Recyclable and Flexible Polyester Thermosets Derived from Microwave-Processed Lignin

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ABSTRACT: Commercial Kraft lignin was successfully valorized into recyclable and flexible polyester thermosets. Kraft lignin was first processed into more well-defined lignin fractions via liquid–solid extraction in green solvents (methanol and ethanol) or microwave-processed in ethanol at different temperatures (80 and 160 °C). The lignin fractions were then cross-linked in one pot with PEG and citric acid into polyester thermosets. In comparison to the thermoset synthesized from the original Kraft lignin, the thermosets synthesized from all the ethanol-extracted fractions were more homogenous and flexible as reflected by a sharper α-transition and over 100% increase in elongation at break. Furthermore, recycling of two of the prepared thermosets was evaluated (i.e., the thermoset prepared from the original lignin and the one prepared from microwave-processed lignin). Both materials could be rapidly recycled back into liquid resins under microwave hydrolysis and recured into thermosets under the original curing conditions. However, good quality films and comparable mechanical properties were only obtained after recurring the recycled resin originally synthesized from the microwave-processed lignin. Microwave processing compared to liquid–solid extraction paved the way for higher yields of narrow dispersity lignin fractions and matching final properties, providing an attractive approach to recyclable flexible lignin thermosets.

KEYWORDS: lignin, thermoset, polyester, microwave, recycling, closed-loop

INTRODUCTION

Lignin, as the most abundant terrestrial aromatic polymer, accounts for 30% of nonfossil organic carbon on Earth. Currently, approximately 70 million tons of technical lignin are produced from the pulp and paper industry, and this material is mainly utilized as low-cost fuel to provide energy for the pulping process. One promising route to valorize technical lignin is taking advantage of lignin’s inherent multifunctionality and its aromatic backbone structure for utilization as a rigid building block candidate to develop thermoset materials (e.g., epoxy, phenolic and polyester thermosets). For the development of lignin thermoset materials, the first step involves selection of suitable lignin because lignin from different pulp processes varies largely in chemical composition, functional group type and content, molecular weight distribution, and solubility. The Kraft lignin has the largest production volume because the Kraft pulping process accounts for 90% of pulp production. Therefore, the Kraft lignin has commonly been chosen as the starting material to develop different classes of thermoset materials. However, the Kraft lignin has a heterogeneous structure, which often results in poor compatibility with other building blocks and limits the development of homogenous materials with reproducible properties. To overcome these issues, a prefractionation of lignin (e.g., by solvent extraction) is commonly utilized to achieve more well-defined fractions with a narrow molecular weight distribution. Depending on solvent selection, lignin with different molecular weights and chemical functionalities could be selectively extracted. However, the yield of each solvent extraction is limited by the lignin solubility in the particular solvent.

The difficulty of recycling thermoset materials with an inherent covalently cross-linked network is well known. One promising solution is to develop degradable thermosets cured by labile bonds, such as ester bonds, disulfides, Schiff bases, and nitrobenzene moieties. Among these labile bonds, the most utilized and economic is the ester bond. Ester bond susceptibility to hydrolysis, especially under basic condition, allows them to be depolymerized into original monomers or other functional intermediates suitable for repolymerization. The possibility to rapidly and efficiently

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hydrolyze ester bonds in thermosets is a highly attractive strategy for recycling cross-linked polyesters. Microwave-assisted degradation has been shown to be an effective tool to valorize common polymers and biopolymers, such as starch, cellulose, polyethylene, and aliphatic polyester thermoplastics, into monomers or other functional building blocks. Microwave-assisted degradation imparts a significantly higher hydrolysis rate compared to conventional heating processes. For example, 35% of poly(ethylene terephthalate) can be degraded back to its original monomers by microwave heating while only 6% monomers were formed during conventional heating under the same conditions. Considering the similar ester functionality, the microwave process also has the potential to be an effective approach for recycling polyester thermosets.

