RIGID POLYURETHANE AND POLYISOCYANURATE FOAMS MADE WITH LIQUID LIGNIN POLYOLS

By

Maureen Setor Afaglo

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ABSTRACT

Lignin is a complex, abundant natural polymer that has attracted significant attention as an alternative to petroleum-based polyols in rigid polyurethane foams, owing to its aromatic structure, high functionality, and high hydroxyl (OH) value. However, the limited reactivity of its sterically hindered phenolic hydroxyl groups towards isocyanates has limited the utilization of solid lignin to approximately 50% polyol substitution, with a noticeable decline in properties beyond that point. Oxyalkylation with cyclic carbonates has emerged as a green and effective method for improving lignin reactivity by converting the phenolic hydroxyl groups into more reactive aliphatic OH groups. This thesis focuses on the development of rigid polyurethane and polyisocyanurate foams using oxypropylated lignin polyols. First, a simple yet novel method was employed to increase the hydroxyl value of lignin polyols by the in-situ generation of propylene glycol. Then, rigid polyurethane (PU) foams were produced by fully replacing petroleum-based polyols with synthesized lignin polyols. The developed lignin polyols had very high reactivity, necessitating the addition of a delayed-action catalyst to control foaming. The lignin-based foams also met most of the standard specifications for type II spray-applied rigid cellular polyurethane thermal insulation and had superior mechanical properties compared to the foam made with conventional fossil fuel-based polyol. The biobased foams, however, had slightly lower thermal stability due to the presence of propylene glycol and other oligomers of propylene carbonate. Finally, urethane-modified polyisocyanurate (PUR/PIR) foams were prepared with oxypropylated lignin polyols. These foams exhibited improved flame retardancy, with significantly shorter burn times than the control, even without the addition of flame retardant, and showed less shrinkage compared to the petrochemical-based foams.

To Yeshua, my loving parents and family.
Thank you for holding me up!

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LIST OF ABBREVIATIONS

^{13}C-NMR: Carbon-13 Nuclear Magnetic Resonance

DBU: 1,8-Diazabicyclo(5.4.0)undec-7-ene

FTIR: Fourier Transform Infrared Spectroscopy

H-NMR: Hydrogen Nuclear Magnetic Resonance

LP: Lignin polyol

NCO: Isocyanate Group

OH: Hydroxyl group

^{31}P-NMR: Phosphorus-31 Nuclear Magnetic Resonance

PC: Propylene Carbonate

PG: Propylene

PIR: Polyisocyanurate

PPHP: Parts Per Hundred Polyol

PU: Polyurethane

PUR/PIR: Polyurethane/Polyisocyanurate

SEM: Scanning Electron Microscopy

TCPP: Tris (chloropropyl) Phosphate

INTRODUCTION

2.1 Polyurethanes

Polyurethanes are one of the largest classes of polymers, with a wide range of applications including foams, coatings, adhesives, and elastomers. Generally, they are formed via a step addition polymerization reaction between polyfunctional alcohols and isocyanates,[1] forming characteristic urethane linkages. Besides the primary urethane-forming reaction, other reactions occur, such as between isocyanates and water resulting in the generation of carbon dioxide, which acts as a blowing agent for expanding the foams, and the trimerization of isocyanates, giving rise to thermally stable isocyanurate rings.[2]

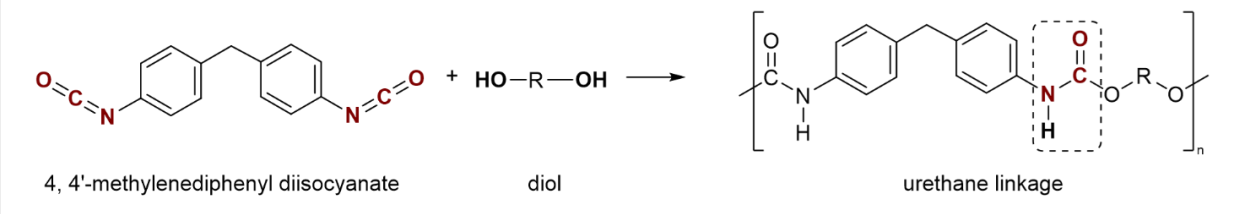

Figure 1: Reaction between isocyanate and diol forming urethane linkages

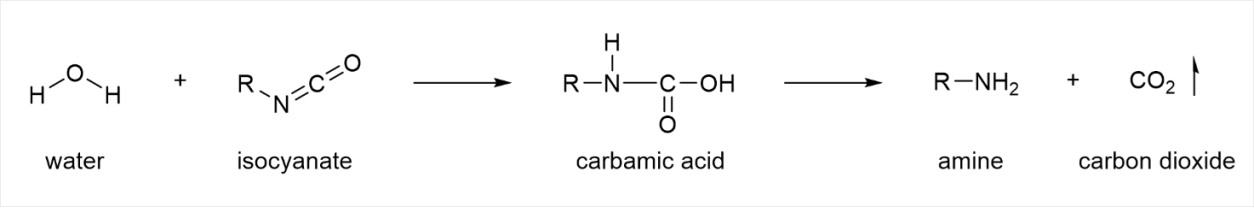

Figure 2: (a) Reaction of isocyanate with water to produce carbon dioxide and amine

Rigid polyurethane foams are among the most efficient insulating materials.[3] They are composed of a solid, continuous phase and a discontinuous gaseous phase.[4] This structure is the result of two competing reactions, namely gelation and blow reactions. Gelation, or the urethane reaction, occurs between the hydroxyl groups of the polyol and NCO groups, and is responsible for the formation of the solid polymer network. The blow reaction leads to the expansion of the foam and the creation of its cellular architecture. This can occur through either of two mechanisms or by a

combination of both. The first involves the exothermic reaction of isocyanate with water, generating carbon dioxide, which lifts and expands the foam. The second mechanism involves the addition of a low-boiling point liquid which causes expansion by vaporizing during PU synthesis. Establishing an equilibrium between gel and blow reactions is crucial to obtaining final products with desired properties.[3] Rapid formation of the polymer network results in high density foams due to low gas entrapment while a faster blow reaction leads to the formation of thin cell walls which are prone to collapse.[5]

2.2 Rigid Polyurethane Foam Components

Urethane chemistry is extremely versatile and highly adaptable to obtaining a vast array of products by varying the proportions and properties of the main components and additives. Polyurethane foams are synthesized from a combination of polyol, surfactants, catalysts and blowing agents, which constitute the B-side resin blend, and isocyanates.

2.2.1 Polyols

Polyols are one of the main starting materials for PU synthesis and are characterized by the presence of hydroxyl (OH) moieties, which serve as reactive sites for the polymerization reaction with isocyanates. Their structure significantly impacts the properties of the final polymer. Polyols used in rigid foams have low molecular weight, high functionality and high hydroxyl value, which yield rigid structures by enhancing crosslinking and increasing the concentration of urethane bonds.[6] Conversely, low functionality, low hydroxyl value, and high molecular weight polyols produce elastic/flexible PU foams since they are composed of long alkyl chains, which allow free rotation about the carbon backbone and minimize crosslinking.[1]

Polyether polyols are the most widely used polyols in rigid foam applications due to their hydrolytic stability and cost-effectiveness. They are synthesized through the polymerization of

propylene or ethylene oxide, which is initiated by high functionality molecules, including glycerol, sorbitol, polyamines, and Mannich bases (produced by the Mannich reaction between phenols formaldehyde and alkanolamines).

Polyester polyols are more frequently used in polyisocyanurate foam formulations since they offer high thermal stability. In addition, the polyester structures have a plasticizing effect, which combats friability caused by a high degree of crosslinking of the isocyanurate rings.[7,8] Polyester polyols were classically synthesized from a combination of adipic acid, phthalic anhydride and glycols/polyols.[7]

2.2.2 Isocyanate

Isocyanates form the second class of monomers used to synthesize PU foams. They are made up of isocyanate (-NCO) groups, which are highly reactive toward active hydrogen-containing functional groups.[9] The electrophilic carbon center of the -NCO group serves as the site for reaction with the oxygen atom of the polyol.[10]

Rigid foams are typically synthesized using aromatic isocyanates such as methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI), since they have a higher reactivity due to the presence of aromatic electron-withdrawing substituents.[1] These structures also provide rigidity to the PU matrix thereby improving foam properties.

Beyond reactions involving polyols, isocyanates react with water to produce carbon dioxide, which causes the expansion of foams. Isocyanate groups are further capable of reacting with each other via dimerization and trimerization reactions. Trimerization is of greater industrial significance, being employed for the synthesis of polyisocyanurate (PIR) foams. PIR foams are highly crosslinked polymers with improved thermal stability over rigid polyurethane foams due to the presence of isocyanurate rings.

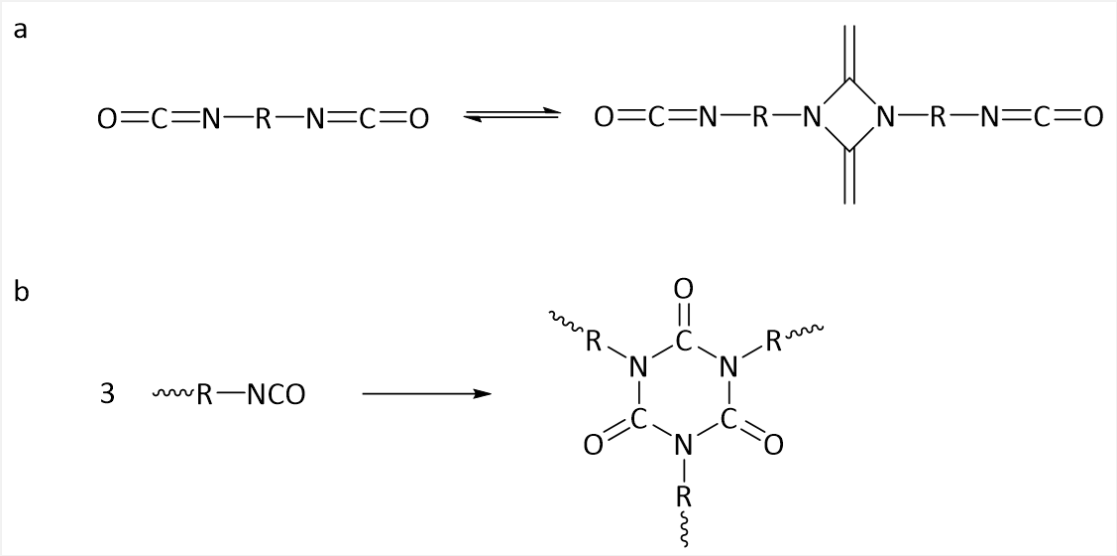

Figure 3: Dimerization (a) and trimerization (b) of isocyanates

2.2.3 Additives

Several additives are included in foam production to tailor final properties or control reaction rates. The main catalysts for PU synthesis include gel-promoting, foaming, or balance catalysts. Amine catalysts accelerate both blow and gel reactions, while organometallic catalysts promote the urethane reaction.[11] In some formulations, balanced catalysts are included to control the competing polymerization and blowing reactions.

Surfactants are a critical component for regulating cellular structure evolution during rigid PU foam synthesis. Typically, these are amphiphilic grafted co-polymers comprising a polysiloxane backbone with polyether grafts.[12,13] Surfactants have two main functions: facilitating the emulsification of incompatible components through a reduction in surface energy of the resin blend prior to polymerization and stabilizing the formation of bubbles in the early stages of the reaction.[13–15]

2.3 Lignin

Lignin is the second most abundant renewable polymer after cellulose. It is a highly branched, aromatic molecule found in plant cell walls and constitutes between 15-35wt.% of biomass on a dry basis.

Lignin is comprised of *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units, which are formed through oxidative radical polymerization of three monolignols, *p*-coumaryl, coniferyl and sinapyl alcohols.[16,17]

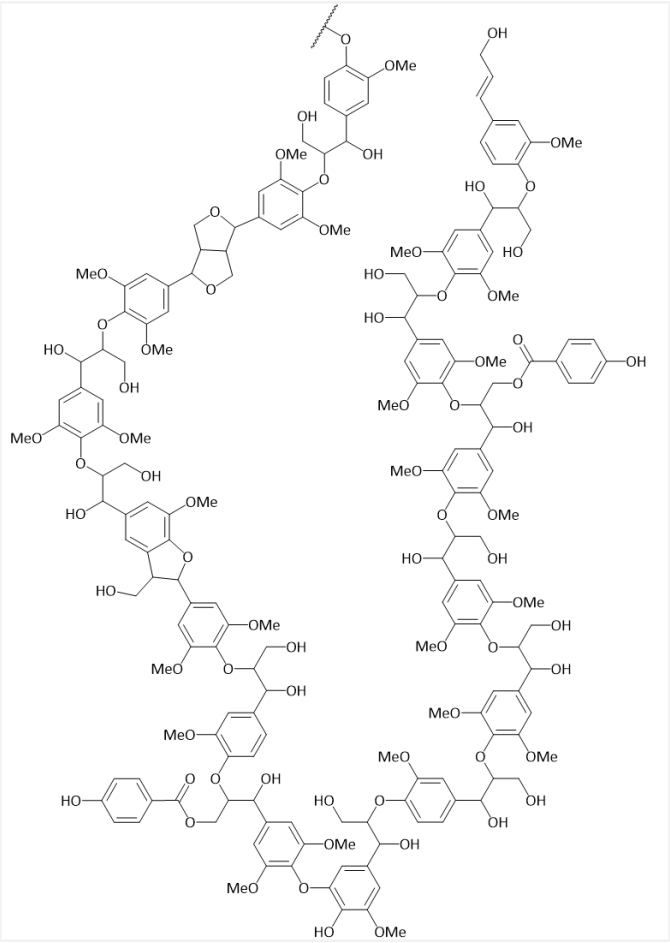

Figure 4: Structure of lignin reproduced from Ralph et al[18]

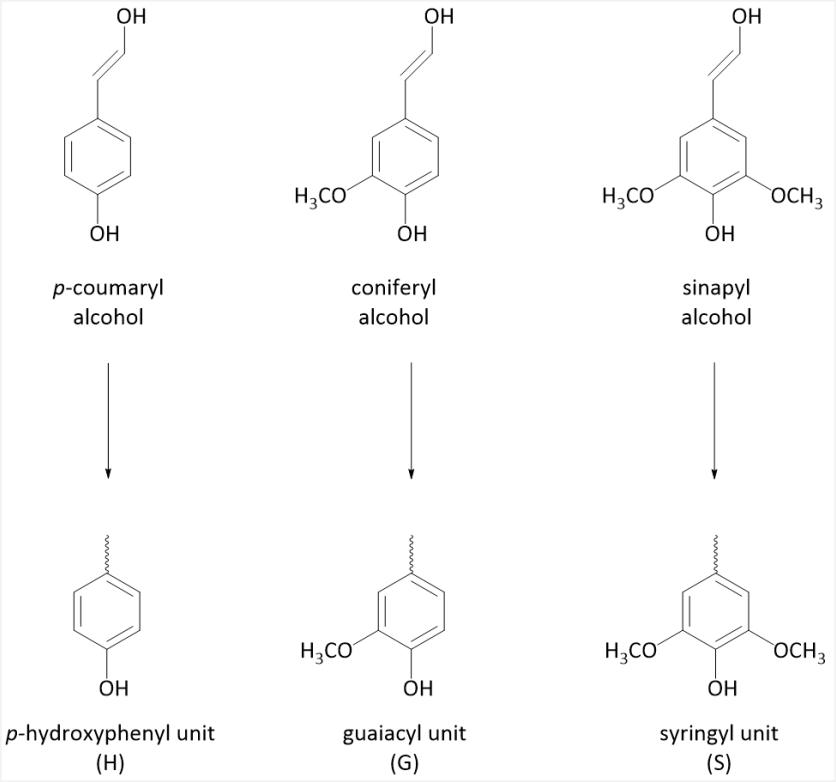

Figure 5: Chemical structure of the three main monolignols adapted from Erdocia et al[19]

The chemical structure of lignin differs considerably among the various types of biomasses due to variations in the proportion of monolignols and the type of interunit linkages formed between them.[20] Softwoods are characterized by a large amount of G units while hardwoods consist of both G and S units. Herbaceous plants contain all three monolignols.[21,22]

2.4 Lignin Isolation Methods

Currently, lignin is produced as a by-product of chemical pulping or biorefinery processes. The extraction process has a significant impact on the physical, chemical and thermal properties of the lignin.[23] Commonly employed extraction methods include Kraft, sulfite, organosolv, hydrolysis and soda processes. Kraft and sulfite pulping involve the use of sulfur-containing compounds for digesting biomass.

