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A Renewable Lignin−Lactide Copolymer and Application in Biobased Composites

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Ⓢ *Supporting Information*

ABSTRACT: The need for renewable alternatives to traditional petroleum-derived plastics has driven recent interest in biobased composite materials that are sourced from carbon-neutral feedstocks. Lignin, an abundant plant-derived feedstock, has been a candidate for renewable materials; however, it is often difficult to blend with other biopolymers. In order to improve the miscibility of lignin with other bioplastics, we developed a catalytic and solvent free method for synthesis of a lignin−PLA copolymer. Graft polymerization of lactide onto lignin catalyzed by triazabicyclodecene (TBD) resulted in a lignin-*g*-poly(lactic acid) copolymer; chain length of the PLA is controlled by varying of the lignin/lactide ratio and preacetylation treatment. End-group analysis reveals high grafting efficiency and preferential grafting on lignin aliphatic hydroxyls over phenolic hydroxyls. The lignin-*g*-PLA copolymers display a glass transition temperature range from 45 to 85 °C and multiphase melting behavior. The lignin-*g*-PLA copolymers are used as dispersion modifiers in PLA-based materials to enhance UV absorption and reduce brittleness without a sacrifice in the modulus of elasticity.

KEYWORDS: *Green materials, Renewable materials, Bioplastics, Biocomposites, Copolymers, Organocatalyst, Graft polymerization*
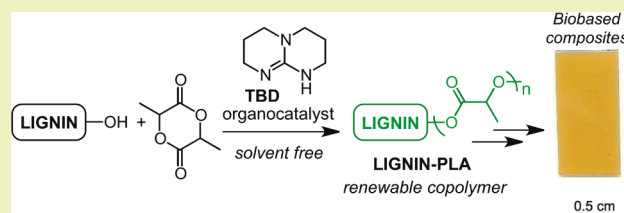
■ INTRODUCTION

The depletion of fossil fuel resources and the environmental impact of petroleum-based plastic materials have driven a strong global interest in renewable biobased polymers and composites derived from natural resources.[1,2] Lignin is the second most abundant renewable biopolymer in nature and an inexpensive and currently underutilized[3] waste product from papermaking and biorefinery industries. These processes produce a lignin fraction that is often relegated to the low-value use of combustion or sold as a natural component of animal feeds. The development of a way to convert lignin to new high-value products will have a crucial impact on biorefinery economics; consequently, the conversion of lignin to value-added chemicals and materials is an active area of research.[3,4] Several laboratories have explored the use of lignin as an inexpensive structural filler, surfactant, and additive in materials applications. For example, lignin is used in biobased polymeric composites to modify material properties such as hydrophobicity, stiffness, and crystallinity relative to neat biopolymers.[5−7] However, the use of unmodified lignin as a filler in thermoplastic polymers often negatively impacts the mechanical properties of the resulting composite materials.[4,6,8,9]

The poor dispersion of lignin in many composites is attributed to its propensity to self-aggregate. Lignin is an irregular polymer made up of substituted phenyl rings and phenolic and aliphatic hydroxyl groups, and aggregation is likely due to intermolecular association from hydrogen bonding between the carboxylic acid groups and various ether oxygens and hydroxyl groups, van der Waals attraction of polymer chains, and π−π stacking of aromatic groups.[10,11] Modification of lignin by esterification[12,13] or etherification[14] has been used to improve its dispersion in thermoplastics and thermosetting materials and leads to improved performance in composite materials. Graft polymerization is an attractive approach to covalently modify the surface of lignin, resulting in a lignin-based copolymer that can be used in a broader range of applications, and allows for the design of novel materials with tailored properties.[15−17] Glasser and co-workers have synthesized multiphase star-like copolymers of lignin-polycaprolactone[18] and lignin-polystyrene[19] that are better dispersed in poly(vinyl chloride)[8] and polystyrene-based[19] thermoplastic materials, respectively, compared to unmodified lignin.

Poly(lactic acid) (PLA) is one of the main biodegradable polymers in the current and emerging bioplastics markets; however, it is not yet considered a direct replacement for conventional synthetic polymers because of its high cost of production and several undesirable attributes including brittleness, poor thermal resistance, limited gas barrier

properties, and poor UV light barrier properties.[20,21] Some laboratories have tried to address these issues by preparing PLA–lignin composites;[22,23] however, these materials often exhibit lower tensile strength and elongation at break than neat PLA. To improve the dispersion of lignin in PLA, lignin-g-PLA copolymers have been synthesized to compatibilize lignin with PLA.[24,25] Our hypothesis is that the introduction of small amount of well-dispersed lignin-g-PLA copolymers should improve UV light barrier properties of the composites without a sacrifice in flexibility. This approach has been successful for generating other types of PLA composites, e.g., PLA–talc reported by Narayan et al.[26] Because ring-opening polymerization (ROP) of lactide is an established method for the synthesis of PLA, we reasoned this process would enable the graft polymerization of PLA onto lignin to generate a lignin-g-PLA copolymer sourced from completely renewable materials. Furthermore, use of an efficient organocatalytic ROP process[27] would leave no metal residues in the resulting biobased composites. Here, we report a simple metal- and solvent-free method for organocatalytic graft polymerization of lactide onto lignin to produce lignin-g-PLA copolymers using triazabicyclodecene (TBD) as a catalyst. The PLA chain length can be controlled by using varying ratios of lignin to a lactide monomer. Further control of the grafted PLA chain length is also accomplished by pre-acetylating the lignin. The ability to control the chain lengths of the grafted PLA enables variable levels of interaction with a surrounding polymer matrix (PLA), allowing properties of the lignin–PLA composite materials to be tuned. We investigated the dispersibility of the grafted lignin–PLA copolymers in a PLA matrix and measured the impact of the modified lignin on the UV–vis absorption spectra and mechanical properties of the resulting composite.

