Fully Biomass-based Biodegradable Polymers from Lignin and Raw Castor oil: Lignin-graft-castor oil

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Lignin is the second most abundant renewable biomass polymer. Although lignin has high potential as a sustainable raw material due to its abundance, low price, and high aromatic concentration, lignin's complex and poorly defined chemical structure and excessive reaction sites limit its applications. Castor oil is a natural vegetable oil that can be converted to many useful chemical such as ethylene brassylate monomer. Although the castor oil-derived ethylene brassylate was studied as a sustainable raw material in a few previous publications, the pristine castor oil has not been directly used to synthesize a sustainable polymer. In this work, we report synthesis and structure-property relationships study of a novel 100% biomass-based polymer, lignin-*graft*-castor oil. In order to prepare the new polymer, natural lignin was chemically modified by a single step with a succinic acid and acetic acid. The acetic acid caps hydroxyl groups on lignin to reduce unnecessarily excessive reaction sites (-OH) with acetyl group. A carboxylic group on the succinic acid provides chemical functionality to link lignin to castor oil. The castor oil was used in its pristine form of vegetable oil without any modification. These two biomasses are covalently linked through esterification in the presence of carbodiimide to prepare a graft copolymer, lignin-*graft*-castor oil. The synthesized series of copolymers showed a range of melting temperatures (57~71 ^{o}C) and glass transition temperatures (39~60 ^{o}C) that enable thermal processing. The mechanical properties can be controlled by changing the crosslinking density and the mass ratio of lignin and castor oil. The copolymer's highest modulus is 228.43 MPa, which is 40% higher than that of commercial low-density polyethylene (LDPE). Furthermore, its physical properties, including density and water contact angle are precisely controllable by the mol % of the capping agent and the mass ratio of capped lignin and castor oil. The lowest and highest densities were 0.96 g/mL and 1.14 g/mL, respectively; the lowest and highest contact angle of the water were 70.5^{o} and 92.9^{o}, respectively. The synthesized fully biomass-based polymer, lignin-*graft*-castor oil, can be an true solution of plastic waste issue, because of their 100% biomass resource with minimal chemical modification to form ester linkage which is readily degradable in natural conditions. In addition, precisely and easily controllable properties offer customized applications in various fields.

Introduction

Biomass-based biodegradable polymer has been gaining high interest as an alternative to petroleum-based non-degradable plastic for the last decade.[1] Because biomass-based biodegradable polymer is a renewable resource leading to sustainable production, reducing the carbon footprint and greenhouse gas emission.[2,3] In addition, environmental pollution caused by non-degradable plastic waste, such as garbage patches in the ocean and microplastics, has a growing impact on our life and ecosystem.[4,5] It is important to know that not all biomass-based polymers are biodegradable.[1] Biodegradability of a polymer is related to the chemical and physical structure, not to the origin of the raw material. Thus, chemical modification or additive could influence on the biodegradability. Examples of biomass-based and non-biodegradable polymers are bio polyethylene (Bio-PE), bio polyethylene terephthalate (Bio-PET), bio trimethylene terephthalate (Bio-PTT), bio polypropylene (Bio-PP), and bio polyamides (Bio-PA).[6] The best solution of petroleum-based non-degradable plastic issue is biomass-based and biodegradable polymers.

Vegetable oils has been studied as a sustainable alternative raw material to petroleum in order to prepare a biomass-based polymer. Chemical structures of vegetable oils contain fatty acids with chain lengths from 12 to 22 carbon atoms and up to three double bonds.[7] Fatty acids are naturally occurring and may be chemically modified to have readily hydrolyzable ester bonds.[8–11] The vegetable oil can be an excellent raw material for sustainable polymers due to its biomass origin, degradability, and chemical availability for further modifications.[12] Among the vegetable oils, castor oil has been used to prepare several biomass-based biodegradable polymers.[13,14] Castor oils have triacylglycerol that consists of various fatty acids and glycerol (Figure 1a). More than 90 % of the fatty acids is ricinoleic acid (12-hydroxy-9-*cis*-octadecenoic acid) in the castor oil.[14]

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Electronic Supplementary Information (ESI) available: FT-IR of lignin-graft castor oil (FigS1), PXRD of lignin-graft-castor oil (Figure S2), and additional mechanical properties test (Figure S3). See DOI: 10.1039/x0xx00000x

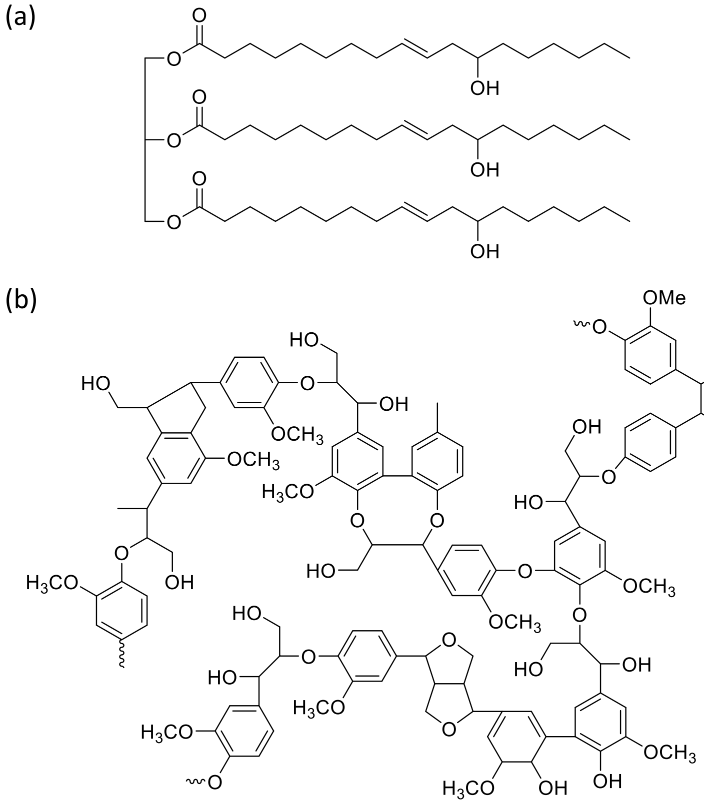


Figure 1. Chemical structures of (a) castor oil and (b) lignin.

Especially, castor oil's hydroxyl group is very useful for further chemical modification (Figure 1a).[15] Other characteristics of castor oil, like high lubricity, high viscosity over a wide range of temperatures, insolubility in aliphatic petrochemical fuels and solvents, and high content of ricinoleic acid make its versatile application possibilities of castor oil in the chemical industry.[16] Castor oil is not a human food. The main application is a lubricant for machinery equipment operating under extreme conditions. For instance, castor oil has already been used as a ancient lubricant in carts and Persian wheels for a long time.[17] Castor oil's other applications includes base oil formulations for lubricants, functional fluids, process oils, feedstock for fuels, reactive components for paints, coatings, inks, polymers, and foams.[17–19]

Lignin is the second most abundant biopolymer found within the cell wall of terrestrial plants.[20] In its native form, lignin has a branched heterogeneous 3D network structure.[21] The structure contains up to three types of aromatic alcohol monomers, termed sinapyl alcohol, coniferyl alcohol, and p-coumaryl alcohol. These monomers are connected by different chemical linkages arising from free radical coupling during biosynthesis.[21] The lignin chemical structure is unable to be precisely defined in a traditional way due to its complexity, and it contains various functional groups, including methoxy groups, phenolic hydroxyl groups, aliphatic hydroxyl groups, and other carbonyl groups.[22]

The abundant amount of hydroxyl groups in lignin offers a chemical modification to control the physical, chemical, and thermal properties of lignin. Esterification, a prototypical derivatization technique for bio-polymers, is an important technology that is applied to biobased materials to make them processable and valuable.[23] Through the esterification method, the modified lignin was used for analysis, as well as the preparation for useful thermoplastic and thermoset polymeric materials.[24] A commonly esterification method is Steglich esterification reacting carboxylic acid compounds with alcohol in the presence of carbodiimide compounds. This approach allows reagents such as short-chain organic acids or long-chain fatty acids that can be derived from biomass (e.g., crops).

