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Kraft Lignin-Based Rigid Polyurethane Foam

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Abstract: Kraft pine lignin was derivatized to a liquid polyol through oxypropylation. The resulting polyol was characterized by GPC, FT-IR, H1, C13, and P31 NMR and was compared to commercial polyols in view of the mechanical property of the corresponding rigid polyurethane foams for the first time. A series of lignin-based PU was synthesized by replacing varying weight percentages of the amount of sucrose polyol and glycerol polyol, two commonly used commercial polyols employed in the control foam preparation. All foams had a low density of \(\sim 30\) Kg m\(^{-3}\) and showed typical linkages of PU in the FT-IR spectra. The diameter of closed-cells was \(\sim 650\) \(\mu\)m for most of the foams as revealed by SEM images. The optimal compressive property of rigid PU foams was obtained using lignin polyol without the addition of any other commercial polyols primarily attributed to the rigidity of lignin aromatic structure and the high functionality of lignin hydroxyl groups.

Keywords Kraft lignin, oxypropylation, lignin polyol, rigid polyurethane foam, optimization

Introduction

Lignin, the most abundant aromatic biopolymer in nature, is a three-dimensional amorphous polymer that is derived from \(p\)-coumaryl alcohol, coniferyl alcohol, and/or sinapyl alcohol.\(^{[1-3]}\) In the secondary cell walls of vascular plants, lignin fills the spaces between cellulose and hemicellulose, providing mechanical strength to the lignocellulose matrix.\(^{[4]}\) The structure and amount of lignin depends not only on the type of plant, but also on a number of other factors: climate, soil, tree age, and component of the tree.\(^{[2,3,5]}\) The largest source of lignin is the Kraft pulping process.\(^{[3]}\) A small amount of lignin in the form of water-soluble lignosulphonates is produced by the sulphite pulping process. Kraft pulping employs sodium hydroxide (\(\sim 20\%\) on oven-dried wood) and sodium sulfide (\(\sim 5\%\) on oven-dried wood) at temperatures between 150–180\(^{\circ}\)C for about 2–3 h to degrade and extract lignin from wood.\(^{[6]}\) As of 2010, the pulp and paper industry generated \(\sim 55\) million tons of lignin each year, most of which is burned in a recovery furnace facilitating the recovery of pulping chemicals and energy.\(^{[7]}\) To date, the existing markets for lignin products remains limited (\(\sim 2\%\)) and focused primarily on low-value products such as agents for dispersing,
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binding, and emulsion stabilization in the form of water soluble lignosulphonates from the sulphite pulping process. Since lignin contains a large number of aliphatic and phenolic hydroxyl groups, researchers have begun to examine the preparation of lignin-modified phenolic resin, epoxy polymer, acrylates, and polyurethanes. These numerous applications can be attributed to polyurethane’s predominant and controlled mechanical and thermal performance depending on the synergistic effect of soft- and hard-segments of the polymer matrix as well as various optional species, such as chain extender, crosslinker, UV absorber, light stabilizer, antioxidant, and flame retardant. Rigid PU foam is a highly crosslinked polymer with a closed-cell structure. Its low density, low thermal conductivity, low moisture permeability, high dimensional stability, and good adhesive property lead to broad uses in construction, refrigeration appliances, and technical insulations.

Polyurethane (PU) is among the most widely used synthetic polymers for assorted applications including coatings, adhesives, elastomers, foams, and fibers. These numerous applications can be attributed to polyurethane’s predominant and controlled mechanical and thermal performance depending on the synergistic effect of soft- and hard-segments of the polymer matrix as well as various optional species, such as chain extender, crosslinker, UV absorber, light stabilizer, antioxidant, and flame retardant. Rigid PU foam is a highly crosslinked polymer with a closed-cell structure. Its low density, low thermal conductivity, low moisture permeability, high dimensional stability, and good adhesive property lead to broad uses in construction, refrigeration appliances, and technical insulations.

