nonlinear negative relationship between T_g and water content in lignin was noted, indicating water as a comparatively good lignin plasticizer, despite the lignin-water incompatibility ($\delta_{\text{H}_2\text{O}} = 47.8 \text{ MPa}^{1/2}$). This effect was attributed to the hydrogen-bonding capacity of water and its ability to swell lignin (139). Moreover, superior plasticization was revealed in the case of combined addition of water and plasticizer, as it was greater than the corresponding individual plasticization effects (138). The plasticizing effect of water was also reported in a later comprehensive study of ~20 plasticizers with wide variations in compatibility with SWKL (Indulin, pine) (135). In this study, the solubility differences between lignin and plasticizers were expressed by their distance in the Hansen space, $\Delta\delta_{3D}$. A negative two-step pseudo-linear correlation between the water content and the T_g of lignin was determined with the initial fast decrease in T_g . This effect diminishes when the water content reaches beyond the lignin saturation level. This change in the rate of lignin plasticization by water was attributed to their intrinsic incompatibility, with $\Delta\delta_{3D} = 26.7 \text{ (J cm}^{-3}\text{)}^{-1/2}$ (135). It was concluded that unsaturated/dry lignin is more readily plasticized by molecules that can interfere with hydrogen bonds in lignin as demonstrated by the superior plasticization effect of water compared to compounds more compatible with lignin in terms of $\Delta\delta_{3D}$. Conversely, saturated lignin is more readily plasticized by more compatible molecules, i.e. those closer to lignin in the Hansen space; for example, lignin-like molecules, such as vanillin, $\Delta\delta_{3D} = 3.9 \text{ (J cm}^{-3}\text{)}^{-1/2}$. This study suggested that lignin plasticization results from the cleavage of hydrogen bonds and some other disentanglement mechanism, as most of the predicted plasticizing values were underestimates of the experimentally determined values. In contrast, for some agents plasticizing results were lower than expected and were attributed to the agent self-interactions (ethylene glycol, for example) or steric hindrance effects. Acetylated lignin samples showed T_g at $\sim 100^\circ\text{C}$ which is close to the T_g of water-saturated lignin confirming that water-based lignin plasticization proceeds through the cleavage of the hydrogen bonds up to lignin saturation point (135).

The first high-lignin content thermoplastics were made using plasticizers. The combined plasticization action of diethylene glycol dibenzoate and indene (combined plasticizers accounted for < 2.5 % mass of blends) resulted in successful blending of underivatized SWKL (pine, *Pinus banksiana*) and PVA with lignin accounting for 85 % of the mass of these blends (134). More generally, these results may be taken as an illustration of the importance of Hildebrand solubility parameter of plasticizers on their efficiency (diethylene glycol dibenzoate, $\delta = 20.7 \text{ MPa}^{1/2}$ and SWKL, $\delta = 24.6 \text{ MPa}^{1/2}$) (78).

In the development of lignin-based thermoplastic blends, various plasticizers may be used to facilitate lignin dispersion in thermoplastic polymers by weakening the strong self-interactions of lignin. They reduce the T_g and enhance the thermal processability of lignin, and their efficiency has been shown to depend on their δ -value.

Table 5. Select Plasticizers Studied for Lignin; Hildebrand Solubility Parameters,

<i>Plasticizer (Content)</i>	<i>Solubility δ (MPa^{1/2})</i>	<i>Lignin Type; (Solubility δ) (MPa^{1/2})</i>	<i>Lignin T_g (°C)</i>	<i>Plasticized Lignin T_g (°C)</i>
Butylbenzyl phthalate (15 %) (136)	20.2	Alcell (28.0)	97	66
Alkylbenzyl phthalate (15 %) (136)	19.5			66
Diethylene glycol dibenzoate (15 %) (136)	20.7			65
Tricresyl phosphate (15 %) (136)	20.2			69
Diethylhexyl phthalate (35 %) (133)	16.8	Indulin (20.5)	142	126
Diethylene glycol dibenzoate (35 %) (77)	20.7			80
Tricresyl phosphate (35 %) (133)	20.2			28
Dimethyl phthalate (20 %) (138)	21.5	Dioxane (22.5)	137	62
Diethyl phthalate (20 %) (138)	20.3			72
Dibutyl phthalate (20 %) (138)	19.2			110
Dihexyl phthalate (20 %) (138)	18.6			117
Diphenyl phthalate (20 %) (138)	26.2			98
Triethyl phosphate (20 %) (138)	19.7			67
Tributyl phosphate (20 %) (138)	18.4			71
Triphenyl phosphate (20 %) (138)	21.3			73
Tricresyl phosphate (20 %) (138)	19.8			101
Cresyldiphenyl phosphate (20 %) (138)	21.7			80
Diphenyl-2-ethylhexyl phosphate (20 %) (138)	19.6			94
Trichloroethyl phosphate (20 %) (138)	22.3			80
Dibutyl maleate (20 %) (138)	18.4			97
o-nitrodiphenyl (20 %) (138)	22.5			80

Esterification

It has been documented that technical lignins can resemble thermoset-like materials at elevated temperatures. At temperatures around or above the T_g , condensation polymerization is induced via free radicals captured by lignin's free PhOH groups, increasing molecular weight and T_g of lignin (140, 141). The abundance of OH groups instigates polar character of lignin limiting its miscibility, and therefore compatibility, with typically hydrophobic polymers, as postulated through the Hansen solubility theory (53, 84). Chemical derivatization of lignin, such as esterification has been explored to improve its thermoplasticity and compatibility (i.e. miscibility) with most commercial polymers, among other purposes (142, 143). It is important to note that this is particularly the case with more hydrophobic polymers, as it has been demonstrated that lignin following acetylation is actually less compatible with PEO than the unmodified lignin (42).