Recently, we have developed lignin polyester thermosets with tunable properties through simply modulating the feed ratio of original Kraft lignin as a building block. Our group also developed a combined microwave-assisted extraction/degradation process for producing high yields of narrow-dispersity lignin fractions with low molecular weight. For example, the reaction process for producing high yields of narrow-dispersity ratio of original Kraft lignin as a building block. Our group also developed a combined microwave-assisted extraction/degradation has been shown to be an effective tool for valorizing common polymers and biopolymers, such as starch, cellulose, polyethylene, and aliphatic polyester thermoplastics, into monomers or other functional building blocks. Microwave-assisted degradation imparts a significantly higher hydrolysis rate compared to conventional heating processes. For example, 35% of poly(ethylene terephthalate) can be degraded back to its original monomers by microwave heating while only 6% monomers were formed during conventional heating under the same conditions. Considering the similar ester functionality, the microwave process also has the potential to be an effective approach for recycling polyester thermosets. Microwave-assisted degradation has been shown to be an effective tool to valorize common polymers and biopolymers, such as starch, cellulose, polyethylene, and aliphatic polyester thermoplastics, into monomers or other functional building blocks. Microwave-assisted degradation imparts a significantly higher hydrolysis rate compared to conventional heating processes. For example, 35% of poly(ethylene terephthalate) can be degraded back to its original monomers by microwave heating while only 6% monomers were formed during conventional heating under the same conditions. Considering the similar ester functionality, the microwave process also has the potential to be an effective approach for recycling polyester thermosets. Recently, we have developed lignin polyester thermosets with tunable properties through simply modulating the feed ratio of original Kraft lignin as a building block. Our group also developed a combined microwave-assisted extraction/degradation process for producing high yields of narrow-dispersity lignin fractions with low molecular weight. For example, the liquid—solid extraction with ethanol at room temperature (RT) with one or two extractions typically resulted in a yield of 37–48%. However, the microwave processing (MwP) in ethanol could increase the extraction yield to 64% while the molecular weight and dispersity remained similar. Therefore, it is important to investigate whether the MwP influences the reactivity of the lignin fractions during thermoset synthesis as well as the final material properties and recyclability of the resulting lignin-based thermosets compared to the thermosets produced from the original lignin or lignin fractions from liquid—solid extraction.

### EXPERIMENTAL SECTION

#### Materials.

The studied lignin was a softwood Kraft lignin that had been separated from Kraft black liquor obtained by the Lignoboost process (LB). The molecular weight and dispersity ($M_w$, dispersity = 4.3) of the used LB lignin were determined by dimethyl sulfoxide (DMSO) size exclusion chromatography (SEC) in our previous work. LB was dried in a fume hood at RT overnight prior to use. Methanol (98.5%, VWR), ethanol (96%, VWR), citric acid (≥99.5%, Fluka), 4-(dimethylamino) pyridine (DMAP) (≥99.0%, Fluka), 1,4-dioxane (≥99.9%, VWR), sodium hydroxide (≥99%, Fluka), and poly(ethylene glycol) (average M$_w$ of 400 g/mol, Sigma Aldrich) (PEG400) were all used as received.

#### Preparation of Lignin Samples for Thermoset Synthesis.

Five different lignin samples were utilized to create thermosets. Two lignin samples were prepared through liquid—solid extraction and two by MwP, that is, by a microwave-assisted extraction/degradation process, according to a previously published procedure. For the two MwP samples, 0.5 g of Lignoboost and 20 mL of ethanol were mixed in a Teflon vessel, which was transferred into a microwave oven. The temperature of the microwave oven was set to 80 or 160 °C. This temperature was reached after 20 min of ramping time, and the extraction/degradation process was allowed to proceed isothermally for additional 20 min. For the two liquid—solid extracted samples, 5 g of Lignoboost was dissolved in 200 mL of methanol or ethanol (to achieve the same solid to liquid ratio), and the suspension was stirred at RT for 2 h to dissolve as much lignin as possible. After MwP or liquid—solid extraction, the soluble fraction was collected by removing the solid residue through filtration. The solvent was subsequently allowed to evaporate at RT for 24 h followed by drying the product fractions at 20 °C for 3 days in a vacuum oven to remove the remaining solvent residue.

