LIGNIN-BASED LOW-DENSITY RIGID POLYURETHANE/POLYISOCYANURATE FOAMS

Christián Henry[a] *and Mojgan Nejad*[*ab]

[a]Department of Forestry, Michigan State University, 480 Wilson Road, East Lansing, MI, 48824, USA

[b]Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, MI 48824, USA

KEYWORDS: Lignin, bio-based, sustainable, foam, polyurethane, polyisocyanurate, low-density

ABSTRACT

In this study, unmodified kraft lignin was utilized to fully replace petroleum-based polyol for the first time in low-density rigid polyurethane/polyisocyanurate (PUR/PIR) foam. The effect of different lignin incorporation levels (0, 25, 50, 75, and 100%) on foam properties was investigated. The developed lignin-based foams were evaluated for their reactivity, polyol viscosity (using a rheometer), apparent density, compression strength (measured with an Instron), closed cell content (using a gas pycnometer), thermal conductivity, fire resistance, and foam morphology (observed through SEM). All of the lignin-based foams met the minimum requirements for rigid foams set by ASTM International standards. Remarkably, the foam made by replacing 100% of

petrochemical polyol with commercially available kraft softwood lignin demonstrated significantly improved fire performance, reducing the burn length by 127%.

INTRODUCTION

Polyurethanes, one of the most versatile polymeric materials, are used in multiple products, including foams, coatings, adhesives, sealants, and elastomers.[1–3] Rigid polyurethane foams (rigid foams) are a collection of multi-purpose polymers consisting of polyurethane (PUR) and polyurethane/polyisocyanurate (PUR/PIR) foams. The raw materials for PUR and PUR/PIR foams are similar, with the main difference being the higher isocyanate index used for PUR/PIR foams (>250) compared to PUR foams (<180).[4] Both foams can have a wide range of properties and are used in various applications such as insulation, construction, and appliances.[1] Due to the combination of strength and low density, the global market of rigid foams have rapidly increased over the last few decades, with their United States resin demand projected to reach 1030 million kg in 2020 (up 34% in 2010).[5]

Commercial polyols used in rigid foam synthesis are currently sourced from toxic and energy intensive starting materials like propylene oxide.[6] Efforts to replace these petro-dependent polyols with lignocellulosic biomass have increased over the years due to their reactive hydroxyl groups being abundantly available and their relative lower cost.[1,7] The incorporation of lignin into rigid PUR foams have been reported to increase char residue,[8] compression strength,[8–10] and biodegradation,[11] while decreasing thermal conductivity,[10] and water absorption.[1,8,12] However, to the best of our knowledge, there is only one study using unmodified lignin in low-density (30-60 kg/m^3) rigid PUR/PIR foams.[13] That study[13] utilized 19 technical lignins to replace 30% of petroleum-based polyol in low-density rigid PUR/PIR foams and reported that the lignin-based

foams that failed in compression strength and/or closed-cell content testing were made with lignins that had lower pH, potassium, sodium, calcium, magnesium, and hydroxyl contents than lignin-based foams that passed all testing.[13]

Comparatively, numerous works exist on lignin-based rigid PUR foams,[11,14–16] mainly utilizing modified lignins, including oxypropylated,[9,10,17–21] liquefied,[8–10,22–26] and various other modification techniques[27–32] like amination,[28] phenylation/epoxidation,[32] and hydroxymethylation.[33] Oxypropylation is one of the most well-known techniques used to change the phenolic hydroxyl (OH) groups of lignin to aliphatic OH groups and prepare liquid lignin polyol for use in rigid foam.[12] The oxypropylation process is conducted at relatively high temperature (150-523 °C), pressure (0.24-1.75 MPa), time (9 min to 5 days), along with high solvent/propylene oxide (50-80%), and catalyst (2-10%) content to liquefy lignin.[9,10,17–21,34–36] Though oxypropylation and other lignin modification techniques can increase the reactivity of lignin, the use of high-energy reaction conditions (high temperature and pressure) and petrochemically sourced solvents (propylene oxide) make these lignin polyols less desirable for commercialization. Lastly, due to the high percentage of propylene oxide/solvent and catalyst used in lignin polyol synthesis, the amount of lignin in the final polyol (10-30%)[19,34] is often lower than or similar to unmodified lignin replacement.