Since lignin has a random non-crystalline network structure, it possesses unique properties that relate to mechanical properties and thermal stability. The natural properties of lignin also contribute to an improvement of moisture and flame resistance of PU foams. Moreover, its aliphatic and phenolic hydroxyl functionalities provide good reacting sites towards isocyanates. Kraft lignin was first incorporated into PU formulations together with a polyether triol and it has been shown to contribute chemically to the formation of a crosslinked network. At low lignin contents, the resulting PUs exhibited considerable toughness at specific values of [NCO]/[OH] ratios. However, at high lignin contents (> 30 wt%), the corresponding PUs were hard and brittle, regardless of the [NCO]/[OH] ratio used. In a later study by Yoshida et al., it was found that PUs prepared with low-molecular-weight lignin (M_w = 620) were more flexible than those obtained with lignin of medium (M_w = 1290) and high values (M_w = 2890). When Kraft lignin content in PUs were higher than 30 wt%, rigid and glassy products were obtained, regardless of the molecular weight of the lignin used. A recent study on the acetic acid lignin-containing PU showed that hydrogen bonding was established between lignin and the polymer matrix and the thermal stability was improved with increasing lignin concentration up to 50%; however, a maximum lignin content of 43.3% can be reached for the continuous film formation.

In order to improve the content of lignin in PU formulation for a product with suitable performance, extensive attention has been directed towards its application as a polyol precursor through liquefaction instead of the direct use of underivatized lignin. Recently, oxypropylation has been recognized as a viable and promising approach to overcome the technical limitations and constraints imposed by the polymeric nature of lignin when directly used as a macromolecule for synthetic purposes. Direct oxypropylation of lignin under alkaline condition was found to be more efficient than acidic condition. After oxypropylation, the starting solid lignin becomes a liquid polyol as a result of the introduction of multiple ether moieties. A study of rigid PU foams obtained from lignin polyols together with 10 wt% of glycerol as a chain extender has shown that it resulted in a rigid PU foam yielding good thermal properties and dimensional stability, even after aging.

In the current rigid polyurethane foam industry, sucrose polyol and glycerol polyol are the most widely used polyols. Whether the use of lignin polyol can result in a product with comparable or even superior properties as compared to the conventional polyols will determine its future applications in this field. Herein, we compared lignin polyol with commercial polyols in view of the mechanical property of the corresponding rigid PU foams for the first time. A series of rigid PU foams was synthesized from commercial polyols and lignin polyol with varying combinations, which started from a control foam...
made from only commercial polyols to a foam solely based on lignin polyol. The results demonstrated the preparation of lignin-based rigid PU foam without the assistance of any other polyols, which provides a significant improvement of the mechanical property of the resulting PU as compared to its commercial counterpart.

Materials and Methods

Materials

A commercial USA softwood Kraft pine lignin (Indulin AT) was used in this study. According to the product description, it was completely free of hemicellulosic materials and had an ash content of 3%. Sucrose polyol (JEFFOL® SD-361), glycerol polyol (JEFFOL® FX31–240), polymeric methylene diphenyl disiocyanate (MDI, RUBINATE® M), dimethylcyclohexylamine (DMCHA, JEFFCAT® DMCHA), Mannich base catalyst (JEFFCAT® TR-52), and silicone surfactant (DABCO® DC5604) were all kindly commercially provided. Sucrose and glycerol polyols have a hydroxyl index of 356 and 246 mg KOH/g, and a functionality of 4.4 and 3.0, respectively. Other chemicals were purchased from Sigma-Aldrich as analytical grade and used as received.

Lignin Oxypropylation

Lignin oxypropylation reaction was carried out in a 160 mL Parr reactor equipped with a thermal mantle, mechanical stir, pressure gauge, and temperature controller. Lignin was dried at 50°C in a vacuum oven for 24 h before use. Lignin, propylene oxide (PO), and KOH were mixed in a glass liner and then sealed in the Parr reactor before heating to 150°C. At first, the pressure gradually rose with increasing temperature, and once it reached 150°C the pressure increased to a maximum value of ~1.75 MPa in seconds and then quickly returned to 0 MPa in less than 9 min, which indicated the completion of the reactants. The formulation of oxypropylation reaction was determined according to the literature, which was able to produce a lignin polyol with an acceptable hydroxyl index between 300 and 800 and a low viscosity for the purpose of rigid PU foam preparation. Table 1 summarizes the reactant formulations and conditions employed.