#### Synthesis of Lignin-based Thermoset Resins.

The four different lignin samples were cured into a polyester thermoset following a previously published procedure. In addition, a fifth thermoset was prepared from the native LB lignin for comparison. Briefly, lignin, PEG, and citric acid were mixed at a 30:30:40 weight ratio equal to 4 g of total products. The product mixture was added to a glass flask along with the DMAP catalyst (1 wt % to the sum of reactants). A minimal amount of 1,4-dioxane to enable a homogenous solution was added (the concentration of the sum of the reactants to solvent was 0.5 g/mL). After 1 h of stirring, the resulting solutions were cast into round aluminum molds (diameter = 70 mm) and left in the fume hood for 24 h to evaporate the solvent. Then, the resins were transferred into a heating oven, and the curing reactions were performed at 110 °C for 48 h to afford the final thermosets with a thickness of approximately 0.1 mm. The thermoset derived from the native LB lignin was denoted as X-LB while X-MFLB and X-EFLB represent the thermosets derived from methanol- and ethanol-extracted lignin, respectively. The thermoset prepared from lignin microwave processed at 80 or 160 °C were denoted as X-EFLB80 and X-EFLB160. The weight loss ratio during the curing process was calculated by the following equation

$$\text{Weight loss ratio} = 1 - \frac{m_f}{m_i} \times 100\%$$

where $m_f$ and $m_i$ represent the sum of the masses of the reactants and the final mass of the thermosets, respectively.

#### Microwave Recycling and Recuring of Recycled Thermosets.

To evaluate the possible chemical recyclability of the lignin-based polyester thermosets, two of the thermosets (X-LB and X-EFLB80) were degraded in a 0.1 mol/L NaOH solution in a microwave oven. The microwave degradation tests were performed by immersing the 0.5 g of the thermosets in 20 mL of a NaOH solution. The temperature was set to 160 °C with a reaction time of 20 min and a ramping time of 20 min. Then, 20 mL of 0.1 M HCl was added to neutralize the pH of the solution, and the water was removed under reduced pressure. The degradation products were collected and weighed. The weight lost during microwave recycling [approximately 30% (w/w)] was compensated by supplying neat reactants of the same initial feed ratio to the mixture. The mixture of recycled and virgin products was dissolved in 10 mL of dioxane, and the sodium chloride from the neutralization step was simultaneously precipitated. The sodium chloride was filtered off, and the solution was transferred into an aluminum mold. The solvent was evaporated overnight in the fume food. Then, the recycled products were cured again according to the procedure described above and denoted as RX-LB and RX-LB-EtOH160.

#### Characterization Techniques.

**Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy.** The PerkinElmer Spectrum 400 FTIR spectrometer (Norwalk, CT) with an attenuated total reflectance (ATR) accessory (gold gate) from Graseby Specac (Kent, United Kingdom) was utilized to confirm the chemical structure of the thermosets. Sixteen scans at a resolution of 4 cm$^{-1}$ were performed.

**Gel Content Test.** The gel content was determined according to a previously reported procedure by extracting rectangular-shaped sample specimens with 1,4-dioxane for 48 h.

**Dynamic Mechanical Thermal Analysis.** TA Instrument Q800 dynamic mechanical analysis in a tension clamp geometry was applied to measure the thermomechanical properties. The samples were cut into pieces that were 40 mm × 5 mm × 0.1 mm. Clamps were attached on both sides of the sample pieces, and the temperature program was run from -50 to 150 °C at 1 Hz with a deflection of 0.1% strain and a 3 °C/min heating rate.