The use of unmodified lignins as polyol replacement in low density rigid polyurethane foams has been reported at ~30% replacement due to the increased polyol viscosity and reduction of foam properties at higher lignin loadings.[12,16] To the best of our knowledge, the maximum amount of unmodified lignin and its effect on foam properties in low-density lignin-based rigid PUR/PIR foams have not been studied. The goal of this work is to elucidate the maximum amount of lignin as polyol replacement in lignin-based PUR/PIR foam while monitoring the effect of lignin loading

on foam properties. To accomplish this, foams were formulated with 0, 25, 50, 75, and 100% lignin as polyol replacement in rigid PUR/PIR foam. The influence of percent lignin loading on polyol viscosity, foam reactivity, morphology, mechanical properties, and horizontal burn were studied.

MATERIALS AND METHODS

Commercial Indulin AT kraft softwood lignin was kindly provided by Ingevity and was sieved (80 μm mesh) and oven dried (80°C) to a constant weight before use. Huntsman Polyurethanes (The Woodlands, TX, USA) graciously supplied all the foam raw materials.[13] Other reagents were purchased from Fisher Scientific (Hampton, NH, USA) and were used as is.

The hydroxyl content of the lignin sample was determined according to previously published methods using ^{31}phosphorus nuclear magnetic resonance spectroscopy (^{31}P NMR).[13,37,38] In brief, lignin was dissolved in a solution of anhydrous pyridine, deuterated chloroform, and dimethylformamide. Cyclohexanol solution consisting of anhydrous pyridine and deuterated chloroform was then added as an internal standard.[13,37,38] Chromium (III) acetylacetonate solution (anhydrous pyridine and deuterated chloroform) was added as a relaxation reagent along with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane as phosphitylation reagent. Spectra were acquired using an Agilent DDR2 500 MHz NMR spectrometer (Billerica, MA, USA).[13] The hydroxyl value of lignin was then calculated by multiplying the measured total hydroxyl content of lignin by the mass of KOH (56.1).[13]

The Polyurethane Foam Cup Test ASTM D7487-13[39] standard was used to formulate foams. The effect of steric hindrance from lignin hydroxyl groups and the increased viscosity of solid lignin addition was decreased by the adjustment of catalyst and viscosity reducer based on the percent weight of lignin (**Table 1**). The percent of viscosity reducer was increased to a higher

weight percentage for 75 and 100% lignin-based foams to account for viscosity increases found in literature. Using a 237 mL cup, polyol, lignin, catalysts, surfactant, blowing agent (n-pentane), viscosity reducer, and flame retardant were mixed to create each B-side polyol blend at a 270 isocyanate index. B-side polyol blends were mixed for about 15 seconds using a high-speed mixer (Camframo overhead mixer) at 3000 rpm.

Table 1. Foam Formulations in Grams

Foam Additive		Lignin polyol replacement (100% Polyol)				
		0%	25%	50%	75%	100%
		Foam Additive (System %)				
100% Polyol	Polyol	29.28	21.3	12.3	5.19	0
	Lignin	0	7.1	12.3	15.56	17.53
Water		0.07	0.07	0.06	0.05	0.04
Viscosity Reducer		2.93	3.55	6.15	15.56	23.37
Surfactant		0.29	0.28	0.25	0.21	0.18
Catalysts		1.84	1.83	1.86	1.83	1.76
Blowing agent		6.44	6.25	5.41	4.56	4.67
Flame retardant		2.93	2.84	2.46	2.07	1.75
PMDI		56.21	56.77	59.2	54.96	50.69
System % Total		100	100	100	100	100

The viscosity of the B-side polyol blend was determined using a Discovery HR-1 rheometer (Waters TA Instruments Newcastle, DE, USA) with a 10 s^{-1} shear rate, at 23°C, for 30 seconds. Viscosities were averaged and reported.

After mixing B-side polyol blends, the isocyanate was then added (3-second pour time) with a 270-isocyanate index and mixed until heat was felt on the outside of the cup (mix time). Foam reaction time was determined by measuring the following: mix, cream, string gel, top of cup, string gel, tack-free, and end of rise times as described in previous literature.[13,39] The mix time indicates the start of the water and isocyanate reaction, cream time shows the onset of foaming, while top of cup time indicates blowing agent activity. Lastly, string gel, tack-free, and end of rise times denote polyol-isocyanate reactions and catalysis.[13,39]

Foam samples were cut to size for each test at least 24 hours after foam formulation. Foams were then kept at room temperature for another 48 hours before being analyzed.