Esterification results in significant changes in lignin properties while it is relatively easy to carry out regarding reagents and reaction parameters. Typically, esterification of lignin is conducted in a reaction with carboxyl acids, their acid halides (often chlorides) or anhydrides (144). Acetylation, perhaps the most widely studied type of lignin esterification, is commonly conducted by using one-to-one mixtures of pyridine and acetic anhydride in laboratory conditions (145). At industrial scale, use of a mixture of alkanolic acid, the corresponding anhydride and metal (sodium or potassium) alkanolate is considered more practical. Studies on acetylation of numerous technical lignins using either pyridine or sodium alkanolate as a catalyst found the same degree of acetylation achieved by the two methods (145). Similar reaction conditions are often employed for esterification reactions that utilize reactants with longer chain lengths. In some cases an additional lignin solvent may be utilized either to reduce or completely replace the need for pyridine, a well-known toxin (36, 146, 147). In one scenario, the esterification reaction was performed under elevated temperatures (60 °C) and in the presence of an argon catalyst to ensure the most favorable reaction kinetics (148). The use of 1-methylimidazole as a catalyst for esterification reactions using acetic, propionic, n-butyric, maleic, and methacrylic anhydrides has led to complete esterification of SWKL and HWKL within 2 h in contrast to 48 h required in the presence of pyridine (84). Subsequently, 1-methylimidazole has been used on a number of different technical lignins (149), also with the goal of optimizing reaction conditions (81). In addition to traditional synthetic chemical reactions to produce esterified lignin, enzymatic approaches have been introduced as well. Lipase-catalyzed transesterification (lipases from *Candida antarctica*, *Pseudomonas cepacia* and *Mucor miehei*) of commercial KL with ethyl oleate (C_{18:1}) was conducted in ionic liquid media resulting in lignin oleate and transesterification yield of up to ~30 % (150). An additional method of producing lignin esters has been explored without the use of any solvents, through microwave assisted acylation with various acid anhydrides. This work produced lignin esters with the degree of substitution varying from as low as 39 % with maleic anhydride, up to 99 % with acetic anhydride (151).

Lignin esterification has been explored as a method to create a more dynamic and valuable material since at least the 1940s. US patents were issued to Lewis and Brauns on “Esters of lignin material” in the 1940s and to Pruett and coworkers on “Lignin and lignin derivatives as copolymerizable colorants for polyesters” in the 1980s. Lewis and Brauns work focused on the production of lignin esters with the reactant chain-length varying from C₂-C₁₈. Lignin esters synthesized by Lewis and Brauns were used in molded plastics and served as plasticizers and internal mold lubricants. On the other hand, lignin esters covered in Pruett’s patent were C₂-C₄ lignin esters utilized in the production of plastic containers with low light transmittance in the UV-range (145, 148). In 2015, a patent was granted to Pietarinen and coworkers for their invention on using tall oil fatty acids (TOFAs; a byproduct of kraft pulping) to replace fatty acid chlorides to produce lignin esterified with at least one fatty acid. The reaction was conducted on acetylated lignin at high temperature to enable distillation of the acetic acid formed during the reaction (152). Lignin esters with TOFA have been examined in barrier surface coating of paper to produce sustainable packaging material and replace synthetic/nonrenewable barrier materials (69, 153, 154).

Increased hydrophobicity and thermal stability, as well as decreased hydrogen bonding and T_g of lignin have been reported following esterification (Figure 3) (146–148, 155). However, a recent TGA study of acetylated lignin and a lignin laurate has suggested that there may be a thermal sensitivity associated with the ester linkage around 200 °C (53). The decrease in T_g (ΔT_g) may be controlled by the extent of the acylation reaction and the size of the moiety added through the ester linkage; short

chain acylation (acetylation) results in ΔT_g of ~ 20 °C versus long chain fatty acid acylation which results in ΔT_g in the range from 20 to 100 °C (148, 156). Acetylation leading to greater compatibility was also reported to affect crystallization behavior of the blends. In experiments with acetylated KL, a decrease in crystallinity of PLA was noticed when compared to the pure polymer or to that of the blend containing underivatized alkaline lignin (36). DSC analysis in another study suggested that the formation of α' crystals was favored over that of α crystals, the tighter and more orderly crystal polymorph, when blends containing acetylated lignin were compared to the pure polymer. Furthermore, underivatized lignin showed the opposite trend, favoring the formation of α crystals over α' crystals (53).