**Tensile Properties.** An Instron 5944 Universal Testing Machine was used to determine the tensile properties of the lignin thermosets using samples with dimensions of 40 mm × 5 mm × 0.1 mm. All tests were performed at 22 °C and 40% relative humidity, seven samples were tested for each thermoset, and the tension strain was 10 mm/min. The tensile properties were calculated according to the ASTM D882-18 standard.

**Size Exclusion Chromatography.** SEC 1260 infinity (Polymer standard service, Germany) equipped with a PSS precolumn, PSS...
water content of the thermosets were also tested using the same nitrogen atmosphere (50 mL/min). The weight loss of lignin and the crucibles and heated from 25 to 650 °C. The sample (∼10 mg) was placed into 70 μL alumina crucibles. The temperature was first cooled to −80 °C and maintained for 2 min prior to heating to 150 °C at 10 °C/min. The samples were run under a nitrogen atmosphere at a flow rate of 50 mL/min.

**Thermal Gravimetric Analysis.** TGA/SDTA 851e (Mettler-Toledo, USA) was applied to evaluate the thermal stability of the thermosets. The sample (∼10 mg) was placed into 70 μL alumina crucibles and heated from 25 to 650 °C at 10 °C/min under a nitrogen atmosphere (50 mL/min). The weight loss of lignin and the water content of the thermosets were also tested using the same instrument by heating isothermally at 110 °C for 1 h.

| Table 1. Characterization of the Original LB Lignin and the Lignin Fractions from the Different Processes as Well as the Gel Contents and Water Production Percentage During the Curing Process |
| sample name | Mn (g/mol) | Mw (g/mol) | D | OH yield (%) | sample name | gel content (%) | water production (wt %) |
|-------------|------------|------------|---|--------------|-------------|-----------------|------------------------|
| LB          | 1900       | 8200       | 4.3 | 12.5 | X-LB        | 89.2           | 29.1                   |
| MFLB        | 1100       | 2800       | 2.5 | 7.4  | X-MFLB      | 84.7           | 23.7                   |
| EFLB        | 720        | 1800       | 2.5 | 4.4  | X-EFLB      | 78.7           | 21.9                   |
| EFLB 370    | 1000       | 3700       | 3.7 | 6.3  | X-EFLB 370 | 80.5           | 20.8                   |
| EFLB 160    | 990        | 2600       | 2.6 | 5.4  | X-EFLB 160 | 76.0           | 19.3                   |

**RESULT AND DISCUSSION**

Lignin thermosets were prepared by one-pot heat curing of lignin, PEG400, and citric acid through an esterification reaction (Figure 1a). In this reaction, citric acid with multiple carboxyl groups and one hydroxyl group is expected to provide sufficient number of cross-link sites as a green cross-linker. PEG 400 with its flexible chain was chosen as an auxiliary alcohol to provide some toughness to the thermosets. Furthermore, PEG with a low molecular weight (i.e., PEG 400) is a good solvent for Kraft lignin, which results in a more homogeneous reaction mixture. According to our previous results for the original LB lignin, good quality films were obtained with a feed ratio of lignin, PEG400, and citric acid of 30:30:40 wt %. Therefore, we continued to use this feed ratio to synthesize lignin thermosets from extracted or microwave-processed lignin fractions. In this work, five lignin thermosets were prepared to evaluate the effect of lignin pretreatment on the thermoset properties. Two thermosets were based on lignin fractions from liquid—solid extraction with methanol or ethanol, and two thermosets were based on lignin fractions from MwP in ethanol at two different temperatures. For comparison, one thermoset was prepared from the original LB lignin. To design materials for a circular economy, the possibility to recycle the fabricated lignin thermosets back to liquid resins via microwave-assisted hydrolysis and reprocessing into new thermosets was evaluated, as illustrated in Figure 1b.

