

Rigid polyurethane foams containing lignin oxyalkylated with ethylene carbonate and polyethylene glycol

Zhang Xuefeng^a, Yunsang Kim^a, Elsayed Islam^a, Madison Taylor^a, Thomas L. Eberhardt^b,
EI Barbary Hassan^a, Rubin Shmulsky^{a,*}

^a Department of Sustainable Bioproducts, Mississippi State University, Starkville, MS 39759, USA

^b USDA Forest Service, Forest Products Laboratory, Madison, WI 53726, USA

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ABSTRACT

A “green” oxyalkylation protocol employing ethylene carbonate (EC), polyethylene glycol 400 (PEG400), and water was developed to convert an industry byproduct, kraft lignin (KL), into biopolyols for the production of rigid polyurethane (RPU) foams. EC served as an oxyalkylation reagent for the derivatization of KL’s hydroxyl (OH) groups. PEG400 and water served as a co-solvent and a reactive additive, respectively, to tailor two properties of the KL-derived biopolyols, those being viscosity and OH number. For the oxyalkylated-KL (OKL), as characterized by ³¹P nuclear magnetic resonance (³¹P-NMR), more than 80% of OH content was aliphatic. The 14-fold increase in reactivity towards isocyanates for the OKL, over that for the unmodified KL, was attributed to the derivatization of lignin phenolic OHs to aliphatic OHs, the latter being more accessible and reactive during the RPU foam production. The preferred oxyalkylation conditions were 170 °C, 30 min, PEG400/EC ratios of 50/50 to 70/30 (wt/wt), and KL mass loadings of 20–50 wt%. Biopolyols synthesized under these conditions exhibited viscosities from 0.5 to 53 Pa·s, OH numbers from 459 to 659 mg KOH/g, and alkalinity numbers below 4 mg KOH/g. The biopolyols were directly used for RPU foam production. RPU foams produced under optimal conditions showed densities from 51 to 60 kg/m³ and compressive strengths from 139 to 204 kPa.

1. Introduction

Lignin valorization has been investigated to improve the economics of biomass conversion and utilization processes for decades. Traditionally, treatment of lignocellulosic biomass primarily focuses on converting the carbohydrates (cellulose and hemicelluloses) to value-added products and chemicals (e.g., wood pulp and bioethanol) through pulping and cellulosic ethanol processes. As a result, a large quantity of lignin is left as a byproduct that is often underutilized (Yan et al., 2018). Even though these lignin byproducts can be burned onsite for power generation, the pulping and bio-ethanol industries have sought non-conventional ways to utilize this material for increased economic return, and because lignin is generated in greater amounts than the mills can use; the price of lignin as a bio-product (\$450/ton) (Kautto et al., 2014) can be significantly higher than the value of lignin as a fuel instead of natural gas (\$165/ton).

Polyurethanes are thermoset polymers that are linked by urethane (-NHCOO-) bridges as a repeating unit. Among industrially relevant polyurethanes, rigid polyurethane (RPU) foams are widely used in residential and commercial applications as thermal insulation materials.

RPU foams are usually synthesized from polyisocyanates and non-renewable petroleum-derived polyols. Extensive efforts have been made to explore green solutions of converting renewable resources to polyols for the production of RPU foams (Septevani et al., 2017; Li et al., 2017; Kirpluks et al., 2018; Czlonka et al., 2018; Bhoyate et al., 2018; Ng et al., 2017). Since industrially isolated lignins usually contain 4.5 to 7.5 mmol/g of OH groups (Balakshin and Capanema, 2015), they hold potential as a sustainable and green source of polyols for the synthesis of RPU foams (Hayati et al., 2018; Zhang et al., 2018). However, the utilization of lignin in the production of RPU foams is still limited due to poor accessibility of sterically hindered phenolic OHs that are inherently lower reactivity with isocyanates relative to aliphatic OHs (Ionescu, 2005). Although liquefaction of lignin with either polyhydric alcohols or ethanol-water mixtures could depolymerize lignin and thereby increase the accessibility of some lignin OH groups (Jin et al., 2011; Mahmood et al., 2016), there is still unrealized potential to increase the reactivity even more by modifying sterically hindered phenolic OHs.

One approach to enhance the reactivity of lignin is oxyalkylation, in which phenolic OHs are derivatized to aliphatic OHs; propylene oxide

* Corresponding authors.

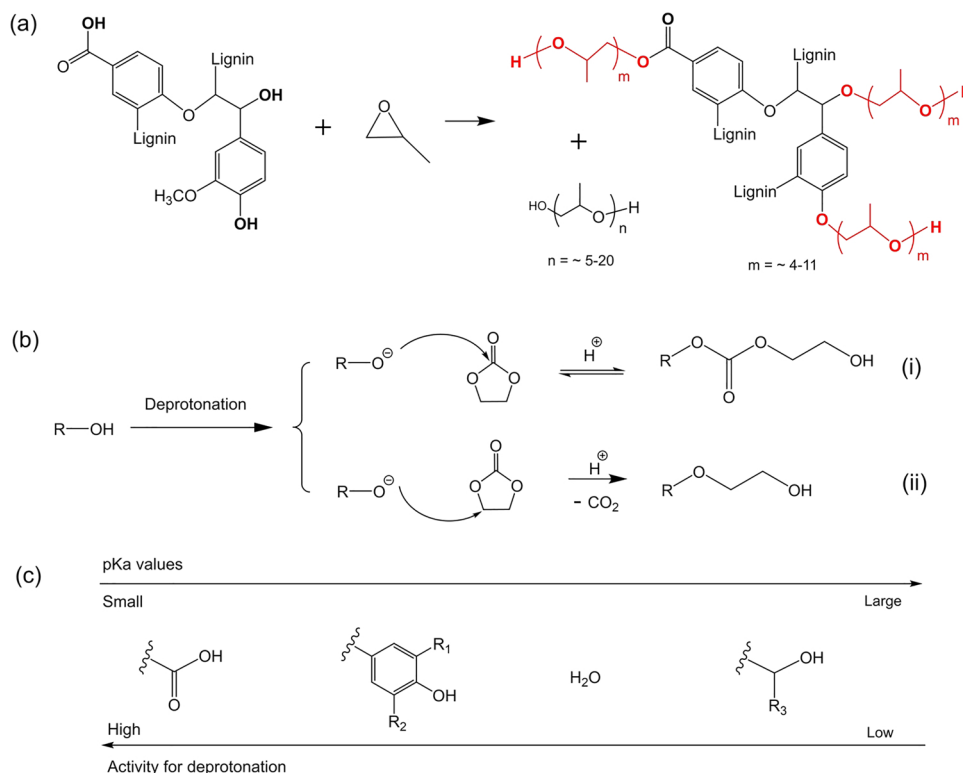
E-mail addresses: xz210@msstate.edu (X. Zhang), rs26@msstate.edu (R. Shmulsky).

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Scheme 1. (a) Oxyalkylation of an industrially isolated lignin with PO for biopolyol production, (b) mechanism of EC ring-opening reactions, (c) deprotonation of different hydroxyl groups.