■ EXPERIMENTAL SECTION

Materials. Lignin (Indulin AT, Westvaco, Charleston, SC) was dried at 50 °C vacuum for 36 h and stored in a glovebox (N_2) prior to use. L-lactide (S,S) (LLA) (Purac Biochem, Netherlands) and triazabicyclodecene (TBD) (Aldrich) were used as received and stored in a glovebox under nitrogen. 2-Chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) (Sigma-Aldrich), cyclohexanol (Alfa Aesar), chromium(III) acetylacetonate (Strem Chemicals), deuterated chloroform (Cambridge Isotope Laboratories), pyridine (EMD Chemicals), acetic anhydride (EMD Chemicals), N-methyimidazole (Acros Organics), p-dioxane (JT Baker), chloroform (Fisher), isopropanol (Fisher), and poly(lactic acid) (2003D) (NatureWorks LLC, MN) were used as received without further purification. Oven-dried glassware and stir bars were used for all polymerization experiments. All polymerization reactions were carried out under inert atmosphere (nitrogen).

Characterization. ^{1}H-nuclear magnetic resonance (NMR) spectra were recorded at room temperature on a Varian 300 (75), 400 (100), or 500 (125) MHz spectrometer, with shifts reported in parts per million downfield from tetramethylsilane and referenced to the residual solvent peak. ^{31}P NMR spectra were obtained on a Varian mercury plus spectrometer, equipped with a four-nucleus switchable and pulse field gradient probe operating at 162 MHz, using methods modified from that of Cateto et al.[28] Experiments were recorded at 25 °C in $CDCl_3$. Chemical shifts were calibrated from the sharp ^{31}P NMR signal at 132.2 ppm arising from the reaction product between residual water and TMDP. Spectra were quantitative with proton broad bands decoupling only during acquisition time. Cyclohexanol was used as an internal standard for the quantitative evaluation of the lignin hydroxyl group content. ^{31}P NMR spectra were obtained with a 100 kHz spectral width, 128,000 data points, 8 s relaxation delay, 0.64 s acquisition time, 8 μs for a 55.4° pulse, and 1 Hz line broadening using 128 scans. Content of different hydroxyl groups were obtained by the

integration values of the spectral regions arising from aliphatic hydroxyls (149–146 ppm), phenolic hydroxyls (144–137.5 ppm), and carboxyls (136–134 ppm) relative to the internal standard (145.5–144.5 ppm).

Differential scanning calorimetry (DSC) was performed on a TA Instruments Q100 and Q2000 DSC using a heating and cooling rate of 10 °C/min and nitrogen flow rate of 50 mL/min. The samples were heated from 0 to 190 °C, cooled to 0 °C, and then heated to 190 °C again. Glass transition temperature (T_g) was determined on the second heating scan if not otherwise specified.

The size exclusion chromatography (SEC) system consisted of a Shimadzu LC-20AD pump, Shimadzu SIL-20AC HT autosampler, CTO-20A column oven, and Shimadzu RID-10A refractive index detector. A Jordi Gel DVB guard column (500 Å) and three Jordi Gel DVB analytical columns (500 Å, 10^4 Å, and 10^5 Å) were used with chloroform as the eluting solvent (1 mL/min) and at 40 °C. The system was calibrated using polystyrene standards from Varian (Calibration Kit S-M2-10, U.S.A.) and Shodex (Showa Denko K.K., Tokyo, Japan). Samples (5 mg) were dissolved in chloroform (1 mL) and then filtered through a 0.22 μm PTFE membrane before injection into the SEC system.

^{31}P NMR spectra and phosphitylation of lignin and lignin-g-PLA copolymer were performed based on modification of the method described by Granata et al.[29] A solvent mixture composed of deuterated chloroform ($CDCl_3$) and pyridine (1.6/1.0, v/v) was prepared and dried over molecular sieves prior to use. This solution was used for the preparation of relaxation reagent solution (RR, chromium(III) acetylacetonate, 5.0 mg/mL) and the internal standard solution (IS, cyclohexanol, 10.0 mg/mL). A total of 15.0 mg of oven-dried sample was dissolved in a $CDCl_3$-pyridine solvent (370 μL) followed by the addition of RR (50 μL) and IS (50 μL). The resulting solution was left to stand for 1 h to ensure total dissolution. TMDP (30 μL) was then added and let stand for at least 7 h to ensure complete derivatization prior to ^{31}P NMR analysis. The phosphitylation of PLA was conducted according to the experimental procedure described above, with a reaction time of 3 days at room temperature. The phosphitylated PLA polymer was analyzed by in situ ^{1}H NMR ($CDCl_3$) (Figure S2, Supporting Information) and ^{31}P NMR ($CDCl_3$) (Figure 3(b)).