A large number of reactive functional groups in lignin lead uncontrolled crosslinking. A crosslinking is a linkage between polymer chains through chemical or physical interaction of a crosslinker that has two or more functional groups.[25] Crosslinking affects properties of the polymer, such as thermal properties. Most of the lignin-based polymers show thermoset behavior due to uncontrolled high density of crosslinking. To solve this problem, our group recently reported a highly efficient crosslinking control method using acetic acid as a capping agent. The capping agent is a functional molecule that reacts with the excess hydroxyl groups of lignin to block (inactivate) the unwanted reactive site. A typical example of the capping agent is acetic acid. Crosslinking degree of lignin-based polymer, lignin-graft-poly(ethylene glycol) (PEG), can be controlled by introducing a capping agent, which was confirmed by precise control of glass transition temperature (T_g) and melting temperature (T_m). The higher amount of capping agent yields a lower crosslinking degree with lower T_m and T_g of lignin copolymer. [26,27]

Polyester is a well-known biodegradable polymer, and therefore it is an environmentally friendly material. Ester bonds can be degradable through hydrolyzed under physiological conditions to break down into smaller fragments.[28] Furthermore, microorganisms such as algae, bacteria, and fungi can break down ester bonds through enzyme (e.g., esterase) mediated processes.[29] Recently, a lignin-based biodegradable polyester, sebacic acid-modified lignin-graft-poly(ethylene brassylate) (PEB) has been reported.[30] The castor oil is a raw materials to derive PEB' monomer, ethylene brassylate. The new polymer, lignin-graft-PEB showed many refine features including biomass-based, degradable ester bonds, controllable mechanical/thermal properties. However, the lignin-graft-PEB uses castor oil-"derived" monomer/polymer which is less sustainable and cost effective due to multistep chemical reaction requirements on PEB part. The best sustainable solution is to use unprocessed castor oil as a raw material (monomer) to directly synthesize biodegradable polymers without multistep reactions.

In 2021, Jedrzejczyk *et al.* reported a biolubricant that is composed of palmitoylated lignin and castor oil.[31] The palmitic acid is a long aliphatic carboxylic acid (Hexadecanoic acid, $CH_3(CH_2)_{14}COOH$). The biolubricant is a mixture of palmitoylated lignin and castor oil without covalent bonding between two components. The palmitoylated lignin showed high dispersity in castor oil because of enhanced lipophilicity. In this study, the lignin blend showed the possibility of replacing petroleum-based lubricant. There are several lignin blends are reported with castor oils. They are epoxide lignin/castor oil,[32] epoxidized kraft lignin/castor oil,[33] lignin/castor oil based polyurethane,[34] and sodium lignosulfonate/castor oil[35]. However, lignin-castor oil copolymer that has covalent links between lignin and castor oil is very rare in literature.

This work reports a new 100% biomass-based polyester, lignin-graft-castor oil that has unprocessed pristine castor oil. The new polymer has features of precisely controllable crosslinking and degradable ester linkage between lignin and castor oil. In addition, the polymer shows a high young's modulus surpassing that of commercial low-density polyethylene (LDPE) and a good thermal processibility. The overall thermal/mechanical properties can be easily and precisely controllable by the amount of capping agent. The new fully biomass-based lignin-graft-castor oil will be a milestone in scalable and cost-effective production of sustainable polymers because the developed polymerization can be done in very moderate reaction conditions without complex steps. The outcome of the reported study will broadly and strongly impact on solving the non-degradable petroleum-based plastic waste issues.

Experimental

Materials.

All chemicals were purchased from MiliporeSigma Ltd. and TCI America and used without further purification unless otherwise stated. Lignin was purchased from TCI America (Product number L0045, softwood lignin). All organic solvents were degassed with bubbling dry nitrogen gas in the presence of a molecular sieve (pore size 3 Å).

In some cases, the cleavage of DMF into a dimethyl carbamoyl radical can occur during certain reactions.[36] The coupling reaction of DMF weakens the sustainable chemistry aspect. To address this concern, the solvent DMF can be replaced by two biobased aprotic dipolar solvents, Cyrene™ and γ-valerolactone (GVL), which have already been reported as alternatives to DMF.[37]

Instrumentation.

NMR tests were carried out on a Bruker Avance 600 MHz spectrometer. FT-IR spectra were obtained from a PerkinElmer Spectrum 100 FTIR spectrometer in attenuated total reflectance (ATR) mode. The molecular weight of polymers and polydispersity index values were determined on an Agilent-Wyatt combination gel permeation chromatography (GPC) instrument containing three successive Agilent PLgel Mixed C columns, an Agilent 1260 infinity series pump, a degasser, and an autosampler. The Wyatt detection unit hosts the Optilab TrEX refractive index detector. Thermal properties were investigated by TA Instruments Q600 simultaneous thermal analyzer (SDT). The SDT instrument simultaneously measured thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC). Low-temperature thermal properties were investigated by TA Instruments Q1000 with RSC 90 refrigeration cooling accessory. Mechanical properties were measured by a Shimadzu tensile-compression tester (model: EZ-LX) equipped with a force transducer (Interface Ltd. model: SM-200 N-168). The PXRD analysis was performed on Rigaku SmartLab Powder X-Ray Diffractometer.

Synthesis of succinic acid-modified lignin (modified lignin) 3.

Ten grams of lignin and succinic acid/ acetic acid mixture (142 mol, mol/mol= 1/5; 1/3; 1/1; 3/1) were added into 190 mL of DMF and stirred for 15 min until perfectly dissolved. Next, the solution was degassed with dry argon gas for 15 min. Then, N, N'-dicyclohexylcarbodimide (DCC, 14.2 g, 68.8 mmol) and 4-dimethylaminopyridine (DMAP, 2.8 g, 22.9 mmol) were added to the mixture solution and degassed for additional 10 min. The dark brown reaction mixture was stirred at room temperature for 48 h, followed by vacuum filtration to remove formed white solids, dicyclohexyl urea (DCU), which is a byproduct of DCC esterification. The dark solution was precipitated in 1M aqueous HCl solution. The yielded slurry-like solution was vacuum filtered to yield 8.6 g of the desired product as a brown solid after drying in vacuo overnight.

General synthesis of succinic acid-modified lignin-graft-castor oil with mass ratio 1: 1 (lignin-graft-castor oil, CL-C11).