(PO) is the most commonly used oxyalkylating reagent (Nadji et al., 2005; Cateto, 2008). The resulting product from PO-oxyalkylation, namely biopolyol, is actually a mixture of oxyalkylated-lignin and poly(propylene oxide) (PPO) diols (Scheme 1a). These PPO diols, arising from the homopolymerization of PO, act as a very useful co-polyol for the synthesis RPU foams. Lignin-based biopolyols derived from PO-oxyalkylation can be used to make RPU foams with comparable properties to those made with synthetic polyols; however, PO is a highly toxic and potentially explosive substance with a low boiling point and a high vapor pressure, which makes its handling dangerous.

In recent years, less toxic and biodegradable cyclic carbonates, such as ethylene carbonate (EC) and propylene carbonate (PC), were used as environmentally friendly alternatives for lignin oxyalkylation (Kühnel et al., 2014, 2017a,b; Duval and Avérous, 2017; Liu et al., 2018). In comparison to PO-oxyalkylation, EC-oxyalkylation is a more complicated process, which involves the deprotonation of OH groups followed by the nucleophilic attack at either alkylene or carbonyl atoms of the EC (Scheme 1b) (Kéki et al., 2001; Tomczyk et al., 2012). The nucleophilic attack at the carbonyl carbon atom (reaction i), namely transesterification, results in a polycarbonate linkage. The nucleophilic attack at the alkylene carbon atom (reaction ii), namely etherification, results in a polyether linkage by CO_2 off-gassing. Due to the transesterification being a reversible reaction, the etherification is favored during EC-oxyalkylation. Alkaline catalysts such as K_2CO_3 , $LiCO_3$, or KOH are usually used to facilitate the deprotonation of the OH groups. Generally, weak nucleophiles such as carboxylic and phenolic OHs are easier to be deprotonated, thereby being more reactive for EC-oxyalkylation than aliphatic OHs. Therefore, EC-oxyalkylation is more effective for the derivatization of phenolic and carboxylic OHs than aliphatic OHs. In addition, EC-oxyalkylation is able to produce selective molecular weight products with one-unit hydroxyalkyl grafts on phenolic OHs, while PO-oxyalkylation of phenolic OHs usually yields heterogeneous products due to uncontrollable multiple-unit oxyalkyl grafting (Clements, 2003).

The different types of OH groups in the lignin, those being aliphatic OHs, phenolic OHs, and carboxylic OHs, lead to a heterogeneous reaction for EC-oxyalkylation. Previous studies have shown the full derivatization of lignin phenolic OHs to aliphatic OHs, with one-unit hydroxyalkyl grafting, to be completed within 15 min (Duval and Avérous, 2017). With long reaction times (e.g., 24 h), aliphatic OHs with 2–4 oxyalkyl units in chains can form through continued grafting (Kühnel et al., 2017b; Duval and Avérous, 2017); however, this is undesirable due to the high energy input, but more importantly, the unfavorable lignin condensation reactions that occur over extended reaction times. The homopolymerization of EC usually requires very long reaction times (e.g., 70–100 h) (Lee and Litt, 2000), which is in contrast to that of PO (e.g., 5–10 min). Therefore, unlike PO-oxyalkylation products, EC-oxyalkylation products cannot be directly used as biopolyols for the synthesis of polyurethanes due to the large amount of unreacted EC with low OH numbers.

In this article, we focused on direct synthesis of biopolyols from EC-oxyalkylation of an industrially isolated lignin, and thereafter, RPU foam production. An alternative EC-oxyalkylation protocol using polyethylene glycol 400 (PEG400) as a co-solvent and water as a reactive additive was developed to tailor the properties of the oxyalkylation products by modulating the OH number and viscosity of the biopolyols. The structure of oxyalkylated lignin derivatives was characterized by ^{31}P -NMR, and their reactivity with isocyanates for polyurethane synthesis was studied. The effects of reaction parameters (e.g., the composition of oxyalkylation co-solvents, reaction temperature, and lignin loading) on the properties of the resultant biopolyols was investigated. Finally, optimal reaction parameters are determined to produce high-quality RPU foams containing lignin oxyalkylated with ECs. To the best of our knowledge, this is the first demonstration of applying EC-oxyalkylated lignin for the production of RPU foams.

2. Experimental

2.1. Materials

A commercial softwood kraft lignin (KL), Indulin AT, was provided by Ingevity Corporation (North Charleston, SC). After grinding the KL in a burr mill, the resultant fine powder that passed a screen of 90 μm aperture was collected, oven dried (103 $^{\circ}\text{C}$ for 24 h), and used for the synthesis of the lignin-based biopolyols. The ash content of KL was determined to be 3.62 wt% following ASTM D1102. The KL molecular weight (Mw) and polydispersity index were determined following our previously reported method (Zhang et al., 2018) to be 4825 g/mol and 5.77, respectively. The polyisocyanates (pMDI) mixture, containing 54% polymeric diphenylmethane diisocyanate and 46% diphenylmethane diisocyanate isomers, was purchased from NCFI polyurethanes Inc. The isocyanate group (NCO) content of pMDI was measured to be 7.61 mmol/g following ASTM D2572-97.

Chemicals for ^{31}P -NMR, being deuterated chloroform (CDCl_3), anhydrous pyridine, chromium acetylacetonate, endo-*N*-hydroxy-5-norbornene-2,3-dicarboximide (NHND, internal standard), 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP, phosphitylation reagent), and chromium acetylacetonate [$\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$, relaxation agent], were purchased from Sigma-Aldrich. Other chemicals, being EC, PEG400, potassium carbonate (K_2CO_3), 1,4-dioxane, phthalic anhydride, acetone, hydrochloric acid (HCl), sulfuric acid (H_2SO_4), sodium hydroxide (NaOH), silicon oil, and dibutyltin dilaurate, were purchased from Fisher Scientific.

2.2. Oxyalkylation of lignin for biopolyol preparation

A mixture of PEG400 and EC (PEG400/EC), as co-solvents, was used for the KL oxyalkylations, in which EC is the lignin oxyalkylation reagent, and PEG400 is a non-reactive modifier for adjusting the viscosity and OH number of oxyalkylation-derived biopolyols. The mass fraction of PEG400 in the co-solvent mixture ranged from 20% to 90%. K_2CO_3 was used as a catalyst with a relative mass that was 0.5% of the co-solvent weight. KL mass loading ranged from 20 to 50%, by weight, of the co-solvent mixture. A small portion of H_2O was added to the co-solvent mixture as a reactive additive to convert excess EC to ethylene glycol (EG), and thereby, to increase the OH numbers of the biopolyols. The amount of H_2O was calculated according to a stoichiometric ratio, based on the assumption of EC grafts only 1 hydroxyalkyl unit per lignin OH during oxyalkylation, as follows:

$$\text{H}_2\text{O}, \text{g} = (\text{M}_{\text{EC}} - \text{M}_{\text{KL-OH}}) \times 18 \quad (1)$$

where M_{EC} is the mole amount (mol) of EC in the co-solvent mixture, $\text{M}_{\text{KL-OH}}$ is the mole amount (mol) of OH groups in KL, 18 is the molecular weight (g/mol) of H_2O .