Increased hydrophobicity following esterification has been supported by a higher water contact angle (157), reduced water vapor transmission rate (WVTR) (69, 153), as well as decrease in the δ_H and δ_P parameters (84). Predicted greater decrease in the δ_H and δ_P parameters than in the δ_D parameter following different types of esterification (with exception to maleation) was confirmed through the use of the Hoy model (84).

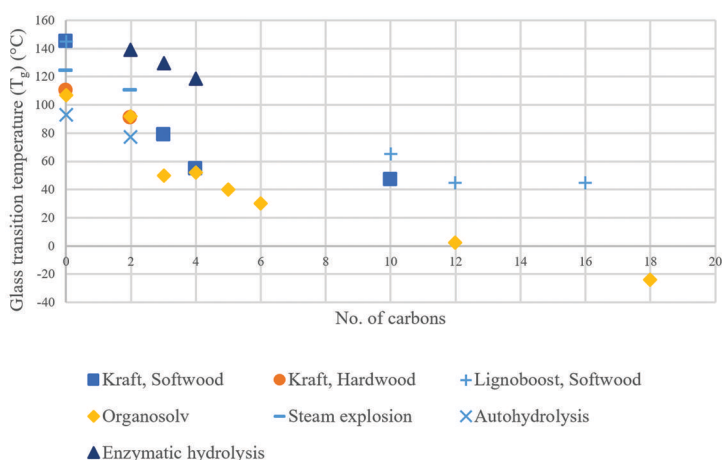


Figure 3. Effect of number of carbons of esterifying agents on the glass transition temperature of different technical lignins. Number of carbons = 0 represents the underivatized lignin (4, 145, 148, 159).

While properties of lignin-based thermoplastic blends change by lignin esterification performed prior to blending, the extent of change has been found to directly correlate with the length of the added chain. Therefore, lignin esters with properties tailored for the given application may be proposed. For example, esterification of SWKL and HWKL utilizing TOFA chlorides (which included saturated C_{16} – C_{20} and more than 85 % unsaturated $C_{18:1}$ – $C_{18:3}$ fatty acids) has been shown to exhibit a favorable reduction in oxygen transmission rate compared to lignin esterified with shorter saturated fatty acids (C_{12} and C_{16}) (69, 153, 154). Lignin esterified with TOFA also exhibited a low T_g , even below 0 °C (69, 153). Due to the more noticeable increase in hydrophobicity with increasing chain length, lignin esterified with C_{17} and $C_{18:1}$ acyl chains have been used as compatibilizers for recycling plastics and producing blends of LDPE either with PP or PS (145). Lignin esters produced with stearoyl chloride (C_{18}) have also been proposed as plasticizers with PS (144). Additionally, miscibility of esterified lignin depends strongly on the chain length. For example, lignin acetate (C_2) was shown to be completely immiscible with poly(ϵ -caprolactone)

(PCL), whereas butyryl and valeryl substitutions were especially effective for the enhancement of miscibility between alkyl-esterified OSL and PCL (158).

Esterification is an effective and well-studied technique utilized to modify polar phenolic and aliphatic OH groups on lignin. Its positive effects include increasing miscibility and compatibility with more hydrophobic commercial polymers (Table 6), which can lead to improved physicochemical properties, such as processability by having a plasticizing effect on lignin, oxygen and water vapor transmittance behavior, and mechanical properties of the resulting thermoplastic.

Etherification

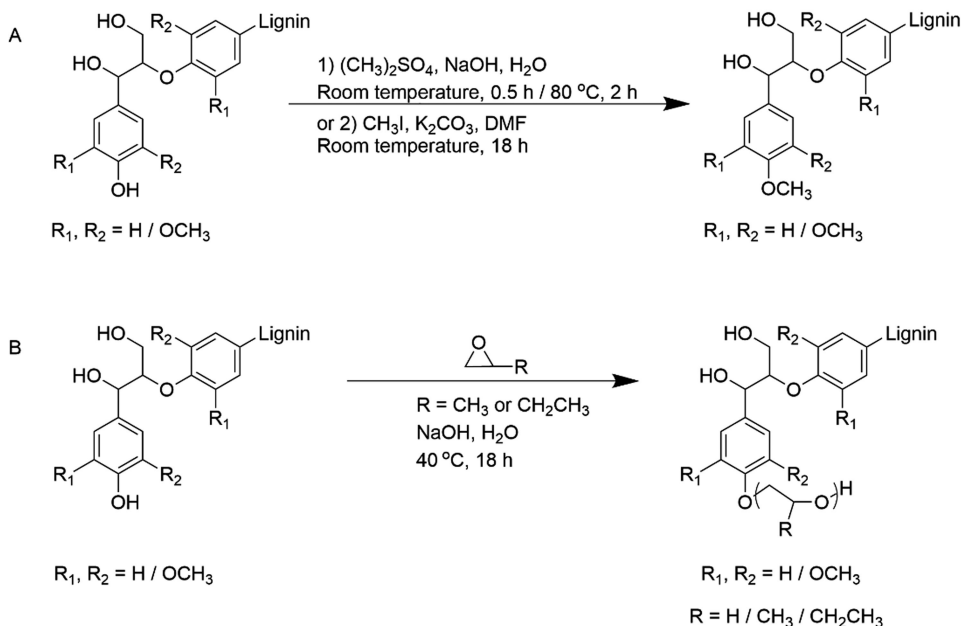


Figure 4. Mechanism for methylation (A) and hydroxyalkylation (B) for lignin. Adapted with permission from Reference (143). Copyright 2012 American Chemical Society.