A general synthesis method of lignin graft copolymer has been reported previously.[30,38–41] Three grams of succinic acid-modified lignin were added to 12 mL of DMF. Three grams of castor oil (3.21 mmol) were added to 12 mL of DMF, respectively. The two solutions of succinic acid-modified lignin and castor oil were mixed and degassed for 10 min. DCC (663 mg, 3.21 mmol, 1 equiv.). was added to the reaction mixture solution. Next, DMAP (131 mg, 1.1 mmol, 0.3 equiv.) was added to the reaction mixture and then degassed for 10 min. The reaction mixture was stirred at 80 °C for 48 h and followed by vacuum filtration to remove DCU. The brown solution was precipitated in cold ether, and then the precipitated brown solid was collected by vacuum filtration (4.31 g, 71.8 % yield). The yield was calculated from the total input mass of succinic acid-modified lignin and castor oil.

In this reaction, castor oil is the only option to synthesize a lignin-based polyester using its pristine form because it is the only one vegetable oil that naturally contains a hydroxyl group in its pristine state. However, soybean oil or other vegetable oil can also be utilized to create a lignin-based polyester after modification. For instance, the unsaturated fatty acids present in soybean oil can undergo oxidation, leading to the introduction of hydroxyl groups along the oil chain.[42] These added hydroxyl groups can then react with the carboxylic acid groups present in lignin to form a lignin-based polyester.

General synthesis of succinic acid-modified lignin-graft-castor oil with mass ratio 1: 5 (lignin-graft-castor oil, CL-C15).

A general synthesis method of lignin graft copolymer has been reported previously.[30,38–41] Two grams of succinic acid-modified lignin were added to 18 mL of DMF. Ten grams of castor oil (10.7 mmol) were added to 18 mL of DMF, respectively. The two solutions of succinic acid-modified lignin and castor oil were mixed and degassed for 10 min. DCC (2.2 g, 10.7 mmol, 1 equiv.) and DMAP (436 mg, 3.6 mmol, 0.3 equiv.) were added to the reaction mixture and then degassed for 10 min. The reaction mixture was stirred at 80 °C for 12 h and followed by vacuum filtration to remove DCU and undissolved black chunk particles. This black chunk particles are high density of crosslinking polymer resulting from the huge excess crosslinker, castor oil. The filtered brown solution was precipitated in cold ether and then the precipitated brown solid was collected by vacuum filtration (1.1 g, 9.2 % yield). The yield was calculated from the total input mass of succinic acid-modified lignin and castor oil. Undissolved products accounted for a large proportion, and it was mixed with DCU. Thus, the amount of undissolved parts can't be determined separately. Several experiments have shown similar yields of soluble products.

NMR analysis.

^{1}H, ^{13}C, and the standard Bruker implementations of two-dimensional Heteronuclear single quantum coherence (HSQC) experiments were used for structural characterization. HSQC cross-peaks were assigned by combining the results and were compared with the literature data.[43–47] Acquisition parameters of each spectrum are as follows: 1H- spectra width 20 ppm, size of FID 65536, acquisition time 2.72, FID resolution 0.37, flip angle 30, relaxation delay of 1s, digital resolution 22, spectral resolution 0.18. 13C- spectra width 240 ppm, size of FID 65536, acquisition time 0.90, FID resolution 1.10, flip angle 30, relaxation delay of 2s, digital resolution 21, spectral resolution 0.24. HSQC(F2*F1)- spectra width 13*165 ppm, size of FID 1024*256, acquisition time (0.065*0.0051), FID resolution (15.25*164.53), digital resolution 22, spectral resolution (7.63*24.32)

DMSO-d_6 was used as the NMR solvent to dissolve unmodified lignin, modified lignin, castor oil and lignin-graft-castor oil at room temperature.

Thermal properties.

The melting temperature (T_m), crystallinity temperature (T_c), and the glass transition temperature (T_g) were analyzed by DSC data. Three cycles were adopted for SDT: cycle 1 heated sample to 200 °C with heating rate 10 °C/min; cycle 2 cooled down to room temperature; cycle 3 was heated to 200 °C with heating rate 10 °C/min and heated to 600 °C with heating rate 20 °C/min. Four cycles were adopted for cytogenic DSC: cycle 1 heated sample to 150 °C from -50 °C with heating rate 25 °C/min; cycle 2 cooled down to -50 °C with cooling rate 25 °C/min; cycle 3 was heated to 150 °C with heating rate 15 °C/min; cycle 4 was cooled sample to -50 °C with cooling rate 15 °C/min.

Mechanical properties.

The polymer samples were prepared in a silicon mold to give a uniform rectangular shape. The samples were heated above the melting points on the hotplate and slowly cooled down. The polymer samples were clamped at one end and pulled at a constant rate (1 mm/min) of elongation at the other clamped end. All tests were performed at room temperature. Each measurement was repeated at least three times, yielding an average and standard deviation. Young's modulus was determined from the slope at the initial range of the stress−strain plot following Hookean behavior. For ductile polymers, the Hookean behavior occurs before 1% of strain in general.[48] The measured maximum tensile strength was the maximum stress value of the obtained stress−strain plot. Energy-to-break was determined from the area under the stress−strain plot.[40]

Powder X-ray Diffraction.

The PXRD analysis was performed with a copper anode-type generator (Cu-Ka, λ =0.154 nm, 40 kV, 15 mA) and a D/teX Ultra detector. The diffraction pattern was scanned over the angular range of 5-90 ° (2θ) with a step size of 0.05 at room temperature.

Contact angle measurement.

Contact angle measurements were performed on lignin-graft-castor oil plate. 50 µL of D. I. water was applied to the plate surface, so the according angle between solid and liquid phases could be recorded. All samples were measured 5 times to minimize systematic errors.

Density tests.

The polymer samples were prepared in a silicon mold to give a uniform rectangular shape. The samples were heated above the melting points on the hotplate and slowly cooled down. The length of length, height, and width of prepared polymer sample were determined by digital caliper and the mass of the sample was determined by balance. The density was calculated by the following equation $density = mass/length \times height \times width$.

Results and discussion

Modification of lignin

The first synthesis step is a modification of natural lignin with acetic acid and succinic acid via carbodiimidemediated esterification (N,N'-dicyclohexylcarbodiimide (DCC) / 4-dimethylaminopyridine (DMAP)), as demonstrated in Scheme 1. The acetic acid reduces excessive numbers of hydroxyl groups on lignin via capping with acetyl groups. Generally, too many hydroxyl groups on lignin lead unwanted crosslinking which is a main reason of weaken mechanical/thermal properties and fast aging of the lignin-based polymer. Succinic acids convert hydroxyl groups on lignin to carboxylic acids for further reactions.[26,30] We have prepared four types of capped lignins with different amounts of capping agent for each as shown in Table 1: 59 mol %, 35 mol %, 27 mol %, and 8 mol % of capping agent. The chemoselectivities of each carboxylic acid's esterification location (aliphatic alcohol vs. phenol) are under investigation in a separate study, which will be reported soon.