Representative Procedure for Synthesis of Lignin-g-PLLA Copolymers (Lignin:Lactide 10:90). Inside a glovebox (N_2), TBD catalyst (100 mg, 1 wt %), lignin (1 g, 10 wt %), and L-lactide (9 g, 90 wt %) were weighed into a reaction vial (25 mL) equipped with a stir bar. The vial was sealed, taken outside the box, and immersed into an oil bath at 130 °C for 3.5 h with stirring. The reaction mixture was then cooled to room temperature and was subsequently quenched by a dichloromethane solution (5 mL) of acetic acid (100 mg). After the residue had completely dissolved, an aliquot was taken out and concentrated in vacuo for ^{1}H NMR analysis (in $CDCl_3$). L-Lactide conversion (83%) was determined by integration of the L-lactide methide signal (5.03 ppm) against the integration of the PLA methide signal (5.16 ppm). The remainder of the crude reaction mixture was then concentrated on a rotary evaporator to a highly viscous solution (approximately 10 mL), which was then precipitated by pipet addition to a stirred methanol solution (1 L). Subsequently, the methanol solution was discarded, and the precipitated polymer at the bottom of the beaker was collected by extraction with dichloromethane. Then polymers were concentrated and dried in vacuo to a constant weight, yielding (6.90 g, 69% yield) pure lignin-g-PLA copolymer. The PLA chain length average was determined by ^{1}H NMR ($CDCl_3$) end-group integration of the PLA (5.16 ppm) methide proton against the end-group methide proton (4.35 ppm) (Figure 1, M_n = 1800 Da). The purified lignin-g-PLA (10/90) copolymer was further characterized by ^{31}P NMR (Figure 3), DSC (Figures 4 and 5), and SEC (Table S1 and Figure S5, Supporting Information). The theoretical M_n value for PLA chains in Figure 2 was calculated by dividing the mmoles of lactide by mmoles of the lignin–OH functionality (obtained by ^{31}P NMR analysis). This maximum M_n for grafted PLA chains was then multiplied by the observed conversion of lactide in the grafting reaction.
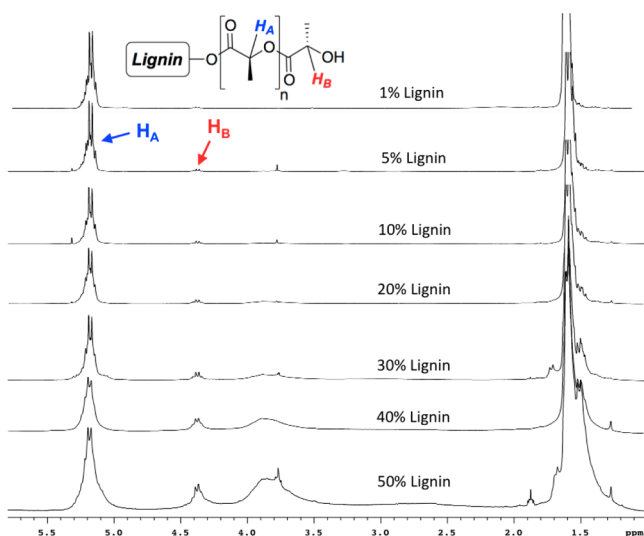
Figure 1. ^{1}H NMR spectrum of lignin-g-PLA copolymers in CDCl$_3$.
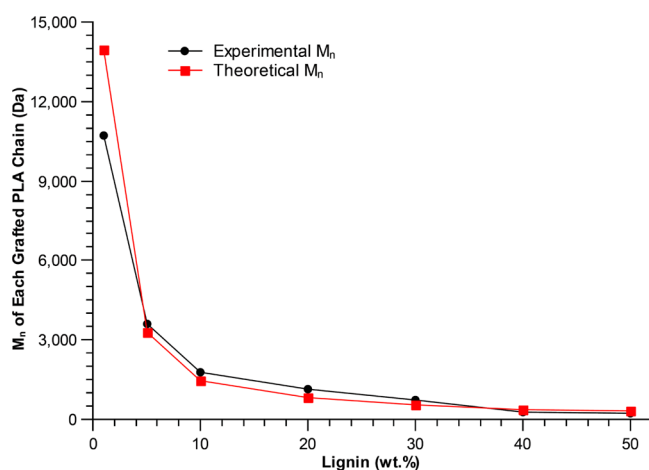

Figure 2. Number-average molecular weight (M_n) of each grafted PLA chain on the starlike lignin-g-PLA copolymers. The experimental PLA chain length was determined by ^{1}H NMR end-group integration. The theoretical value was determined as described in the Experimental Section.

The lignin-g-PLA copolymers (30−50 wt % lignin) were synthesized as above but were instead purified by dialysis (MW cutoff 1000 Da) over methanol (1 L) changed twice over 12 h. The remaining contents of the dialysis bag were extracted with dichloromethane and concentrated in vacuo, yielding the pure copolymers.

General Procedure for Acetylation of Lignin (DA=75%). The procedure was modified from a previously reported acetylation method.[13] To 1.0 g of lignin was added acetic anhydride (Ac$_2$O, 2.6 mL, 28.0 mmol, 5.5 eq, based on 5.10 mmol OH/g lignin) and diluted to a final volume of 4.0 mL using p-dioxane in a 7 mL scintillation glass vial equipped with a stir bar. The reaction was sealed and stirred at 50 °C for 2 h. No special care was taken to ensure that the reaction was moisture- or air-free. Acetylated lignin was recovered by precipitation initiated by addition of 45 mL of deionized (DI) water to the crude reaction mixture. The resulting suspension was transferred to a 50 mL falcon tube and subjected to centrifugation at 4000g for 15 min. The supernatant was decanted and discarded. The residue was resuspended in an additional 45 mL of DI water and subjected to another round of centrifugation. After two rounds of centrifugation, the resulting product was freeze dried, followed by drying in a vacuum oven (50 °C) prior to subsequent analyses and used as a substrate for

copolymerization with L-lactide. ^{31}P NMR analysis revealed 75% degree of acetylation (DA).