Acetylation Procedure for GPC Analysis

Acetylation of the GPC samples was carried out according to a published method. In brief, dry lignin/oxypropylated lignin (~20 mg) was added to a solution of acetic anhydride

<table>
<thead>
<tr>
<th>Kraft lignin (g)</th>
<th>Propylene oxide (mL)</th>
<th>Potassium hydroxide (g)</th>
<th>T_{set} (°C)</th>
<th>T_{max} (°C)</th>
<th>P_{max} (MPa)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>40</td>
<td>0.5</td>
<td>150</td>
<td>285</td>
<td>1.75</td>
<td>~9</td>
</tr>
</tbody>
</table>

1T_{set} is the reaction initiation temperature.
2Reaction time was recorded from the initiation temperature to the pressure reaching zero.
and pyridine mixture (1:1, v/v, 2 mL) and then stirred at room temperature for 72 h. The solvent mixture was removed under reduced pressure at 50°C. The acetylated product was dissolved in chloroform (50 mL) and washed with water (20 mL). The chloroform phase was dried over anhydrous MgSO4 and then concentrated under reduced pressure. The dry acetylated lignin/oxypropylated lignin was then dissolved in THF (∼1 mg mL⁻¹) for GPC analysis.

**Phosphitylation Procedure for Quantitative ³¹P NMR Analysis**

The lignin phosphitylation procedure for ³¹P NMR analysis was accomplished following a published method. Briefly, a relaxation reagent solution (chromium (III) acetylacetonated, 3.6 mg mL⁻¹) and an internal standard solution (N-hydroxy-5-norborene-1,3-dicarboximide (NHND), 4 mg mL⁻¹) were prepared in a mixed solvent of pyridine and CDCl₃ (1.6:1, v/v). The lignin sample (20–25 mg) was dissolved in the solvent (0.50 mL) in a vial sealed with a Teflon-faced septum, followed by the addition of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) (0.10 mL), which was stirred for 10 min prior to NMR analysis.

**Optimization Experiments**

A control foam was prepared from sucrose polyol, glycerol polyol, and polymeric MDI. Sucrose polyol was then gradually replaced by lignin polyol in weight percentages of 10%, 30%, 60%, and 100% since they have a similar hydroxyl index. The last foam was made with only lignin polyol without the addition of any other commercial polyols. Table 2 summarizes the amounts of each component used for individual foam preparation. DMCHA (1.80 g) and Mannich base catalyst (0.90 g) as catalysts, pentane (10.00 g) as a blowing agent, and surfactant (1.50 g) were used at the same amounts for all formulations. The value of [NCO]/[OH] ratio was set at 1.2.

**Preparation of Kraft Lignin-Based Rigid PU Foam**

A rigid PU foam was prepared by a one-shot method, which was described in our previous study. Briefly, it is formed by first mixing polyol(s) with catalysts and surfactant for ~1 min, followed by adding pentane and polymeric MDI under strong stirring until foaming

<table>
<thead>
<tr>
<th>Lignin polyol (wt%¹)</th>
<th>Sucrose polyol (g)</th>
<th>Glycerol polyol (g)</th>
<th>Polymeric MDI (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>25.00</td>
<td>15.00</td>
<td>36.37</td>
</tr>
<tr>
<td>10</td>
<td>22.50</td>
<td>15.00</td>
<td>36.66</td>
</tr>
<tr>
<td>30</td>
<td>17.50</td>
<td>15.00</td>
<td>37.24</td>
</tr>
<tr>
<td>60</td>
<td>10.00</td>
<td>15.00</td>
<td>36.07</td>
</tr>
<tr>
<td>100</td>
<td>0.00</td>
<td>15.00</td>
<td>39.24</td>
</tr>
<tr>
<td>Only lignin polyol</td>
<td>0.00</td>
<td>0.00</td>
<td>42.20</td>
</tr>
</tbody>
</table>

¹Weight percentage is based on 25.00 g of sucrose polyol used in the control foam.
was induced. All foams cured at room temperature for at least 48 h prior to characterizations, which allowed for the complete reaction of diisocyanate forming hard, rigid polyurethane foams.