Previously, it was reported that lignin's number average molecular weight and polydispersity index (M_w/M_n, PDI) were 24,000 g/mol and 2.4 repectively.[30,39,41,49] An average number of hydroxyl groups in a single lignin molecule is 86.[30,39,41,49] The total mole amount of all carboxylic acids ([succinic acid]+[acetic acid]) were three equivalents of mole amount of all hydroxyl groups on lignin (86 per one molecules) during modified the lignin. We used 83 mol%, 75 mol%, 50 mol%, and 25 mol% of the capping agent (acetic acid) to synthesize the capped lignin. Note that, this mole % is input amount of capping agent for the lignin modification. For example, 25 mole % acetic acid condition uses 25 mole % of acetic acid and 75 mole % of succinic acid to modify hydroxyl groups on lignin. Outcome of each capping agent roughly reflected the input amount of capping agents: 59 mol %, 35 mol %, 27 mol %, and 8 mol % as shown in Table 1. The report uses outcome mole % of the capping agent for all discussions.
The ^1H NMR spectra of modified lignins are shown in Figure 2. The ethane protons from succinic acid ($R\text{-}CH_2\underline{\mathbf{CH_2}}\text{-}COOH$, **b1**) are

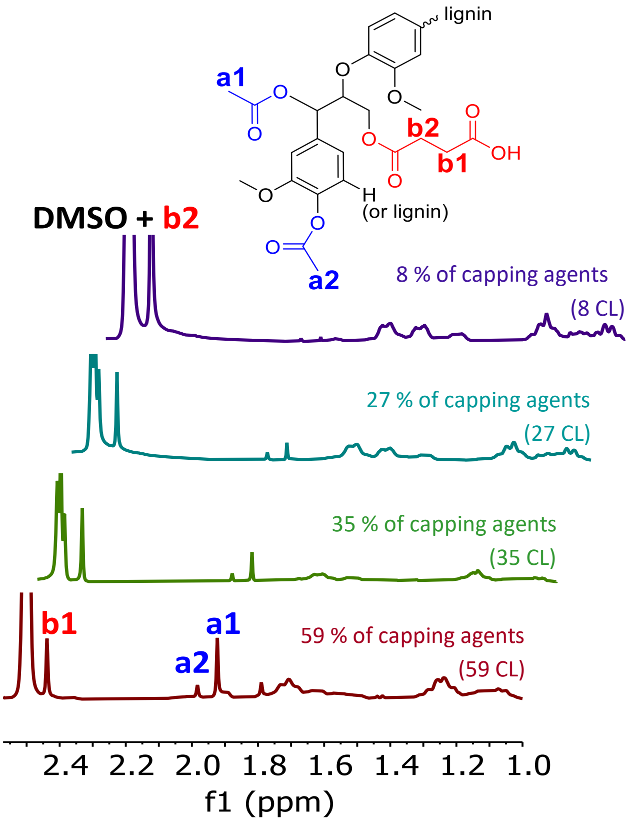
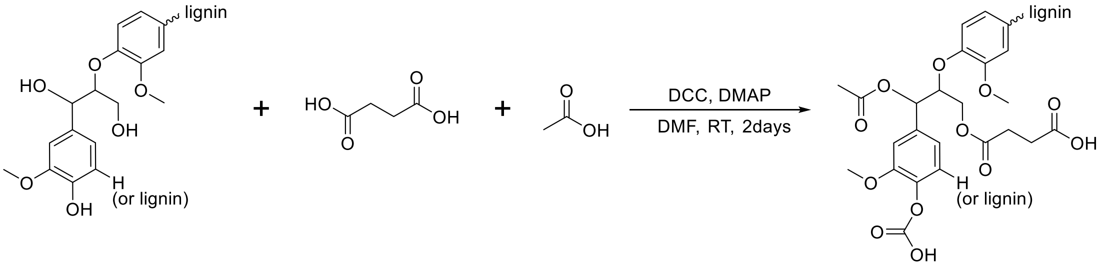
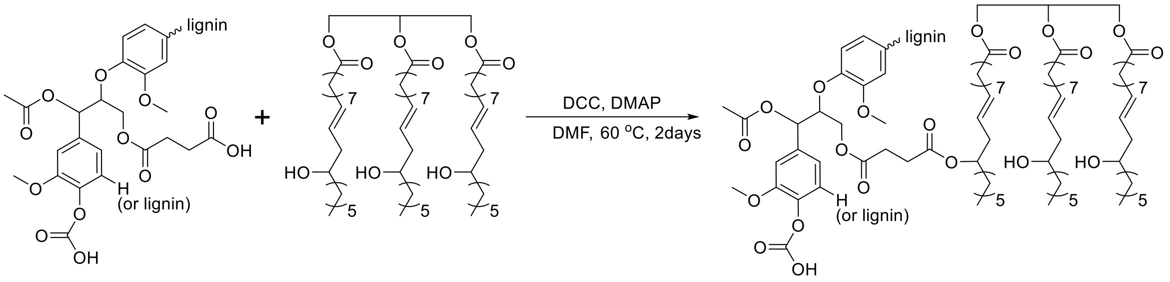


Figure 2. ^1H NMR spectra in d_6-DMSO of capped lignin with different amounts of capping agents.



Scheme 1. Chemical modification of lignin with acetic acid (capping agent) and succinic acid (carboxylic acid terminal on lignin) to prepare capped lignin that is enabled to control crosslinking degree.



Scheme 2. Graft copolymerization of castor oil onto modified lignin.

displayed at 2.43 ppm and the ester bond protons from succinic acid (R-COO-$\underline{\mathbf{CH_2}}CH_2$-COOH, **b2**) are displayed at 2.5 ppm which is partially overlapped with D_6-DMSO. As shown in the Figure 2, the signal from b1 is getting stronger as the carboxylic acid amount increases on the modified lignin (small signal for 59 CL, then large signal for 8 CL). The methyl protons from acetic acid are displayed at the two different chemical shifts depending on their reaction site. The peak for acetyl proton, a1, is located at 1.92 ppm and the peak for acetyl proton, a2, is located at 1.98 ppm. The acetyl signal (a1 and a2) becomes strong as the acetic acid is used more (strong in 59 CL then weak in 8 CL). These two opposite trends of acetyl and carboxylic acid supports that capping of unwanted hydroxyl group on lignin has occurred successfully with precise control rate. The reacted mole ratios of capping agents are 8 %, 27 %, 35 %, and 59 %. The modification rates were calculated by the integration ratio of peak b1 with peak a1 + peak a2.

Graft copolymerization of castor oil onto modified lignin.

Hydroxyl groups on castor oil were reacted with carboxylic acids on lignin via carbodiimide-mediated esterification (DCC / DMAP), as demonstrated in Scheme 2. In this graft copolymerization, we used four different types of capped lignin, 8 %, 27 %, 35 %, and 59% from the previous lignin modification step. Another experimental condition is two different weight ratios of lignin and castor oil, 1 to 1 and 1 to 5 (lignin : castor oil = 1 : 1 and 1 : 5).

The synthesized lignin-graft-castor oils are named "**X**CL-C**Y**", where X= mole % of capping agent; Y= mass ratio of lignin to castor oil. For example, 8CL-C15 indicates a copolymer of lignin which capped 8 mol% and castor oil with a 1:5 (capped lignin: castor oil) weight ratio. The molecular weight of castor oil is 927 g/mol, and this is relatively small molecular weight of many commercial polymers. Thus, we have defined that the prepared lignin-graft-castor oil is a graft copolymer. The graft copolymers exhibit a controllable and diverse degree of crosslinking due to the control of the ratio of active groups to protecting groups. The slightly crosslinked lignin-graft-castor oil behaves like a linear graft polymer and remains soluble in organic solvents such as DMF and DMSO. In contrast, as stated in the experimental section, highly crosslinked lignin-graft-castor oil with a large amount of castor oil (CL-C15s) also forms insoluble gels, creating a dense network structure.