Mechanical Properties of PLA−Lignin Composites. A total of 2.1 g PLA was blended with non-modified lignin (0.021−0.105 g) or lignin-g-PLA copolymer (0.21−0.2625 g) in chloroform (15 mL) at room temperature for 15 h. Then, the polymer mixture was precipitated by the addition of isopropanol (100 mL). The precipitated polymers were dried in a vacuum oven (80 °C) for 3 days prior to use. PLA−lignin composites were obtained by hot pressing the dried precipitate (PHI-Tulip Model 225H-X6-13, U.S.A.) at 190 °C using three pressure stages: 0 ton pressure for 30 s, 0.1 ton for 1 min, and then 0.5 ton for 2 min. The hot-pressed specimen (∼60 mm × 100 mm × 0.25 mm) was then cut into sample strips (10 mm × 100 mm) using a razor blade for tensile testing. Tensile tests were carried out using Instron 5565 (TA Instruments) to measure tensile modulus, strength, and strain of composites. The space between the grips was 50 mm and served as the gage length for deformation measurements. A constant deformation speed of 5 mm/min was used. The specimens were conditioned at room temperature under 54% RH for 2 days prior to testing. Four to five replicate specimens were tested and analyzed.

Optical Properties of PLA−Lignin Composites. A total of 500 mg PLA was blended with unmodified lignin (5 mg) or lignin-g-PLA copolymer (50 mg) in chloroform (10 mL) at room temperature for 2 h. Then, the polymer mixture was precipitated by methanol (100 mL) and dried in a vacuum oven (55 °C) prior to use. A total of 50 mg of PLA−lignin blends were then hot pressed at 180 °C using three pressure stages: 0 ton pressure for 30 s, 0.1 ton for 1 min, and then 0.5 ton for 2 min into films 0.04−0.05 mm in thickness. The films were conditioned at room temperature under 0% RH for 3 days prior to testing. Because poly(ethylene terephthalate) (PET) is a commonly used material for packaging and and also used for light-sensitive products because it has good UV light barrier properties,[20] we are interested in comparing the UV light barrier properties of PLA−lignin composites to PET. The PET materials were obtained from poly(ethylene terephthalate) (PET) bottles (Fiji bottled water) and then hot pressed by the same procedure into films with 0.04 mm in thickness. Optical properties of PLA, PLA−lignin, and PET films were measured by an Agilent Cary 6000i UV−vis−NIR spectrophotometer. The specimens were scanned from 200 to 800 nm at room temperature.

■ RESULTS AND DISCUSSION

Graft Polymerization of PLA onto Lignin via Ring-Opening Polymerization. The diverse chemical functionalities of lignin, including a mixture of aliphatic hydroxyls, phenolic groups, and carboxylic acid etc., presents a challenge for synthetic modification, both in terms of functional group tolerance and selectivity. Previously described ring-opening polymerization (ROP) protocols on lignin with caprolactone[18] and styrene[19] utilized chemical pretreatment (hydroxypropylation), followed by fractionation processes as a method to convert lignin into a functionally more homogeneous material prior to its use in polymerization. From a practical and economic standpoint, the need for chemical pretreatment and purification of lignin prior to use limits the attractiveness of this approach. Thus, we investigated whether lignin could be used directly in graft polymerization reactions for production of new biobased polymeric materials.

In order to create a lignin-g-PLA copolymer that would perform well in a PLA composite, we turned to graft polymerization of PLA onto an unmodified lignin substrate. This approach was especially attractive because there are well-established methods for ROP of lactide to make PLA. In particular, a metal-free approach developed by the Waymouth and Hedrick laboratories has been used to polymerize L-lactide (LLA), caprolactone, and valerolactone.[30] We discovered that

Scheme 1. Ring-Opening Polymerization of Lactide (LA) on Lignin Using Triazabicyclodecene (TBD) Catalyst
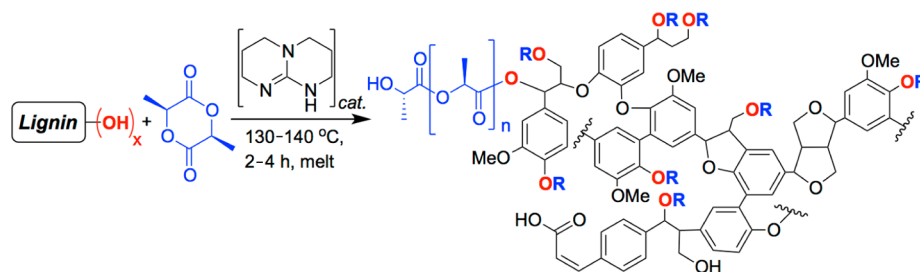
the organocatalytic ring-opening polymerization of lactide could be done in the melt with catalytic triazabicyclododecene (TBD) in the presence of lignin (1−50%) to cleanly generate a novel lignin-g-PLA copolymer (Scheme 1 and Table S1, Supporting Information).

Analysis of the isolated copolymers by ^{1}H NMR spectroscopy indicated efficient surface modification of lignin (Figure 1). The resonances at 5.3−5.1, 4.4−4.3, and 4.0−3.5 ppm (CDCl$_3$) are assigned to the protons of the PLA repeating unit (H$_A$), end group of PLA (H$_B$), and lignin, respectively. These spectra could also be used to calculate average PLA chain length in the copolymer by ^{1}H NMR end-group integration; as the weight fraction of lignin relative to lactide monomer increased, the resulting shorter PLA grafted chains decreased in length (shown in Figure 2), suggesting that initiation of PLA polymerization at each lignin−OH group effectively competes with extension of the PLA chain.

By varying the lignin content from 1 to 50 wt % in the graft polymerization process, the chain lengths of the grafted PLA could be controlled from number-average molecular weight (M_n) 200−11,000 Da (Figure 2). The observed M_n of the grafted PLA chains were in close agreement with the theoretical value predicted from the number of active hydroxyls on lignin determined by phosphitylation of the lignin substrate and analysis by ^{31}P NMR spectroscopy (Table 1).

