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Lignin-Based Polyurethanes from Unmodified Kraft Lignin Fractionated by Sequential Precipitation

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ABSTRACT: Lignin-based polyurethanes were synthesized from three unmodified softwood Kraft lignin fractions as the primary hydroxyl group providers which constituted >40% of the polymeric materials. High-, medium-, and low-molecular-weight Kraft lignin fractions were prepared by sequential precipitation from the acetone–methanol cosolvent by adding hexane as an antisolvent. A polyether, poly(ethylene glycol), and a polyester, poly(trimethylene glutarate), were selected as secondary polyols to form the soft segments in the lignin-based network. At a fixed NCO/OH ratio (1:1), the effects of lignin macromolecular features and their intermolecular interactions with the secondary polyols on mechanical and thermal properties of the lignin-based polyurethanes were investigated by tensile tests, DMA, SEM, and TGA. Owing to the unique association behavior of macromolecular lignin, the sequential precipitation method was able to produce Kraft lignin fractions possessing very high molecular weights. The morphological study revealed that the polyurethane network was assembled by cross-linking nanosized lignin complexes through urethane links. It was found that the mechanical properties of the lignin-based polyurethanes can be tuned by lignin molecular weight and the incorporation of a secondary polyol. Compared to poly(trimethylene glutarate), poly(ethylene glycol) interacts strongly with associated lignin complexes through hydrogen bonding. It promoted dissociation of the lignin complexes and consequently improved reactivity between lignin and diisocyanate. Moreover, at PEG/lignin = 1:4 (w/w), the soft segments formed by PEG enhanced the stiffness of the lignin-based polyurethanes; when the PEG content was increased to PEG/lignin = 2:3 (w/w), plastic deformation can be observed for the stress–strain curves of all corresponding lignin-based polyurethanes.

KEYWORDS: lignin-based polyurethane, lignin refinery and valorization, nanoparticles, mechanical properties, intermolecular interactions



INTRODUCTION

Lignin, the most abundant aromatic biopolymer, incorporates ~20% of the total carbon fixed in terrestrial plants through photosynthesis. It can be biodegraded by various microorganisms in the carbon recycling of land ecosystems.^{1,2} To meet the demand for 79 billion liters of second-generation biofuels, the annual production of lignin will reach 62 million tons in the United States by 2022.³ Instead of combusting these coproduct lignins as low-cost fuels, one of the most efficient valorization pathways is to blend or cross-link them into polymeric materials such as thermoset resins,^{4–7} foams,^{8–10} coatings,^{11–13} adhesives,^{14–16} and thermoplastics.^{17–21} Petrochemical-based polyurethanes are built with small blocks of a polyol such as polyesters or polyethers connecting through urethane bridges (–NHCO–O–). The annual production of polyurethane products was 2.4 billion tons with \$281 billion in

revenues in 2014.²² Owing to its abundance in hydroxyl groups and rigid aromatic backbone, Kraft lignin, the coproduct of Kraft pulping, has been applied as a sustainable alternative polyol in polyurethane synthesis, and the hard segments composed of macromolecular lignin were expected to reinforce the elastomer.^{5,23–25}

In the Kraft pulping process, the wood chips are cooked in sodium hydroxide and sodium bisulfide aqueous solution at 170 °C for ~2 h. Under such severe pulping conditions, Kraft lignin turns into a more heterogeneous polymer, compared to native lignin, possessing more free phenolic hydroxyl groups, new stilbene-like structures, and sulfur-based impurities.^{26,27} The

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refining of technical lignin can be classified into two methods: sequential precipitation^{28–30} and solvent extraction.^{31–33} The homogeneity and purity of technical lignin samples can be improved by both methods. However, sequential precipitation of dissolved lignin usually generates fractions possessing significantly higher molecular weights and polydispersity as lignin macromolecules are prone to associate during this process, and the formed associated lignin complexes cannot be disrupted in dilute alkaline solution unless it was heated to 80 °C.³⁴