The synthesized lignin-graft-castor oil was characterized by ^{1}H NMR spectroscopy and HSQC 2D NMR. Figure 3 shows ^{1}H NMR spectra of capped lignin, castor oil, and lignin-graft-castor oil (35CL-C11). In Figure 3a, the ethane protons from succinic acid (R-CH$_2$$\underline{\mathbf{CH_2}}$-COOH, **b1**) are displayed at 2.43 ppm. Hydroxyl protons of castor oil (proton '20' in the chemical structure) were observed at 4.36 ppm in Figure 3b. After graft copolymerization, signals of 'b1' were changed to 2.5ppm due to the newly formed ester bond. This new b1 signal is overlapped with d_6-DMSO and 'b2'. This signal overlapping is a serious huddle for accurate analysis of product. Therefore, we analyzed the sample with HSQC 2D NMR in the following section. The peak attributed to proton '20' almost disappeared, as hydroxyl groups of castor oil was consumed by esterification with carboxylic acid of the succinic acid terminal as shown in Figure 3c.

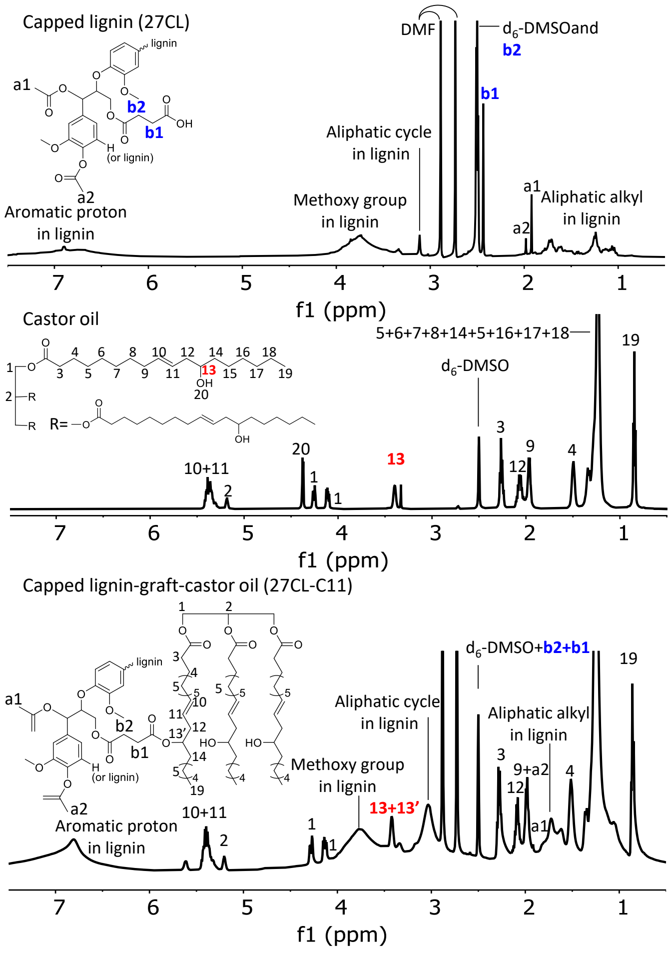


Figure 3. ^{1}H NMR of (a) capped lignin (35CL), (b) castor oil, and (c) lignin-graft-castor oil (35CL-C11)

For a more detailed investigation, we analyzed samples with HSQC 2D NMR, as shown in Figure 4. Figure 4a, b, and c show HSQC spectra of capped lignin (35CL), castor oil, and lignin-graft-castor oil (35CL-C11), respectively. In Figure 4a, the signal from ethane protons of succinic acid (R-CH_2<u>**CH_2**</u>-COOH, **b1**) is displayed at δ_C/δ_H 29.03/2.43 and the signal from ester bond protons of succinic acid (R-COO-<u>**CH_2**</u>CH_2-COOH, **b2**) is displayed at δ_C/δ_H 34.52/2.50. The signal at δ_C/δ_H 69.98/3.40 in Figure 4b is attributed to castor oil's proton '13' (-RCHR-OH). After copolymerization, the signal corresponding to proton' **b1**' was shifted to δ_C/δ_H 28.88/2.50 and the signal of ester bond protons from castor oil (R-COO-<u>**CH**</u>-R, **13'**) was observed at δ_C/δ_H 65.15/3.37 in a yellow highlighted circle. The signal from newly formed ester link that is in yellow highlighted circle is the most significant spectrometric evidence of covalent linkage between lignin and castor oil. Also, the newly formed ester bonds are also confirmed by FT-IR spectrum. The peak of newly formed ester bonds is displayed at 1565 cm^{-1} (Figure S1 in Supporting information)

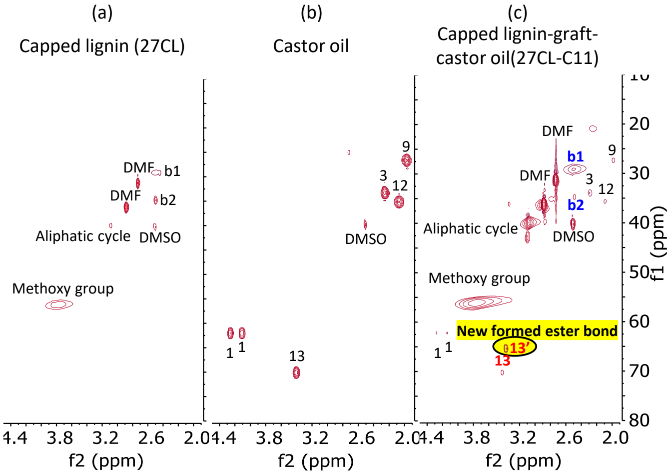


Figure 4. HSQC of (a) capped lignin (35CL), (b) castor oil, and (c) capped lignin-graft-castor oil (35CL-C11), the signal of new synthesized ester bond protons from castor oil (R-COO-<u>**CH**</u>-R, **13'**) was observed at δ_C/δ_H 65.15/3.37 in a yellow circle.

Thermal properties of lignin-graft-castor oil.

Thermal property studies of the synthesized lignin-graft-castor oil were conducted by a differential scanning calorimeter (DSC). All characterization were performed after purification to remove unreacted castor oil and small molecule reagents. We focused on understanding the crosslinking density effect of lignin-graft-castor oil on thermal properties, including T_g and T_m. The reported DSC data (Figure 5) was collected on the 2nd heating cycle. The presence of melting temperature in 2nd heating cycle provides that the lignin-graft-castor oil is a thermoplastic polymer and can be processed multiple times.

As shown in Figure 5a, the T_g of CL-C11s (entries 1-4 in Table 1) is increased progressively from its low crosslinking degree (59CL-C11, entry 1 in Table 1) to the higher crosslinking degree (8CL-C11, entry 4 in Table 1). The T_g of the 59CL-C11 (entry 1 in Table 1) is 49.5 °C which is the lowest value. The T_g increased to 51.8 °C (35CL-C11, entry 2 in Table 1) and 54.6 °C (27CL-C11, entry 3 in Table 1) with the higher crosslinking density on lignin-graft-castor oil. The highest T_g is 59.6 °C from 8CL-C11 (entry 4 in Table 1). This polymer has the highest crosslinking density among all copolymers. This trend explains that the high crosslinking density reduces the mobility of the polymer chains, which result in high thermal properties.[48]

In Figure 5a, T_m of CL-C11 is not observed. This phenomena is related to a crystallinity of copolymers. The lignin-graft-castor oil has crystalline region (long aliphatic alkyl chain on castor oil) and amorphous region (lignin). Because of the small amount of castor oil, CL-C11s showed amorphous properties, which is indicated in the PXRD data (Figure S2 black line). On the other hand, CL-C15s show higher crystallinity due to a larger amount of castor oil (Figure S2 red line), T_m of CL-C15s can be observed in Figure 5b.