A summary of the lignin sample characteristics including molecular weight, dispersity, and functionality is given in Table 1. Full characterization of the lignin samples was presented in a previous study. In general, the lignin samples from liquid—solid extraction and MwP had significantly lower weight average molecular weights, polydispersities, and lower hydroxyl group content than the original lignin. The liquid—solid extraction with methanol resulted in a higher yield, higher weight and number average molecular weight, and higher content of hydroxyl groups compared to lignin fraction from liquid—solid extraction with ethanol. When comparing the lignin samples from liquid—solid extraction with ethanol and MwP in ethanol, the number average molecular weight of the lignin samples after both processes was similar while a much higher yield and moderately higher hydroxyl group content were observed after MwP. The MwP temperature also influenced the outcome. A higher microwave temperature (160 °C) resulted in a higher yield, lower weight average...
molecular weight, and lower amount of hydroxyl group compared to the lignin samples processed at a lower temperature (80 °C).

**Cross-link Density of Lignin-based Thermosets.** The cross-link density is an important indicator for thermosets because it influences the mechanical and thermal properties of the materials. In our system, water was the only side product that formed during the curing process, and the water evaporated during the reaction. Therefore, water production during curing also reflects the number of crosslinks formed. Both the weight loss during curing and gel content were utilized to estimate the cross-link density, Table 1. The lignin thermoset prepared from original LB had the highest water production during curing, indicating the highest cross-link density. This result can be explained by the larger content of hydroxyl groups in original LB inducing more crosslinks in the formed thermosets. As a result, X-LB had slightly higher thermal stability compared to the other prepared thermosets (Figure S2). Although the number of hydroxyl groups differed somewhat depending on the processing of the lignin samples, the measured weight losses were quite similar for all the thermosets prepared from the lignin fractions from the different processes. With the exception of EFLB, the gel content calculations were generally consistent with the weight loss during curing. This discrepancy could be ascribed to the lower number and weight average molecular weight of EFLB, which means more crosslinks may be needed before an insoluble cross-link structure is formed. Therefore, the cured EFLB exhibited a lower gel content with the same cross-link density compared to other lignin resins.

**Chemical Structure of Lignin-based Thermosets.** The chemical structure of the lignin thermosets was determined using Fourier transform infrared (FTIR) spectroscopy (see Figure 2, and the full spectrum in Figure S3). In general, all the thermosets had an ester −C==O absorption band at 1730 cm⁻¹, indicating that the esterification reaction was complete, and the lignin was successfully incorporated into all thermosets.

**Thermomechanical Properties of the Lignin-based Thermosets.** The influence of the differently processed lignin fractions on the thermoset relaxation transitions and modulus were investigated by a dynamic mechanical thermal analyzer. The changes in storage modulus (G') and loss factor (tan δ) as a function of temperature are presented in Figure 3a,b. The dynamic mechanical properties of the thermosets are summarized in Table 2. The thermosets synthesized from ethanol-treated lignin samples (both solvent extracted and microwave processed) showed one transition temperature around Tg ≈ 45 °C while the thermosets synthesized from original Lignoboost lignin or the methanol-extracted lignin sample exhibited broadened transition peaks. This result is most likely caused by the higher dispersity of the methanol-treated sample and original Lignoboost lignin, yielding more heterogeneous resins and subsequently thermosets. However, the yield of the lignin fraction from ethanol extraction was much lower compared to the yield from the methanol-extracted fraction. By introducing MwP of the lignin in ethanol, the lignin yield increased by over 50% compared to liquid-solid extraction with ethanol. At the same time, the results indicate that although the yield increased because of MwP, a more homogeneous thermoset structure was obtained.

The storage modulus of the thermosets exhibited different trends in the glassy and rubbery states. In the glassy state (20 °C), X-MFLB and X-EFLB had the highest (190 MPa) and lowest (70 MPa) storage modulus values, respectively, and no obvious relationship between the different lignin resin characteristics (molecular weight, dispersity, and number of functional groups) and the storage modulus of the resulting thermoset was observed. In the rubbery state (50 °C), the storage modulus of the thermosets decreased in the following order: X-LB > X-MFLB > X-EFLB > X-EFLB₈₀ > X-EFLB₁₆₀.