2.4.1 Kraft Pulping

Kraft pulping is the most dominant pulping technique, which involves delignification of biomass using an aqueous solution of sodium sulfide (Na_2S) and sodium hydroxide (NaOH), known as white liquor, at elevated temperatures (160-180°C) and pressure (800kPa).[24] The cleavage of α- and β- aryl linkages[25,26] results in fragmentation of the lignin molecule and generation of phenolic OH groups.[19] Kraft lignins are characterized by the presence of impurities, including sugars (1-2.3 wt.%) and sulfur (1-3 wt.%).[26,27]

2.4.2 Sulfite Pulping

The sulfite process involves the digestion of biomass using a solution of sulfur dioxide (SO_2) and a sulfite base (SO_3).[28] The introduction of sulfonate groups onto lignin during the cooking process enhances the hydrophilicity of lignin, making it highly soluble in water with poor solubility in organic solvents.[29] Lignosulfonates are further characterized by a high concentration of sodium and other impurities.[19,30–32]

2.4.3 Organosolv Process

Organosolv pulping processes utilize aqueous solutions of organic solvents, often with organic or inorganic acid catalysts to cleave linkages between lignin, cellulose and hemicellulose.[33–35] The most widely employed solvents include ethanol and methanol.[34–36] Organosolv lignins have characteristically narrow ranges of molecular weights, lower ash content and low levels of impurities, compared to those isolated using the kraft and sulfite processes.

2.4.4 Hydrolysis

Hydrolysis is a method for breaking down lignocellulosic biomass by solubilizing cellulose and hemicelluloses in wood using acidic media, alkali, enzyme or steam explosion.[37] Generally, lignin obtained through this process has a high concentration of sugars (10 - 22.4 wt.%), low sulfur and

ash content, and molecular weight between 5,000 and 10,000 g/mol.[38] Hydrolysis lignins also have a lower glass transition temperature than other types of technical lignin due to the presence of carbohydrate impurities.[39]

2.5 Lignin as a Polyol Replacement in Rigid PU Foams

Significant research efforts have been directed towards investigating lignin's potential as a bio-based polyol feedstock in PUs due to the presence of multiple hydroxyl moieties and its abundance in nature. Lignin has an aromatic structure, high functionality, and OH content, rendering it an attractive alternative to petroleum polyols for PU rigid foam synthesis. Incorporating lignin into PU rigid foams has followed two approaches: 1) direct substitution of technical lignin in the PU matrix or 2) chemical modification to improve its reactivity with isocyanate.

2.5.1 Direct Substitution

Technical lignins have been incorporated directly into PU polymers as renewable alternatives to petroleum-derived polyols, with varying levels of success. In rigid PU foams, the substitution of petroleum-based polyols with approximately 30 wt.% of lignin has been found to produce foams with improved compressive strength, thermal stability, morphological structure and flame retardancy.[40–42] However, higher loading levels (>50 wt.%) were linked to increased density, brittleness, and deterioration in cellular structure and mechanical properties.[42–44] This decline is largely due to the heterogeneous reactivity of OH groups towards isocyanate and the solid nature of lignin. The hydroxyl moieties in lignin demonstrate varying reactivity towards isocyanate: aliphatic OH groups react quickly, followed by aromatic hydroxyl groups, which are more acidic and sterically hindered, and finally carboxylic hydroxyl groups.[45,46] Additionally, the solid nature of technical lignins leads to particle agglomeration which increases the viscosity of the polyol

blend and prevents effective mixing with isocyanates. Lignin particles also serve as nucleating sites during bubble formation which results in distortion of the cells.[43,47]

2.5.2 Chemical Modification of Lignin

Several lignin derivatization methodologies have been introduced to overcome the challenges posed by the direct incorporation of solid lignin into PU rigid foams, notably variation in reactivity of hydroxyl groups towards isocyanates and solubility. These strategies can be classified into three broad categories: 1) depolymerization, 2) modification of native hydroxyl groups, and 3) creation of new active sites.[23,43] Of these methods, the depolymerization and modification of OH groups through oxypropylation are the most studied by various researchers.

Depolymerization/ fragmentation of biomass involves cleavage of the ether linkages by thermochemical means, resulting in the production of oligomeric products with low polydispersity.[48,49] Among possible depolymerization routes, liquefaction is one of the most utilized processes.[5] Liquefaction produces liquid, hydroxyl rich products through simultaneous depolymerization and solvolysis.[50,51]

2.6 Oxyalkylation

2.6.1 Alkylene Oxides as Oxyalkylating Reagents

Oxyalkylation with alkylene oxides, specifically propylene oxide (PO), is a well-known method for modifying hydroxyl groups of lignin. The process involves the etherification of lignin by reacting it with PO in the presence of a basic catalyst (usually KOH), under high pressure and temperature (6-20 bar and 150-180°C) for a time ranging from a few minutes to several hours.[52–55] The ring-opening polymerization reaction converts sterically hindered phenolic hydroxyl groups into more reactive secondary aliphatic OH groups by extension with poly(propylene) oxide chains. Homopolymerization of alkylene oxides was consistently observed to accompany the main

grafting mechanism due to transfer reactions,[56] Other hydroxyl-bearing biomass residues, including tannin, chitin and sugar beet pulp, have been successfully modified by oxyalkylation with other alkylene oxide compounds (e.g. ethylene oxide and butylene oxide).[57–63]

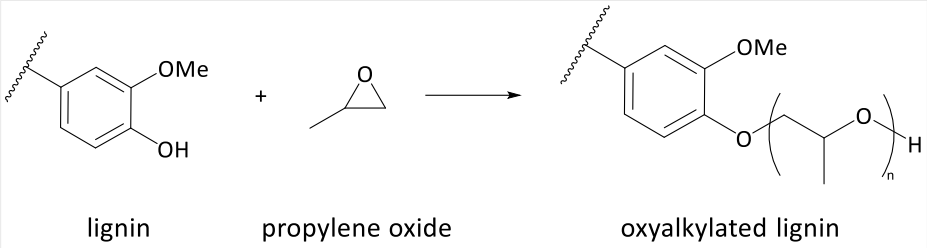

Figure 6: Oxyalkylation of lignin using propylene oxide adapted from Gouveia et al[53]

Alkoxylated lignin polyols have been used as polyol replacements in rigid polyurethane foams at different substitution levels, with evidence of improved properties.[64–71] Cateto et al.[71] fully replaced conventional polyols with lignin polyols synthesized from four technical lignins. The lignin-based foams had low densities (19.4-25.1 kg/m^3) with most having better insulation performance than the control sample. The control sample, however, had a higher compressive modulus than all the biobased samples. Nadji et al.[70] also produced rigid PU foams from four oxypropylated lignin samples. The softwood lignin sample had low density (30 kg/m^3) and thermal conductivity (0.024 W/mK). The other samples were found to have low dimensional stability. Li and Ragauskas[68] prepared rigid foams by substituting 10-100% of polyols with propoxylated lignin polyol. Foam made with only lignin polyol had a higher compressive strength (~140 kPa) than the control sample (~100 kPa). Widespread adoption of propoxylation has, however, been limited due to high toxicity and high vapor pressure of propylene oxide (PO), which necessitates the use of pressurized reactors to ensure safe handling.

2.6.2 Cyclic Carbonates as Oxyalkylation Reagents

Oxyalkylation with cyclic carbonates instead of their oxirane counterparts has been extensively studied towards the preparation of biobased polyols for polyurethane synthesis. These compounds have higher boiling points, lower toxicity, improved biodegradability, and established pathways for synthesis from carbon dioxide, which makes them more sustainable alternatives.[72–74]

The reaction proceeds by two distinct pathways, etherification or transesterification, depending on the type of hydroxyl group being modified. Etherification is initiated by the deprotonation of phenolic or carboxylic hydroxyl groups, followed by nucleophilic attack at the alkylene site on the cyclic carbonate.[72,75–77] This leads to the creation of aliphatic OH groups through chain extension with hydroxyalkyl units and the liberation of carbon dioxide (Figure 7). Aliphatic hydroxyl groups however, favor the reversible transesterification route through nucleophilic attack on the carbonyl carbon,[75,78] yielding carbonate linkages (Figure 8).

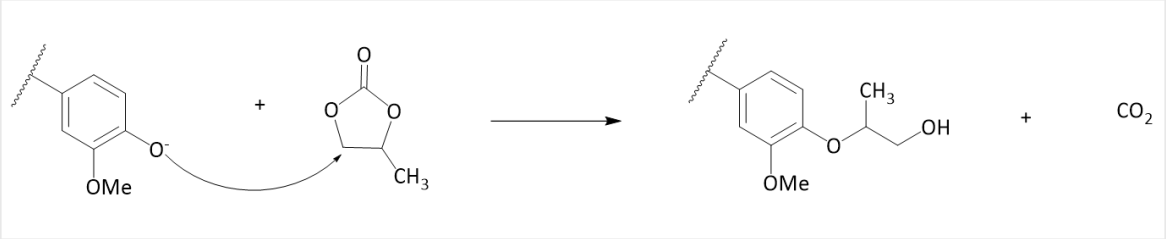

Figure 7: Mechanism for etherification of phenolic OH groups in lignin, adapted from Duval et al[75]

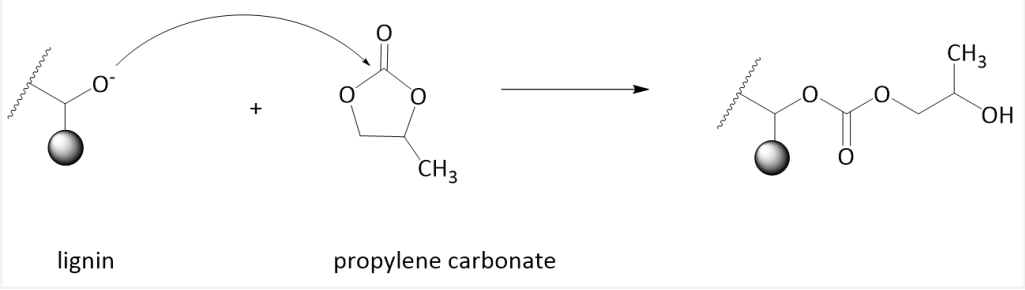

Figure 8: Mechanism for transesterification of aliphatic OH groups during oxyalkylation adapted from Duval et al[75]

Previous studies have investigated the effects of process conditions, catalyst type and structure of cyclic carbonate on the hydroxyalkyl products.[75,77,79] Oxyethylated polyols showed the highest reactivity due to the formation of only primary aliphatic OH groups. Oxyalkylation with asymmetrical carbonates (e.g. propylene carbonate, glycerol carbonate, and vinyl ethyl carbonate) produced both primary and secondary aliphatic hydroxyl moieties.[75]

2.7 Synthesis of Rigid PU Foam Using Oxyalkylated Lignin Polyols

Vieira et al.[80] prepared rigid PU foam by substituting 25-100 wt.% of conventional polyol with hydroxypropyl lignin polyol (5.5 molar equivalents of PC). The lignin polyol had ~20% lignin content, a hydroxyl value of 257 mg KOH/g, and a viscosity of 5,300 mPa.s. Compared to the control (120 - 160kPa), the lignin-based foam with 100% substitution had a significantly lower compressive strength (80 - 120 kPa) which they attributed to a disrupted cellular structure and the plasticizing effect of PC oligomers in their liquid lignin polyol. They also reported that lignin-based foams were less thermally stable than the control foam. In another study by the same group,[81] the oxypropylated lignin-based foam (100% substitution) showed marginally improved flame retardancy over the petroleum-based foam.

Other studies employed polyethylene glycol (PEG) as a co-solvent during oxyalylation which reduced the amount of cyclic carbonate needed for the reaction and simultaneously increased polyol hydroxyl value. Zhang et al.[82] incorporated water and PEG 400 as reactive additive and co-solvent respectively. The produced polyols had hydroxyl values ranging between 459 - 659 mg KOH/g, and viscosity between 500-5,300 mPa.s. The effects of lignin loading in the polyol and PEG content on the density and compressive strength of foams were determined. Foam density ranged between 51-66 kg/m³ as PEG content in the polyol increased from 20-90 wt.%, while the compressive strength declined from 377 to 137kPa. Increasing lignin loading in the polyol, from

20 - 50% wt.%, increased density, from 54 to 57 kg/m³, and decreased compressive strength of foams from 182 to 139 kPa.

Duval et al.[83] employed a similar methodology, incorporating PEG of different molecular weights (150 - 400 g/mol) as a co-solvent in lignin oxyalkylation with ethylene carbonate. The polyols had 20 - 25wt.% lignin, with hydroxyl values ranging from 300 to 700mg KOH/g and viscosity, 500-30,000 mPas. Rigid PU foams produced by substituting 25% of polyether polyol with the synthesized polyols had densities ranging from 27 to 28.5 kg/m³ and compressive strengths between 214 - 244 kPa.

Similar trends were observed in all the above studies involving the synthesis rigid PU foam using oxyalkylated lignin polyols. In all instances, the lignin fraction in the polyols was limited to approximately 30 wt.% of polyols to control viscosity. Mechanical properties of the foams were also lower than in the control foams in some of the studies.[81,83] Finally, the amount of lignin in the foam remained low due to the low substitution ratio of the lignin polyol in the foam and the addition of PEG during oxyalkylation.

This study therefore seeks to address the limitations identified in previous publications, including the low hydroxyl value of oxyalkylated lignin polyols, the low fraction of lignin and the large amount of residual cyclic carbonate in the polyols, without the addition of other co-solvents.