Etherification is another approach for lignin derivatization and improving its thermal processability. Etherification includes alkylation and alkoxylation, which are conducted via the mechanism of nucleophilic aromatic substitution (S_NAr) to produce lignin ethers and hydroxyalkyl lignins, respectively (19); thus masking the PhOH groups on lignin and reducing the degree of intramolecular hydrogen binding; thus, the T_g. In fact, alkoxylation converts the PhOH groups to less acidic secondary aliphatic OH (19, 160), causing the same effects. These groups can further serve as reaction sites providing uniform functionality for additional lignin modification, such as in synthesis of lignin copolymers, as described in the later section on lignin copolymers (161). Lignins etherified by various etherifying agents have been blended with numerous polymers, such as PP, PEO, PLA, PVA, and polypropylene carbonate (PPC). Though most studies employ kraft lignin, more recent attempts of using biorefinery lignins have been described.

Alkylation (Figure 4 A), most frequently as methylation can be performed by various reagents, including dimethyl sulfate, methyl iodide, or dimethyl carbonate in aqueous alkali solutions or in organic solvents such as dimethylformamide/dimethyl sulfoxide (DMF/DMSO). Dimethyl sulfate has been found to be a more effective methylation agent than methyl iodide (143). Other alkylating

agents such as 1-iododecane (C_{10}) and 1-iodohexadecane (C_{16}) have been used (162), but in a limited capacity. Moreover, studies on blending these alkylated lignins with other polymers have not been commonly performed.

Hydroxyalkylation (Figure 4 B) is the reaction with alkylene oxides such as ethylene oxide (EO), propylene oxide (PO) or butylene oxide (BO) performed in aqueous alkali solution or organic solvents, with hydroxypropylation being the most common method (13).

Both methods of etherification selectively substitute PhOH groups. The reagents act as internal plasticizers for lignin altering its physical and chemical properties. The main effects include increased solubility in organic solvents such as tetrahydrofuran (THF) (used in SEC) (163), chloroform (used in NMR) (164), DMF, dioxane, and a decreased T_g , as well as improved the melt flow index (MFI) (13).

Etherification with alkylene oxides, specifically EO has been conducted at pilot plant scale, and hydroxyethyl and hydroxypropyl lignin have been produced commercially (13, 70).

Degree of substitution can be controlled by the amount of reagent, as well as the chain length of the reagent. Increase in the etherification degree results in a larger change in T_g of lignin. Comparing the effects of EO, PO, and BO, the longer chain etherifying agents cause a greater change than the short chain (13). Therefore, the greater the etherifying degree and chain length, the more drastic effect on T_g is observed (Figure 5).

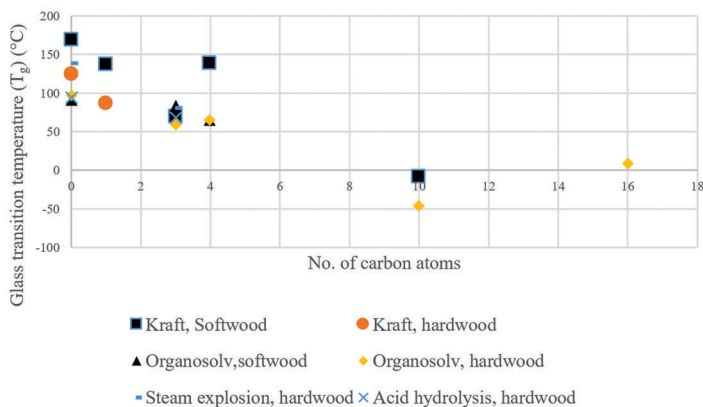


Figure 5. Effect of number of carbons of etherification agents on the glass transition temperature of different technical lignins. Number of carbons = 0 represents the underivatized lignin (4, 162).

Comparative studies of methylation and hydroxypropylation have been performed. The average chain length of the grafted polypropylene glycol in hydroxypropylation reaction was found to affect the molecular weight, T_g , and functionality of the final lignin derivatives. Comparison of methylated and hydroxypropylated SWKL (HP-SWKL) demonstrated a decrease in T_g , but the former was more thermally stable (141). However, as expected both methods successfully replace PhOH groups of lignin, but no change was observed in the content of lignin aliphatic OH groups.