Polyurethanes have been synthesized with lignin fractions obtained by successive extraction with various organic solvents, from which the molecular weights of lignin fractions were hardly surpassing 10000 g/mol.^{27,35–38} The studies of the relationship between lignin structure and material properties of lignin–PUs indicated that polyurethanes prepared from low- and medium-molecular-weight lignin fractions were more flexible and tougher; however, when the lignin content was above 30–35%, the lignin–PU networks were too brittle to be tested regardless of the NCO/OH ratio applied.^{35,37} For the lignin-based PU elastomer using 2,4-diisocyanate-terminated poly(propylene glycol) tolylene (PPGTDI) as the soft segments, the PU elastomer with the best mechanical properties was prepared with low-molecular-weight (600 g/mol) lignin which was able to form a homogeneous network with PPGTDI.³⁸ In fact, it has been demonstrated in the study of thermoplastics containing 85 wt % of unmodified Kraft lignin that the tensile strength and modulus increased linearly with the apparent molecular weight of lignin that was simply manipulated by the degree of association between lignin components.²⁰ In the present work, a softwood Kraft lignin sample was refined by sequential precipitation from an acetone–methanol–hexane cosolvent system. The lignin-based polyurethane was fabricated with three fractions with high, medium, and low molecular weights. It was demonstrated that the mechanical properties of the polyurethanes were tuned by lignin molecular weight and the intermolecular interactions between lignin and the secondary polyols.

EXPERIMENTAL SECTION

Materials. A commercial softwood Kraft lignin sample was purified and fractionated according to the procedures described in a previous publication.³⁹ Kraft lignin (2 g) was suspended in 20 mL of acetone–methanol (7:3, v/v) (AM) cosolvent under vigorous stirring for 30 min at room temperature. The insoluble fraction denoted as AM-ins was collected by centrifugation at –4 °C for 30 min. Hexane (2 mL) was added as the antisolvent to the supernatant, and the resulting precipitated fraction (AMKL-66k) was collected by centrifugation (4000g, –4 °C). This procedure was repeated by adding 4, 6, and 13 mL of hexane. The precipitated Kraft lignin fractions were labeled according to their weight-average molecular weight, such as AMKL-54k, AMKL-15k, and AMKL-4k. After the addition of 13 mL of hexane, the final soluble fraction (designated as AMKL-1k) was dried in a vacuum oven under reduced pressure at 35 °C. The chemicals and solvents used in this work, if not specified, were purchased from Sigma-Aldrich and Fisher Scientific and were used as received.

Characterization of Lignin Fractions. The hydroxyl groups of Kraft lignin fractions were analyzed quantitatively by using ³¹P NMR. The molecular weights and distribution of acetylated Kraft lignin fractions were determined by GPC analysis. The detailed methods were published in a previous paper.³⁹

Preparation and Characterization of Lignin–Polyurethane Film. The synthesis of lignin-based PU film was performed by solution casting from tetrahydrofuran (THF) in the presence of 1.5% dibutyltin dilaurate as the catalyst. In addition to AMKL fractions, poly(ethylene

glycol) (MW = 4000, Alfa Aesar) or poly(trimethylene glutarate) (MW = 4000, Scientific Polymer Products, Inc.) was used as a secondary polyol. The polyols were dissolved in THF at 60 °C, and then 4,4'-methylenebis(phenyl isocyanate) (MDI) which was dissolved in THF at room temperature was added to produce a mixture with a mass concentration of 0.26 g/mL THF. After mixing with the catalyst, the viscous fluid was transferred to a 50 mm × 20 mm Teflon mold and cured in a desiccator for 2 days. The high-molecular-weight Kraft lignin fraction, AMKL-54k, was not soluble in THF by itself or in the presence of PTMG, and the corresponding PU films (HLPU0 and HLPU3) were not homogeneous; therefore, their mechanical behaviors were not presented in this work.

The lignin-based PU films were die-cut into dog-bone-shaped testing specimens by using a toggle press (Pioneer Die-TECS) equipped with an ASTM D-638 Type IV specimen die. The die-cut specimen was kept in between two glass boards for 3 days, and then it was further cured in an air-circulated oven at 155 °C for 3 h. The tensile test was performed using a dual column Instron 5567 tensile tester with a 500 N static load cell at a strain rate of 0.1 mm/min.

The Fourier transform infrared (FTIR) spectra of Kraft lignin fractions and lignin-based polyurethanes were collected from 4000 to 600 cm⁻¹ with 32 scans on a Spectrum One FTIR system (PerkinElmer) equipped with a universal attenuated total reflection (ATR) accessory.

The fracture surface of the lignin-based PU was smoothed by ultramicrotome cutting using a 45° glass blade on a Leica EM UC7 ultramicrotome according to the method described in a previous paper.¹⁸ After 2 day relaxation in a dust-free Petri dish, the ultramicrotome-cut surface was imaged with variable pressure SEM in the backscattered mode.