2.8 Objectives

The primary objective of this work was to develop lignin-based rigid polyurethane foams by entirely replacing petroleum-based polyols with oxypropylated lignin polyols. More specifically, the following objectives were proposed:

- Synthesize liquid lignin polyols through oxyalkylation with propylene carbonate (PC) with the goal of reducing the quantity of residual PC in the polyol

- Develop a method to increase the hydroxyl values of liquid lignin polyols
- Formulate rigid polyurethane foams by substituting 100% of conventional petroleum-based polyols with lignin polyols
- Investigate the effect of lignin polyol incorporation on foam performance

MATERIALS AND METHODS

3.1 Materials

Hardwood hydrolysis lignin was provided by Sweetwater Energy and used as received without drying or further purification.

Polymeric methylene diphenyl diisocyanate (pMDI) with NCO content of 31.1%, petroleum-based polyol with hydroxyl number of 350 mgKOH/g and propylene carbonate were kindly supplied by Huntsman Polyurethanes. 1,8-Diazabicyclo (5.4.0) undec-7-ene (DBU) was purchased from Tokyo Chemical Industry (TCI). Catalysts and surfactants were provided by Evonik.

Reagents for NMR and GPC analysis, cyclohexanol with 99% purity, HPLC-grade pyridine, 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) and deuterated dimethyl sulfoxide (d_6-DMSO) were obtained from Signa-Aldrich. Deuterated chloroform, Chromium (III) acetylacetonate, HPLC-grade tetrahydrofuran, and acetic anhydride were purchased from Fisher Scientific.

3.2 Lignin Characterization

3.2.1 Elemental Analysis

The lignin sample was conditioned according to the Association of Official Analytical Chemists (AOAC) Official Methods 922.02 and 980.03 before being submitted to an external laboratory for analysis of C, H and N compositions along with other impurities such as sodium and potassium. A Thermo Scientific iCAP 6000 series 6500 Duo Spectrometer was used to perform Inductive-Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) testing.

3.2.2 Ash Content

The ash content of lignin was determined following the method outlined in TAPPI T 211 om-9.84. Five ceramic crucibles were dried at 105°C until a constant weight was achieved and weighed to

the nearest 0.1mg. Two grams of oven-dried lignin were measured into each crucible before being transferred into a muffle furnace. The samples were gradually heated to 525°C at a rate of 5°C /min and held at a constant temperature for 4 hours. After cooling, samples were transferred to a desiccator and weighed. The ash content was calculated using the following equation

$$\text{Ash content (\%)} = \frac{m_{c,2} - m_{c,i}}{m_{c,1} - m_{c,i}} \quad (1)$$

Where,

$m_{c,i}$ = initial mass of crucible

$m_{c,1}$ = mass of crucible plus lignin sample

$m_{c,2}$ = mass of crucible plus residual ash

3.2.3 Molecular Weight Distribution Analysis

The molecular weight distribution of the lignin sample was determined using gel permeation chromatography (GPC). Lignin was first acetylated, to ensure complete solubility in tetrahydrofuran (THF). 40mL of a solution of pyridine and acetic anhydride (50-50 v/v%) was added to 1g of lignin and mixed at room temperature for 24 hours. The sample was then precipitated with 0.1M hydrochloric acid, washed with deionized water, and dried. HPLC-grade THF was added to the precipitated sample at a concentration of 5mg/mL after which the solution was passed through a 0.45µm syringe filter. 25µL of the filtrate was injected into a Waters GPC with a e2695 separation module comprising three 300mm × 7.8mm Ultrastyragel columns in series (5k-600kÅ, 500-30k Å and 100-10k Å). THF was employed as the mobile phase at a rate of 1mL/min. Polystyrene standards with molecular weights ranging between 162 and 16200 Da were used as calibration standards. Data was recorded and analyzed using Empower GPC software.

3.2.4 Phosphorus-31 Nuclear Magnetic Resonance Spectroscopy (^{31}P-NMR)

The hydroxyl content (OH) of the lignin sample was determined using ^{31}P-NMR spectroscopy according to published procedures.[84,85] First, a solvent solution was prepared with chloroform and pyridine (1:1.6 v/v). 22.1mg of cyclohexanol was dissolved in 1000µL of the solvent solution to prepare the internal standard solution. The relaxation agent solution was prepared by dissolving 5-7 mg of chromium (III) acetylacetonate in 1000µL of the solvent. 30mg of oven-dried lignin was dissolved in 500µL of the solvent and mixed at 3000rpm with a vortex. Then, 100µL of the internal standard and relaxation agent were added and mixed. Finally, 100µL of TMDP was added and vortexed. 650µL of the sample was transferred to a 5mm Wilmad NMR tube and analyzed in an Agilent DDR2 500 MHz NMR spectrometer equipped with 7600AS, running VnmrJ 3.2 A. Spectra collection parameters were set to 128 scans with a relaxation delay of 5s and pulse angle of 90°. Data was processed using MestreNova software (Mestrelab Research S.L. Version 14.1.1-24571). The OH content was calculated by determining the ratios of various regions corresponding to lignin OH moieties over the region of the internal standard peak (145.3-144.9 ppm). The specific regions of integration for lignin OH groups are: aliphatic (149.1-145.4 ppm), condensed phenolic (144.6-143.3 and 142.0 -141.2 ppm), syringyl phenolic (143.3-142.0 ppm) guaiacyl phenolic (140.5-138.6 ppm), *p*-hydroxyphenyl phenolic (138.5-137.3 ppm) and carboxylic acids (125.9-134.0 ppm).

3.2.5 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectra of unmodified lignin samples was collected on a PerkinElmer Spectrum Two spectrometer in Attenuated Total Reflectance (ATR) mode. 16 scans were recorded between 450-4000cm^{-1} at a resolution of 4cm^{-1}.

3.2.6 Carbon-13 (^{13}C-NMR) Nuclear Magnetic Resonance Spectroscopy

The structure of lignin prior to modification was investigated further using proton and carbon-13 NMR methods. 40mg of lignin was dissolved in 60µL of deuterated dimethyl sulfoxide (DMSO-d_6) and vortexed. 600µL of the solution was transferred into a 5mm Wilmad NMR tube. The following collection parameters were used: 2s relaxation delay with 6000scans for ^{13}C-NMR.

3.3 Lignin Polyol Synthesis

3.3.1 Lignin Oxyalkylation

Lignin was oxyalkylated using propylene carbonate in the presence of Diazabicyclo(5.4.0)undec-7-ene (DBU) catalyst. 100g of lignin (5.43 mgKOH/g, 1 molar eq.), PC (4 molar eq.) and DBU (0.025 molar eq.) were charged into a 0.6L capacity reactor (PARR, model 4524). The reactor was first purged with nitrogen to eliminate air and heated to 150°C under constant stirring. After 3 hours, the reactor was cooled to 80°C and the polyol product recovered.

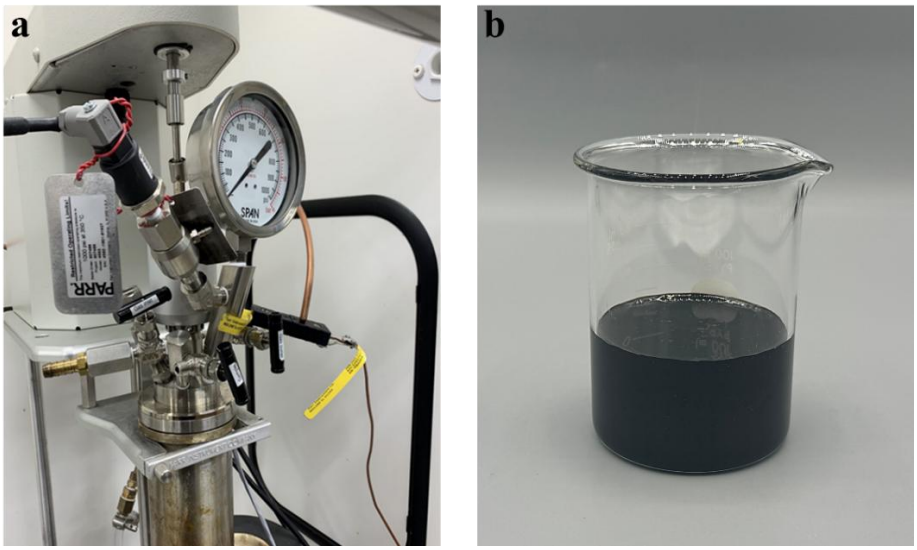

Figure 9: (a) Parr reactor used during oxyalkylation (b) lignin polyol

3.3.2 Hydrolysis of Propylene Carbonate (PC)

100 g of oxypropylated product was transferred into a 250ml 3-necked round bottom flask fitted

with a condenser. Water was added and the mixture was heated at 150°C for 30 minutes with constant stirring to facilitate the hydrolysis of PC to propylene glycol (PG).

The exact quantity of water needed for the reaction was calculated using the procedure outlined below. For clarity and brevity, oxypropylation and subsequent PC hydrolysis reactions will be referred to as steps 1 and 2 respectively.

The mass fraction of PG produced during oxyalkylation (step 1) was determined as follows:

$$\mathrm{OH_{LP}} = \mathrm{OH_L x_L} + \mathrm{OH_{PG} x_{PG,step\ 1}} \quad 3$$

Where,

OH_{LP} = hydroxyl value of polyol

OH_L = hydroxyl value of unmodified lignin

$\mathrm{x_L}$ = mass fraction of lignin

$\mathrm{OH_{PG}}$ = hydroxyl value of propylene glycol

$\mathrm{x_{PG,step1}}$ = mass fraction of propylene glycol produced in Step 1.

The mass of PG required, $\mathrm{x_{PG\ target}}$, to achieve a desired hydroxyl value, was calculated in a similar way.

Thus, for a desired hydroxyl value, the mass of water m_{water} is found as

$$\mathrm{m_{PG,step\ 2}} = \mathrm{m_{PG\ target}} - \mathrm{m_{PG,step\ 1}} \quad 4$$

$$\mathrm{m_{water}} = \frac{\mathrm{m_{PG,step\ 2}}}{\mathrm{M_{PG}}} \times 18 \quad 5$$

Where,

$\mathrm{m_{PG\ target}}$ = total mass of PG required to achieve a desired hydroxyl value

$\mathrm{m_{PG,step2}}$ = mass of PG which must be produced in Step 2

After the reaction completion of the reaction, the mixture was cooled and evaporated at 120°C under vacuum conditions for 5 minutes. Polyols with hydroxyl values between 300-500 mg KOH/g

were produced to test the efficiency of PG generation.

3.4 Polyol Characterization

3.4.1 Structural Analysis of Lignin Polyols

Structural elucidation of lignin polyols was carried out using FTIR, ^{31}P-NMR and ^{13}C-NMR spectroscopy following the procedures outlined for unmodified lignin

3.4.2 Viscosity

The viscosity of lignin polyols was measured using a TA Instruments Discovery HR-1 hybrid rheometer equipped with 40mm stainless Peltier plates with a 1 mm gap. Viscosities were measured using a constant shear rate of $100s^{-1}$ over a 60-second interval and average values were reported.

3.4.3 Fraction of Modified Lignin in Polyol

The mass fractions of modified lignin in the polyols were determined through gravimetric analysis. 15ml of hydrochloric acid solution (pH = 2) was added to 1 g of each lignin polyol, and the samples were stirred continuously until complete dissolution was achieved. Pyrex ASTM 10-15 M Gooch crucible filters were dried overnight in an oven and weighed. The samples were transferred into crucibles, filtered and dried in a vacuum oven at 105°C for 24 hours. Three replicates were prepared for each polyol. The fractions of modified lignin were determined according to the equation below:

$$Modified\ lignin\ fraction\ (\%) = \frac{m_{c,f} - m_{c,i}}{m_{polyol}} \times 100 \qquad 2$$

Where,

$m_{c,i}$= initial mass of oven-dried crucible

$m_{c,f}$= mass of dried crucible plus precipitate

m_{polyol}= exact mass of polyol prior to precipitation

3.5 Rigid Polyurethane Foam (RPUF) Preparation

Predetermined quantities of lignin polyol, water, catalysts and surfactant, were weighed into an 8-oz cup and homogenized with a high-speed mixer (Camframo overhead mixer), at a stirring rate of 2000 rpm for about 10s. N-pentane was added and mixed. pMDI was immediately added to the resin blend, stirred and the foam was allowed to rise freely. Larger samples were prepared by pouring the reacting mixture into silicone molds (7.62 mm × 7.62 mm × 7.62 mm). After at least 48 hours, foam samples were cut to size for each test and conditioned at room temperature prior to testing. Detailed formulations for each foam are listed in Table 1.

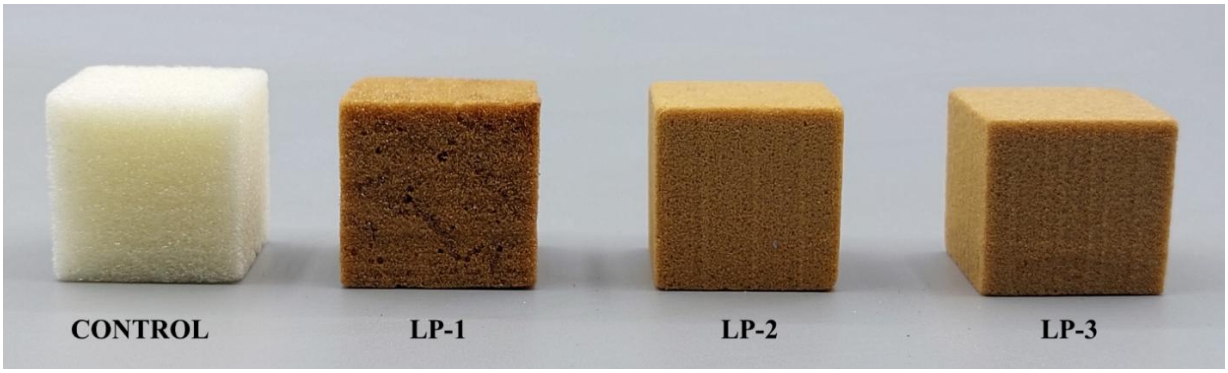

Figure 10: Rigid PU foam samples synthesized with petroleum-based and lignin-based polyols (LP-1, LP-2 and LP-3)

Table 1: Rigid PU foam formulations for control and lignin polyol-based foams

Component	**Control**		**LP-1**		**LP-2**		**LP-3**	
	pphp	Foam Composition (%)	pphp	Foam Composition (%)	pphp	Foam Composition (%)	pphp	Foam Composition (%)
Polyol	100	42.71	100	50.46	100	44.02	100	38.90
Water	0.25	0.11	0.25	0.13	0.25	0.11	0.25	0.01
Surfactant	1	0.43	1	0.5	1	0.44	1	0.39
Catalysts	2	0.85	2	1.01	2.3	1.01	2	0.89

Table 1 (cont'd)

n-Pentane	**20**	**8.54**	**20**	**10.09**	**7.5**	**3.30**	**7.5**	**2**
pMDI	120-index	51.12	140-index	37.81	120-index	51.12	120-index	55.83

3.6 Rigid PU Foam Characterization

3.6.1 Polyol Reactivity

The reactivity profile for the foams was investigated by measuring cream, gel, top of cup, tack-free, and end of rise times with a stopwatch.[86] The cream time is the point at which a color change is observed, indicating the start of the isocyanate-water reaction. Gel time indicates the time at which 'strings' of the tacky foaming mixture can be pulled from the foam surface when touched with a tongue depressor. The top of cup time represents the time at which the crown of the expanding foam reaches the rim of the cup. Finally, the tack-free time is the time at which the foam surface is no longer sticky/ tacky.