In a typical example, oven-dried KL (4–10 g), PEG400/EC (20 g), K_2CO_3 (0.1 g), H_2O (0.02–2.89 g) were loaded into a 50 mL polypropylene screw-cap centrifuge tube and premixed thoroughly using a Genie-2 vortex mixer at 50 $^{\circ}\text{C}$ for at least 2 h to ensure a good dispersion of lignin and catalyst in the PEG400/EC. The mixture was then transferred into a 60 mL stainless-steel reactor which was tightly sealed before being placed in an oven (100 $^{\circ}\text{C}$ for 10 min) for preheating. The oxyalkylation reaction was initiated by removing the reactor from the oven and immediately immersing it into a preheated oil bath at 140–170 $^{\circ}\text{C}$. After being kept in the oil bath for a preset time (10–30 min), the reactor was then immediately removed and cooled in tap water (25 $^{\circ}\text{C}$) to terminate the reaction. Note that during the reaction, the reactor was gently shaken in the oil bath every 5 min using a pair of tongs. Biopolyols were obtained upon recovery from the reactor. All experiments were conducted with 3 replicates.

2.3. Characterization of biopolyols

The viscosity of the biopolyols was determined at 25 $^{\circ}\text{C}$ at a shear rate of 20 s^{-1} using an AR 1500EX (TA Instruments) rheometer equipped with a rotator spindle with a diameter of 40 mm. The water content of biopolyols was determined using a HANNA HI 903 volumetric Karl Fischer titrator following ASTM D4672-18. The alkalinity number of the biopolyols was determined in accordance with ASTM D4662-08. Approximately 3 g of biopolyol was dissolved in 20 mL of 1,4-dioxane/water (80/20, wt/wt). Titration was conducted using a 0.1 N standard HCl solution and the equivalence point was indicated by a digital pH meter. The OH number of the biopolyols was determined in accordance with ASTM D4274-05D. Specifically, 0.5–1.5 g biopolyol was dissolved in a 25 mL phthalation reagent (containing 115 g of phthalic anhydride and 700 g of pyridine) and heated at 100 $^{\circ}\text{C}$ for 60 min. This was followed by adding 20 mL of 1,4-dioxane and 5 mL of deionized water. Titration was conducted using a 0.5 N NaOH solution to the equivalence point indicated by a digital pH meter. Alkalinity and OH numbers were calculated using formulas from respective ASTM standards.

Finally, FTIR spectra of the biopolyols were recorded in the attenuated total reflectance (ATR) mode on a PerkinElmer Spectrum Two spectrometer in the range 450–4000 cm^{-1} as an average of 10 scans with a 4 cm^{-1} resolution. The results for biopolyol viscosity, water content, alkalinity number, and OH number presented are the means of three replicates.

2.4. Characterization of oxyalkylated lignin

In order to investigate the structure and reactivity of KL after oxyalkylation, the oxyalkylated-KL (OKL) product was separated by precipitation from the biopolyol. For the precipitation of OKL, 1 g of biopolyol was washed with 10 mL of chloroform in a 50 mL polypropylene screw-cap centrifuge tube. After vigorously shaking the mixture for 1 min by hand, and then allowing it to stand for 3 min, the OKL floating on the chloroform was collected with a spatula, and washed again (2 times). The chloroform-washed OKL was transferred to a clean centrifuge tube and then exhaustively washed 4 times with approximately 50 mL deionized water. Each water wash was followed by centrifugation at approximately $100 \times \text{g}$ using a Clay Adams Dynac 0101 centrifuge for 5 min to collect the precipitated OKL.

The composition of OH groups in OKL was determined by ^{31}P -NMR following a procedure derived from previously established protocols (Granata and Argyropoulos, 1995; Zhang et al., 2018). Briefly, 20 mg oven-dried OKL sample was added in 0.5 mL of pyridine/ CDCl_3 solution (1.6/1, v/v) containing 1 mg/mL $\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$ and 2 mg/mL NHND; the mixture was vigorously shaken (Vortex Genie 2 mixer) until dissolved. Then, 0.1 mL TMDP was added into the OKL solution for lignin phosphitylation. Phosphitylated lignin was immediately used for ^{31}P -NMR analysis using a Bruker Avance 300 MHz NMR spectrometer with a 90 $^{\circ}$ pulse angle, 5 s pulse delay, 125–155 ppm scanning range, and 128 scans. TMDP was used as the phosphitylation reagent because it provided a good separation of phenolic OH and aliphatic OH signals in the spectra. For comparison, the composition of OH groups in KL was also tested with the same procedure.

The reactivity of OKL to isocyanates was tested by reacting OKL with pMDI in a 1,4-dioxane/pyridine mixture solution. Specifically, 0.2 g of oven-dried OKL was added to 3 g of 1,4-dioxane/pyridine solution (2/1, wt/wt) in a glass vial and vigorously shaken by Vortex Genie 2 mixer until dissolved. Then, a predetermined amount of pMDI (equivalent amount to the total OH content of OKL) was added into the OKL solution followed by vigorous shaking (Vortex Genie 2) to initiate crosslinking reactions between pMDI and OKL. The set time at the end of the reaction was defined by the time from mixing pMDI and OKL, to when the resultant polyurethane resin solidified. The gel-like resin was solidified further upon suspension in 15 mL of acetone, which

Table 1
RPU foam formulation used in this study.

Component	Parts by mass
Biopolyol	100
pMDI	Equivalent amount for NCO-index of 120
Silicon oil surfactant	2
Dibutyltin dilaurate catalyst	1
Blowing agent (water)	1.5
Alkalinity neutralizing agent (H ₂ SO ₄)	Equivalent amount to K ₂ CO ₃ contained in biopolyol

extracted/diluted the reaction solvents; Soxhlet extraction with acetone for 2 h removed all residual 1,4-dioxane and pyridine. The extracted resin was dried at 50 °C under vacuum for 12 h. FTIR spectra of the oven-dried resin were then recorded on a PerkinElmer spectrometer in ATR mode (10 scans with a 4 cm⁻¹ resolution). For comparison, the reactivity of KL was also tested with the same procedure.

2.5. Preparation of rigid polyurethane (RPU) foams

A formulation for producing the RPU foams is listed in Table 1. The isocyanate index (NCO-index) for all the RPU foams was set to 120 and calculated using the following equation:

$$\text{NCO-index} = [W_{\text{pMDI}} \times \text{NCO}_{\text{pMDI}} / (W_{\text{Biopolyol}} \times \text{OH}_{\text{Biopolyol}} + W_{\text{Water}} \times \text{OH}_{\text{Water}})] \times 100 \quad (2)$$

where W_{pMDI} , $W_{\text{Biopolyol}}$, and W_{Water} are the weight (g) of pMDI, biopolyol, and water (blowing agent), respectively; NCO_{pMDI} is NCO content of pMDI (7.61 mmol/g); $\text{OH}_{\text{Biopolyol}}$ and OH_{Water} are the OH content (mmol/g) of biopolyol and water (111 mmol/g) (Huang et al., 2017; Ionescu, 2005), respectively. Because at the optimized condition the biopolyol water content is low, the original water content in biopolyol was excluded for the NCO-index calculation.