The viscoelastic properties of the lignin-based PU films were evaluated by using a Pyris Diamond dynamic mechanical analyzer (PerkinElmer) equipped with a dual cantilever. The sample was cut into a 50 × 10 × 1 mm³ (length × width × thickness) strip; dynamic mechanical analysis (DMA) was performed in single bending mode at a frequency of 1 Hz, and the temperature was increased from 30 to 200 °C at a heating rate of 2 °C/min.

Thermal gravimetric analysis (TGA) of lignin-based PU samples was performed on a PerkinElmer Pyris 1 TGA heating from 25 to 900 °C at 10 °C/min. During the heating process, the sample was incubated at 105 °C for 15 min to remove moisture and solvent residue. The mass loss of lignin-based PUs approached 100% by the end of the TGA experiment when performed in air.

RESULTS AND DISCUSSION

Properties of Lignin Fractions. The heterogeneity of polymeric lignin enabled the softwood Kraft lignin fractions with specific structural features to sequentially precipitate from acetone–methanol cosolvent by adding hexane as the polarity and hydrogen-bonding capacity of the cosolvent system were gradually decreased. The mass yield, weight-average molecular weight (M_w), and polydispersity of each fraction are summarized in Table 1. The first three fractions in Table 1 exhibited unprecedently high M_w (43000–66000) and a very

Table 1. Mass Yield, Weight-Average Molecular Weight (M_w), and Polydispersity (PDI = M_w/M_n) of Kraft Lignin Fractions

fraction	yield (%)	M_w (g/mol)	PDI
AM-ins	6.0	42963	16.6
AMKL-66k	4.0	65521	17.2
AMKL-54k	21.5	53625	15.2
AMKL-15k	14.0	14488	6.2
AMKL-4k	25.5	3790	2.0
AMKL-1k	26.5	1322	1.6

broad molecular weight distribution. The fractions AM-ins and AMKL-66k were found enriched with carbohydrates and partially soluble in pyridine.³⁹ Therefore, in this work, they were ball milled for 1 h before acetylation and ³¹P NMR analysis. It has been reported that ball milling can degrade lignin macromolecular structures through cleavage of the β -O-4' alkyl aryl ether interunit linkage.⁴⁰ However, the mild mechanical treatment improved the accessibility of lignin so that fractions AM-ins and AMKL-66k were dissolved in pyridine completely. Fraction AMKL-54k, which accounted for 21.5% of the parent Kraft lignin sample, was the most abundant high-molecular-molecular weight fraction. In general, that Kraft lignin fractions with higher M_w were less tolerant to the addition of hexane, and they possessed higher frequencies of aliphatic hydroxyl groups than the lower-molecular-weight ones (Table 2). The strong

Table 2. Hydroxyl Group Contents of Kraft Lignin Fractions Determined by ³¹P NMR Analysis

sample	hydroxyl group (mmol/g)			total
	aliphatic	phenolic	carboxylic	
AM-ins	3.13	2.39	0.31	5.83
AMKL-66k	2.70	2.59	0.29	5.58
AMKL-54k	2.14	2.83	0.32	5.29
AMKL-15k	1.88	3.16	0.39	5.43
AM-4k	1.79	3.74	0.43	5.96
AM-1k	1.22	4.30	0.64	6.16
PEG	0.40			0.40
PTMG	1.51		0.57	2.08

intermolecular interactions among individual lignin components are mainly composed of noncovalent π - π stacking between aromatic rings and intermolecular hydrogen bonding, and the hydrogen bonds formed through aliphatic hydroxyl groups are more stable.⁴¹ Therefore, the unexpected high molecular weights of Kraft lignin fractions prepared by sequential precipitation were contributed by the unique association behavior of lignin macromolecules.^{34,42}

Lignin-Based Polyurethane Composition and Synthesis. The lignin-based PU films were polymerized with the selected Kraft lignin fractions, secondary polyols, and MDI by using an overall NCO/OH ratio of 1.0. As shown in Table 3, the lignin-based PU films were denoted based upon the molecular weight range of the Kraft lignin fraction such as high-, medium-, and low-molecular-weight lignin-based PU (HLP, MLPU, and LLPU).