3.6.2 Fourier Transform Infrared Spectroscopy (FTIR)

The infrared spectra of RPUR were collected on PerkinElmer Spectrum Two FT-IR Spectrometer, in Attenuated Total Reflectance (ATR) mode. 5mm sections were cut from each specimen and loaded into the FTIR, ensuring good contact with the crystal. 15 scans were recorded for each sample between 450-4000cm^{-1} wavelength and with a resolution of $4cm^{-1}$.

3.6.3 Apparent Density

The apparent density of foam samples was calculated according to ASTM D1622-20.[87] Five 1-$inch^3$ (25.4mm × 25.4mm × 25.4 mm) specimens were measured for each foam sample. Specimen dimensions (length, width and height) were measured using calipers, with three measurements recorded for each dimension. Each sample was then weighed using a digital scale. The density was

calculated based on equation 3 below and reported in units of kilogram per cubic meter (kg/m^3). Five replicates were measured for each sample.

3.6.4 Compressive Strength

Compressive strength was determined using an Instron 5565 universal testing machine, following the procedure outlined in ASTM D1621-16.[88] At least five 1-inch cube (25.4mm × 25.4mm× 25.4 mm) specimens were compressed to 13% strain, perpendicular to the rise direction.

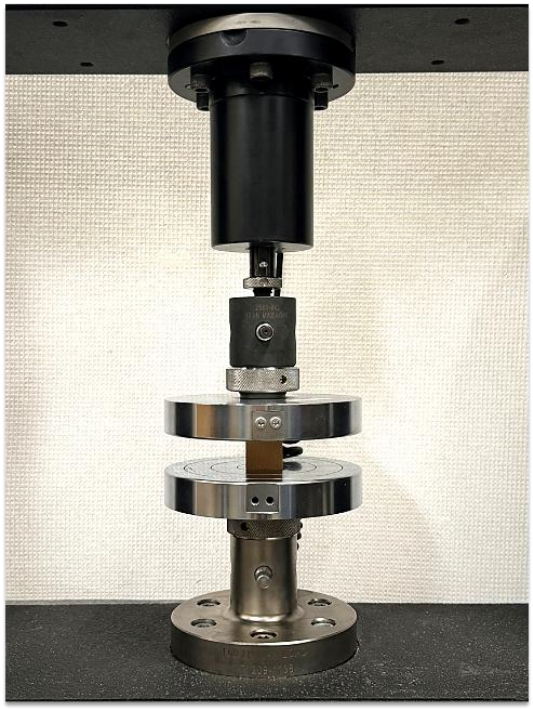

Figure 11: Compressive strength testing of rigid PU foam

3.6.5 Cell Morphology

Foam morphology was investigated using a JEOL 6610 LV scanning electron microscope (SEM). Specimens were cut with a razor in the direction perpendicular to foam rise and coated with gold nanoparticles in an argon atmosphere using an EMSCOPE SC 500 sputter coater. Images were collected with an accelerating voltage of 10kV, spot size of 30, and at 35x and 100x magnifications. SEM images were analyzed in Image J software.

3.6.6 Closed Cell Content

The closed cell percentage was measured using a Micromeritics AccuPyc II 1340 gas pycnometer.[89] In accordance with micromeritics Foam Pyc method B, analysis was performed in a nitrogen atmosphere with 10 purges cycles, 27.58kPa purge, and cycle fill pressure at 0.01kPa/min.

Closed cell content determination followed a 3-step process. In the first step, the empty sample cup was first weighed. Foam samples were ground and packed into the sample cup until it was two-thirds full and weighed. The cup was inserted into the cell chamber of the pycnometer, capped, and the bulk density was determined. The sample cup was emptied completely and weighed again. Two 1-inch cubes were weighed in the cup, and the cup was transferred into the instrument. The material parameters, that is geometry, bulk density and cube mass, were programmed into the software and analyzed. After the second analysis step, the cubes were removed and cut into 16 equally sized cubes (8 cubes per sample) and returned to the sample cup. The final analysis was performed to determine the closed cell percentage.

3.6.7 Thermal Conductivity

The thermal conductivities of the control foam and optimized lignin foam were measured by an external facility, following the procedure outlined in ASTM C518-21.[90] Specimens were cut to size (130 mm× 130 mm× 28 mm) and analyzed using a Netzsch HFM 446/S Lambda model heat flow meter instrument, at a nominal mean temperature of 23.9°C.

3.6.8 Thermogravimetric Analysis (TGA)

The thermal stability of PU rigid foam samples was analyzed using a TA instruments TGA 55 thermogravimetric analyzer under oxygen flow. 5-8 mg of each specimen was loaded into a platinum pan and heated to 800 °C, at a heating rate of 10 °C/min.

3.6.9 Horizontal burning characteristics

The burning behavior of PIR foams was determined according to a modified version of ASTM D4986[91]. At least five test specimens, measuring 13mm × 13mm × 80mm were marked at 25 and 60 mm and burned for 30 seconds with a Bunsen burner. The burn length and burn time for the foams were recorded.

RESULTS AND DISCUSSION

4.1 Lignin Polyol Synthesis

4.1.1 Oxyalkylation

Oxypropylation presents a simple method for overcoming the limitations posed by the direct incorporation of technical lignins, by simultaneously converting phenolic OH groups into more reactive aliphatic groups and producing a liquid polyol by grafting ether units onto the lignin molecule. Based on the previously published work, 1,8-Diazabicyclo(5.4.0)undec-7-ene (DBU) was employed as the catalyst due to its selectivity towards the deprotonation of phenolic OH groups over aliphatic groups.[77,78,92] The initial oxypropylation reaction was performed at 150°C for 1.5 hours with a 0.05 equivalent molar ratio of catalyst, leading to near-complete derivatization of the phenolic OH groups into aliphatic (LP-1). This polyol exhibited very high reactivity during foam formulation, which was also reported by previous studies.[64,81,83] Subsequently, the catalyst content was reduced from 0.05 to 0.025 molar equivalent, and the reaction time was increased to 3h to achieve a similar degree of conversion.

4.1.2 Hydrolysis of Propylene Carbonate

The polyols directly obtained after oxypropylation had lower hydroxyl values than unmodified lignin, due to self-condensation of lignin, which is consistent with previously published literature.[70,80] These polyols also had a large quantity of unreacted PC, as shown in Table 2. Unlike alkylene oxides, oxyalkylation with PC is not accompanied by homo-polymerization since it is less thermodynamically favorable[82,93]. Excess PC in the polyol poses a challenge during foam formulation due to the plasticizing effect of PC on the PU matrix.[94] Efforts to reduce the amount of residual cyclic carbonate (ethylene carbonate) used through the addition of PEG as a co-oxyalkylating reagent led to an increase in polyol viscosity, further reducing the amount of lignin

in the foam.[82,83]

The hydrolysis of 5-membered cyclic carbonates yields corresponding vicinal diols, accompanied by the release of carbon dioxide.[95–97] High temperatures,[95] and alkali catalysts,[97,98] greatly accelerate the reaction. By taking advantage of this reaction, we were able to a) reduce the amount of excess PC that remained in the lignin polyol after oxypropylation, and b) by adding water, increase the OH value of lignin polyols through the in-situ production of chain extender diol, which increases the concentration of hard segments by forming urethane linkages with isocyanate.[99–103]

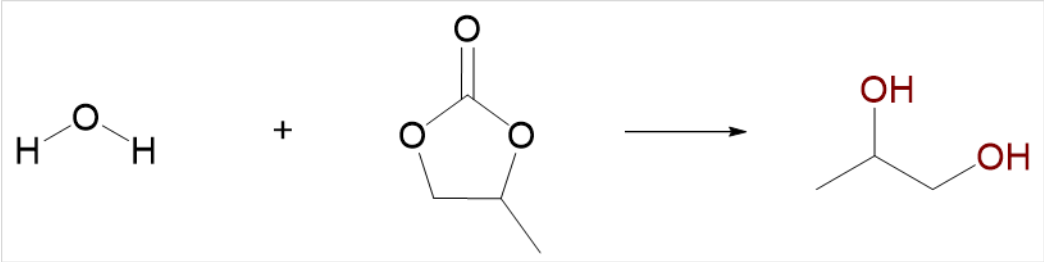

Figure 12: Ring opening reaction of propylene carbonate with water, producing propylene glycol

The specific quantity of water needed to achieve a desired OH value was calculated by stoichiometry, with the assumption that full consumption of water was attained within the reaction time (30 minutes). Three polyols with hydroxyl values ranging from 200-500 mg KOH/g were produced to test the efficiency of this procedure and determine the range of hydroxyl values that could be achieved within the reaction time. The target hydroxyl value and actual OH value achieved are provided in Table 2.

LP-2 and LP-3 achieved OH values slightly higher than the target since water was added in a slight excess to minimize the production of other oligomers.[97] Additionally, after heating the polyol under vacuum conditions, no water was evaporated into the collecting chamber, proving full consumption. Higher OH values (>500 mg KOH/g) were found to require longer reaction times (45 - 60 minutes) to ensure that the target OH value was achieved.

Table 2: Summary of polyol properties

Polyol ID	Target OH value (mg KOH/g)	Achieved OH value (mg KOH/g)	Viscosity (mPa.s)	Lignin Fraction (%)
Control	-	360	2,500	-
LP-1	-	201	1,493 ± 20	38
LP-2	350	379	1,781 ± 11	41
LP-3	450	472	3,249 ± 30	41

4.2 Polyol Characterization

4.2.1 Structural Analysis of Polyols using FTIR

FTIR spectroscopy was used as a qualitative means of verifying the chain extension reaction in LP-1. The following spectral changes confirmed the success of the chain extension reaction: (a) increased stretching of the C-H region (2800 - 3000cm $^{-1}$) and increased CH_3 bending at 1387 cm^{-1} due to the creation of CH, CH_2 and CH_3 groups[52,104]; (b) increase in the C-O ether absorption peak at 1046 cm^{-1} [70]; and (c) creation of ether linkages proven by the increased stretching in the phenyl-alkyl region (1179cm^{-1}). Following the hydrolysis reaction, the spectra for LP-2 and LP-3 showed (a) an increase in the hydroxyl region (b) the creation of methylene, methine and methyl groups, evidenced by increased stretching between 2800-3000 cm^{-1}, and (c) reduction in the intensity of the carbonyl peak at 1784 cm^{-1} confirming the ring opening of PC by water. The decrease of the PC-associated peak (between 1000-1250 cm^{-1}) and increase in the PG-related peak at 1456 cm^{-1} also confirmed the occurrence of the hydrolysis reaction in LP-2 and LP-3.

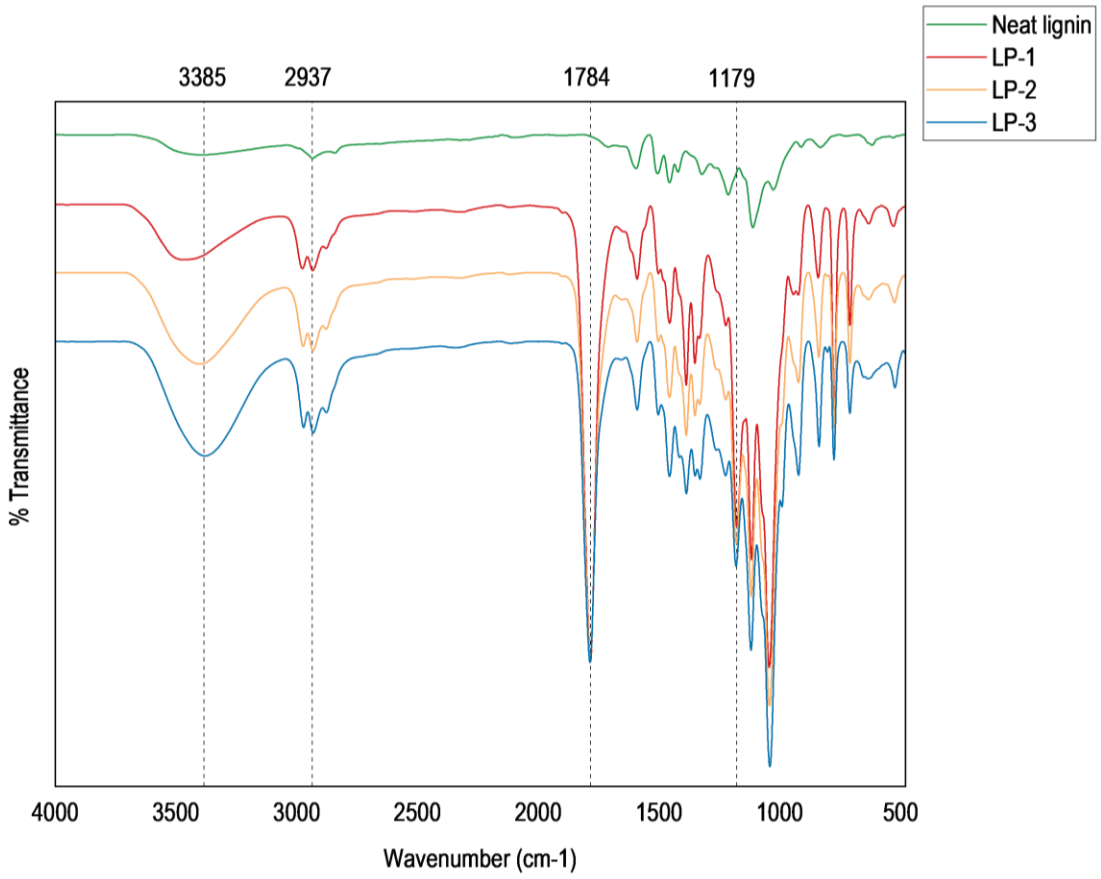

Figure 13: FTIR spectra of neat lignin, LP-1, LP-2 and LP-3

Further investigation of the structural composition of the polyols was carried out using ^{31}P- and ^{13}C-NMR techniques.