Methylating agents dimethyl sulfate and methyl iodide are highly toxic and hazardous. In contrast, dimethyl carbonate is of low toxicity, noncorrosive, and has been suggested as a biodegradable alternative for lignin methylation. Dimethyl carbonate is produced by catalytic synthesis from carbon dioxide and methanol (4, 19, 165, 166). Similarly, propylene oxide is risky to handle owing to its high vapor pressure (588 hPa at 20 °C), flammability, toxicity, and carcinogenicity. In contrast, five-member cyclic organic carbonates with low toxicity and vapor

pressure (0.04 hPa at 20 °C), high boiling points and flash points have been proposed as alternatives. They also have the added advantage of being biodegradable (167). Moreover, reactions with these reagents can take place at high temperatures at atmospheric pressure; thus, they do not require pressurized reactors. Their high boiling points also afford them the ability to act as solvents and reagents (168).

Varying ratios of unmodified and methylated HWKL and PEO were extruded to make PEO-lignin blends. Based on the presence of a single T_g for all compositions, it was concluded that lignin and PEO were miscible. A strong hydrogen bond between the aromatic hydroxyl proton of the unmodified lignin and the ether oxygen of PEO was observed (Table 4). Since the PhOH groups are replaced by methoxy groups, the formation of hydrogen bonds between methylated lignin and PEO is less likely, as confirmed by the FT-IR results. Moreover, blends with the lignin-to-PEO ratio > 1 demonstrated superior mechanical properties to pure lignin and PEO polymers. This was attributed to PEO disrupting the intermolecular bonds of lignin and the supramolecular lignin complexes (42).

Dichloromethane and chlorobenzene were used as alkylating and arylating reagents, respectively, to modify sugarcane bagasse biorefinery lignin to produce PP-lignin blends via melt extrusion (lignin content 5–25 %). Improvements in thermal stability with increasing lignin content for both alkylation and arylation were observed. Crystallinity was improved with the addition of alkylated lignin (up to 15 % lignin content) compared to pure PP. In addition, MFI of the lignin blends remained stable with five extrusion cycles, while pure PP showed a continuous increase. However, tensile strength was compromised with only a slight improvement in Young's modulus. The authors concluded that both alkylated and arylated lignins are viable processing stabilizers for PP; however, lignin content above 15 % in PP-lignin blends was not beneficial (169).

Alkylation of HWKL with bromododecane was performed prior to producing lignin-PP blends. The compatibility of alkylated lignin and PP was superior to that of unmodified lignin-PP blends. The SEM micrographs of alkylated lignin-PP blends showed a homogenous blend with a single T_g and better thermal stability. Although, with increasing lignin content, tensile, flexure, and impact strength decreased, a higher impact strength at 10 % lignin content was observed. Blends with higher lignin content were also more brittle, as indicated by the high elastic modulus, but had better damping effect (absorption of energy) demonstrated by the wide $\tan \delta$ peaks (170).

HP-SWKL was blended with PVA (the degree of hydrolysis from 0 to 96 %; hence, various MW (3,500–96,000), T_g s (32–77 °C), and δ (19.6–25.8 MPa^{1/2})) by solvent casting. HP-SWKL had an assigned δ value of 22.7 MPa^{1/2}. All blends displayed similarly homogenous morphology, indicating that hydrogen bonding between the polymers can occur over a wider range of solubility parameters than previously expected. The authors also observed changes in crystalline structure indicated by the changes apparent in the melt endotherm in the DSC. A decrease in melt endotherm peak area indicates polymer-polymer interactions resulting in a disorder in the crystal, thereby reducing crystallinity. Increasing lignin content resulted in an increase of T_g of the blends. This was attributed to the hydrogen bonding between OH groups of HP-SWKL and PVA, yielding quasi cross-links and increasing the T_g (96).

Up to 40 % HP-KL was incorporated in to PPC via melt extrusion (171). As in most cases, PPC-lignin blends showed superior thermal properties to neat PPC. In addition, a significant improvement was seen in tensile strength, Young's modulus, storage modulus, and elongation at break with increasing lignin content. However, water contact angle measurements showed that the wettability of the blends increased with HP-lignin content. This was viewed positively by the authors,

as it would aid in biodegradability of the material, as corroborated by the results of soil biodegradation tests.

HP-KL has been blended (up to 30 % HP-KL) with biodegradable copolyester from 1,4-butanediol, adipic acid, and terephthalic acid to produce films by melt-blowing on an industrial scale (172). It has been demonstrated that lignin provides resistance against photodegradation and compostability to these films, which have been already used in the semi-commercial production of waste bags (Xylobags). Other injection-molded products have also been produced from HP-KL (Figure 6).



Figure 6. Prototype and semi-commercial products made from HP-KL-polymer blends. Reprinted with permission from Reference (172). Copyright 2017 W.G. Glasser.

Four cyclic carbonates - ethylene, propylene, vinyl ethylene, and glycerol were studied as low cost, non-toxic, and green alternative etherifying agents for lignin (168). A complete conversion of PhOH was within short reactions times. Cyclic carbonates were reported to react with aliphatic and carboxylic OH groups, unlike conventional etherifying agents, which selectively replace PhOH groups.