Characterizations

All prepared lignin polyols were extracted three times with hot hexane under reflux to obtain pure oxypropylated lignin by removing poly(propylene oxide) (PPO) according to the literature.\textsuperscript{34–36}

The molecular weight of Kraft lignin before and after oxypropylation was examined by GPC employing an Agilent Technologies 1200 series analysis system consisting of an autosampler, a UV detector, and four columns of Styrage HR 0.5, HR 2, HR4, and HR 6 (Waters, Inc., Milford, MA) linked in series using THF as the eluent (1.0 mL min$^{-1}$). The acetylated sample was dissolved in THF (1 mg mL$^{-1}$), filtered through a 0.45 µm filter, injected (20 µL) into the GPC system, and detected by a UV detector at 270 nm. A calibration curve was constructed based on eight narrow polystyrene standards ranging in molar weight from 1.5 × 10$^3$ to 3.6 × 10$^6$ g mol$^{-1}$. Data collection and processing were performed using Polymer Standards Service WinGPC Unity software (version 7.2.1, Polymer Standards Service USA, Inc., Warwick, RI). Molecular weights (M$\text{n}$ and M$\text{w}$) were calculated by the software relative to the universal polystyrene calibration curve. Polydispersity index (PDI) was determined by dividing M$\text{w}$ by M$\text{n}$.

FT-IR spectra of Kraft lignin before and after oxypropylation were recorded between 4,000 and 600 cm$^{-1}$ with a resolution of 4.0 cm$^{-1}$ and 64 scans on a Magna 550 FT-IR Spectrometer. KBr powders were used to obtain lignin (1%, w/w) pellets with a thickness of 1 mm.

All NMR experiments were performed with a Bruker Avance-400 spectrometer (Billerica, MA, USA). $^1$H NMR spectra were acquired on dry samples (~20 mg) in DMSO-d$_6$ (450 µL) applying a 90° pulse angle and a 15 s pulse delay at 25°C. Quantitative $^{13}$C NMR spectra were also collected on dry samples (80–120 mg) dissolved in DMSO-d$_6$ (450 µL). An inverse-gated decoupling pulse sequence was used and 10,000 scans were collected at 100.59 MHz operating frequency, a 90° pulse angle, and a 12 s pulse delay at 25°C. Quantitative $^{31}$P NMR spectra were acquired using an inverse-gated decoupling pulse sequence with a 90° pulse angle, a 25 s pulse delay, and 200 scans at 25°C.

SEM images of the prepared rigid PU foams were taken by a Hitachi S-800 FE-SEM. Five samples (5 mm × 5 mm × 1 mm) were cut from different parts of each foam using a sharp blade and were placed on one side of a double-side carbon tape. Samples were coated with a gold palladium sputter coater to prevent charge build-up during imaging. Images were taken under an accelerating voltage of 10 kV and magnification of 40. The average diameter value of five samples was determined for each foam.

The density of each foam was calculated as the average value of mass divided by volume of five samples with a sample size of 25 mm × 25 mm × 15 mm.

Mechanical Testing

Compression testing was carried out on a MTS Insight 2 universal test machine according to ASTM C365/C365M-05. Five specimens with a square section of 25 mm × 25 mm and a thickness of 15 mm were cut off from each foam. The crosshead speed was 4 mm min$^{-1}$. Tests were terminated when it reached a densification level of 80%. Specimen displacement was recorded from the crosshead movement by a data acquisition system. The intersection
point between the initial slope and the plateau slope was determined as the yield strength and the initial slope of the stress-strain curve was termed as the compressive modulus. The average value of five data points of each foam together with the standard deviation (S.D.) was recorded for comparison.

Results and Discussion

Characterization of Oxypropylated Kraft Lignin

Oxypropylation, the chain extension reaction of Kraft lignin, is always accompanied by the homopolymerization of propylene oxide through transfer reactions following the anionic grafting mechanism.\[27,37\] The resulting polyol is, in fact, a mixture of oxypropylated lignin and PPO oligomers. In other words, the PPO oligomers exist either as the grafts of lignin or a polymer by itself. These independent PPO oligomers are normally left in the final mixture because they constitute a very useful bifunctional co-polyol, decreasing the viscosity and glass transition temperature of the lignin polyol.\[27\] The oxypropylation with lignin is illustrated in Figure 1.