Table 1. Effect of Pre-Acetylation on Chain Length of Each Grafted PLA Chain of Lignin-g-PLA Copolymers (5 wt % lignin)

type of Lignin	neat lignin	pre-acetylated lignin[c]
M_n of each grafting PLA chain (Da)[a]	3600	6408
aliphatic OH 149−146 ppm[b]	2.01	0.66
phenolic OH 144−137.5 ppm[b]	3.10	0.58
total OH 149−137.5 ppm[b]	5.10	1.24
COOH 136−134 ppm[b]	0.40	0.35

[a]Number-average molecular weight (M_n) is determined by ^{1}H NMR end-group integration. [b]Hydroxyl (OH) group content in units of mmol/g. [c]Degree of acetylation (DA) of the pre-acetylated lignin is 75%. DA is determined by dividing the acetylated OH group content (5.10 − 1.24 = 3.86 mmol/g) of the pre-acetylated lignin by that of the unmodified lignin (5.10 mmol/g).

To assess the efficiency of the grafting method, we phosphitylated the PLA-grafted lignin and compared the ^{31}P NMR spectra to that of phosphitylated lignin and PLA. In Figure 3(a), the resonances at 149−146, 144−137.5, and 136−134 ppm (CDCl$_3$) are assigned as the phosphotriesters of the aliphatic hydroxyl (OH), phenolic OH, and carboxylic groups of lignin, respectively.[29] The ^{31}P chemical shifts of phosphotriesters derived from the terminal hydroxy group of PLA occur

at 146.2−146.5 ppm (shown in Figure 3(b)). The absence of ^{31}P resonances corresponding to aliphatic and phenolic lignin OH signals (149−146 and 144−137.5 ppm, respectively) in Figure 3(c) and the presence of ^{31}P resonances corresponding to PLA terminal hydroxyls at 146.5 ppm (at 5 wt % lignin) indicates that all detectable OH groups of lignin are covalently modified by PLA chains in the 5 wt % lignin-g-PLA copolymer. For higher lignin loadings (30%), some lignin phenolic OH functionality is unmodified, as indicated by the broad peak at 140−139.5 ppm (Figure 3(d) and Table S2, Supporting Information). Organocatalytic ROP is efficient with aliphatic alcohol initiators,[30] but less is known on the use of phenolic initiators.[31] Our study suggests that phenols are slower initiators than aliphatic alcohols but are in part acting as initiators in the polymerization. This was also supported by control experiments of TBD-catalyzed lactide polymerization (130 °C, 4 h, melt) with aliphatic (benzyl alcohol) and phenolic initiator (3-ethyl-phenol) at a target degree of polymerization (DP) of 25 (Table S3, Supporting Information). Initiation by benzyl alcohol resulted in an observed M_n of 3600 Da, whereas 3-ethyl-phenol as initiator gave a higher M_n (7200 Da). The presence of the phenolic end group was confirmed by ^{1}H NMR on the isolated PLA and integrated (1:1) against the methide alcohol end group (Figure S1(b), Supporting Information). This suggests that phenols may be acting as initiators in the polymerization of LA, using the above-described conditions, although with lower efficiency than aliphatic alcohols.

In order to increase the length of PLA chains while keeping the lignin content high in the copolymer, we hypothesized that grafted PLA chain length could be controlled by appropriate tailoring of the lignin OH content. Thus, we prepared a series of lignin samples with varying degrees of acetylation (Table S4 and Figure S3, Supporting Information). Lignin (75% acetylated) was used in the synthesis of lignin-g-PLA copolymer (5 wt % lignin). Table 1 shows that a significant increase in molecular weight of each grafted PLA chain was observed in the resulting lignin-g-PLA copolymer (M_n 6408) compared to the neat lignin (Indulin AT) (M_n 3600).

The lignin-g-PLA copolymers were found to be soluble in common organic solvents such as chloroform and tetrahydrofuran in contrast to unmodified lignin; a trend of increasing solubility was observed as the PLA chain length increased.