In conclusion, etherification can successfully mask PhOH groups of lignin, improve solubility in organic solvents (Table 6), and decrease T_g to facilitate lignin use in thermoplastic applications. Methylation and hydroxypropylation are the most studied methods, and in addition to PhOH, the latter also has the potential to replace aliphatic OH. However, methylated lignin has demonstrated better thermal stability. The reagents used in methylation and hydroxypropylation are hazardous. Therefore, dimethyl and five-member cyclic carbonates generated from CO_2 have been proposed as non-toxic, environmentally friendly alternatives. In almost all cases, addition of lignin improves thermal properties. However, mechanical properties are often compromised with higher lignin loadings, which is a challenge yet to be overcome.

Table 6. Effects of Lignin Esterification and Etherification on Solubility

<i>Lignin</i>	<i>Hansen Solubility Parameters</i>			<i>Hildebrand or Total Hansen Solubility Parameter (MPa^{1/2})</i>
	δ_d (MPa ^{1/2})	δ_p (MPa ^{1/2})	δ_h (MPa ^{1/2})	
Unmodified SWKL (84)	16.7	13.7	11.7	24.6
Acetylated SWKL (84)	16.1	12.0	10.2	22.5
Propionated SWKL (84)	16.3	11.5	9.7	22.1
Butyrated SWKL (84)	16.4	11.1	9.3	21.9
Maleated SWKL (84)	15.6	13.2	10.7	23.0
Methacrylated SWKL (84)	15.9	11.7	9.2	21.8
Unmodified HWKL (84)	16.7	13.5	11.3	24.3
Acetylated HWKL (84)	16.1	12.1	10.3	22.6
Propionated HWKL (84)	16.3	11.5	9.7	22.2
Butyrated HWKL (84)	16.4	11.1	9.3	21.9
Maleated HWKL (84)	15.6	13.1	10.7	23.1
Methacrylated HWKL (84)	15.9	11.7	9.2	21.8
Indulin Kraft (173)	N/A	N/A	N/A	22.5
Hydroxypropyl Indulin Kraft (96)	N/A	N/A	N/A	22.7

Lignin Copolymers

The typical multifunctional structure of lignin enables an alternative approach to lignin modification by covalently linking lignin (or its derivatives) with immiscible polymers (graft copolymerization) to synthesize a thermoplastic copolymer, or to facilitate blending of lignin with other thermoplastic polymers (56). Most notably, the OH groups on the lignin (PhOH groups on unmodified lignin, or artificially created secondary aliphatic OH groups on derivatized lignin) are utilized for lignin copolymerization. Lignin graft copolymers can be synthesized via two approaches: “grafting onto”, and “grafting from” (Figure 7). In the first approach, polymers are coupled to the OH or other functionalities by techniques such as diisocyanate and boron mediated coupling and azide alkyne Huisgen cycloaddition (click chemistry). In the second approach, monomers are polymerized directly from lignin cores via free radical polymerization (FRP), ring opening polymerization (ROP), chemo-enzymatic polymerization, and atom transfer radical polymerization (ATRP) (174). Lignin graft copolymers have been employed in synthesis of thermoplastic materials as a strategy for lignin derivatization, and facilitating eventual blend formation between the graft copolymer and previously incompatible polymers (“*binary/multi-component blends*”) or as thermoplastic materials by themselves (“*one component blends*”).

Lignin Graft Copolymers in Binary Blends

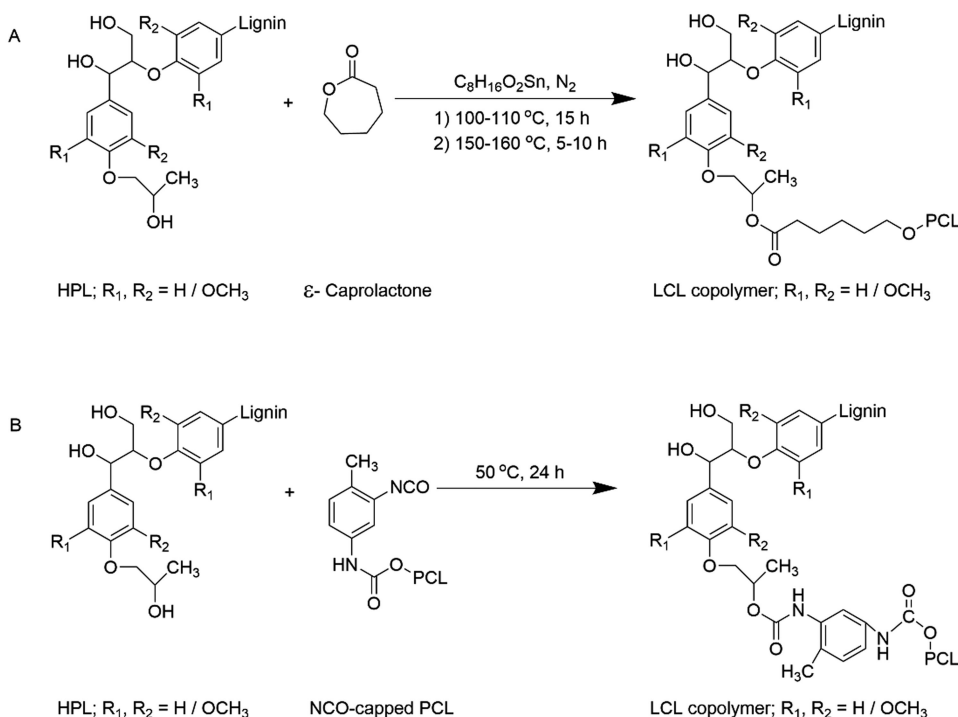


Figure 7. Copolymerization of hydroxypropylated lignin with ϵ -caprolactone monomer (grafting from) (A) and NCO-capped poly(ϵ -caprolactone) prepolymer (grafting onto) (B) to form lignin-caprolactone copolymer (LCL). Adapted with permission from Reference (161). Copyright 1994 American Chemical Society.