Table 3. Formulations of Kraft Lignin-Based PUs^a

KL-PU	KL fraction	PEG/KL	PTMG/KL	KL (wt %)
MLPU0	AMKL-15k			60
LLPU0	AMKL-4k			57
HLP1	AMKL-54k	1:4		52
MLPU1	AMKL-15k	1:4		52
LLPU1	AMKL-4k	1:4		50
HLP2	AMKL-54k	2:3		43
MLPU2	AMKL-15k	2:3		43
LLPU2	AMKL-4k	2:3		42
MLPU3	AMKL-15k		1:4	52
LLPU3	AMKL-4k		1:4	50

^aFor 2 g of Kraft lignin-based PU films, the molar ratio of $NCO_{MDI}/(OH_{KL} + OH_{PEG/PTMG}) = 1:1$, and the PEG/KL and PTMG/KL are weight ratios (w/w).

MLPU, and LLPU). The lignin-based PUs labeled as PU0 were prepared as a control set that used Kraft lignin as the only OH group provider. The sets of PU1, PU2, and PU3 were synthesized in the presence of secondary polyol (PEG or PTMG) according to the formulations listed in Table 3. Because of their low yields and poor solubility in THF, fraction AM-ins and AMKL-66k were not applied in PU synthesis here. On the other hand, fraction AMKL-1k, which possessed the most abundant phenolic hydroxyl groups, failed to form PU networks with adequate mechanical strength for tensile testing.

The dissolution behavior of AMKL fractions in THF varied depending on their molecular weight and content of aliphatic hydroxyl group. In general, fractions with lower molecular weight and fewer aliphatic hydroxyl groups, such as AMKL-15k and AMKL-4k, were more readily soluble in THF at 60 °C. For the high-molecular-weight fraction (AMKL-54k), THF alone was not a good solvent, but the presence of PEG enabled it to dissolve completely in THF. However, when PTMG was applied as the secondary polyol, fraction AMKL-54k remained partially soluble in THF at 60 °C. The ether oxygen in PEG was able to form a strong hydrogen bond with the lignin aromatic hydroxyl proton, which allowed PEG to disrupt the associated lignin complexes and facilitate dissolution of fraction AMKL-54k in THF.^{19,43} Under the condition that the phenolic hydroxyl group was substituted through alkylation, PEG can still interact more strongly with alkylated Kraft lignin derivatives than polyesters like PTMG.²¹

The FTIR spectra of the medium-molecular-weight Kraft lignin fraction, AMKL-15k, before and after reacting with MDI in the presence or absence of different secondary polyol are presented in Figure 1. The broad band at 3415 cm^{-1} arising

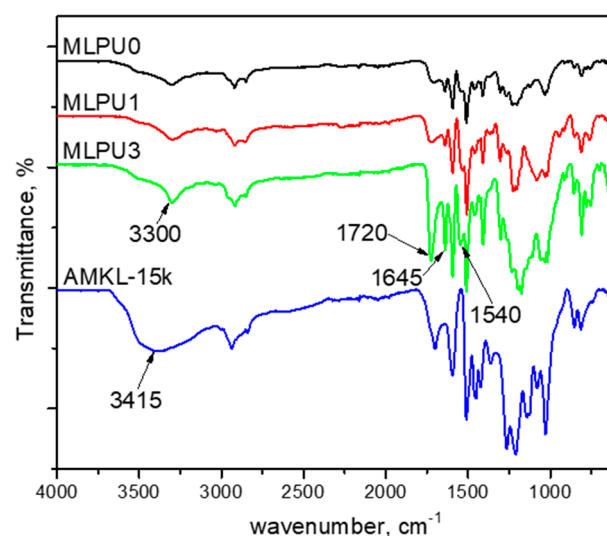


Figure 1. FTIR spectra of Kraft lignin fraction AMKL-15k and its derived medium-molecular-weight lignin-based PUs (MLPU) with or without secondary polyols.

from the asymmetric stretching of O-H bond of lignin shrank significantly after reacting with MDI. Meanwhile, the absorption of isocyanate group at 2270 cm^{-1} was not observed in any lignin-PU spectra in Figure 1, which can be viewed as a sign of successful formation of lignin-based PU network with a complete consumption of isocyanate groups.^{38,44} In addition, the new bands at 3300 and 1540 cm^{-1} which were ascribed respectively to N-H stretching and angular deformations of

N–H bond coupled with the stretching of C–N bond can be observed clearly in all lignin–PU spectra.⁴⁵ In the spectra of MLPU0 and MLPU1, the distinguishable bands at 1720 and 1645 cm^{-1} were related to C=O stretching vibrations in the urethane bridge.⁴⁵ Their intensities increased dramatically in the spectrum of MLPU3 due to the contribution from the stretching of C=O bond in the ester group of PTMG.