4.2.2 Results of ^{31}P-NMR Analysis

^{31}P-NMR was employed to verify the structures formed during both steps of polyol synthesis. ^{31}P-NMR analysis of LP-1 (Figure 14) showed near-complete disappearance of phenolic and carboxylic hydroxyl groups, confirming the results seen in the IR spectra. The broad signal in the primary aliphatic region of unmodified lignin completely disappeared and was replaced by a new peak between 147.2-147.4 ppm, corresponding to primary hydroxyl groups.[75,76] Another band appeared between 145.5 - 146 ppm, assigned to secondary hydroxyl groups.[75,76] Both primary and secondary hydroxyl moieties were produced during oxypropylation of lignin since moisture in the

lignin sample would generate propylene glycol by reacting with PC. The intensities of both primary and secondary hydroxyl peaks followed an increasing trend in LP-2 and LP-3, signaling the successful hydrolysis of PC in the second step, yielding primarily 1,2- propanediol. An unidentified peak was observed between 146.7 - 146.9 ppm in LP-1, possibly arising from other oligomers (e.g. dipropylene glycol) which are formed due to side reactions.[105,106] Interestingly, its intensity decreased gradually as the polyol OH value increased from LP-2 to LP-2.

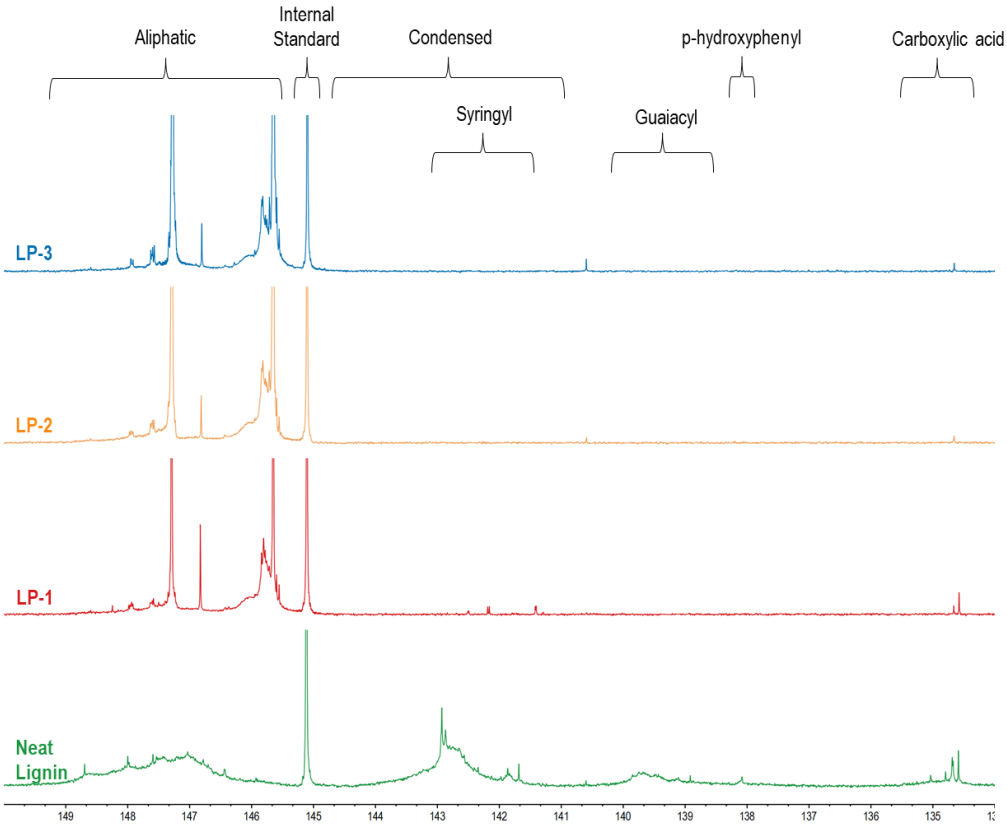

Figure 14: ^{31}P-NMR spectra of unmodified lignin, LP-1, LP-2 and LP-3

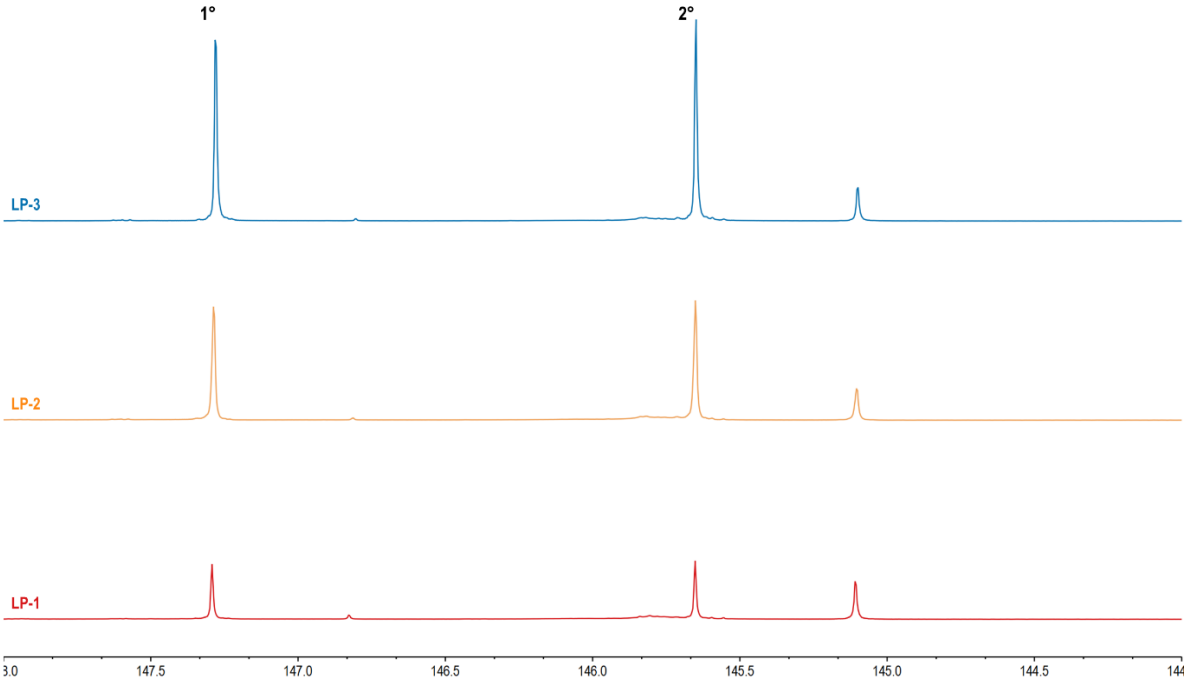

Figure 15: ^{31}P-NMR of LP-1, LP-2 and LP-3, showing primary (1°) and secondary (2°) aliphatic OH groups

4.2.3 ^{13}C-NMR analysis

Further structural elucidation of lignin polyols was performed using ^{13}C-NMR. Analysis was conducted on modified lignin fractions isolated by gravimetric analysis and the unmodified lignin. Successful etherification of lignin was confirmed by two major changes: a) new signals in the aliphatic region corresponding to methyl (15.4 - 21.7 ppm), methylene (77.2 - 79.4 ppm) and methine (62.8 - 66.1 ppm) carbons from the hydroxypropyl units which were grafted unto lignin and b) the simultaneous disappearance of the signal at 148 ppm assigned to C3/C5 phenolic syringyl units and increased intensity at 152 ppm assigned to etherified C3/C5 syringyl units.[78] As expected, the precipitate from LP-2 showed almost no deviation from that of LP-1, since no further modification was performed on lignin.

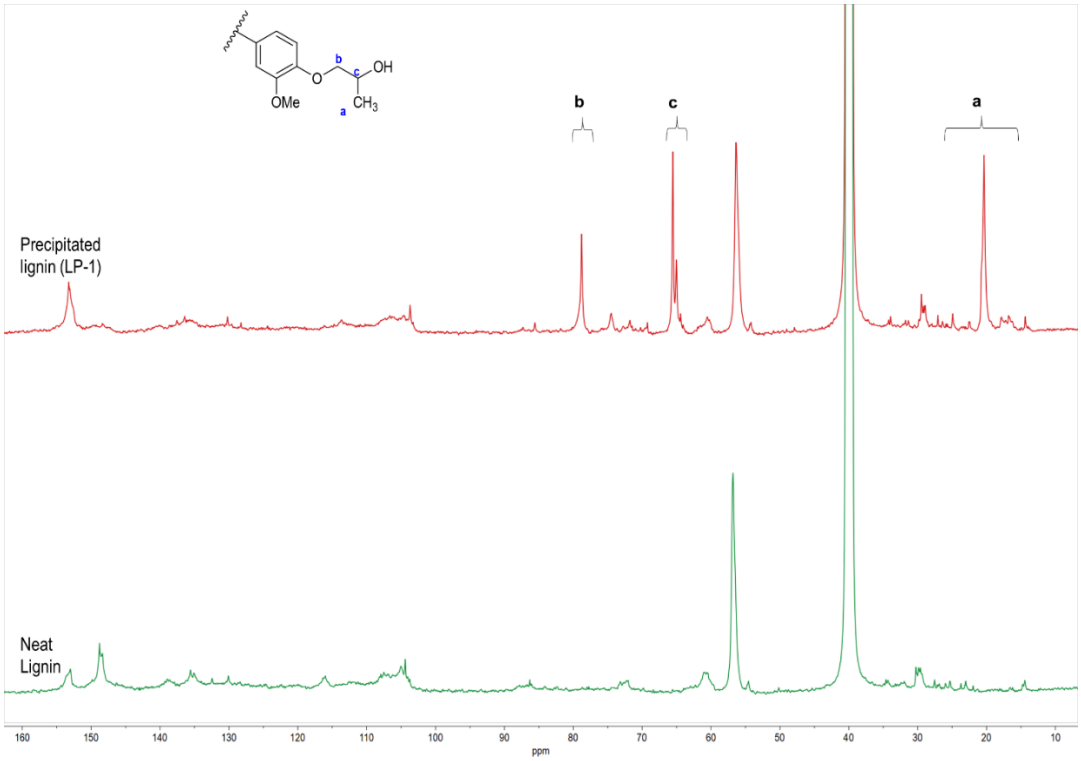

Figure 16: ^{13}C-NMR Spectra of neat lignin and modified lignin precipitated from LP-1

LP-1 and LP-2 were analyzed following the same procedure. In LP-1, the signals at 20.25 and 67.41 ppm were attributed to propylene glycol produced during oxyalkylation, since lignin was not fully dried before use. Analysis of LP-2 indicated the consumption of PC by the decrease in intensities at 19.17 ppm, 71.02 ppm and 74.67 ppm. The increased intensity of the signals at 20.25 ppm and at 67.41 ppm, attributed to methyl and methine carbons in PG respectively, which further proved the occurrence of the hydrolysis reaction.

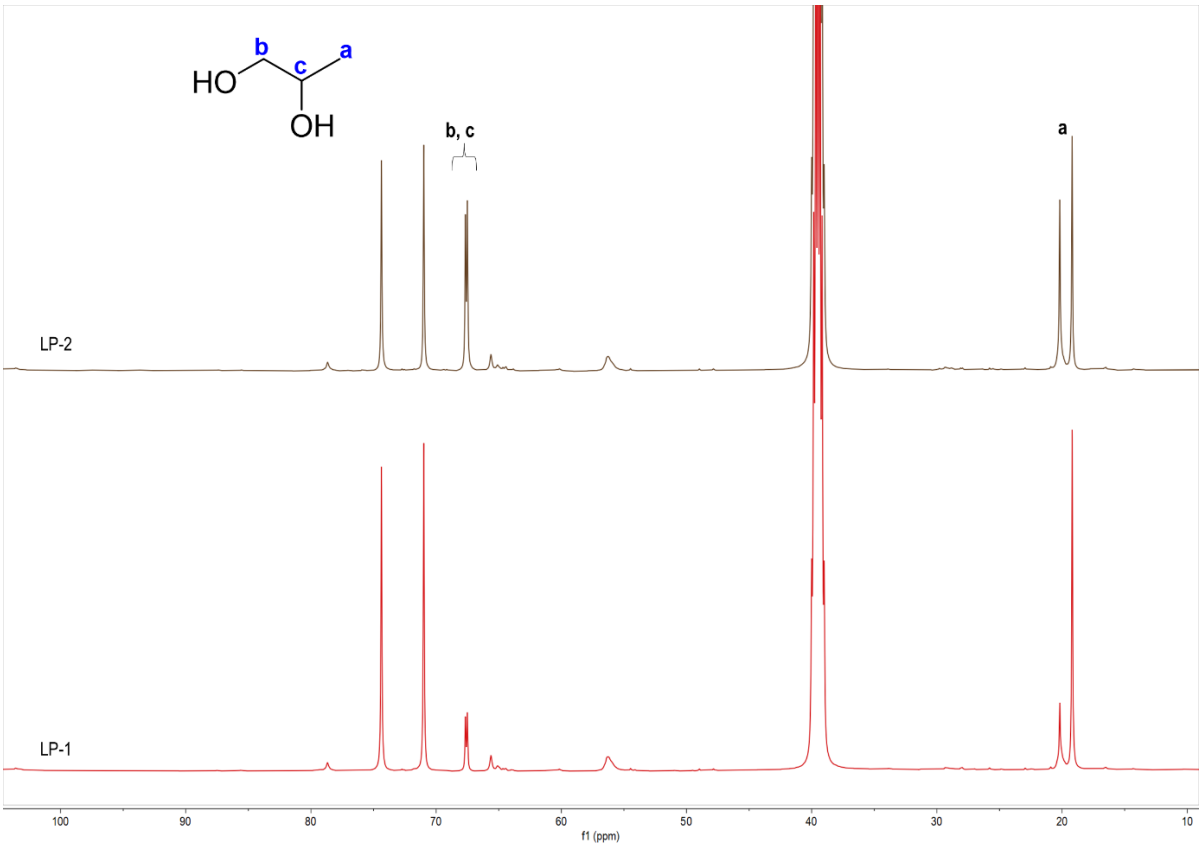

Figure 17: ^{13}C-NMR analysis of LP-1 and LP-2

4.3 Polyurethane Foam Synthesis and Characterization

Rigid polyurethane foams were prepared using petroleum-based polyol (Control), LP-1, LP-2, and LP-3. Foams based on LP-2 represent the optimized formulation and were fully characterized.

4.3.1 Foam reactivity

Lignin-based foams showed very rapid gelation and foam expansion, consistent with published literature,[80,82,83] which was attributed to the higher reactivity of newly created aliphatic hydroxyl groups. Residual DBU in the polyol was also postulated to speed up the gelation reaction, resulting in rapid formation of the polymer network. Strategies employed in other studies to control foam kinetics include neutralizing the prepared polyol with an acid,[80,82] and reducing the amount of catalyst used by up to 75%,[83] which limited overall foam expansion and did not significantly slow down foaming kinetics enough to prepare larger foam samples.

In our study, a reactive acid-blocked amine catalyst was added to the optimized formulation to control reaction kinetics without sacrificing foam expansion. These are employed to inhibit reactivity and improve flowability during PU synthesis.[107] The incorporation of a small quantity of delayed-action catalyst (0.3pphp) produced a noticeable increase in cream time, that is the time corresponding to the start of the water-isocyanate reaction, in LP-2 than was observed in LP-1. Increasing the amount beyond 0.4 pphp, however, lessened the extent of foam expansion due to the reduced rate of blowing.