This method consists of creating lignin graft copolymers, which are then blended with other polymers. In one study, multiphase block co-polymer was formed between HP-SWKL (Indulin) and PCL, which was then blended with PVC. HP-SWKL served as the core, while PCL served as the flexible arm segments (2-7 per core) of star-like lignin-polycaprolactone (LCL) co-polymer. Both, anionic copolymerization between HP-SWKL and CL (Figure 7 A), and grafting with monoisocyanate (NCO)-terminated PCL were reported (Figure 7 B). The resulting copolymer architecture was found to be dependent on the average molecular weight, molecular weight distribution, lignin content, and T_g of the starting lignin and its derivatives, presenting an opportunity to customize the copolymer properties per specific requirements. The copolymer was characterized by FT-IR, GPC, DSC, and optical microscopy. During eventual blending of LCL copolymer and PVC, the blend was found to benefit significantly from the innate compatibility between PCL and PVC (56). An improved compatibility between the components was evidenced by a single T_g of the blend, as measured by DSC, and supported by DMTA. Copolymerization of lignin was also found to help with the mechanical properties of the blend, where inclusion of LCL in the formulation (up to 50 %) improved the elongation from 200 to 600 %, as compared to pure PCL. LCL was also found to slow down the characteristic crystallization of PCL in PCL-PVC blends, which leads to their embrittlement (56). Hence, LCL was beneficial to reduce the effects of aging on the thermoplastic blend. ‘Grafting onto’ approach via ROP was employed to synthesize lignin-g-poly-L-lactide (lignin-g-PLLA) copolymers from soda lignin which were then blended with

PLA (5-15 % copolymer) (132). The lignin-g-PLLA-PLA blends showed a tensile strength that was higher than that observed for pristine lignin-PLA blends, and comparable to that observed for neat PLA. Most importantly, lignin-g-PLLA-PLA blends showed UV-blocking properties that increased with increasing content of the copolymer in the blend. In a similar fashion, synthesis of dodecylated (C₁₂ esterified) alkaline lignin-g-PLA-PLA blends (50 % copolymer) was reported, with effective UV-blocking properties, and a high elongation, up to 40 times elongation at break of the neat PLA (175). ‘Grafting from’ approach was used in synthesis of OSL- and biorefinery-lignin-based copolymers (lignin-g-polyacrylate) by FRP, initiated by calcium chloride and hydrogen peroxide. The resulting lignin-g-polyacrylate copolymers were blended with PLA, providing a UV-blocking effect and enhancing mechanical properties (54). Apart from the UV-blocking and anti-aging properties, lignin copolymers have also been reported to possess antioxidant, biodegradable, and biocompatible properties (52). Specifically, a lignin-PCL-co-lactide copolymer (lignin-PCLLA) from alkali lignin via solvent-free ROP, was further blended with PCL or PLA to produce electrospun composite fibers for medical applications (52).

Lignin Graft Copolymers as One Component Blends

Examples of one-component blend are lignin-PS (up to 19.6 % lignin) and lignin-polymethyl methacrylate (PMMA) (up to 22.1 % lignin) copolymers prepared by ATRP between KL and the corresponding synthetic polymers (‘grafting from’) (176). Both copolymers were reported to exhibit 10 times increase in toughness, while the lignin-PMMA copolymer showed twice the elongation as compared to the non-grafted, binary blend system. Lignin-PMMA copolymers were reported to have higher elongation and toughness values than lignin-PS copolymers. The mechanical properties of the blends were found to be mostly dictated by lignin than by the synthetic polymers. A single T_g , which was higher than T_g s of individual homopolymers, was reported for the copolymers indicating presence of strong interactions between lignin and the polymers. Transmission electron microscopy (TEM) showed a uniform dispersion of the components in the blend. In another example of one component blend between lignin and PS, styrene was ‘grafted onto’ HWKL (average T_g ~65-85 °C (19)) via ATRP to synthesize a lignin-g-PS copolymer (177). A single T_g was observed at ~107 °C. Thermal decomposition behavior of the copolymer showed a similar trend as of pure PS. ‘Grafting from’ via ATRP was employed in synthesis of another one component blend between HWKL and *N*-isopropylacrylamide (NIPAM) (178). The thermal decomposition temperature of the lignin-g-poly(NIPAM) copolymer was reported to be significantly higher than poly(NIPAM). The copolymer showed a thermally activated phase transition from hydrophilic to hydrophobic above 32 °C, similar to poly(NIPAM) (lower critical solution temperature, LCST ~32 °C). The use of ATRP (activator regenerated electron transfer – ARGET ATRP) has also been employed in combination with the convenience and cost-effectiveness of photo cross-linking, to synthesize UV-cross-linkable lignin-g-PS(co-acryloyl benzophenone) copolymers (174). The photo-cross-linking ability was provided by inclusion of acryloyl benzophenone (ABP), a UV-sensitive compound as a comonomer. The resulting copolymer exhibited enhanced thermoplasticity as compared to the unmodified kraft lignin, and higher thermal stability than PS homopolymer. Lignin copolymerization has also been reported to be employed along with fractionation approach to enhance lignin compatibility (24, 132). Sequentially fractionated and cross-linked HWKL was reacted with dicarboxy-terminated polybutadiene (PBD) to form lignin-PBD copolymers (12-38 % lignin) (24). The resulting copolymer films from HMW-fractions of lignin showed a two-phase viscoelastic behavior. Increasing