Lignin oxypropylation was accomplished following the conditions summarized in Table 1. Most of the propylene oxide reacted either to form the lignin grafts or the homopolymer of PO, which are two competitive reactions during oxypropylation. The traces of PO were removed by placing the lignin polyol in a vacuum oven at 40°C until a constant weight was achieved. The weight of the crude product equals the total weight of the starting Kraft lignin and propylene oxide. The potassium ion remained with the lignin polyol for PU preparation. Pure oxypropylated lignin was separated from the PPO oligmers by extracting the polyol mixture with hot hexane under reflux three times, according to the procedure described by Pavier and Gandini.\[37\] They were subsequently vacuum-dried until a constant weight was achieved and the PPO content was determined to be 46 ± 5 wt%.

The original Kraft lignin has a broad molecular weight distribution and the large molecules degraded to some extent during oxypropylation resulting in a smaller polydispersity index (M_w/M_n) of the oxypropylated lignin. The detailed data were summarized in Table 3. The amount of PPO grafts per oxypropylated lignin macromolecule was determined to be ∼38.9 wt% in average according to the M_n values of the original and oxypropylated Kraft lignin.

FT-IR spectra of the original and the oxypropylated Kraft lignin are shown in Figure 2. The spectra are normalized to the intensity of the lignin aromatic ring vibrations at 1503 cm⁻¹. The bands at 1119 and 1160 cm⁻¹ were attributed to the OCH₃ groups of the propylene oxide side chain and the aromatic O-H vibrations were found at 3400 cm⁻¹.

![Figure 1. Reaction involved in lignin oxypropylation.](image-url)
Table 3
Molecular weight change of Kraft lignin after oxypropylation (samples were acetylated for GPC analysis)

<table>
<thead>
<tr>
<th></th>
<th>Kraft lignin</th>
<th>Oxypropylated lignin</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_w$ (g mol$^{-1}$)</td>
<td>$7.6 \times 10^3$</td>
<td>$4.2 \times 10^3$</td>
</tr>
<tr>
<td>$M_n$ (g mol$^{-1}$)</td>
<td>$1.1 \times 10^3$</td>
<td>$1.8 \times 10^3$</td>
</tr>
<tr>
<td>$M_w/M_n$</td>
<td>7.0</td>
<td>2.4</td>
</tr>
</tbody>
</table>

1600 cm$^{-1}$.[38] In both spectra, the O–H stretching vibration is easily seen at $\sim 3450$ cm$^{-1}$ and the intensity remains generally the same. However, the oxypropylated Kraft lignin exhibits increasing band intensity at 2868–2937 cm$^{-1}$ which is assigned to the O–H stretching vibration in methylene groups.[38] Moreover the increasing band intensity at 1034–1096 cm$^{-1}$ in the spectra of oxypropylated Kraft lignin, corresponding to the aliphatic C–H and C–O stretching vibrations, are also due to the PPO grafts.[39]

Compared to the starting Kraft lignin, the oxypropylated lignin exhibited apparent differences in the $^1$H NMR spectral data (Figure 3). Introducing large amounts of PPO grafts generated peaks of CH$_3$ groups at 1.0 ppm, CH$_2$ groups at 3.4 ppm, and CH groups at 3.7 ppm, which were also seen by Nadji et al.[30] Protons from aromatic rings ($\sim 6.3–7.7$ ppm) were clearly identified although the relative signal intensity was diminished due to the dominance of PPO grafts.

![Figure 2. FT-IR spectra of Kraft lignin (bottom) and oxypropylated lignin (top).](image_url)
Figure 3. $^1$H NMR spectra of Kraft lignin (top) and oxypropylated lignin (bottom).