![Figure 2. ATR–FTIR spectrum of all lignin thermosets under transmission mode.](image-url)

![Figure 3. Storage modulus (a) and tan delta (b) as a function of temperature for the thermosets composed of different lignin types.](image-url)
This order is consistent with the $T_g$ trend obtained from differential scanning calorimetry (DSC) analysis (Figure S4), which reflects the gel content of the thermosets. Therefore, the difference in the thermoset storage modulus could be, at least partly, explained by their differences in cross-link density.

**Tensile Properties of the Lignin Thermosets.** The tensile properties of the thermosets were evaluated, and the determined values with standard deviations are reported in Figure 4 and Table 3. All thermosets synthesized utilizing the different lignin fractions showed an elongation at break above 200%, which is approximately twice the elongation at break of X-LB. At the same time, their tensile stress and Young’s modulus were lower than those of the lignin thermoset based on the original LB lignin. Similar results were obtained for other lignin epoxy and polyurethane thermoset systems, where the decreasing molecular weight for lignin decreased the stiffness of the thermoset. This behavior was explained by the fact that lignin with a higher molecular weight is anticipated to have larger intermolecular interactions (noncovalent stacking between aromatic rings and intermolecular hydrogen bonding) among individual lignin components. In our system, this behavior may also be because of the lower cross-link density of the lignin thermosets prepared from lignin fractions from liquid–solid extraction or Mwp. In comparison to the liquid–solid extraction, the Mwp resulted in a higher yield while the narrow dispersity and functionality of the lignin fractions were retained. Although small variations were observed in the modulus and elongation for the fabricated thermosets, the properties were not significantly different for thermosets prepared from the methanol- and ethanol-extracted or microwave-processed fractions. This result indicated good system robustness, where some variations in the extraction process can be tolerated without significant changes in material properties. In comparison to previously reported results for lignin thermosets, the studied lignin thermosets exhibit relatively high elongation at break. For example, previously reported elongation at break values of 41% for lignin polyester thermosets, 47% for epoxy thermosets, and 330% for hyperbranched polyester thermosets have been reported. To conclude, the thermoset prepared from the liquid–solid extracted or microwave-processed fractions had a higher elongation at break compared to the thermosets based on the original LB lignin. In general, the thermoset based on the different extracted/microwave-processed lignin fractions exhibited similar mechanical behaviors.

**Microwave Recycling and Recuring of the Thermosets.** Considering the principles of sustainability and environmental responsibility, we further investigated whether the fabricated thermosets could be chemically recycled and reprocessed. According to a previous research, polyester thermosets can be recycled into pristine building blocks or oligomeric resin by cleaving ester bonds, and then, the obtained resins can be repolymerized into new thermosets to achieve a closed loop process. We therefore speculated that a similar process (see Figure 5a) could be used to recycle the lignin thermosets prepared here. The applied microwave-assisted process was effective, and the thermosets became fully soluble in an alkaline aqueous solution during microwave heating at 160 °C within 20 min.