lignin content resulted in increasing storage modulus at rubbery plateau. Lignin-PCL one component blends have also been reported, in a solvent-free bulk polymerization between KL and CL, via ROP (179). Formation of the copolymer was confirmed by change in the solubility of the copolymer in organic solvents. The resulting copolymer showed an enhanced thermal processability and extrusion behavior compared to pristine lignin. Biorefinery lignin-g-PCL copolymers have also been reported to possess UV-blocking effect (180).

Lignin copolymerization has also been used to achieve improvement in the biodegradability of the blends. Graft copolymers between SWKL and 1-ethenylbenzene (10–51 % lignin), synthesized by FRP was reported to be biodegradable by white rot (*Pleuroteus ostreatus*, *Phanerochaete chrysosporium*, and *Trametes versicolor*), and brown rot fungi (*Gloeophyllum trabeum*). The rate of biodegradation was found to increase with increasing lignin content (58).

Lignin grafts offer an effective approach for creating thermoplastic blends between lignin and commercial off-the-shelf polymers, through the formation of covalent linkages that facilitate the blend formation, and improving the thermomechanical properties of the resulting blends. This is a unique approach, especially for creating single component blends from polymers that are otherwise immiscible with each other.

Lignin Elastomers

Thermoplastic elastomers are a class of materials combining both thermoplastic and elastomeric properties (181). Stable, high-functioning lignin-based thermoplastic materials can offer an alternative to the synthetic elastomers (182). Lignin-based thermoplastic elastomers can be synthesized by blending lignin with rubbers/polymers, or by chemically linking them together. An example of the former is an elastomer formulation (50 % lignin) prepared by blending acrylonitrile butadiene rubber (NBR-33; $\delta = 19.2\text{--}20.3 \text{ MPa}^{1/2}$) and various types of lignin (HWOSL, HWSL, SWKL, and methanol-fractionated SWKL) (182). Among these, HWOSL lignin provided characteristics similar to an elastomer containing organic fillers (5–7 MPa tensile failure stress, 500–600 % elongation). Methanol-fractionated SWKL-NBR blend also showed good mechanical properties.

Chemical synthesis was used to produce lignin-based elastomers as multi-armed star shaped lignin-g-PMMA-co-BA copolymers via ATRP (< 1 % lignin) (181). It was reported that the mechanical properties of these copolymers were significantly improved as compared to the linear PMMA-co-BA polymers. The T_g of lignin-g-copolymers was found to be similar to that of linear PMMA-co-BA polymer. The copolymers showed a higher thermostability than unmodified lignin, possibly due to their star-shaped architecture, which restricts the chain mobility. They also showed a higher storage modulus and stress at break as compared to the linear PMMA-co-BA polymer. Creep-recovery tests confirmed the property of a rubber-like elasticity. Inclusion of lignin was also shown to impart UV-absorbing capacity to the formulation. In another innovative study, EHL was linked with MA-grafted saturated polyolefin elastomer (POE-MA) rubber matrix (30 % lignin), by constructing coordination-based energy sacrificial bonds at the interface between lignin and POE (183). The coordination bonds were reported to facilitate lignin dispersion into the rubber matrix, and help orient the chains during stretching. The resulting formulation showed 100 % increase in the toughness, and 35 % increase in the stress at break, as compared to the formulation without lignin. The material also showed excellent shape memory performance.

Conclusions

Lignin shows tremendous potential as a biopolymeric component in the formulation of thermoplastic materials. Although it can form miscible blends with a few polymers, it largely shows immiscibility/incompatibility with most polymers, due to its multifunctional, polar structure characterized by strong self-interactions (such as hydrogen bonding). Several strategies dealing with this incompatibility exist as discussed within this chapter. Inclusion of lignin in the thermoplastic formulation not only helps in lowering the cost and the carbon footprint of plastics, but also provides additional benefits such as thermomechanical stability, flame retardancy, biodegradability, UV-protecting, antioxidant and anti-weathering capacity. These benefits make lignin-based thermoplastics attractive alternatives for petroleum-based thermoplastics, in numerous applications from packaging to the biomedical field.

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