In a typical RPU foam production process, approximately 12 g biopolyol was premixed with catalyst, surfactant, neutralizer (H₂SO₄), and blowing agent (H₂O) in a 650 mL disposable polypropylene beverage cup. Mixing with a Cole-Parmer compact digital mixer at 2500 rpm for 1–3 min gave a homogenous biopolyol mixture. The absolute amounts of the other reagents were adjusted to maintain the proportions shown in Table 1. Adding H₂SO₄ to the biopolyol mixture to neutralize residual K₂CO₃ was essential for the preparation of foams. After that, a predefined amount of pMDI (calculated from NCO-index) was added into the cup, followed by stirring the mixture at 2500 rpm for another 18–25 s. The foam was allowed to freely expand in the cup and allowed to cure for at least 1 day before being removed and cut into specimens for further analysis.

2.6. Characterization of RPU foams

The density and compressive strength of RPU foams were measured in accordance with ASTM D 1622-08 and ASTM D 1621-10, respectively. RPU foam samples were tested on at least 9 replicates with the dimension of 25 × 25 × 22 mm³ (22 mm in the foam rise direction). Compressive strength testing was conducted using Instron 3382 universal testing machine with a crosshead displacement rate of 2 mm/min.

In order to analyze the significance of differences in the density and the compressive strength of RPU foams among different groups, analysis of variance (ANOVA) was implemented. SAS software (SAS Institute, Cary, NC, USA) was used to perform the ANOVA with a least significant difference (LSD) test at a significance level of 0.05.

3. Results and discussion

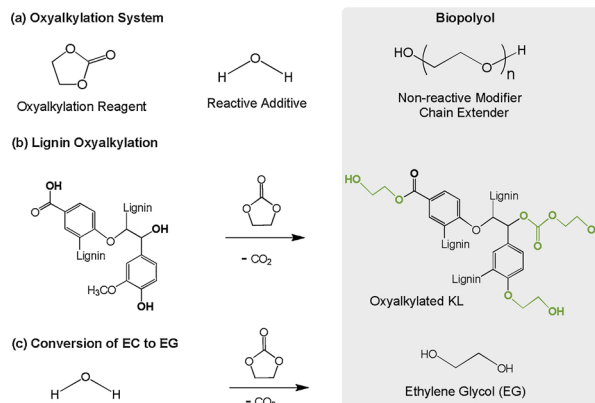
3.1. Characterization of oxyalkylated lignin

In the recent literature, oxyalkylation of lignin with cyclic carbonates was found to modify various types of OH groups in lignin, albeit by different mechanisms (Scheme 2a), those mainly being a deprotonated carboxylic/phenolic OH group attack of the cyclic carbonate followed by CO₂ off-gassing, or a deprotonated aliphatic OH group attack resulting in a polycarbonate linkage (Kühnel et al., 2017b). Due to the high deprotonation activity of carboxylic and phenolic OH groups, the previous mechanism is highly favored over the other. Modification of the phenolic OHs was of particular interest in the current study to increase the reactivity of the lignin as a biopolyol for RPU foams; however, it should be noted that products by lignin oxyalkylation with EC cannot directly be used as a polyol for RPU foam preparation due to the lack of EC homopolymerization leaving a considerable amount of unreacted EC contained in the product, even if the reaction was conducted at 170 °C for 5 h, as shown in Fig. S1 in the Supporting Information (SI).

Therefore, in this study, we reduced the amount of EC used for lignin oxyalkylation by substituting 20–80 wt% of EC with PEG400 to serve both as a non-reactive modifier during lignin oxyalkylation, and

as a chain extender in RPU foam synthesis. After this substitution, the equivalent weight of EC to lignin OH groups was in the range of 1.1–8.5 mmol/mmol, which is much lower than that of 10–50 mmol/mmol used in the previous studies (Kühnel et al., 2014, 2017b, 2017a; Duval and Avérous, 2017). In addition, a small amount of H₂O was added to consume residual EC, converting it into ethylene glycol (EG) to increase the biopolyol OH number for polyurethane synthesis (Scheme 2c). The amount of water added was equivalent to residual EC after oxyalkylation, with the assumption of only a one-unit hydroxyalkyl graft on each lignin OH group. The main reactions during lignin oxyalkylation in the new oxyalkylation system are shown in Scheme 2.

In order to confirm that phenolic OHs in lignin were modified in our new oxyalkylation system with less EC, ³¹P NMR analyses of the KL and oxyalkylated-KL (OKL) were conducted (Fig. 1). In general, the spectra can be divided into the regions of aliphatic (150–145 ppm), phenolic (145–136.4 ppm), and carboxylic OHs (136.4–133.6). The comparison of the oxyalkylated KL (OKL) spectrum with KL spectrum showed a significant increase in intensity at around 146.3 ppm, and a significant



Scheme 2. Oxyalkylation of lignin with EC and PEG400 co-solvent system.

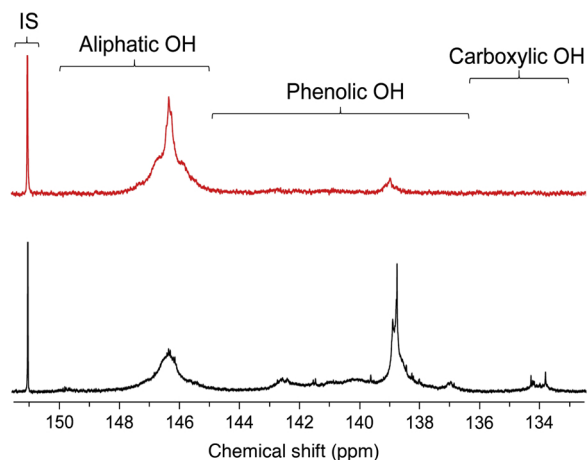


Fig. 1. ^{31}P NMR spectra of OKL and KL in CDCl_3 with NHND as an internal standard. Oxyalkylation condition of OKL: 60 wt% PEG400, 20 wt% lignin loading, 170 °C for 30 min.

decrease in intensity at around 139 ppm, indicating the conversion of phenolic OHs to aliphatic OHs.