According to Figure 5b, a higher crosslinking density of CL-C15s (entries 5-8 in Table 1) leads to a higher T_m. The T_m of the 59CL-2P11 (entry 5 in Table 1), which has the lowest crosslinking

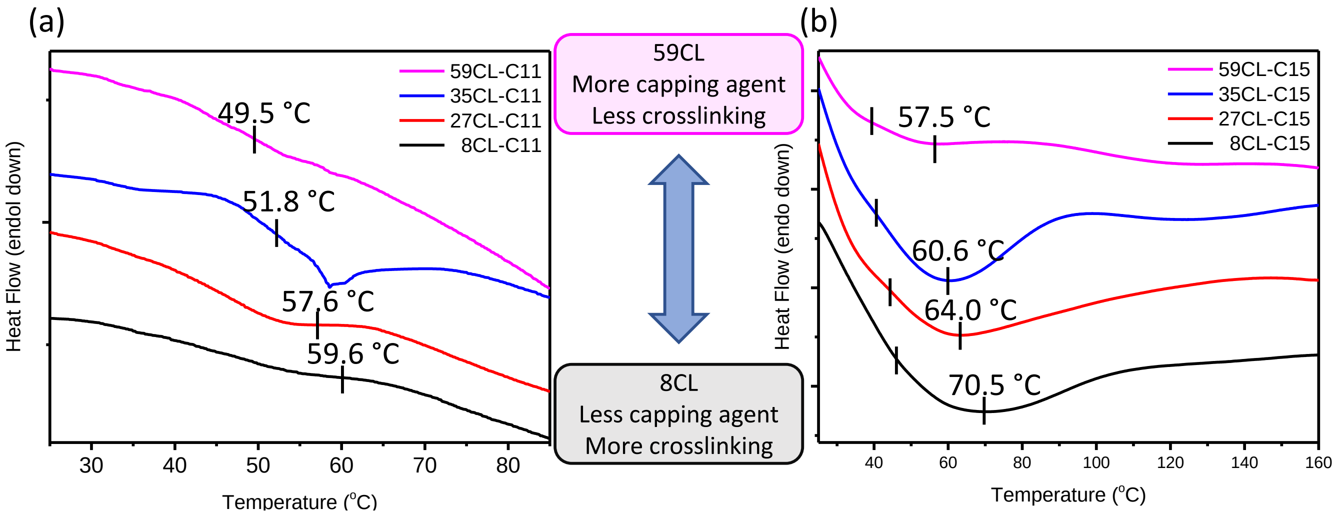


Figure 5. (a) DSC curves of CL-C11s (entries 1-4 in Table 1), (b) DSC curves of CL-C15s (entries 5-8 in Table 1).

Table 1. Thermal properties of lignin-graft-castor oil

Entry	Mass ratio (lignin: castor oil)	Mol % of capping agent [a]	Sample code [b]	T_m (°C)	T_g (°C)
1	1:1 (CL-C11)	59 % (low crosslinking)	59CL-C11	N/D[c]	49.5
2		35 %	35CL-C11	N/D	51.8
3		27 %	27CL-C11	N/D	57.6
4		8 % (high crosslinking)	8CL-C11	N/D	59.6
5	1:5 (CL-C15)	59 % (low crosslinking)	59CL-C15	57.5	39.8
6		35 %	35CL-C15	60.6	42.0
7		27 %	27CL-C15	64.0	42.8
8		8 % (high crosslinking)	8CL-C15	70.5	45.1

[a] Acetic acid was used as a capping agent. [b] XCL-CY, where X= mole % of capping agent; Y= mass ratio of capped lignin with castor oil (8CL-C11 (entry 1 in Table 1) indicates a copolymer of capped lignin which capped 8 mol% and castor oil with a 1:5 weight ratio. c) Not detected

density among the four samples, is 57.5 °C. The T_m increased to 60.6 °C for 35CL- C15 (entry 6 in Table 1), 64.0 °C for 27CL- C15 (entry 7 in Table 1), and 70.5 °C for 8CL-C15 (entry 8 in Table 1), with higher crosslinking density. The higher crosslinking between copolymers reduces the free volume and lead the higher T_m of lignin-graft-castor oil.

The T_g of CL-C15s followed the same trend as that of CL-C11s, which have higher T_g with higher crosslinking density (Figure 5b). The T_g of CL-C15 with the smallest crosslinking density (59CL-C15) is 43.0 °C. The 35CL-C15, 27CL-C15, and 8CL-C15 showed increased T_g with the higher crosslinking density on lignin-graft-castor oil to 47.1 °C, 48.2 °C, and 51.5 °C, respectively.

Mechanical properties of lignin-graft-castor oil

Figure 6a-c show the images of tested polymer samples: 35CL-C11 (entry 2 in Table 1), 27CL-C11 (entry 3 in Table 1), and 8CL-C11 (entry 4 in Table 1). The 59CL-C11 (entry 1 in Table 1) was too brittle to form a stable solid shape for the mechanical property test due to too little amount of castor oil. All prepare samples were tested by a static tensile test to obtain stress-strain curves as shown in Figure 6d.

Figure 6d shows the stress-strain curves of CL-C11s to demonstrate the effect of crosslinking density. 27CL-C11 (Figure 6d red line, entry 2 in Table 2) demonstrated overall superior mechanical properties to 35CL-C11 (Figure 6d black line, entry 1 in Table 2) and 8CL-C11 (Figure 6d blue line, entry 3 in Table 2). The Young's modulus, calculated from the initial linear elastic part of the stress-strain curves, is 228.43 ± 13.67 MPa, maximum tensile strength is 1.71 ± 0.09 MPa, and energy to break is 0.023 ± 0.006 MPa. However, 35CL-C11, which has lower crosslinking density, shows lessened mechanical properties. Young's modulus is 164.56 ± 13.10 MPa, maximum

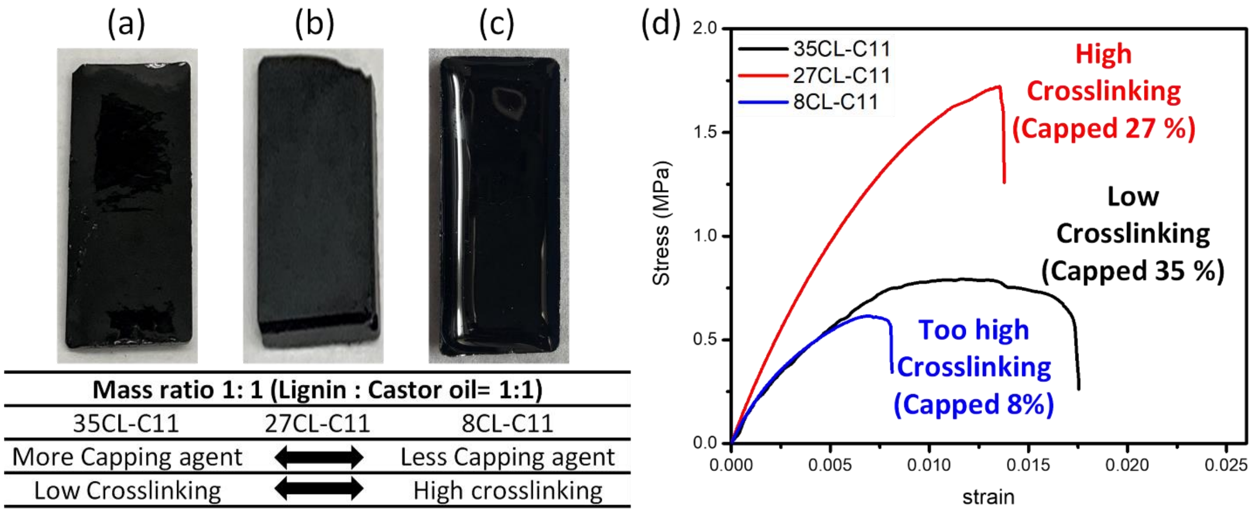


Figure 6. Images of (a) 35CL-C11 (entry 2 in Table 1), (b) 27CL-C11 (entry 3 in Table 1), (c) 8CL-C11 (entry 4 in Table 1), (d) Strain-stress curves of CL-C11s (entries 1-3 in Table 1); The plot shows a single experiment and not an average value. Table 2 includes average values of the test.