The signals in the $^{13}$C NMR spectra (Figure 4) can be divided into three main types: 1) those corresponding to carbonyl and carboxyl carbons (160–200 ppm); 2) those associated to aromatic carbons, which can be divided further into substituted (125–160 ppm) and protonated carbons (100–125 ppm); 3) and those assigned to aliphatic carbon atoms, which allow the observation of the main linkages between phenylpropane units (10–100 ppm). The strong signal at 56–57 ppm was readily assigned to the methoxyl group in guaiacyl units.$^{[40]}$

In the spectrum of oxypropylated lignin the grafted PPO oligomers chains generated intense aliphatic carbon peaks. CH$_3$ resonances were identified at 17 and 20 ppm, respectively, for the pendant and terminal methyl groups. CH$_2$ and CH resonances were identified between 71.4 and 77.4 ppm. The terminal CH-OH carbons were identified at 65 and 67 ppm.$^{[41]}$

Quantitative $^{31}$P NMR was used not only to investigate the structure change of the Kraft lignin before and after oxypropylation, but also as a direct and fast tool for hydroxyl index calculation. The spectrum of Kraft lignin shows aliphatic, condensed phenolic, guaiacyl, and a small amount of carboxylic hydroxyl groups, while the spectrum of oxypropylated lignin exhibited only aliphatic and carboxylic hydroxyl groups, as can be seen in Figure 5. This indicates a successful chain extension reaction, after which all phenolic hydroxyl groups have been converted into aliphatic hydroxyl groups of the PPO grafted units. The detailed signal assignments and hydroxyl value analysis of the $^{31}$P NMR spectra of Kraft lignin and oxypropylated lignin are summarized in Table 4. The hydroxyl index ($I_{OH}$), a term often used in PU research, is defined as the weight of KOH (mg) that will neutralize the acetic anhydride capible of reacting by acetylation with 1 g of polyol.$^{[15]}$ Here, $I_{OH}$ of Kraft lignin polyol was determined as the result of the total hydroxyl value (mmol g$^{-1}$) multiplied by the molecular weight of KOH, which is 387 mg KOH/g.
Characterization of Oxypropylated Kraft Lignin-Based Rigid PU Foams

Polyurethane synthesis is essentially a formation of urethane linkages between polyols and isocyanates. However, linkages other than urethane bonds may also be formed, such as allophanate bonds, which can arise from the reaction of excess diisocyanates with urethane groups.[25] Moreover, isocyanate dimerization and trimerization reactions can also occur. Figure 6 shows all possible reactions.

Kraft lignin-based rigid PU foams of varying formulations were prepared under the same experimental conditions. The densities of all foams were measured to be $\sim30$ kg m$^{-3}$. However, the SEM images in Figure 7 show a difference in close-cell diameter between 60%, 100% (750 $\mu$m) Kraft lignin-based foams, and other foams (650 $\mu$m). Moreover,
Table 5
Different cream times of rigid PU foams prepared with varying lignin polyol contents

<table>
<thead>
<tr>
<th>Lignin polyol (wt%)</th>
<th>Cream time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>40</td>
</tr>
<tr>
<td>10</td>
<td>38</td>
</tr>
<tr>
<td>30</td>
<td>34</td>
</tr>
<tr>
<td>60</td>
<td>26</td>
</tr>
<tr>
<td>100</td>
<td>23</td>
</tr>
<tr>
<td>Only lignin polyol</td>
<td>17</td>
</tr>
</tbody>
</table>

shrinkage occurred with the two foams that have larger cell sizes when cured at room temperature. The cream time corresponding to the start of the bubble rise decreased with increasing lignin polyol contents, as shown in Table 5. This result suggests that the lignin polyol has a higher reactivity towards polymeric MDI under the same reaction conditions.

**Mechanical Testing of Oxypropylated Kraft Lignin-based Rigid PU Foams**

A key objective of this study was to optimize the mechanical properties of the Kraft lignin-based PU foams as a function of the starting reagents formulation. It was investigated by compression testing, which generated the stress-strain curves of all prepared foams.