The composition of lignin OH groups was further analyzed from the integrated areas in the spectra and shown in Fig. 2. KL contains 5.33 mmol/g OHs (Fig. 2b), in which the ratio of aliphatic, phenolic,

and carboxylic OHs were 33%, 62%, and 5% (Fig. 2a), respectively. For all the tested conditions of temperature (140–170 °C, Fig. 2a), PEG400 ratio (20–90 wt%, Fig. 2c), and lignin loading (20–50 wt%, Fig. 2e), the oxyalkylation resulted in the OKLs having over 80% OH groups as being aliphatic. Given the negligible differences in the proportion aliphatic OHs at the various temperatures used, effective oxyalkylation can be achieved at temperatures over 140 °C using the 30 min reaction time. This result was different from Duval and Avérus (2017) and Kühnel et al. (2017a), which achieved 100% aliphatic OHs in EC-oxyalkylated lignin. This difference can be attributed to the lower amount of EC used in the current study, that corresponding to an EC to lignin ratio in the range of 1.1–8.5 (Fig. 2a, c and e). Although EC-oxyalkylation effectively derivatized lignin phenolic and carboxylic OHs, the oxyalkylated lignin (OKL) was found to have lower OH content than the starting KL. The OH content of KL was slightly decreased from 5.33 mmol/g to 5.10 mmol/g at 140 °C, and further decreased to 4.97 mmol/g at 170 °C, corresponding to an overall 6.8% OH content reduction (Fig. 2b). As the amount of PEG400 increased from 20 to 90, the total OH content of OKL decreased slightly from 5.05 to 4.71 mmol/g, with the total OH content being reduced by 11.7% at the highest wt% of PEG400 (Fig. 2d). The total OH content of OKL was significantly decreased from 4.97 to 2.71 mmol/g with the increasing lignin loading from 20 to 50 wt% (Fig. 2f). At lignin loading of 50 wt%, the total OH content of OKL was reduced by 49% (Fig. 2f). Overall, the reductions of lignin OH content can be attributed to the condensation reactions of lignin intermediates, which was more remarkable at higher

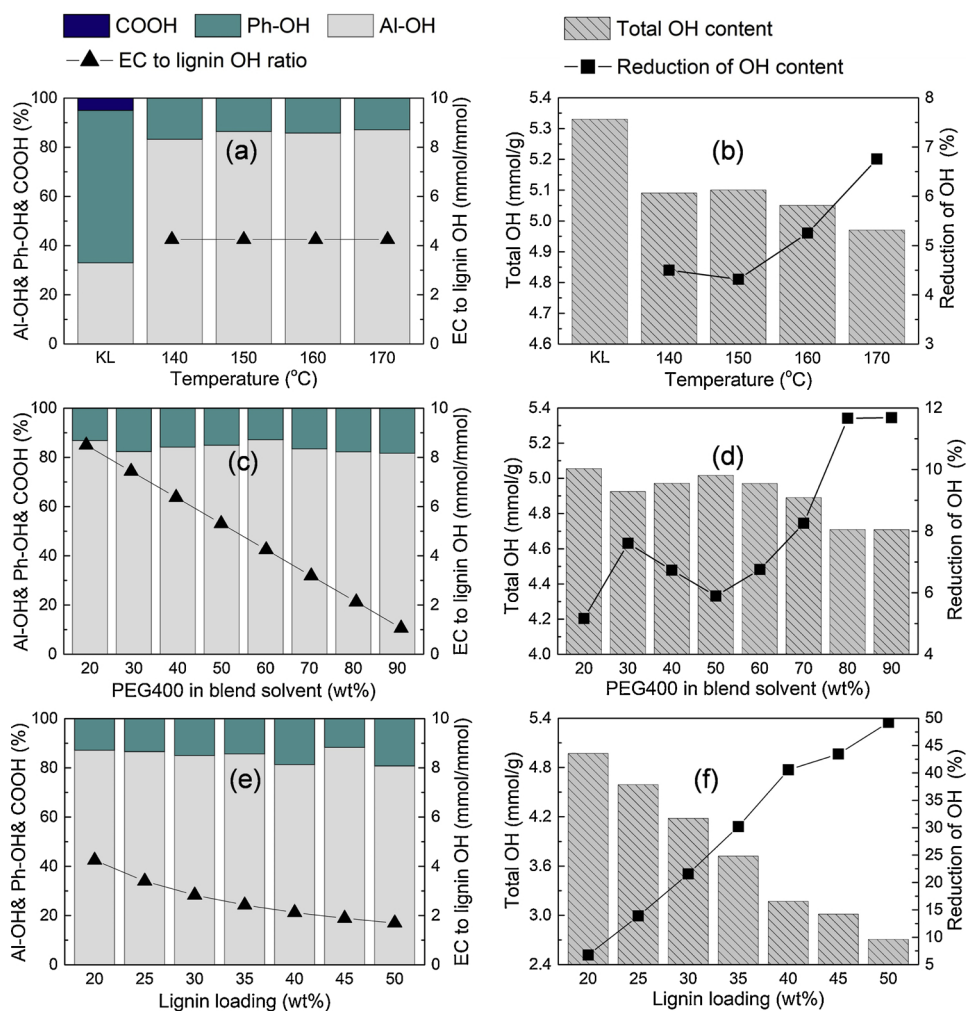


Fig. 2. Effect of temperature on OKL hydroxyl composition (a) and content (b), effect of PEG400 ratio on OKL hydroxyl composition (c) and content (d), effect of lignin loading on OKL hydroxyl composition (e) and content (f).

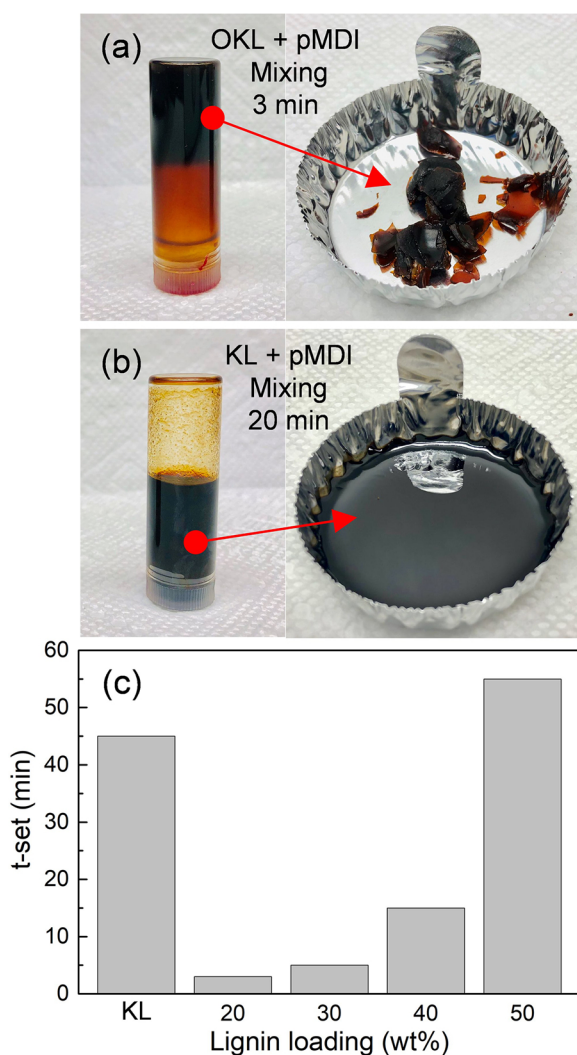


Fig. 3. (a–b) Photographs of mixtures of (a) OKL (60 wt% PEG400 in co-solvent, 20 wt% lignin loading, 170 °C, 30 min) and (b) KL with pMDI in a dioxane/pyridine solution; (c) t-set for KL and OKL with different lignin loadings (oxyalkylation condition: 170 °C for 30 min with 60 wt% PEG400).

lignin loading. Although oxyalkylation reduced total OH content of the lignin, more than the 80% proportion of aliphatic OHs in the OKLs was anticipated to result in overall reactivities being higher than that for KL.