Thermal Properties of Lignin-g-PLA Copolymers. Lignin has a relatively high glass transition temperature (T_g = 150 °C (Figure S4, Supporting Information)) as compared to commercial bioplastics, e.g., PLLA (63 °C),[32] PCL (−60 °C),[33] and PHBV (−9−9 °C).[34] The condensed rigid phenolic moieties and strong intermolecular hydrogen bonding interactions restrict the thermal mobility of lignin molecules and result in its high T_g. The incorporation of lignin into these
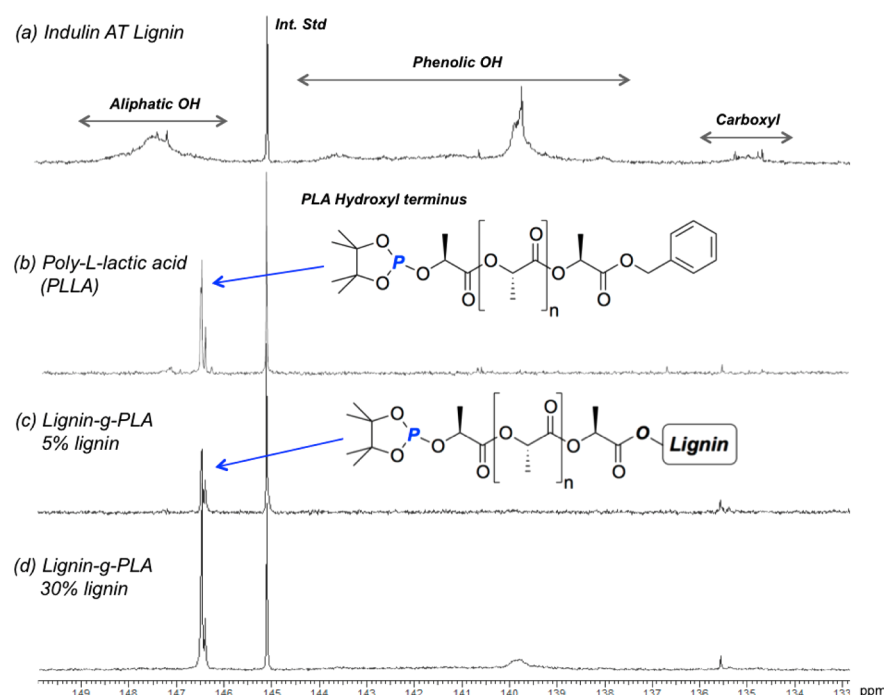
Figure 3. ^{31}P NMR spectrum of (a) lignin, (b) PLA, and lignin-*g*-PLA copolymers with (c) 5 wt % lignin and (d) 30 wt % lignin, derivatized by 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane. Int. Std: internal standard (cyclohexanol).
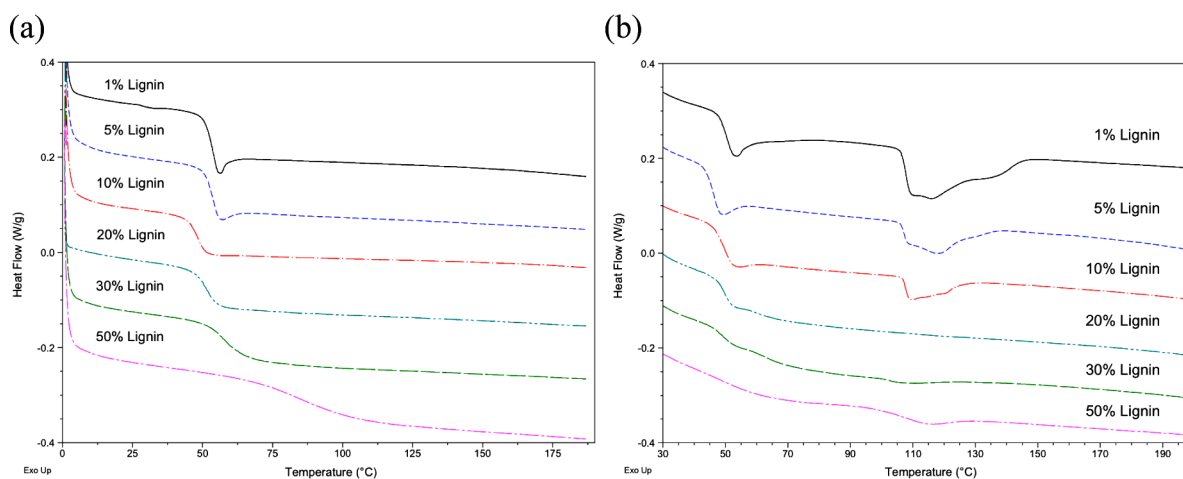

Figure 4. DSC curves of lignin-*g*-PLA copolymers on the second heating scan (a) and after annealed at 90 °C for 14 h prior to the DSC scanning from room temperature to 200 °C at 10 °C/min (b).

polymeric materials is expected to affect their thermal properties. DSC analysis of the lignin-*g*-PLA copolymers clearly shows that the incorporation of lignin significantly influences the glass transition temperatures (T_g) of the lignin-*g*-PLA copolymers (Figure 4(a)). Glass transition temperatures for lignin-*g*-PLA copolymers ranging from 45−85 °C were observed depending on the initial lignin/LA ratio (Figure 5 and Table S1, Supporting Information).

At low lignin content (1−5 wt %), the measured T_gs do not differ significantly from that of polylactide (63 °C). At higher lignin content (>10%), where the length of the grafted PLA chains are lower than M_n = 2000 (Figure 2), the T_gs increase as the weight fraction of lignin increases (Figure 5). The lignin segment, which possesses a relatively high T_g compared to PLA, contributes to the increased T_gs of copolymers. For lignin contents from 10−40 wt %, the T_gs increase from about 45 to

75 °C; at 50 wt % lignin, the transition is sufficiently broad that it is difficult to identify the T_g. Because lignin is an inhomogeneous waste material, the increase of the lignin content resulted in decreased homogeneity of the resultant copolymers. When the lignin-*g*-PLA copolymers are annealed at 90 °C for 14 h before the DSC scan (Figure 4(b)), an endotherm is observed with an onset of approximately 110 °C for samples containing 1−10% lignin. The endotherm is likely due to the melting of PLA crystals (T_m of PLA = 90−185 °C).[35] The incorporation of lignin in the PLLA structure reduced the crystallization of PLA during annealing treatment. The gradual disappearance of the melting peak could be the result of the decreasing PLA chain length at higher lignin content. The PLA chain of the copolymer below the critical molecular weight of ~DP14 likely does not form the crystal structure.
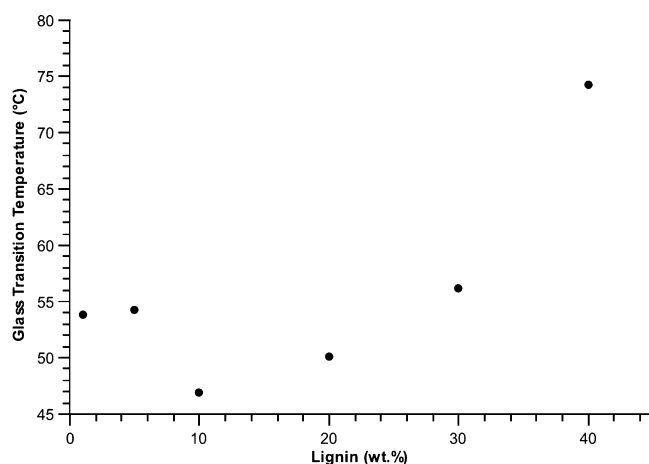
Figure 5. Glass transition temperature (T_g) of lignin-g-PLA copolymers on the second heating scan.