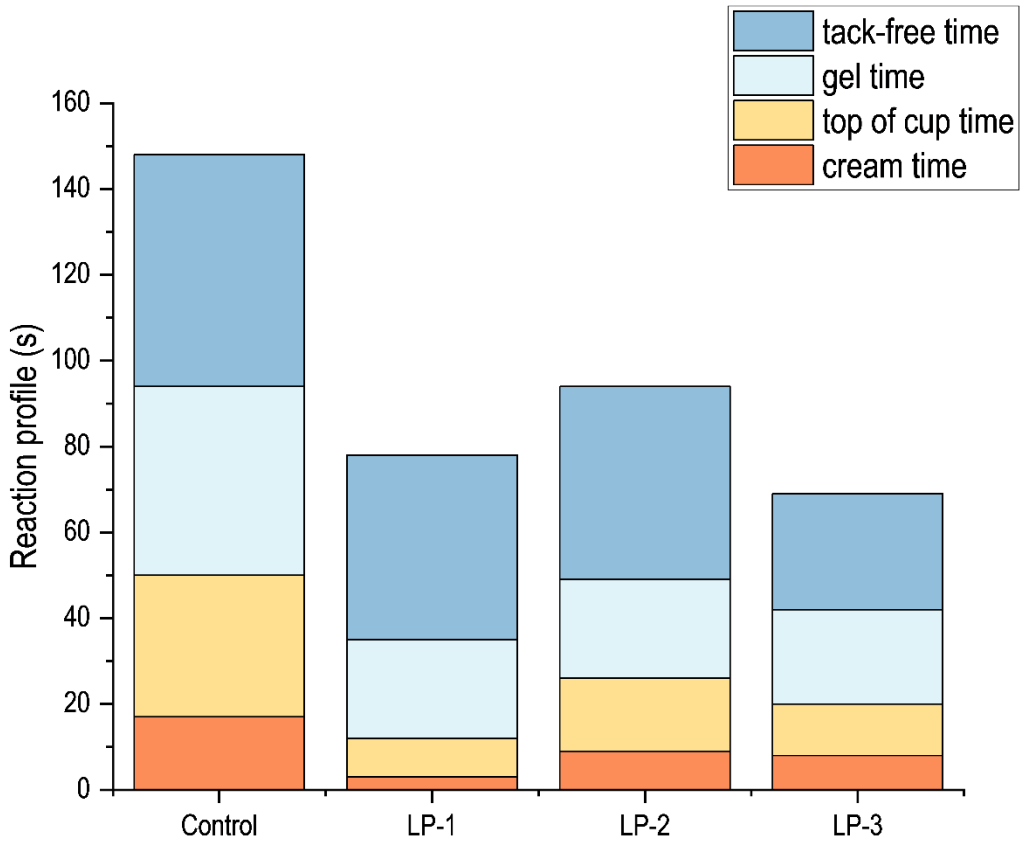

Figure 18: Reactivity profile of control and lignin polyol-based foams formulated with LP-1, LP-2 and LP-3

4.3.2 Analysis of Foam using FTIR Spectroscopy

The synthesized foams were analyzed using FTIR spectroscopy to confirm the successful

polymerization reaction between polyols and isocyanate. As seen in Figure 19, characteristic absorption bands in all prepared PUR foam samples provide evidence of urethane formation: N-H stretching (3339 cm^{-1}) and bending vibrations (1512 cm^{-1}), and stretching vibration of C=O moieties (1708 cm^{-1}). The low-intensity peak at 2286 cm^{-1} associated with unreacted NCO groups, was present in the lignin-based samples as well as the control sample. In the lignin-based foams, higher absorption was observed in this area as the polyol OH value increased. This is because the isocyanate was supplied in a slight excess (120-index), meaning more -N=C=O groups were made available than was required for the reaction. The bands at 1790 cm^{-1} and 1113 cm^{-1} were present only in lignin-based foams and correspond to carbonate structures originating from PC.

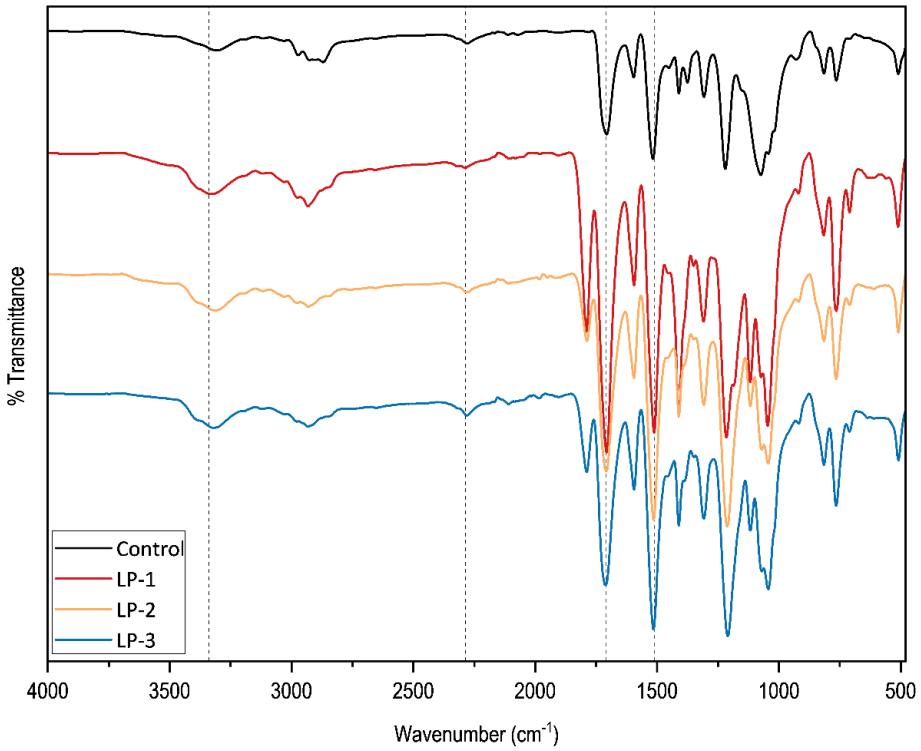

Figure 19: FTIR spectra of Control foam and lignin-based foam formulated with LP-1, LP-2 and LP-3

4.3.3 Apparent Density

As previously discussed, all lignin-based polyols were characterized by high reactivity, which led to the rapid formation of the foams. As such, higher densities were expected compared to the control due to inefficient mixing and emulsification of the resin blend, which could result in poor distribution of the blowing agent. Higher reactivity could also result in increased loss of pentane used as physical blowing agent due to higher reaction exothermicity. The efficiency of the surfactant in emulsifying incompatible components in the B-side resin is also extremely essential to ensure proper distribution of the blowing agent as well as homogenous cell structure.

Using the same initial quantity of pentane as in the control sample resulted in visibly large pores in some areas of the foam, due to an uneven distribution of the blowing agent and high reactivity of the lignin polyol. This further proved the incompatibility of the lignin polyol with the physical blowing agent and the inefficiency of the selected surfactant in emulsifying the resin blend. Hence, the amount of pentane was reduced from 20 pphp to 10 pphp in subsequent formulations with LP-2 and LP-3. A delayed action catalyst was also added to the foam formulation to combat the effect of residual DBU.

Despite the use of a lower amount of pentane, a slight decrease in density was observed between LP-1 and LP-2. This was attributed to the addition of the delayed catalyst, which allowed more time for the components to be properly mixed, ensuring that the blowing agent was more evenly distributed. Regarding LP-3, the lower density can be attributed to increased cell distortion resulting from the higher OH value (472 mg KOH/g), as illustrated in Figure 23.

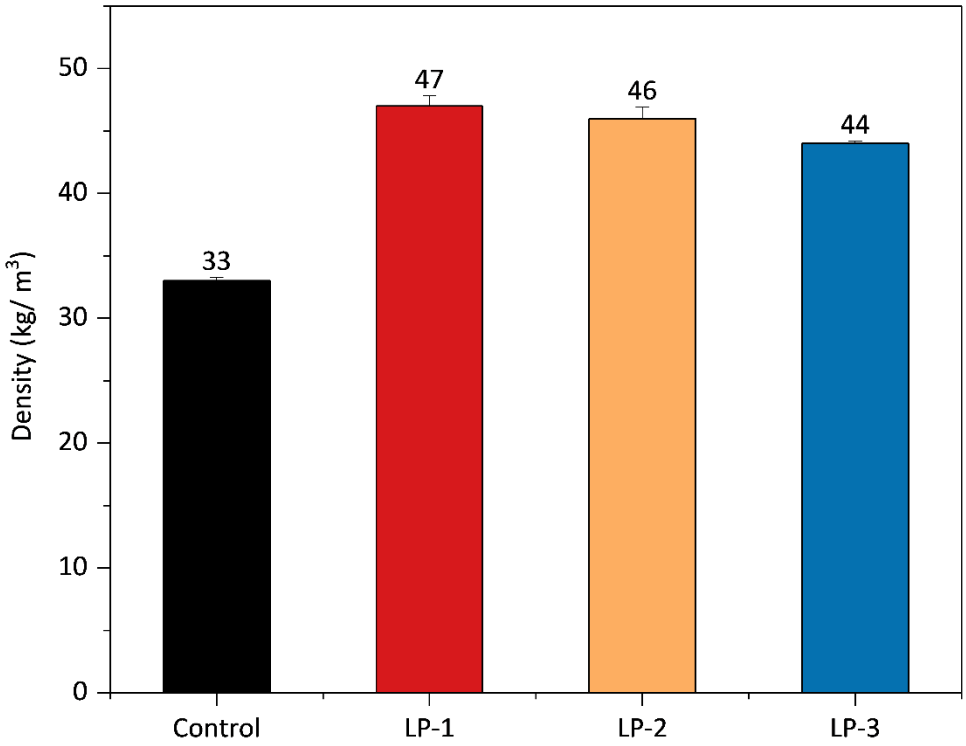

Figure 20: Density for control foam and lignin polyol-based foams formulated with LP-1, LP-2 and LP-3

4.3.4 Compressive Strength

The compressive strength of foam based on LP-1 (188 kPa) was significantly lower than that of LP-2, despite its higher density, due to the low OH value of the polyol and the presence of a large quantity of unreacted PC. High polyol hydroxyl values are essential for the formation of compact foams by increasing the extent of urethane formation.[108,109] Residual PC also has a plasticizing effect on foams,[94] thereby increasing flexibility and decreasing compressive strength. Incompatibility of the blowing agent with the polyol, which led to the heterogeneous distribution of pentane in the foam matrix, could further impact the proper formation of bubbles, decreasing compressive strength. LP-2-based foam, on the other hand, exhibited a higher compressive strength due to the conversion of residual PC to PG, which increased the polyol OH value while

reducing the amount of PC. The generated PG further functioned as a chain extender, with the ability to react with isocyanate, thereby increasing the extent of hydrogen bonding and rigidity of the foam. An unexpected decrease in compressive strength was obtained in the foam made with LP-3. Generally, increasing the polyol OH value results in higher compressive strength and vice versa. In the case of foam prepared with LP-3, the reduction could be explained by the higher reactivity of the polyol. The oxypropylation reaction generates a highly reactive polyol whose activity is further accelerated by the presence of unreacted DBU. Initially, this provides many advantages as discussed above, but further increasing the polyol OH value, coupled with the high functionality of lignin, could result in excessive crosslinking, which further disrupts bubble formation, as observed in Figure 23.

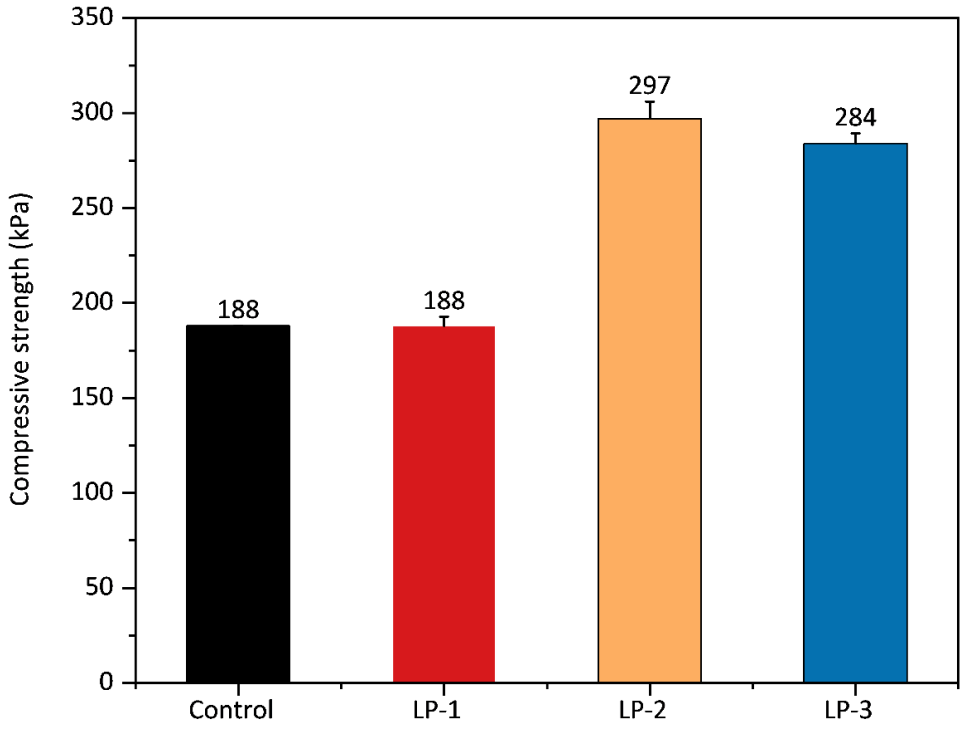

Figure 21: Compressive strengths for control foam and lignin polyol-based foams formulated with LP-1, LP-2 and LP-3

4.3.5 Thermal Analysis of Foams

Thermogravimetric analysis (TGA) of the foam samples was carried out to evaluate the impact of lignin polyol addition on the thermal stability of the foams, and assess whether an improvement in thermal stability was observed by hydrolysis of PC to PG. Thermo-oxidative degradation of all rigid PU foams followed a three-step process typical of urethanes:[110] (a) the evolution of low molecular weight constituents such as water, (b) urethane bond degradation, and (c) polyol decomposition and char formation. The onset of degradation of lignin-based foams was much lower than the petroleum counterpart, indicating lower thermal stability. While the aromatic backbone of unmodified lignin confers moderate thermal stability at elevated temperatures,[111] oxypropylation introduces segmental mobility through chain extension, which interferes with hydrogen bonding interactions.[112,113] Additionally, oxypropylation produces polyols with both primary and secondary OH groups, the latter being attributed to higher flammability in foams.[114] Furthermore, hydrolysis lignins have been shown to possess lower thermal stability than other industrial lignins due to co-existing carbohydrate impurities.[39] This could also contribute to the decomposition patterns observed in the lignin foams.