Material Properties of Lignin-Based PU. The mechanical properties of lignin-based polyurethanes were investigated by a tensile test as summarized in Table 4. In Figure 2A, simple

Table 4. Ultimate Tensile Strength (σ_{max}), Elongation at Break (ϵ_{break}), and Young's modulus (E_{Young}) of Polyurethanes Synthesized with Kraft Lignin Fractions of Different Molecular Weights in the Presence or Absence of Secondary Polyols

sample	σ_{max} (MPa)	ϵ_{break} (%)	E_{Young} (MPa)
MLPU0	27.7 ± 2.7	4.2 ± 0.5	779 ± 40
LLPU0	26.8 ± 3.3	4.6 ± 1.1	662 ± 15
HLPU1	43.2 ± 6.6	6.6 ± 1.1	961 ± 5
MLPU1	38.1 ± 4.5	5.2 ± 1.1	839 ± 51
LLPU1	35.3 ± 4.1	5.4 ± 1.6	750 ± 21
HLPU2	40.6 ± 0.5	24.7 ± 0.6	664 ± 15
MLPU2	37.0 ± 0.1	26.6 ± 0.0	676 ± 8
LLPU2	32.8 ± 0.5	34.5 ± 8.2	611 ± 17
MLPU3	17.7 ± 4.6	3.3 ± 0.2	658 ± 209
LLPU3	16.8 ± 6.0	2.6 ± 0.8	679 ± 79

formulations that employed medium-molecular-weight (AMKL 15k) and low-molecular-weight (AMKL-4k) Kraft lignin fractions as the only OH group provider were able to generate rigid polyurethane films with ultimate tensile strength (σ_{max}) of 25–30 MPa and elongation at break (ϵ_{break}) < 5%. For the set of PU1 demonstrated in Figure 2B, the soft segments formed by the additional 13 wt % PEG improved the material strength of the cross-linked lignin-based PUs, and σ_{max} of MLPU and LLPU was enhanced by more than 40%. HLPU1 containing 50 wt % lignin and 13 wt % PEG exhibited promising σ_{max} that approached 50 MPa; nonetheless, its ϵ_{break} (<7%) like MLPU1 and LLPU1 was refrained by the rigidity of lignin components. Further increasing the PEG content to 28 wt % significantly improved the ductility of the corresponding lignin-based PUs without weakening the strength of the materials (Figure 2C). Plastic deformation can be clearly observed in the stress–strain curves of the PU2 set, and particularly LLPU2 exhibited ϵ_{break} > 40% accompanied by moderate σ_{max} around 33 MPa. Young's modulus (E_{Young}), which is referred to as the modulus of elasticity, measures the stiffness of an elastic material. Here, E_{Young} of PU0 and PU1 sets showed a unanimous dependence on the molecular weight of Kraft lignin fractions as shown in Table 4. As more PEG was introduced to PU2 set, the associated lignin complexes were disrupted into smaller size by the strong intermolecular interactions between lignin and PEG; consequently, E_{Young} decreases and the difference of E_{Young} value among PU2 samples was diminished. Unlike PEG, the polyester (PTMG) soft segments seemed to be detrimental to MLPU3 and LLPU3 due to its weak intermolecular interactions with lignin components (Figure 2D). The reactivity of aliphatic OH with NCO is much higher than that between phenolic OH and NCO.⁴⁶ As the Kraft lignin fraction molecular weight decreased from 54K (AMKL-54k) to 4K (AMKL-4k), the aliphatic OH content decreased by 20%, the phenolic OH content increased

by 32%, and the total OH content increased by 13% (Table 2). However, the change in molecular weight was more than 10-fold and had an overwhelming impact on the material properties of lignin–PU. By comparison of the tensile behaviors of lignin-based PUs synthesized with different Kraft lignin fractions and secondary polyols, it can be concluded that PUs can be reinforced by increasing the molecular weight of lignin; the material ductility can be tuned synergistically by PEG content and lignin molecular weight.