Optical and Mechanical Properties of PLA Composites with Lignin-g-PLA Copolymers.

The optical and mechanical properties resulting from blending the unmodified lignin and lignin-g-PLA copolymers with commercial PLA were studied in hot-pressed films. Table 2 illustrates the composition

Table 2. Composition and Abbreviation for PLA–Lignin Composites

abbreviations	lignin[a] (wt %)	PLA (g)	unmodified lignin (g)	lignin-g-PLA copolymers (g) 10:90[b]	lignin-g-PLA copolymers (g) 40:60[b]
PLA	0	100	—	—	—
PLA1L	1.0	100	1	—	—
PLA5L	4.8	100	5	—	—
PLA1C	0.9	100	—	10	—
PLA5C	4.4	100	—	—	12.5

[a]Lignin content in the composites. [b]Lignin:L-lactide weight ratio.

and abbreviation for the PLA–lignin blends. Figure 6 shows that the unmodified lignin forms aggregated particles in the PLA matrix (Figure 6(b,c)). The presence of polar groups on lignin favors self-aggregation because they can form clusters of lignin through hydrogen bonding.[10] Grafting PLA chains switches the polarity of lignin from hydrophilic to hydrophobic; thus, lignin-g-PLA copolymer interacts more favorably with a surrounding hydrophobic PLA matrix and displays increased dispersion in the PLA materials (Figure 6(d,e)). The interfacial interaction between the grafted chains and polymeric matrix could be further tailored by varying the species of the grafted monomers and chain lengths to achieve good dispersion of lignin particles in a wide range of thermoplastic materials.

The absorption of UV light is an important property for designing packaging materials to protect light-sensitive products from damage during storage. It is reported that PLA materials have better UV light barrier properties than low density polyethylene (LDPE) but worse than those of PET, cellophane, and polystyrene (PS).[20] We investigated the light barrier properties of PLA films with unmodified lignin and lignin-g-PLA copolymers and compared those to PET films (shown in Figure 7). The PLA film shows no ultraviolet (UV) light transmission in the lower range of UV-C (100–230 nm), while the PET film does not transmit both UV-C (100–280
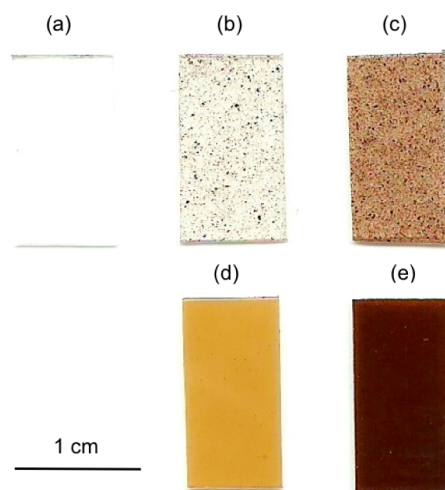

Figure 6. Images of PLA–lignin composites samples suggest increased dispersion of lignin in composites made from lignin-g-PLA copolymer compared to those made with unmodified lignin: (a) PLA, (b) PLA1L, (c) PLA5L, (d) PLA1C, and (e) PLA5C. The lignin contents for (b)/(d) and (c)/(e) are 0.9–1.0 and 4.4–4.8 wt %, respectively.
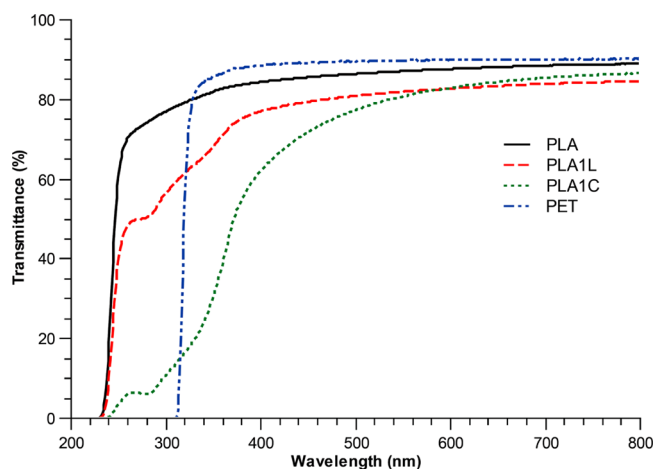

Figure 7. UV–vis spectrum for PLA, PET, and PLA–lignin composites with unmodified lignin (PLA1L) and lignin-g-PLA copolymers (PLA1C). The amounts of lignin in the PLA films with unmodified lignin (PLA1L) and with lignin-g-PLA copolymers (PLA1C) are 1% and 0.9%, respectively.

nm) and UV-B (280–315 nm). By adding a low amount of lignin (0.9 wt %) with PLA grafted on the surface into the PLA films, the PLA–lignin films (PLA1C) show UV light barrier properties, which block nearly all UV-C and UV-B and half of UV-A (315–400 nm). The unmodified lignin (PLA1L) did not significantly reduce the UV light transmission because of the poor dispersion in the PLA materials. Most of the UV light passes through the films without encountering and being absorbed by the unmodified lignin. However, the lignin-g-PLA copolymer acts as a well-dispersed UV blocker that can potentially be applied in the biocompatible packaging and surface coating industry for preventing damage and extending shelf life of light sensitive products.