In order to verify increased reactivity of lignin by oxyalkylation, both KL and OKL were reacted with pMDI in a dioxane/pyridine mixture solution. For the OKL prepared at 170 °C for 30 min with 60 wt% PEG400 in co-solvent and 20 wt% lignin loading, when mixing with pMDI, it only took 3 min to become a solid gel-like polyurethane resin (Fig. 3a and video in Supplementary materials). The mixture of KL and pMDI remained in liquid state after 20 min mixing (Fig. 3b); the time (t-set) needed for the mixture to become the solid gel-like polyurethane (PU) resin was 45 min. This result indicates the reactivity of OKL towards pMDI about 14 times higher than that of KL. As lignin loading increased from 20 wt% to 50 wt%, the t-set increased from 3 min to 55 min (Fig. 3c), this can be attributed to lower OH content of OKL at higher lignin loading.

The crosslinking densities of OKL- and KL-derived PU resins were further characterized by FTIR. Fig. 4 shows the FTIR spectra of KL, OKL, and the PU resins derived from them. In comparison with KL, the OKL spectrum shows a small peak at 1740 cm^{-1} that indicates the presence of carbonate linkages from the transesterification reaction (reaction ii in Scheme 1b) between lignin OH groups and EC; however, the

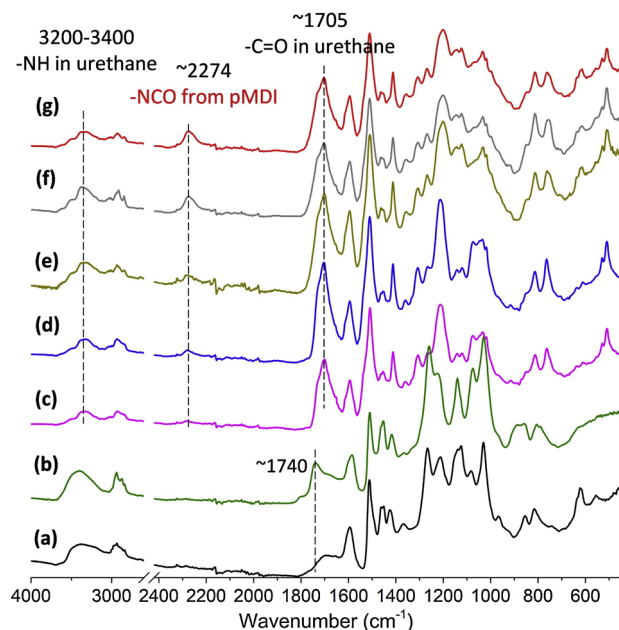


Fig. 4. FTIR spectra of (a) KL; (b) OKL with 20 wt% lignin loading; (c–g) OKL-derived PU resins with (c) 20 wt%, (d) 30 wt%, (e) 40 wt%, (f) 50 wt% lignin loading; and (g) KL-derived PU resin. Oxyalkylation was conducted at 170 °C for 30 min with 60 wt% PEG400.

intensity at 1740 cm^{-1} is much lower than the previous reports from Kühnel et al. (2017a) and Duval and Averous (2017). This suggests the derivatization of lignin OH groups mainly occurred through etherification reaction. For OKL- and KL-derived PU resins, the urethane-related linkages such as N–H (3200–3400 cm^{-1}) and C=O (~1705 cm^{-1}) can be observed in their spectra. The NCO peak at ~2274 cm^{-1} in both resins indicates the residual isocyanates from the pMDI. In comparison with KL-derived PU resin (spectrum g in Fig. 4), the OKL-derived PU resin derived from 20 wt% lignin loading (spectrum c in Fig. 4) has a much smaller NCO peak, which suggests the higher crosslinking density of the OKL-derived PU resin. The higher crosslinking density of the OKL-derived PU resin (with 20 wt% lignin) is attributed to the higher amount of aliphatic -OHs in OKL. On the other hand, as lignin loading increased from 20 wt% to 50 wt%, the intensity of NCO peak of OKL-derived resins showed an increasing trend (Fig. 4 spectra c–f), indicating a lower crosslinking density at higher lignin loadings. At higher lignin loadings (especially at 50 wt%), OKL exhibits a lower OH content (Fig. 2f), indicating a more condensed lignin structure was formed; this is probably responsible for the reduction of crosslinking density in OKL-derived resins at higher lignin loadings.

3.2. Properties of biopolyols and RPU foam

3.2.1. Effect of oxyalkylation temperature

Fig. 5a shows the effect of reaction temperature on the viscosity and water content of biopolyols. As the temperature increased from 140 to 170 °C, the biopolyol viscosity increased from 0.29 to 0.53 Pa·s, while the water content decreased from 3.65 to 0.18 wt%. Fig. 5b shows the effect of reaction temperature on biopolyol OH and alkalinity numbers. As the temperature increased from 140 to 170 °C, the OH and alkalinity numbers of biopolyol increased from 323 to 569 mg KOH/g and from 2.4 to 3.2 mg KOH/g, respectively. The increases in biopolyol viscosity and OH numbers with rising temperature can be attributed to the conversion of EC to EG (Scheme 2); this is because EG has a much higher viscosity (16.1 mPa·s) and OH number (1807 mg KOH/g) than that of EC (2.5 mPa·s and 0 mg KOH/g, respectively). The corresponding FTIR spectra of lignin-based biopolyols are given in SI (Fig. S2) and show that increasing temperature facilitates the conversion of

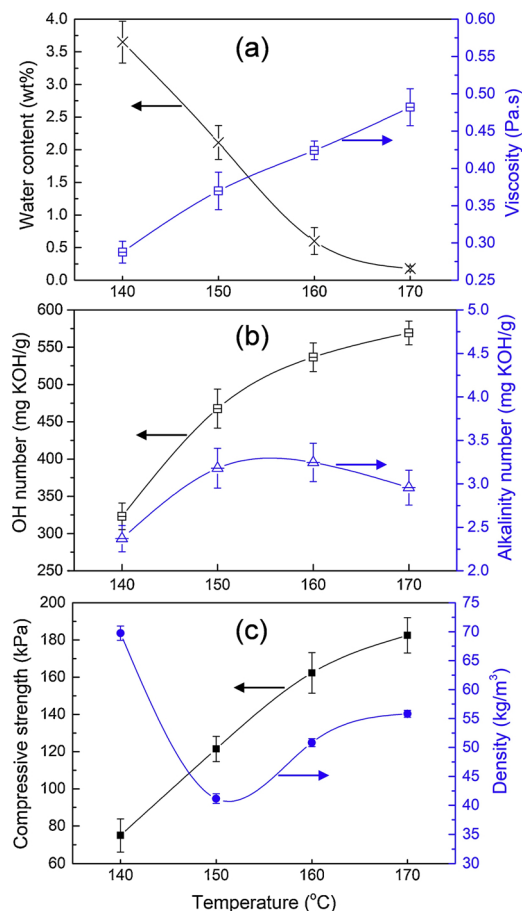


Fig. 5. Effect of oxyalkylation temperature on (a) water content and viscosity, (b) OH and alkalinity numbers of biopolyol, and (c) compressive strength and density of RPU foam. (reaction conditions: 20 wt% KL mass loading, co-solvents containing 40 wt% EC and 60 wt% PEG400, 30 min). Standard error bars in the plots were calculated using the standard deviations of these replicates.