For highly cross-linked materials, the glass transition state can be flat and broad in DSC analysis. Alternatively, DMA has been used as a sensitive technique to investigate the thermal mechanical of cross-linked polymeric materials. The storage and loss moduli (E' and E'') are measured as a function of increasing temperature, and the glass transition temperature (T_g) can be determined through the peak of loss factor, $\tan \delta = E''/E'$. As shown in Figure 4, in the glass state where all relaxation modes were frozen, like the E_{Young} obtained in tensile testing, the dynamic moduli were also influenced by the molecular weight of Kraft lignin fractions applied in polyurethanes. The average values of E' in the temperature range between 30 and 40 °C (E'_{30-40}) were 22.1 and 15.5 GPa for MLPU0 and LLPU0, respectively. After the addition of 13 wt % PEG, E'_{30-40} decreased to 19.4, 18.7, and 16.3 GPa for HLPU1, MLPU1, and LLPU1, respectively. The gaps of the dynamic moduli (E' and E'') for HLPU1, MLPU1, and LLPU1 were reduced significantly as the associated lignin complexes were disrupted by PEG (Figure 3). On the other hand, blending with PTMG led to an opposite effect: HLPU3 and LLPU3 became stiffer as their E'_{30-40} increased to 33.1 and 20.3 GPa, respectively. In fact, the efficiency of the secondary polyol acting as a plasticizer can be evaluated by its impact on the T_g of the lignin-based polymeric materials.²¹ At the same incorporation level (13 wt %), PEG was able to lower the T_g of lignin-based PU by ~30 °C; nevertheless, PTMG hardly changed T_g because of its weaker interactions with lignin macromolecules.

The SEM micrographs revealed three distinct surface morphologies of the MLPUs prepared with different formulations (Figure 4). After 2 day relaxation in a dust-free environment, an evenly distributed nodular feature can still be clearly observed on the ultramicrotome-cut surface of MLPU0 which was synthesized with lignin as the only hydroxyl group provider. It has been reported that the fresh ultramicrotome-cut surfaces of lignin-based thermoplastics were composed of nanosized (9–15 nm) complexes formed by associated lignin components under an atomic force microscope (AFM).^{17,18} In lignin-based PUs, these nanosized complexes were cross-linked through urethane bridges (–NHCO–O–).⁴⁷ However, they were not found on the ultramicrotome-cut surface of MLPU1 and MLPU3 in Figure 4B,C. In fact, the lignin nanoparticles coalesced in the presence of the miscible secondary polyols. The terrace surface morphology of MLPU3 confirmed that it was mechanically more brittle than MLPU1.

The TGA thermograms of lignin-based PU exhibited three thermal degradation stages in air (Figure 5). The initial peak around 250 °C was caused by degradation of MDI,⁴⁸ and this peak was shifted to lower temperature range as the MDI content increased in the lignin-based PU. The second stage (~350 °C) that was not observed in the TGA curves of Kraft lignin was caused by oxidative degradation of the urethane group.^{39,48} It was broadened up to 400 °C as a result of incorporating PEG or PTMG, and the curve pattern was strongly influenced by the thermal degradation behavior of the