Apparent density was determined according to ASTM D1622[40] following a previously published method.[13] Each sample was measured volumetrically to 0.01 significant figures (three times per side) using a digital caliper and weighed using a digital scale (0.0001). The average of at least five foam samples were used to calculate apparent density, and results were reported in kg/m^3.

Thermal conductivity was evaluated using a TA Instruments FOX 200 heat flow meter instrument according to ASTM C518.[41] Plate temperatures of 12.8°C and 35°C (mean plate temperature of 23.9°C) along with 15cm x 10cm x 5cm samples were used.

Closed-cell content was determined using a micromeritics gas pycnometer (AccuPyc II 1340, Norcross, GA, USA) [13] according to ASTM D6226-15.[42] Following micromeritics method B[43] and previously published literature,[13] experimental conditions included nitrogen atmosphere with 10 purges, 10 cycles, 27.58 kPa purge, and cycle fill pressures at 0.03 kPa/min.

The compression strength was determined using an Instron 5565 universal testing machine (Norwood, MA, USA) following ASTM D1621-16.[44] Twenty-five-millimeter cube samples were tested using a 2.5 mm/min strain rate (13% initial thickness) perpendicular to the foam rise direction.[13]

The fire properties of control and lignin-based foams were determined according to ASTM D4986-18,[45] Standard Test Method for Horizontal Burning Characteristics of Cellular Polymeric Materials. In brief, at least ten 125 mm by 13 mm by 13 mm samples were burned for 30 s in a laboratory fume hood, free of induced/forced draft, with a Bunsen burner (natural gas supply). The foams were marked at 25- and 100-mm lengths, then volume and weights were measured. After burning, the foam weights and burn lengths were remeasured and used to calculate the burn length and percent weight loss of foam.

The morphology of foams was determined using a scanning electron microscope (SEM) and a digital light microscope. For SEM analysis, the foam samples were cut, flash-frozen in liquid nitrogen, and cut with a razor blade. Cut samples were then placed on double-sided carbon conductive tape attached to a metal stub and sputter-coated with gold using an EMSCOPE SC 500 (Emzer, Barcelona, Spain) with a 3-minute coat time and 20 mA dissociation. After mounting, the gold-coated samples were analyzed on a JEOL JSM 6610LV (Akishima, Tokyo, Japan) microscope using 10 kV accelerating voltage, 13 mm working distance, 30 spot size, at 200 x magnification. Each foam's cell size (diameter, strut width, and perimeter) was measured following a modified version of ASTM D3576-15[46] using three-millimeter foam slices cut 25mm below the top of the foam.[13] At least 20 cells from each set of foams were averaged and analyzed perpendicular to foam rise using a Dino-Lite Edge digital microscope (Torrance, CA, USA).

RESULTS AND DISCUSSION

Quantitative ^{31}P NMR analysis was utilized to determine the hydroxyl content of lignin before incorporation into foam (Table 2). The industry-recommended commercial polyester polyol that was used in this study had a hydroxyl value (OHV) of ~248 mgKOH/g. In general, commercial polyols used in rigid foams typically have OHV between 200-550 mg KOH/g.[4,47] The kraft softwood lignin used in this study had an OHV of 327 mgKOH/g, which was in an acceptable range for rigid foam formulation (Table 2).

Table 2. Hydroxyl Content of Kraft Lignin

Hydroxyl content of kraft softwood lignin analyzed by ^{31} P NMR (mmol/g)					
Aliphatic	**Condensed Phenolic**	**Guaiacyl**	***P*-Hydroxyphenyl**	**Carboxylic Acid**	**Total OH***
2.10 ± 0.03	1.11 ± 0.11	1.98 ± 0.17	0.24 ± 0.04	0.40 ± 0.06	5.83 ± 0.17