Despite having lower onset thermal degradation temperatures, lignin-based rigid PU foams presented a slower degradation pattern than the control sample in the region corresponding to urethane bond decomposition (250-350°C). This is a consequence of the aromatic structure of lignin,[80] as well as higher crosslinking densities stemming from the high functionality of lignin. It was expected that foams based on higher-OH polyols would exhibit increased thermal stability and decompose more slowly due to the higher concentration of PG, which increases the concentration of urethane linkages. However, a slight decrease in the onset temperature at each degradation step was observed as the polyol OH value increased, hinting at a further decline in

thermal stability. As also reported in previous publications,[81,115] the presence of small molar mass molecules led to a decrease in thermal stability. Thus, the increase in PG and possibly other PC-oligomers could be responsible for this trend.

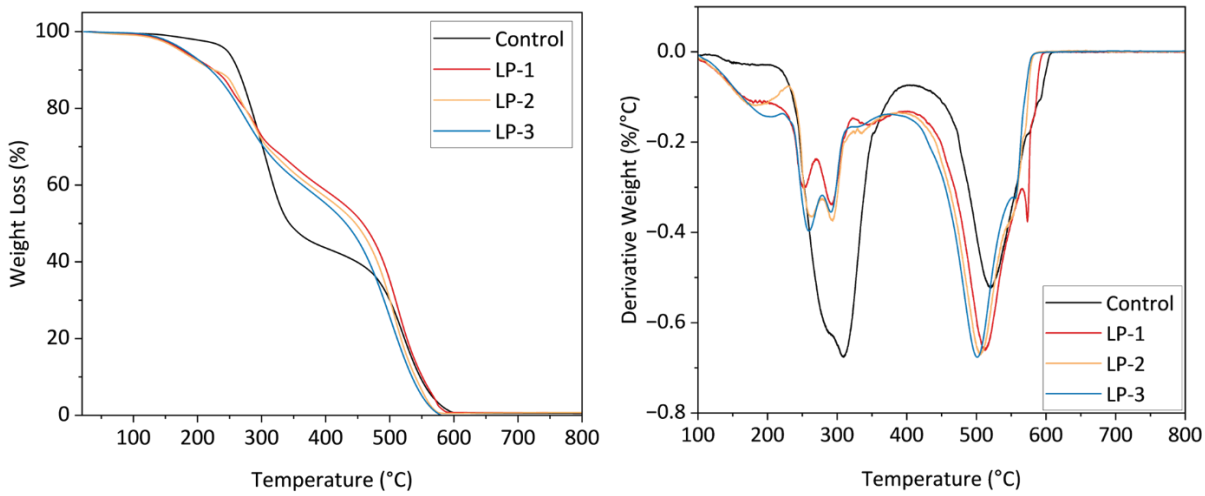

Figure 22: TGA (a) and DTGA (b) curves of control, LP-1, LP-2 and LP-3 foams in air

4.3.6 Cell Morphology

The evolution of cellular structure in rigid PU foam is influenced by the interplay of various factors, including reaction kinetics, polyol viscosity, and the amount and type of surfactant. Establishing a balance between the gel and blow reactions is essential in obtaining a homogenous cellular structure. The gelation rate determines the speed at which the polymer network forms around the growing bubbles.[116] Fast gelation causes the formation of smaller cells and minimizes the effects of cell drainage and bubble coalescence,[5] but results in a higher density. In the case of increased blowing action, rapid foam expansion produces larger, more elongated cells and foams with a lower density.[115,117] Higher polyol viscosity yields smaller, less heterogeneous cells, resulting from limited coalescence and bubble expansion. A further increase in viscosity however, leads to the formation of less uniform cells, which are more damaged due to reduced blowing activity.[118]

Scanning electron microscopy was used for the morphological investigation of control and lignin-based foams. SEM micrographs of the foams revealed a more heterogeneous cell distribution in the lignin-based foams as shown in Figure 23. These also generally had a larger proportion of smaller cells compared to the control, which can be attributed to higher polyol reactivity resulting from the conversion of phenolic OH groups into aliphatic hydroxyl groups, thereby accelerating gelling activity and network formation, and producing finer cells. The delayed action catalyst also possibly contributed to the generation of smaller cells by inhibiting the blowing reaction. The broader distribution in cell diameter was further attributed to the incompatibility of pentane with the polyol and insufficient activity of the surfactant, which impacted the proper distribution of pentane.

The degree of cell homogeneity in the lignin-based foams decreased with the increasing OH value of polyols. LP-1 presents more uniform cells with less damage than LP-2 and LP-3. The foam based on LP-3 had noticeably more irregular and damaged cells. Given the high reactivity of the polyol, increasing the OH value further led to extremely fast polymerization, disrupting proper bubble formation and coalescence.

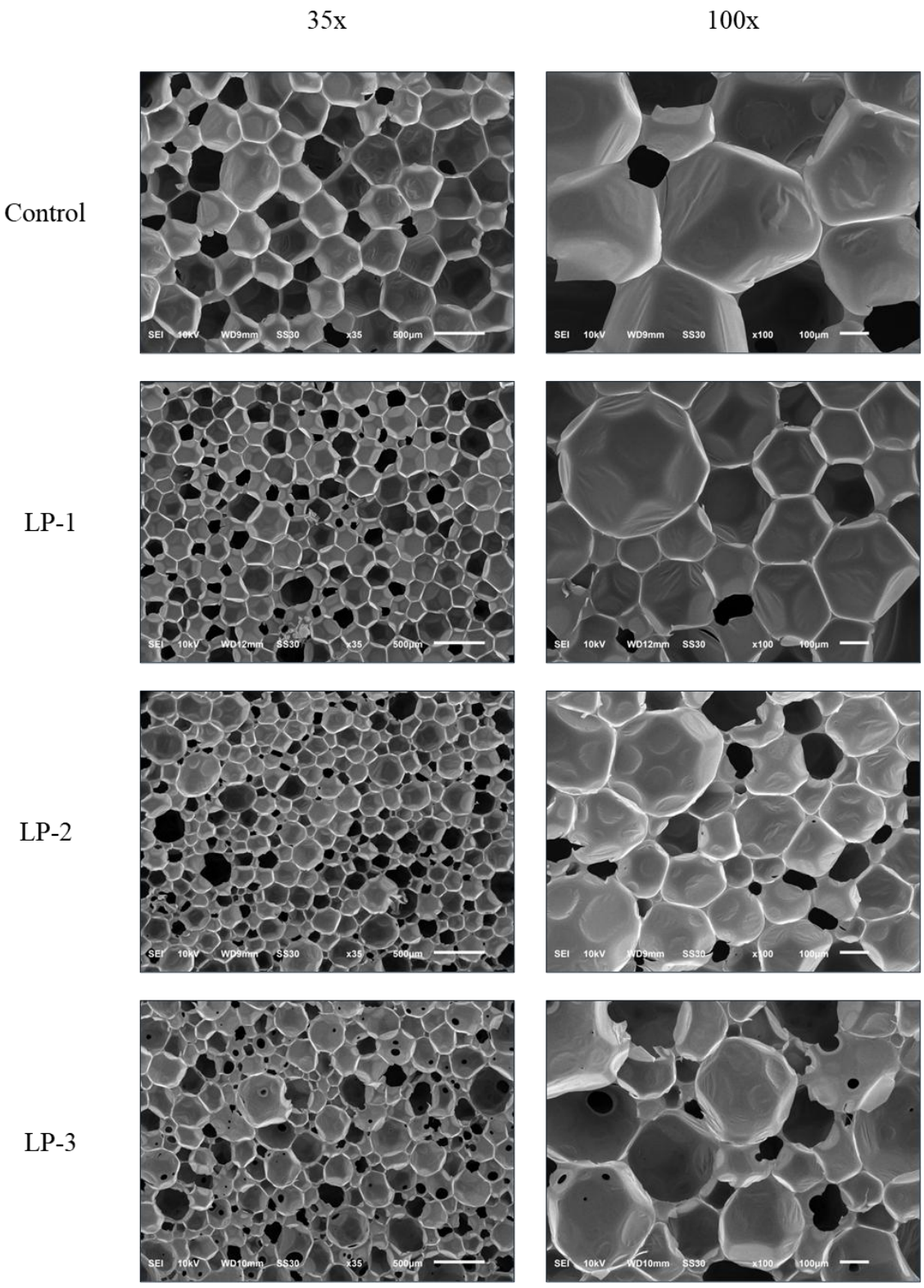

Figure 23: Scanning Electron Micrographs of Control, LP-1, LP-2 and LP-3 rigid PU foams taken at 35x and 100x magnifications

4.3.7 Closed Cell Content

The closed cell percentage of the control and LP-2 based foams were measured using a gas pycnometer. The closed cell content is significantly dependent on cell morphology, with smaller, homogenous cells being linked to higher closed cell content. A high closed cell percentage is also necessary to maintain the insulation efficiency of rigid foams by slowing down the rate of substitution of entrapped gases with air, an occurrence that increases the thermal conductivity of the foam.

The optimized lignin-based foam produced in this study had a higher closed cell content (92%) than the control foam (90%). Given that the control polyol (360 mg KOH/g) and lignin polyol (379 mg KOH/g) had similar hydroxyl values, the difference was attributed to the higher reactivity of the lignin polyol, which led to faster gelation and the production of finer cells. The high functionality of the lignin polyol, coupled with the presence of PG, also speeds up network formation through enhanced crosslinking in the foams. The faster rate of network formation thus produced higher closed cell content.

4.3.8 Thermal Conductivity

Thermal conductivity is an important property for insulating materials: low thermal conductivity ensures efficient insulating properties and vice versa. In rigid PU foam synthesis, good insulating performance is achieved through the addition of physical blowing agents (n-pentane), which are characterized by low thermal conductivities. These compounds do not participate in the reaction but are vaporized by the heat evolved and become trapped in the cells, along with carbon dioxide produced in the blow reaction. The addition of physical blowing agents is especially important since the entrapped gases account for approximately 70% of the total thermal conductivity of rigid PU foams.[119] Thermal conductivity is also affected by the cell size and distribution, and the

proportion of closed cells in the foam.

Given the higher closed cell content and smaller cells, the LP-2 foam was expected to have a lower thermal conductivity. However, it had a slightly higher thermal conductivity (0.0327 W/mK) than the control (0.0309 W/mK). As discussed earlier, the amount of pentane used in the lignin-based foam was reduced significantly due to the incompatibility of the lignin polyol with pentane. Also, the high reactivity of the polyol gave rise to two phenomena that potentially led to a reduction in thermal conductivity: inefficient mixing of the components, leading to heterogeneous distribution of the blowing agent; and high exothermicity, which could lead to excessive loss of the blowing agent. The combination of these factors explains the higher thermal conductivity of the bio-based foams . The increased thermal conductivity could also be attributed by the higher density of the lignin foam, which increases conduction through the solid polymer matrix, leading to a reduction in the thermal conductivity.[120] Foams based on this technology thus hold significant potential for use as thermal insulation materials.

4.4 Synthesis and Characterization of Polyisocyanurate Foam

Polyisocyanurate (PIR) foams are recognized as superior insulation materials, offering improved thermal and dimensional stability, as well as lower flammability, compared to PU foams.[2,114,121] They are obtained by the trimerization of -N=C=O groups into trisubstituted isocyanurates in the presence of trimerization catalysts.[3,121] Although the thermal properties of pure PIR foams are desirable, the high degree of crosslinking that characterizes these polymers causes high brittleness and friability. To circumvent these problems, PIR foams were modified through the introduction of other chemical groups, including urethane, epoxy and amide groups.[121–123]

Urethane-modified polyisocyanurates (PUR/PIR) are hybrid polymers formed by reacting polyols with an excess of isocyanate, resulting in the formation of both urethane and isocyanurate groups. The foams provide a compromise between mechanical strength and thermal stability, with reduced friability. Aromatic polyester polyols with low functionality are the most commonly used class of polyols in PUR/PIR foam production, since the polyester structures have a plasticizing effect on the foams.[7]

The incorporation of unmodified lignin in PUR/PIR foams yielded the same trends as with PUR foams: substituting beyond 50 wt.% of polyol led to a significant decline in foam properties.[40,44] These studies further found that the aromatic structure of lignin contributed to improved flame retardancy. In this study, a preliminary investigation on formulating thermally stable PUR/PIR foams using oxyalkylated lignin polyol was conducted. Lignin polyol with a hydroxyl value of 472 mg KOH/g (LP-2) was used in formulating the bio-based foam, while the control foam was prepared with a polyester polyol with a hydroxyl value equal to 227 mg KOH/g.

4.4.1 Foam Formulation

PUR/PIR foams are formulated using higher isocyanate indices than PU foams since NCO groups are consumed through urethane and isocyanurate formation. In this study, an NCO/OH molar ratio of 270 was utilized. One key observation after foam formulation was the higher friability of the lignin polyol-based foam. This is the result of a greater degree of crosslinking stemming from the higher hydroxyl value and functionality of the lignin polyol. The specific formulations used are included in Table 4.

Table 3: PUR/PIR foam formulations

	Control Foam		**Lignin Polyol-Based Foam**	
Component	pphp			
Polyol	100	100	100	100
Water	0.25	0.25	0.25	0.25
Viscosity reducer	10	10	-	-
Surfactant	1	1	1	1
Trimerization catalysts	4.8	4.8	4.3	4.3
Polyurethane catalysts	1.5	1.5	4.3	4.3
TCPP	-	1	-	1
n-Pentane	22	22	20	20
Isocyanate	270-index	270-index	270-index	270-index

4.4.2 Evaluation of Thermal Stability

The thermo-oxidative stability of the PUR/PIR foam samples was evaluated using TGA, up to 800°C. Thermal degradation in urethane-modified isocyanurate foams follows the same trend as in polyurethane foams, beginning with the evolution of low molecular weight compounds, followed by the decomposition of urethane linkages, and finally, isocyanurate trimer

decomposition.[124] The weight loss (TGA) and derivative weight loss (DTGA) thermograms in Figure 24 show the higher thermal stability of the lignin-based foam compared to the control sample. This is especially evident in the region corresponding to urethane bond decomposition (between 200-300°C), where the lignin polyol-based foam exhibits significantly lower weight loss than the control. This can be attributed to the aromatic structure of lignin as well as the high functionality and high OH value of the polyol, factors that increase the degree of crosslinking. In the second major decomposition region representing isocyanurate trimer decomposition (500-550°C), a slight decrease in weight loss and increase in degradation temperature is exhibited in the lignin-based foam (522°C) compared to the control (516°C).