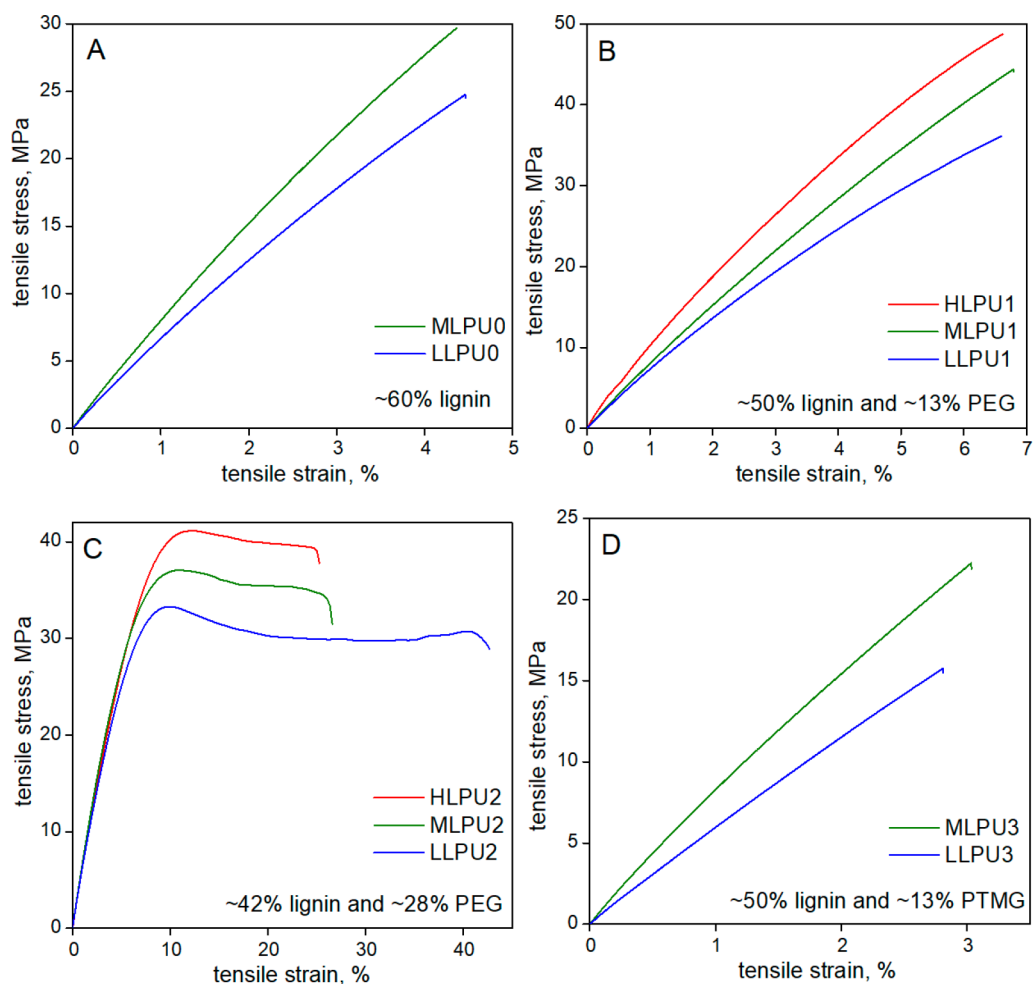


Figure 2. Tensile behavior of Kraft lignin-based polyurethanes containing (A) ~60 wt % lignin, (B) ~50 wt % lignin and ~13 wt % PEG, (C) ~42 wt % lignin and ~28 wt % PEG, and (D) ~50 wt % lignin and ~13 wt % PTMG.

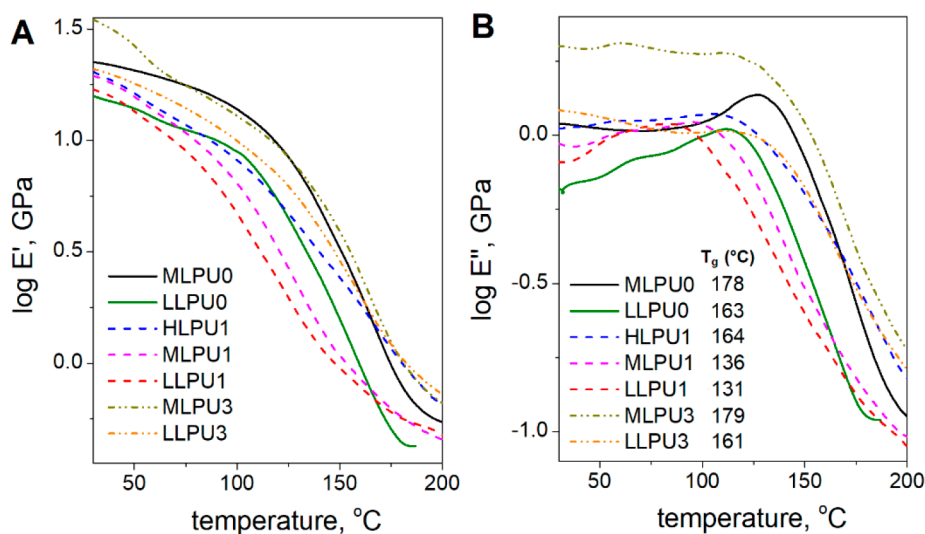


Figure 3. Dynamic moduli E' (A) and E'' (B) at 1 Hz, measured as a function of increasing temperature, for the Kraft lignin-based polyurethanes.

secondary polyol. The major oxidative decomposition of lignin occurred during the third stage (~600 °C). In general, the PU produced from higher-molecular-weight lignin fraction were more resistant to thermal degradation regardless its formulation.