The mechanical properties of tensile modulus of elasticity, tensile strength, and strain at ultimate tensile strength of PLA–lignin composites were evaluated by tensile tests of hot-pressed films (Figure 8). Li et al.[23] reported that the tensile strength and elongation at break of PLA–lignin composites decreased
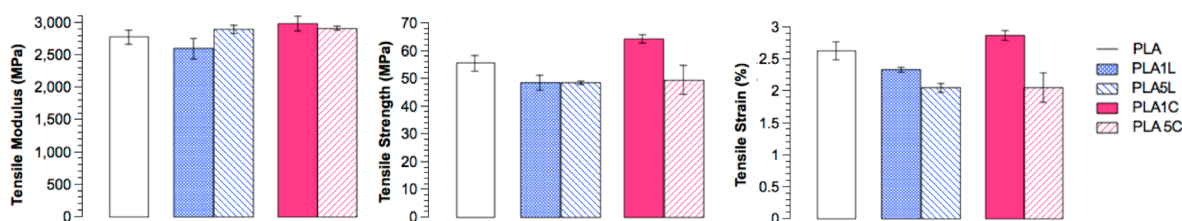
Figure 8. Mechanical properties of PLA−lignin composites. The lignin content in the PLA1L/PLA1C and PLA5L/PLA5C are 0.9−1.0 and 4.4−4.8 wt %, respectively.

with increasing lignin content, while the Young's modulus in tension remained constant up to a lignin content of 20 wt %. Ouyang et al.[22] also found that the tensile strength and elongation at break decreased with the addition of lignin in a PLA matrix but that Young's modulus in tension increased (20%) with 20 wt % lignin addition. In the experiments reported here, the incorporation of lignin-*g*-PLA copolymers (lignin:lactide 10:90) into PLA (PLA1C) resulted in a modest increase in the tensile strength (+16%) and strain (+9%) without a sacrifice in the tensile modulus (Figure 8). However, the tensile strength and strain for the PLA composites with unmodified lignin (PLA1L and PLA5L) and lignin-*g*-PLA copolymers with a higher wt % of lignin (lignin:lactide 40:60)(PLA5C) decreased compared to the neat PLA materials (PLA). The mechanical property results show that lignin-*g*-PLA copolymers with appropriate grafted PLA chain lengths can be utilized as well-dispersed polymeric plasticizers for improving flexibility and toughness of brittle PLA materials.

The tensile modulus of elasticity for PLA−lignin composites was estimated by the rule of mixtures (Table 3). The

Table 3. Comparison of Estimated and Experimental Modulus of Elasticity for PLA−Lignin Composites

materials	experimental modulus of elasticity (MPa)	estimated modulus of elasticity (MPa)[a]
lignin	4500	−
PLA	2764 ± 111	−
PLA1L	2586 ± 161	2780
PLA5L	2886 ± 63	2843
PLA1C	2968 ± 116	2779
PLA5C	2902 ± 35	2838

[a]Tensile modulus of elasticity is predicted by the rule of mixtures: $E_c = E_{PLA}V_{PLA} + E_{lignin}V_{lignin}$, where E_c is the modulus of the composites, E_{PLA} and E_{lignin} are the modulus of PLA (2764 MPa) and lignin (4500 MPa),[36,37] and V_{PLA} and V_{lignin} are the volume fractions of PLA and lignin.

experimental modulus of elasticity for both PLA composites with unmodified lignin (PLA1L and PLA5L) and lignin-*g*-PLA copolymers with a higher wt % of lignin (lignin:lactide 40:60)(PLA5C) were in close agreement with the estimated value. The slight positive deviation of modulus of elasticity from the estimated value of PLA1C suggests the lignin-*g*-PLA copolymer with appropriate grafted PLA chain lengths might have a synergistic reinforcement effect on the modulus of elasticity of the PLA materials. The reinforcing effect of the new filler lignin-*g*-PLA on the PLA composite not only depends on the stiffness of the lignin component but also on the interfacial interaction between the lignin-*g*-PLA and PLA materials.

CONCLUSIONS

The present study demonstrates that PLA can be directly grafted onto unmodified lignin by ring-opening polymerization with an organic catalyst. Graft polymerization of lactide onto lignin catalyzed by triazabicyclodecene in the melt provides lignin-*g*-PLA copolymers with controllable PLA chain lengths. End-group analysis by ^{31}P NMR revealed a high grafting efficiency and preferential grafting on lignin aliphatic hydroxyls over phenolic hydroxyls. The lignin-*g*-PLA copolymers displayed increased glass transition temperatures from 45 to 85 °C with increasing lignin content from 10% to 50%. The PLA composites with a 10% lignin-*g*-PLA copolymers (lignin:lactide 10:90) addition (PLA1C) block nearly all UV-C (100−280 nm) and UV-B (280−315 nm) and half of UV-A (315−400 nm). The incorporation of lignin-*g*-PLA copolymers (PLA1C) shows an increase in the tensile strength (+16%) and strain (+9%) without a sacrifice in the tensile modulus. The synthesized lignin-*g*-PLA copolymers with appropriate grafted PLA chain lengths can be utilized as dispersion modifiers in PLA-based biobased composite materials, improving UV absorbance as well as mechanical properties.

ASSOCIATED CONTENT

Ⓢ Supporting Information
Tabulated data related to the structural and mechanical characterization of lignin-*g*-PLA copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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