After the microwave recycling process, a yield of 65% or 63% weight percentage of the X-LB and X-EFLB$_{160}$ thermosets was recovered. To compensate for the weight loss, pristine resins with the same ratio as the original feed ratio were supplied to afford the same total initial weight, and the mixture was recurred into thermosets under the same conditions used for the original pristine thermosets. Figure 5b shows a comparison of the FTIR spectrum of the pristine X-EFLB$_{160}$ thermoset, the recycled resin mixture, and the thermoset based on the recycled resin mixture. The results showed that the ester C=O band at 1731 cm$^{-1}$ shifted to the carboxylic C=O band at 1721 cm$^{-1}$ and the OH band at 3446 cm$^{-1}$ increased after microwave degradation, which indicates cleavage of the ester bond as the main degradation mechanism. After the recuring process, the carbonyl bond shifted back to 1731 cm$^{-1}$, and the different extracted/microwave-processed lignin fractions were retained.
Flexible and recyclable polyester thermosets were successfully fabricated by utilizing refined lignin fractions derived from liquid—solid extraction or MwP of Kraft lignin. In comparison to the thermoset synthesized from the original unrefined Kraft lignin, the chemical structure of the thermosets derived from the lignin fractions was similar, but the cross-link densities were somewhat lower. A sharp $\alpha$-transition temperature peak indicated that thermosets produced from the ethanol-extracted lignin fractions were generally more homogenous compared to the thermoset produced from the original Kraft lignin. All the thermosets synthesized from the different lignin fractions exhibited similar stress—strain behavior with over 200% elongation at break. This value is more than twice the value determined for thermosets synthesized from the original Kraft lignin. Furthermore, the similar stress—strain curves indicate good robustness against the type of extraction process. The fabricated thermosets, modeled by X-EFLB and X-EFLB$_{160}$, could be rapidly recycled back to liquid resins by microwave heating and cured into new thermosets. However, because of the somewhat higher molecular weight and viscosity of the recycled resins compared to the corresponding original resins, good quality cured films were only produced from the recycled resins originating from X-EFLB$_{160}$. The RX-EFLB$_{160}$ recycled thermoset exhibited mechanical properties in between the original X-EFLB and X-EFLB$_{160}$ thermosets with an intermediate elongation at break (140%) and tensile strength (2.8 MPa). To conclude, the polyester thermosets synthesized from ethanol-extracted lignin fractions from both extraction processes were more homogeneous and exhibited higher flexibility and better recyclability than thermosets produced from the original unrefined Kraft lignin. MwP gave higher yields of narrow dispersity lignin fractions compared to normal liquid—solid extraction without sacrificing the final properties of the thermoset. This approach provides a promising route to recyclable flexible lignin thermosets.

**CONCLUSIONS**

Flexible and recyclable polyester thermosets were successfully fabricated by utilizing refined lignin fractions derived from liquid—solid extraction or MwP of Kraft lignin. In comparison to the thermoset synthesized from the original unrefined Kraft lignin, the chemical structure of the thermosets derived from the lignin fractions was similar, but the cross-link densities were somewhat lower. A sharp $\alpha$-transition temperature peak indicated that thermosets produced from the ethanol-extracted lignin fractions were generally more homogenous compared to the thermoset produced from the original Kraft lignin. All the thermosets synthesized from the different lignin fractions exhibited similar stress—strain behavior with over 200% elongation at break. This value is more than twice the value determined for thermosets synthesized from the original Kraft lignin. Furthermore, the similar stress—strain curves indicate good robustness against the type of extraction process. The fabricated thermosets, modeled by X-EFLB and X-EFLB$_{160}$, could be rapidly recycled back to liquid resins by microwave heating and cured into new thermosets. However, because of the somewhat higher molecular weight and viscosity of the recycled resins compared to the corresponding original resins, good quality cured films were only produced from the recycled resins originating from X-EFLB$_{160}$. The RX-EFLB$_{160}$ recycled thermoset exhibited mechanical properties in between the original X-EFLB and X-EFLB$_{160}$ thermosets with an intermediate elongation at break (140%) and tensile strength (2.8 MPa). To conclude, the polyester thermosets synthesized from ethanol-extracted lignin fractions from both extraction processes were more homogeneous and exhibited higher flexibility and better recyclability than thermosets produced from the original unrefined Kraft lignin. MwP gave higher yields of narrow dispersity lignin fractions compared to normal liquid—solid extraction without sacrificing the final properties of the thermoset. This approach provides a promising route to recyclable flexible lignin thermosets.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsapm.0c00130.

TGA of lignin and lignin thermosets; full FTIR spectrum of lignin thermoset; DSC of lignin thermosets; digital picture of recycled X-LB and X-EFLB$_{160}$ FTIR spectrum of pristine thermosets, recycled resin and recycled thermosets for X-LB; and SEC analysis of the pristine resins (LBr and EFLB160r) and recycled resins (R-LBr and R-EFLB160r) for X-LB and X-LBEtOH160 (PDF)

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