CONCLUSION

Refinery by solvent fractionation for well-defined structural features and purity is vital for valorization of technical lignins. In this study, lignin-based polyurethanes were fabricated with high-, medium-, and low-molecular-weight Kraft lignin

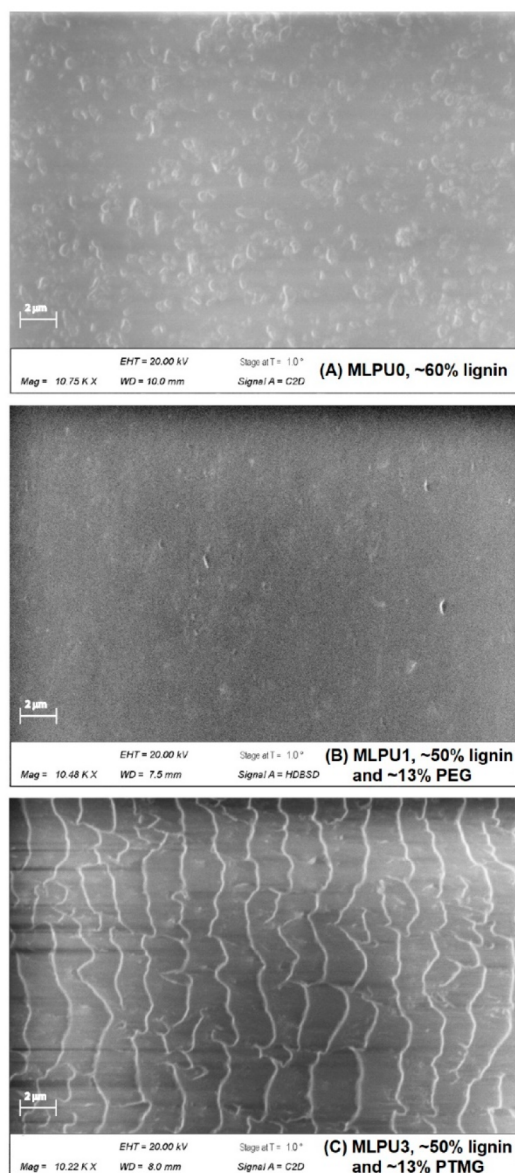


Figure 4. Ultramicrotome-cut surface micrographs, scanned by SEM (2 μm size bar), for medium-molecular-weight Kraft lignin-based polyurethanes: (A) MLPU0, (B) MLPU1, and (C) MLPU3.

preparations obtained by sequential precipitation from the organic cosolvent system. Two secondary polyols, PEG and PTMG, were blended with Kraft lignin fractions before PU synthesis to improve the latter one's miscibility and reactivity with MDI in THF. The efficiency of the secondary polyol depends on the strength of its intermolecular interactions with the nanosized lignin complexes. The insight into formulating potential lignin-based polymeric materials has been provided by the unique physicochemical property of lignin. Herein, the mechanical properties of lignin-based polyurethanes were influenced by the synergetic effects of lignin structural features and the secondary polyol. It can be concluded that increasing the lignin molecular weight was able to improve the material stiffness or resistance to deformation of lignin-based polyurethanes. On the other hand, the incorporation of an efficient secondary polyol such as PEG can reduce the brittleness and enhance the ductility of lignin-based polyurethanes.

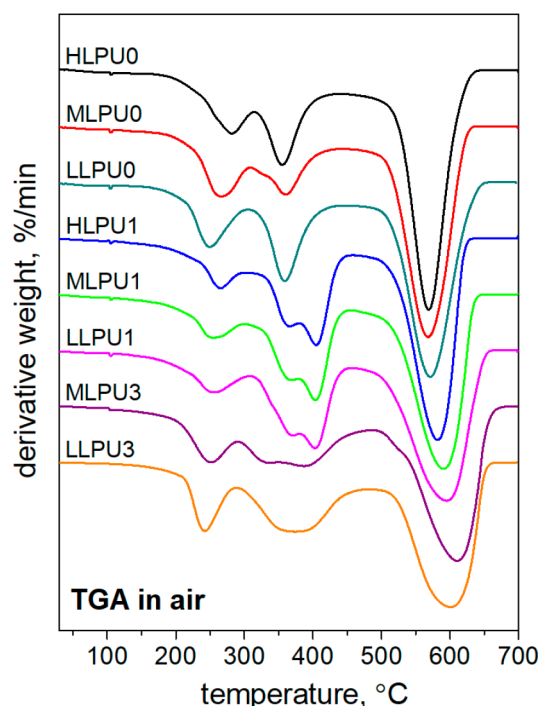


Figure 5. Derivative weight (%/min) of Kraft lignin-based polyurethanes measured by TGA, as a function of increasing temperature.

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Notes

The authors declare no competing financial interest.

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