EC to EG. At lower temperatures, *i.e.*, 140–160 °C, the conversion of EC to EG was incomplete and left a considerable amount of water, so the optimal oxyalkylation temperature appears to be 170 °C.

RPU foams were directly synthesized using biopolyols from lignin oxyalkylation. Representative pictures of RPU foams produced from lignin-based biopolyols are shown in SI (Fig. S3). Compared to conventional RPU foam made with PEG400 that is white, lignin-based RPU foams are brown, resulting from the brown color of the KL.

Fig. 5c shows the effect of oxyalkylation temperature on the density and compressive strength of RPU foams. As the temperature increased from 140 and 170 °C, the density and compressive strength of RPU foams ranged from approximately 41 to 69 kg/m³ and 75 to 182 kPa, respectively. The RPU foams obtained from the oxyalkylation at 140 °C exhibited the highest density. This can be attributed to the substantial shrinkage after foam production. This shrinkage was likely due to a considerable amount of unconverted EC and water contained in the biopolyol derived at 140 °C. Water serves as a chemical blowing agent during foam synthesis, which could react with pMDI and generate CO₂ to expand the foam cells; however, too much CO₂ would induce the breakage of foam cells, thereby decrease the rising volume of the foams. As the temperature increased from 150 and 170 °C, the foam density was increased from 41 to 56 kg/m³. This can be attributed to the decrease in water content in biopolyols when temperature rises. The compressive strength of RPU foams increased from 75 to 182 kPa with an increased temperature from 140 to 170 °C. Strong linear correlations are found between RPU foam compressive strength and biopolyol OH number ($R^2 = 0.99$). This linear relationship indicates that higher OH

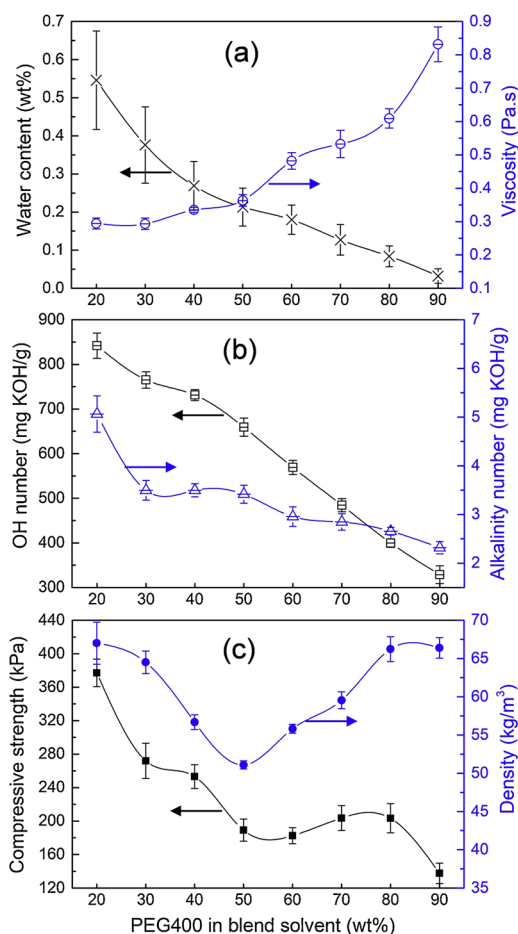


Fig. 6. Effect of PEG400 content on (a) water content and viscosity, (b) OH and alkalinity numbers of biopolyol, and (c) compressive strength and density of RPU foam. (Reaction conditions: 20 wt% KL mass loading, 170 °C, 30 min). Standard error bars in the plots were calculated using the standard deviations of these replicates.

numbers contribute to more compact and denser structures leading to higher compressive strength RPU foams. Therefore, the increase in compressive strength with the increase in temperature from 150 to 170 °C was attributed to the increase in foam density. Analysis of the data by ANOVA suggested that the effect of reaction temperature on the compressive strength and density of RPU foams was significant ($p = 0.00$).

3.2.2. Effect of PEG400 content in the co-solvent

This study focuses on direct utilization of oxyalkylation-derived biopolyols for the production of RPU foams. In the PEG400/EC co-solvent system, PEG400 serves as a non-reactive modifier during lignin oxyalkylation that adjusts the OH value and viscosity of the biopolyols, aside from serving as a chain extender in RPU foam synthesis that plays an important role in enhancing the structural homogeneity and mechanical properties of RPU foams. Fig. 6a shows the effect of PEG400 content in the co-solvent system on the water content and viscosity. Although water added into the co-solvent system was calculated to be equivalent to the amount of EC after one-unit hydroxyalkyl grafting onto lignin OH groups, a small amount of water remained in the biopolyols. The water contents of the biopolyols decreased from 0.55 to 0.03 wt% with the increase of PEG400 from 20 to 90 wt%. This can be attributed to more water being added when the co-solvent contained more EC. It worth noting that the biopolyol water content was less than 0.2% when PEG400 content was above 60 wt%, negating any need for water removal before RPU foam production. Biopolyol viscosity

increased from 0.29 to 0.83 Pa·s with the rise of PEG400 from 20 to 90 wt%, which can be also attributed to the higher viscosity of PEG400 than EC, as well as EG.

Fig. 6b shows the effect of PEG400 content on the OH number and alkalinity number of biopolyols. As the content of PEG400 in the co-solvent increased from 20 to 90 wt%, the OH number of the biopolyol decreased from 842 to 329 mg KOH/g. This decrease is attributed to the lower OH number of PEG400 than EG (as a reaction product of EC and H₂O). A strong linear correlation between biopolyol OH number and the content of PEG400 was observed ($R^2 = 0.99$), suggesting little influence of PEG400 on the oxyalkylation reaction. Biopolyol alkalinity number decreased from 5.1 to 2.3 mg KOH/g with the increase of PEG400 from 20 to 90 wt%. The reduction in the alkalinity number of the biopolyol might be ascribed to the condensation reactions and carbonate transesterification reactions between PEG400 and lignin intermediates (Duval and Avérous, 2017; Kühnel et al., 2017b) that occur more easily at high PEG400 concentration.