Table 2. Mechanical properties of lignin-graft-castor oil

Entry	Sample Code [a)]	Young's modulus (MPa)	Max. tensile strength (MPa)	Strain at break (L/ΔL, no unit)	Energy to break (MPa)
1	35CL-C11	164.6±13.1	0.79±0.01	0.021±0.003	0.013±0.002
2	27CL-C11	228.4±13.7	1.71±0.09	0.020±0.005	0.023±0.006
3	8CL-C11	212.5±19.5	0.66±0.10	0.009±0.001	0.005±0.001
4	35CL-C15	123.4±14.1	0.55±0.01	0.160±0.075	0.049±0.015
5	27CL-C15	147.8±16.0	0.65±0.07	0.210±0.035	0.088±0.054
6	8CL-C15	50.0±6.0	0.46±0.12	0.027±0.003	0.008±0.002

a) XCL-CY, where X= mole % of capping agent; Y= mass ratio of capped lignin with castor oil, Standard derivations are in parenthesis.

tensile strength is 0.79 ± 0.01 MPa, and energy to break is 0.013 ± 0.002 MPa. Mechanical strength, stiffness, and toughness of lignin-graft-castor oil are improved by higher crosslinking density.

Although the 8CL-C11 has the highest crosslinking density, it shows diminishing mechanical properties due to the overly crosslinking. The overly crosslinked polymer caused the unbalanced distribution of crosslinking points in the copolymer, which hindered normal movements of copolymer chains.[50–53] During the tensile process, stress is focused on the overly crosslinking region, which eventually results in catastrophic decreasing of overall mechanical properties, including Young's modulus, maximum tensile strength, strain at break, and energy to break.

The effect of grafting density on mechanical properties are also studied (Figure S3 in Supporting information). The 27CL-C11 (lower grafting density) showed higher young's modulus and higher maximum tensile strength and the 27CL-C15 (higher grafting density) showed higher strain. The mechanical properties of all CL-C11s and CL-C15 s are summarized in Table 2.

For comparison, previously reported lignin-graft-poly (caprolactone) showed the Young's modulus of 24.6 MPa[54] and a tensile strength of 1.22 MPa.[55] The new synthesized lignin-graft-castor oil showed overall superior mechanical properties than lignin-graft-poly(caprolactone). Although the maximum tensile strength of newly synthesized lignin-graft-castor oil was lower than previous reported lignin-graft-PEB[30], the maximum tensile strength could be greatly improved by allowing a small amount of reinforcing agent (1 wt % or less).[56]

Density and surface hydrophilicity of lignin-graft-castor oil

Figure 7a and b show CL-C11 an d CL-C15 samples in D. I. water containing vials. Figure 7a shows the CL-C11 samples submerged on the bottom of D. I. water containing vial, while Figure 7b shows CL-C15 samples floated on the surface of D. I. water. According to literature, the pure castor oil's density is 0.959 g/mL, and the lignin's density is 1.350-1.500 g/mL.[57] Thus, CP-C11s with a higher wt % of lignin exhibit higher densities than 1, whereas CP-C15s with a higher wt % of castor oil exhibit lower densities than 1. All tested polymer samples do not include any voids (air bubbles) in the solid structure.

As shown in Figure 8a, the measured densities of 35CL-C11 (entry 1 in Table 3), 27CL-C11 (entry 2 in Table 3), and 8CL-C11 (entry 3 in Table 3) are 1.138, 1.142, and 1.139 g/mL, respectively. In the CL-C11 series (35CL-C11, 27CL-C11, and 8CL-C11), the number of castor oil molecules is smaller than the number of reaction sites on modified lignin. Thus, the numbers

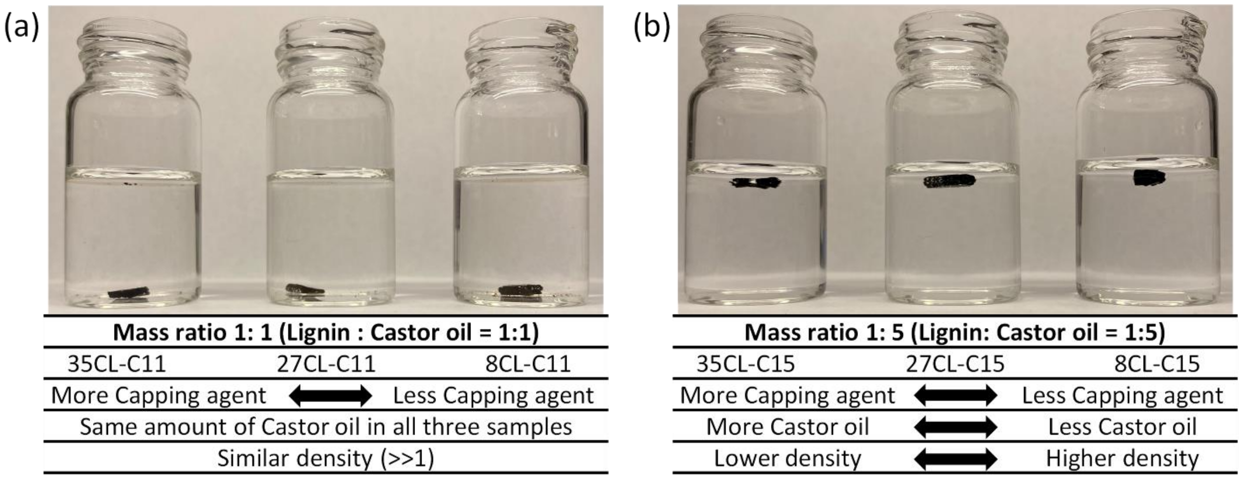


Figure 7. Images of (a) CL-C11 (entries 1-3 in Table 3) samples in D. I. water, and (b) CL-C15 (entries 4-6 in Table 3) samples in D. I. water