![Quantitative 31P NMR spectra of Kraft lignin (bottom) and lignin polyol (top). TMDP:2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane.](image-url)
Table 6
Yield strength and compressive modulus of prepared rigid PU foams

<table>
<thead>
<tr>
<th>Lignin polyol (wt%)</th>
<th>Strength (MPa)</th>
<th>Modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.10 ± 0.01</td>
<td>1.45 ± 0.07</td>
</tr>
<tr>
<td>10</td>
<td>0.10 ± 0.01</td>
<td>1.56 ± 0.05</td>
</tr>
<tr>
<td>30</td>
<td>0.11 ± 0.01</td>
<td>1.58 ± 0.05</td>
</tr>
<tr>
<td>60</td>
<td>0.10 ± 0.01</td>
<td>1.13 ± 0.01</td>
</tr>
<tr>
<td>100</td>
<td>0.09 ± 0.01</td>
<td>1.11 ± 0.03</td>
</tr>
<tr>
<td>Only lignin polyol</td>
<td>0.14 ± 0.01</td>
<td>3.41 ± 0.39</td>
</tr>
</tbody>
</table>

shown in Figure 8. According to the literature,[42] density plays an important role in the mechanical performance of rigid PU foam and their relationship can be depicted by Power law. However, in the present study, the density of all prepared foams was very close to 30 kg m$^{-3}$ and therefore the mechanical property was simply and directly compared in terms of yield strength and compressive modulus, which are summarized in Table 6. Both the strength and modulus were slightly increased at 10% and 30% lignin polyol contents, and then dropped below the values of the control foam at 60% and 100% lignin polyol contents. The drop could be due to the high content of low functionality polyols; i.e.,

![Figure 6. Possible reactions involved in the preparation of PU.](image-url)
Figure 7. SEM images of rigid PU foams prepared with (a) 0, (b) 10, (c) 30, (d) 60, (e) 100 wt% of Kraft lignin polyol based on the weight of sucrose polyol of the control foam, and (f) only lignin polyol.

PPO oligomers and glycerol polyol, which are generally not favorable polyols for highly crosslinked PU synthesis. The optimal properties were obtained with foam prepared with only lignin polyol without the addition of any other commercial polyols. Its yield strength and compressive modulus were improved by 44% and 135%, respectively, as compared to the control foam. It could be primarily attributed to the rigidity of lignin aromatic structure and the high functionality of lignin hydroxyl groups, which introduced more crosslinking to the PU network resulted in a higher crosslinking density compared to the control foam.
Conclusions

Oxypropylation of Kraft pine lignin was proved to be a successful way to modify solid lignin into a liquid polyol, which possessed a suitable hydroxyl index between 300 and 800 for rigid PU foam preparation. Additionally, oxypropylation made it possible to incorporate a higher content of lignin in the PU formulation, and also provided superior and a better control of the properties of polyol and resulting PU, comparing to directly reacting solid lignin with disiocyanate,[43] polyethylene glycol/glycerol and disiocyanate,[44] or polyether triol and disiocyanate, [17,18] as previously reported by other researchers. This study has shown that it is not only feasible to use lignin polyol solely for rigid PU foam making without the addition of any other polyols or chain extenders, e.g., glycerol,[28] but also afford a rigid PU foam with better mechanical properties than its commercial counterpart. The results suggest a broad application of lignin polyol in the future polyurethane industry.

References

standardisation, production and applications adapted to market requirements (EUROLIGNIN).
10. Stewart, D. Lignin as a base material for materials applications: Chemistry, application and
12. Cateto, C.A.; Batteiro, M.F.; Rodrigues, A.E. Monitoring of lignin-based polyurethane synthesis
to polyurethanes and Appendix 1: Calculations. In The Huntsman Polyurethanes Book; Randall,
17. Yoshida, H.; Morck, R.; Kringstad, K.P.; Hatakeyama, H. Kraft lignin in polyurethanes I. Me-
chanical properties of polyurethanes from a kraft lignin–polyether triol–polymeric MDI system.
Effects of the molecular weight of Kraft lignin on the properties of polyurethanes from a Kraft
25. Saraf, P.V.; Glasser, W.G. Engineering plastics from lignin. III. Structure property relationships
27. Cateto, C.A.; Barreiro, M.F.; Rodrigues, A.E.; Belgacem, M.N. Optimization study of lignin
29. Cateto, C.A.; Barreiro, M.F.; Rodrigues, A.E.; Brochier-Salon, M.C.; Thielemans, W.; Belgacem,
M.N. Lignins as macromonomers for polyurethane synthesis: A comparative study on hydroxyl
30. Nadji, H.; Bruzzese, C.; Belgacem, M.N.; Benaboura, A.; Gandini, A. Oxypropylation of lignins