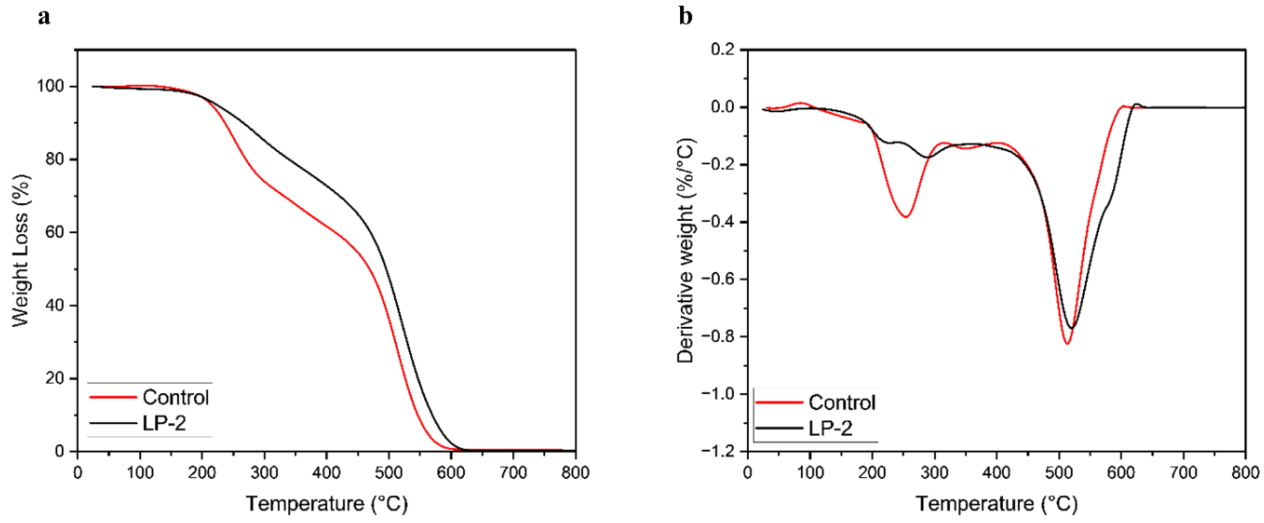

Figure 24: TGA (a) and DTGA (b) curves of Control and Lignin polyol-based foams in air

4.4.3 Burning Behavior of PUR/PIR foams

The prepared foam samples were subjected to the horizontal burning test to evaluate their flame retardancy. The lignin-based samples had significantly shorter burn times than the control, and the flame did not spread beyond the 25mm mark, as shown in Figure 25. Additionally, the flame was extinguished almost immediately after the removal of the flame source. These results could be attributed to the char-promoting nature of lignin and the higher crosslinking density of the foam.

Lignin is widely regarded as enhancing flame retardant properties of polymeric materials due to the high carbon content, which promotes charring.[40,125,126] The char layer formed acts as a barrier, cutting off the oxygen supply to the foam and limiting the spread of the flame. Besides the modification that arises from oxypropylation, that is grafting of an aliphatic chain which reduces the thermal stability of the foam, the aromatic backbone of lignin remains intact. This could enhance the flame retardancy in combination with the presence of isocyanurate trimers. Furthermore, the high functionality of lignin and the high OH value of the polyol enhanced crosslinking, which led to the formation of a more compact polymer and inhibited flame spread.

Table 4: Burning behavior of control and lignin polyol-based PUR/PIR foams without flame retardant

	Flame time to 25mm (s)	**Burn time after flame removal (s)**	**Burn length (mm)**
Control	5 ± 0.96	13 ± 2.21	60 ± 6.34
Lignin polyol-based	7 ± 1.10[a]	2 ± 0.83	33 ± 0.84

a = flame did not reach the 25mm mark

Finally, the nature of the charred layer offers more insight into the flame performance of the samples. Considering the control foam, a noticeable change in dimensions and structure is observed after the removal of the flame. The foam based on lignin, however, presents only a slight change in morphology. This pattern was observed in both the samples prepared with and without Tris (chloropropyl) phosphate (TCPP), which is a commonly used flame retardant in PU foams.

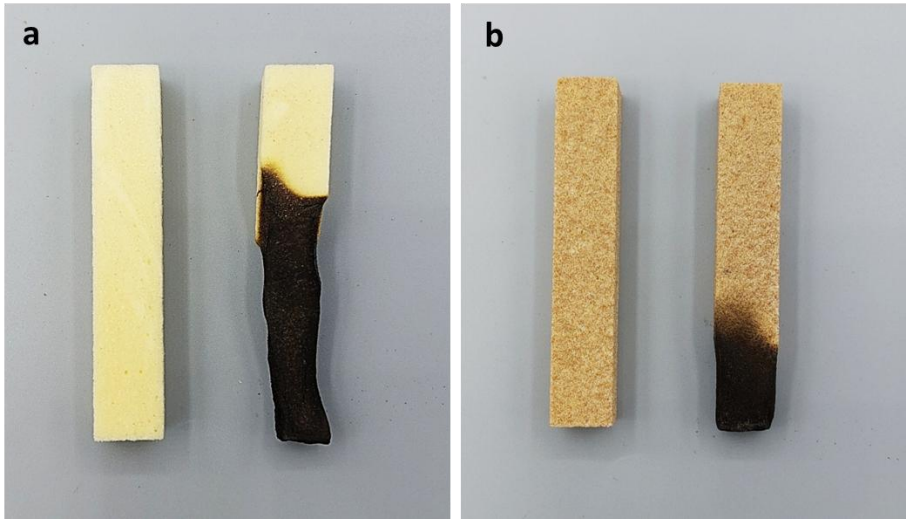

Figure 25: Petroleum-based (a) and lignin-based (b) PUR/PIR foam samples before (left) and after (right) burning (without flame retardant)

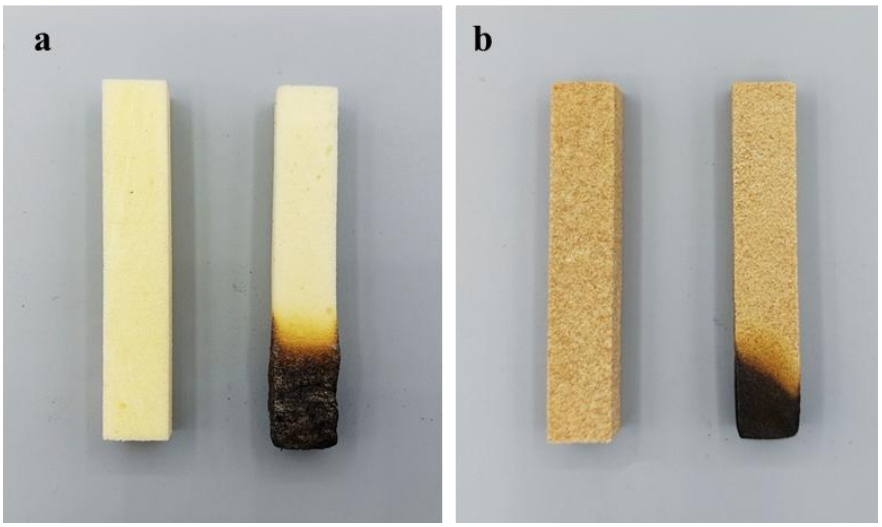

Figure 26: Petroleum-based (a) and lignin-based (b) PUR/PIR foam samples with halogenated flame retardant before (left) and after (right) flame test (burning)

CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

The use of lignin as a polyol replacement in rigid polyurethane foams has been investigated due to its renewable nature, high hydroxyl value, high functionality, and flame retardant properties. The direct incorporation of solid lignin in rigid PU foams is, however, limited to approximately 50% lignin loading due to a decline in properties. Oxypropylation is a practical methodology for modifying sterically hindered phenolic hydroxyl groups in lignin by converting them into aliphatic groups. While the modification results in increased reactivity of the polyol, issues persist, namely, (i) the low hydroxyl value of the polyol, (ii) a large amount of unreacted propylene carbonate (PC), and (iii) the low amount of lignin in the final polyol.

In this study, a simple, effective method is proposed for increasing the hydroxyl value of oxypropylated lignin polyol by the hydrolysis of excess PC into propylene glycol. This procedure is beneficial since it simultaneously reduces the amount of residual PC and allows for higher lignin loadings to be achieved, without using other solvents. Furthermore, propylene glycol functions as a chain extender, which increases the proportion of hard segments in the foam. Using this methodology, lignin polyols with up to 41 wt.% of modified lignin were produced with hydrolysis lignin, having hydroxyl values ranging between 300 - 500 mg KOH/g.

Rigid PU foams were synthesized by entirely replacing petroleum-based polyols with lignin polyols, which satisfied most of the requirements for type II spray-applied rigid cellular polyurethane thermal insulation. Firstly, the optimized lignin polyol-based foam had 17% lignin content, which is an increase over the amount achieved in previous studies (~10%). The foam showed a three-fold increase in compressive strength and a 45% decrease in density, in comparison to a similar study conducted by our lab using solid lignin. Additionally, smaller cells and a higher

degree of homogeneity in cell size distribution were observed, which is a significant improvement over morphology after incorporating solid lignin. The thermal conductivity was however higher, due to the incompatibility of the polyol with pentane. Finally, the lignin-based foam had slightly lower thermal stability than the control foam, which was attributed to small molecular weight compounds present in the polyol.

Oxyalkykated lignin polyol was further employed as a polyol substitute in urethane-modified isocyanurate (PUR/PIR) foams. The foams showed improved flame retardancy with less reduction in dimensions compared to the control, due to the high functionality and aromatic structure of lignin, even without the addition of tris(chloropropyl) phosphate (TCPP). The lignin-based foams were however more friable.

5.2 Future Work

Future studies can build on these achievements and further improve the performance of lignin-based foams directed at:

1. Developing a more effective strategy for controlling the fast rate of the polyurethane reaction due to high reactivity of liquid lignin polyols .
2. Investigating mechanisms for improving the thermal stability of PU rigid foams based on hydroxypropyl lignin polyol.
3. Incorporating higher amounts of lignin in the polyols while maintaining viscosities suitable for rigid PU and PUR/PIR foam synthesis.
4. Optimizing lignin-based PUR/PIR foam formulations to improve friability.
5. Using other lignin types for polyol synthesis and subsequent foam formulation

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APPENDIX

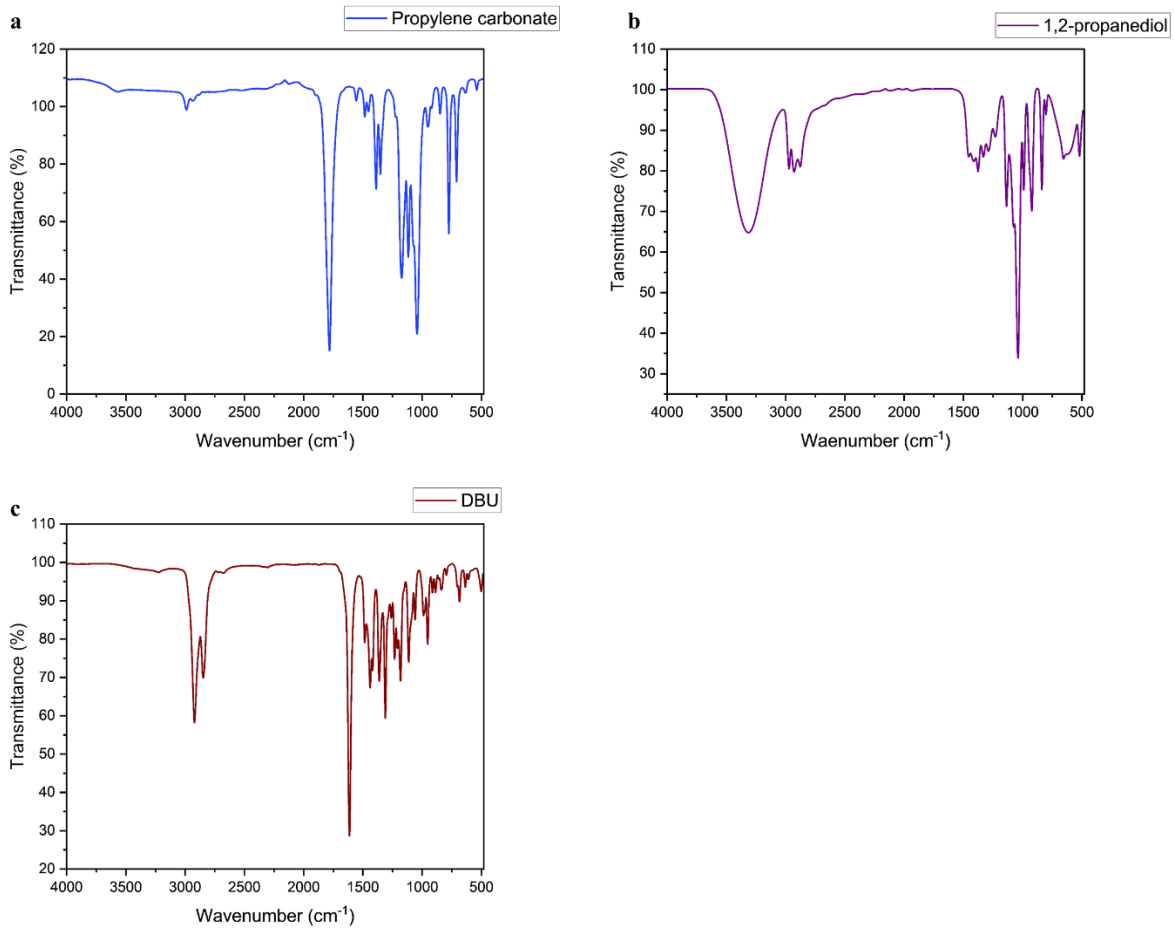

Figure 27:FTIR spectra of (a) propylene carbonate, (b) 1,2-propanediol and (c) DBU

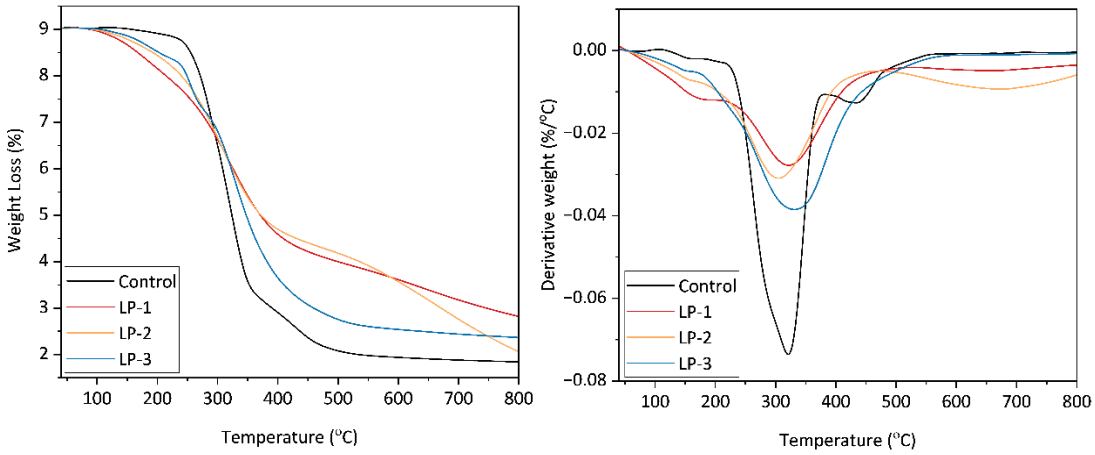

Figure 28: Thermogravimetric analysis of control and lignin-based foam in nitrogen