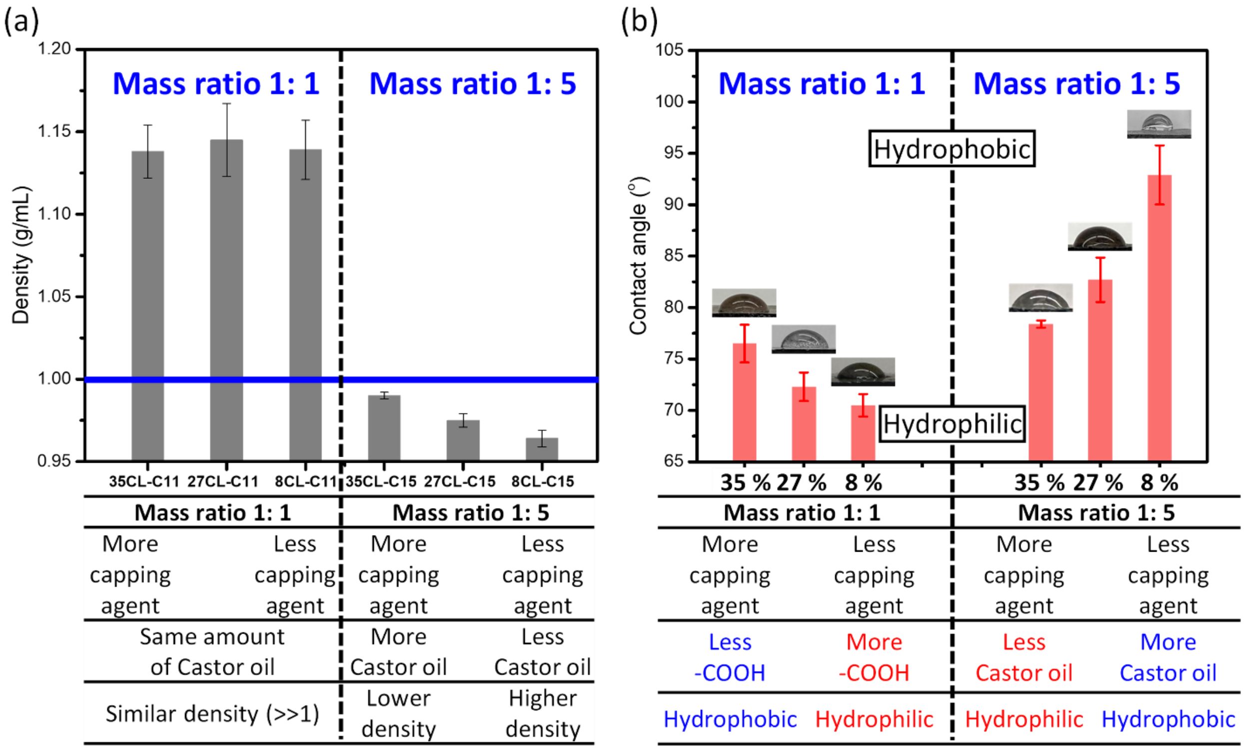


Figure 8. (a) Densities of lignin-graft-castor oil and (b) Contact angle of lignin-graft-castor oil

of castor oil molecules are the same within all CL-C11 series (35CL-C11, 27CL-C11, and 8CL-C11). The similar amount of castor oil led to the same densities of copolymers.

However, densities of CL-C15s (35CL-C15, 27CL-C15, and 8CL-C15) are reduced as the amount of capping agent decreases in modified lignins. In the CL-C15 series (35CL-C15, 27CL-C15, and 8CL-C15), the number of castor oil molecule is much larger than the number of rection sites. Hence, the amounts of reacted castor oil on CL-C15 series (35CL-C15, 27CL-C15, and 8CL-C15) are determined by the amount of capping agent of capped lignin (i.e., large capping agent amount → low amount of available COOH sites on modified lignin → low amount of castor oil on lignin-graft-castor oil). As a result, higher amount of capping agent in capped lignin showed lower densities of copolymers.

To investigate the hydrophilicity of copolymer, the water contact angle on the surfaces of lignin-graft-castor oil was measured, as shown in Figure 8b. The contact angle of 35CL-C11 (entry 1 in Table 3), 27CL-C11 (entry 2 in Table 3), and 8CL-C11 (end entry 3 in Table 3) are 76.5 ° (low hydrophilicity), 72.3 °, and 70.5 ° (high hydrophilicity), respectively. Higher hydrophilicity of lignin-graft-castor oil with higher capping agent is because of increase in surface hydrophilicity resulting

Table 3. Densities and contact angle of capped lignin-graft-castor oil

Entry	Sample Code	Grafting density	Capping agent	Castor oil	Density (g/mL)	Contact angle (°)
1	35CL-C11	Low grafting density	More capping agent ↕	Same amount of castor oil in all three samples	1.138±0.016	76.5±1.84
2	27CL-C11				1.142±0.022	72.3±1.39
3	8CL-C11		Less capping agent		1.139±0.018	70.5±1.10
4	35CL-C15	High grafting density	More capping agent ↕	Less castor oil ↕	0.990±0.002	78.4±0.36
5	27CL-C15				0.975±0.004	82.7±2.16
6	8CL-C15		Less capping agent	More castor oil	0.964±0.005	92.9±2.87

from an increase in carboxylic acid concentration on lignin. Note that the use of large capping agent amount (e.g., 35CL-C11) leads low carboxylic acid amount on a modified lignin and lignin-graft-castor oil molecule. Hence, the use of more capping agent decreases the polarity (low carboxylic acid amount) on lignin-graft-castor oil polymer surface, resulting in a larger contact angle (low hydrophilicity on surface).[7]

On the other hand, the contact angle of CP-C15s (entries 4-6 in Table 3) shows completely opposite trend. Because all carboxylic acids on modified lignin are completely consumed by excess castor oil (lignin:castor oil = 1:5), the main control factor of hydrophilicity is the amount of castor oil in lignin-graft-castor oil. Note that "vegetable oil" has a hydrophobic nature (not miscible to water). Low capping agent condition (8CL-C15) has low hydrophilicity (high contact angel, 92.9 ^{o}) due to larger amount of castor oil in lignin-graft-castor oil. On the other way, high capping agent condition (35CL-C15) has high hydrophilicity (low contact angel, 78.4 ^{o}) due to smaller amount of castor oil in lignin-graft-castor oil.

The last trend of surface hydrophilicity is overall comparison between C15 series and C11 series (lignin:castor oil = 1:5 vs. lignin:castor oil = 1:1). CL-C15s show overall higher contact angle than CL-C11s because of the higher amount of castor oil in lignin-graft-castor oil.

Conclusions

In this report, we successfully synthesized a 100% biomass-based degradable polymer, lignin-graft-castor oil. The new sustainable polymer shows excellent and precisely controllable thermal / mechanical properties, density, and surface hydrophilicity. The new polymer is composed of two biomass, lignin and castor oil, and these two biomasses were covalently linked via ester bonds. All products, natural lignin, castor oil, modified lignin, and lignin-graft-castor oil, were precisely characterized by ^{1}H NMR, ^{13}C NMR, HSQC 2D-NMR, and FT-IR spectroscopy to determine synthesized chemical structures. The lignin-graft-castor oil is a thermoplastic polymer that can be recycled multiple times for a sustainable economy. The thermal property studies showed a clear trend with precise controllability in T_g and T_m via crosslinking conditions depending on amount of capping agent. The lignin-graft-castor oil has comparable mechanical properties to a commercial LDPE. The highest modulus is 228.43 MPa, which is higher than that of LDPE. The new polymer showed controllable mechanical properties by changing the crosslinking density and the mass ratio of lignin and castor oil. Furthermore, density and contact angle of water showed highly controllable properties via mol% of a capping agent and wt% of castor oil. The new polymer, lignin-graft-castor oil, is a promising new sustainable and degradable polymer that can replace petroleum-based polymers in broad applications.

Conflicts of interest

There are no conflicts to declare

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