Fig. 6c shows the effect of PEG400 content on the density and compressive strength of RPU foams. The density of RPU foams initially decreased with increasing PEG400, with a minimum of 51 kg/cm³ occurring at 50 wt%. Above 50 wt%, the density of RPU foams returns back to 66 kg/m³ at 90 wt% of PEG400. Reduction in density usually comes from increased foam cell expansion during the foaming process. In comparison with EG, PEG400 is a long-chain polyol which could allow more expansion of the foam cell. Thus, increasing PEG400 in the biopolyols, up to 50 wt%, likely contributed to increasing cell expansion, resulting in the reduction of foam density. Rising RPU foam density after 50 wt% of PEG400 may be explained by a threshold for OH number being reached, causing a decrease in initial crosslinking density. For instance, when the initial crosslinking density was too low to produce strong cell walls for maintaining the CO₂ gas generated during foam formation, the release of CO₂ from foam cells resulted in decreased foam expansion volume (Sonjui and Jiratumnukul, 2015). Additionally, the increase of foam density with the increase PEG400 content from 50 to 90 °C was also attributed to a decrease in biopolyol water content.

As PEG400 content increased from 20 to 90 wt%, the compressive strength of RPU foams ranged from 377 to 137 kPa (Fig. 6c). From 20% to 50 wt% of PEG400, the compressive strength is inversely proportional to the PEG400 content, which can be attributed to reduced foam density; however, when foam density increased after 50 wt% of PEG400, the compressive strength of RPU foams seems to remain relatively unchanged. We believe that an increased amount of long-chain PEG400 possibly conferred mechanical flexibility to RPU foams. Increased foam flexibility counteracts the compressive gain from the increase in foam density, thereby leading to a marginal fluctuation in the compressive strength of RPU foams. Further increases in PEG400 to 90 wt% caused a significant decrease ($p = 0.01$) in foam compressive strength.

3.2.3. Effect of lignin mass loading

Fig. 7a shows the effect of KL mass loading on the water content and viscosity of biopolyols. As the KL loading increased from 20 to 50 wt%, the water content of biopolyol ranged from 0.18 to 0.07 wt%, while biopolyol viscosity increased exponentially from approximately 0.5 to 53 Pa·s. Although a highly viscous biopolyol may not be suitable as an additive in polymer applications, the biopolyol viscosity of 53 Pa·s is still acceptable for the preparation of polyurethane foams. It is worth noting that the EC-oxyalkylated biopolyols obtained from this study have a much lower viscosity than the biopolyols derived from PO oxyalkylation with the same amount of lignin mass loading (Cateto, 2008; Cateto et al., 2014; Nadji et al., 2005), suggesting that even greater amounts of lignin can be used in EC oxyalkylations.

Fig. 7b shows the effect of KL mass loading on biopolyol OH and alkalinity numbers. As KL mass loadings increased from 20% to 50%, the alkalinity of biopolyol remained around 2.8 mg KOH/g, while the

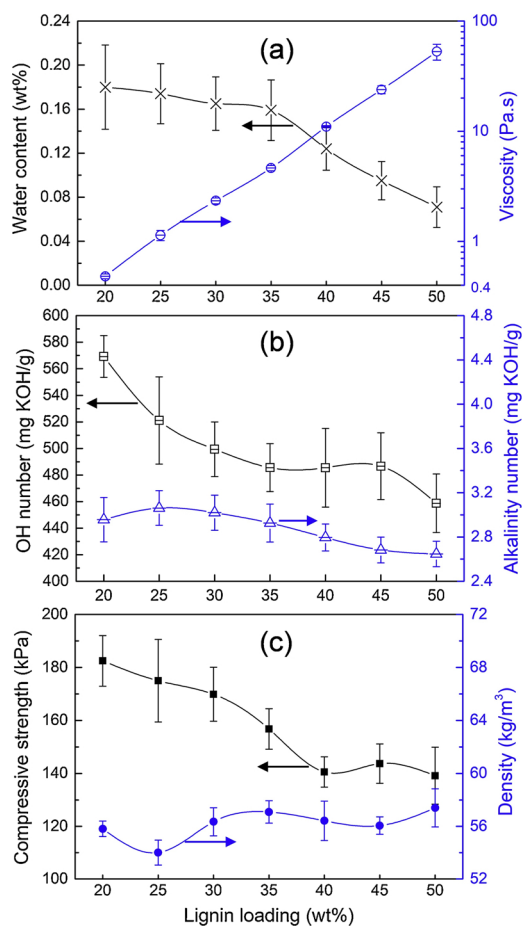


Fig. 7. Effect of KL mass loading in biopolyol on (a) water content and viscosity, (b) OH and alkalinity numbers of biopolyol, and (c) compressive strength and density of RPU foam. (Reaction conditions: co-solvent containing 40 wt% EC and 60 wt% PEG400, 170 °C, 30 min). Standard error bars in the plots were calculated using the standard deviations of these replicates.

OH number of biopolyols decreased from 569 to 452 mg KOH/g. The decrease in OH number can be caused by the consumption of EC for lignin oxyalkylation and/or lignin condensation reactions that occur more readily at high KL mass loadings.

As shown in Fig. 7c, the density of RPU foams ranged from 54.0 to 57.4 kg/m³ when KL mass loading in biopolyol was between 20% and 50%, this could be attributed to a higher water content of biopolyols at higher lignin loading. ANOVA showed that the effect of KL mass loading on foam density was insignificant ($p = 0.42$). The compressive strength of RPU foams gradually decreased from 182 to 139 kPa. ANOVA showed that the effect of KL mass loading on foam compressive strength was significant ($p = 0.00$). The decrease in compressive strength was probably due to either the lower OH values of biopolyol or the less homogeneous foam cellular structure at higher KL mass loading. It is worthwhile to note that the compressive strength of RPU foams containing up to 50% lignin remained greater than the minimum compressive strength (> 130 MPa) required for insulation applications, such as the core layer in structural insulated panels used for building construction (Zhang et al., 2019).

4. Conclusions

This study reports a novel EC-oxyalkylation protocol to convert KL into biopolyols for the production of RPU foams. More than 80% of lignin OH groups was in the form of aliphatic OHs that allowed for the high reactivity of the derivatized lignin in the formation of the RPU

foams. Using the resultant lignin-based biopolyols, RPU foams were successfully produced. The properties of produced biopolyols and RPU foams were influenced by oxyalkylation parameters such as reaction temperature, PEG400 ratio, and lignin mass loading. In order to produce biopolyols of suitable material properties for RPU foams, optimized oxyalkylation conditions include reaction temperature of 170 °C for 30 min, PEG400 proportion of 50–70 wt%, and KL mass loading of 20–50 wt%. Combined properties of the lignin-based RPU foams suggest that lignin oxyalkylation with EC and PEG400 is a promising route that leads to a cleaner production of high-quality bio-based RPU foams.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.indcrop.2019.111797>.

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