*Hydroxyl value 327 mgKOH/g

The viscosity of polyol systems determines mixing efficiency along with foam uniformity and quality.[48] To achieve sufficient mixing and dispensing in polyols for rigid foams, viscosity of polyol blends is recommended to be less than 20,000 cP. (20 Pa·s), with lower viscosities being more favorable.[49] The effect of unmodified lignin addition on polyol blend viscosity from 0-100% loading is reported for the first time (Table 3). Although polyol viscosity increased with lignin addition from 0 to 100% loading, it should be noted that viscosity measurements were performed at room temperature. Li et al.[50] reported that the viscosity of lignin-based polyols significantly decreased by heating the polyol blend to 50°C, a method often used in the foaming industry,

turning a completely solid polyol into a liquid with a viscosity of 6.3 Pa·s.[50] This indicates that the viscosities of polyol blends containing 75% and 100% lignin polyol could easily meet the viscosity requirements by heating the polyol blends to a slightly higher temperature (50°C).

Table 3. Polyol Blend Viscosities

Lignin (%)	**0%**	**25%**	**50%**	**75%**	**100%**
Polyol Blend Viscosity (Pa·s)	1.24[a]	4.29[a]	6.84[a]	25.93[b]	46.12[c]

*Values with the same letter are not significantly different ($p < 0.05$)

Figure 1 shows the formulated lignin-based foams and control foam that has no lignin (made with entirely petroleum-based polyol). The foaming reactions of control and lignin-based foams represented by end of rise, tack free, string gel, top of cup, cream, and mix times are reported in Figure 2. Although the addition of lignin into foam increased reaction times, all the foams had suitable reaction times for rigid foam synthesis.[39,51] Our previous study was the only other study which incorporated unmodified lignin into low-density rigid polyurethane/polyisocyanurate (PUR/PIR) foams. We used 19 technical lignins to replace 30 wt.% of petrochemical polyol with lignin and found that foams with higher reaction times (~357 s) had significantly worse compression strengths, closed cell contents, and cell morphologies.[13] All control and lignin-based foams were well below this reaction time by 27-75%.

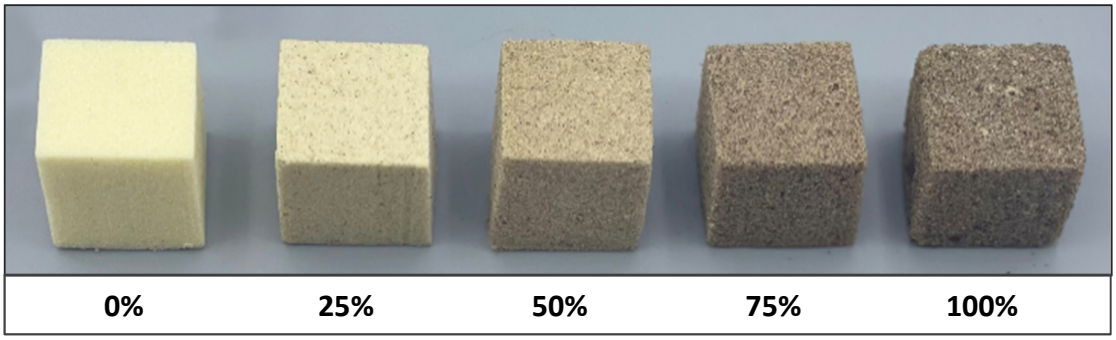


Figure 1. Image of formulated PUR/PIR foams with 0-100% lignin

The 100% lignin-based foam outperformed various lignin-based low-density rigid polyurethane (PUR) foams in reaction time. Haridevan et al.[52] dispersed up to 6% kraft lignin powder (356 hydroxyl value) in a 80/20 mixture of commercial aromatic polyester polyol/glycerol and formulated low-density rigid polyurethane foams.[52] The 6% lignin polyol dispersion based foam had a 240 s tack free time[52] while our 100% lignin-based foam was 70% lower (Figure 2). The cream and end of rise times of 100% lignin-based foam was even superior to liquefied lignin polyol by over 95% and 80% respectively.[50] Li et al.[50] fractionated miscanthus giganteus lignin using a multistep process and formulated foams with the resultant biopolyol at 50, 80, and 100% petrochemical polyol replacement.[50] Cream times for these foams ranged from 166-290 s and end of rise times ranged from 445-451 s.[50] Both of these studies incorporated less actual lignin as polyol replacement (6-40%) and used energy intensive lignin dispersion/modification methods (≥ 6 h processing times).[50,52]

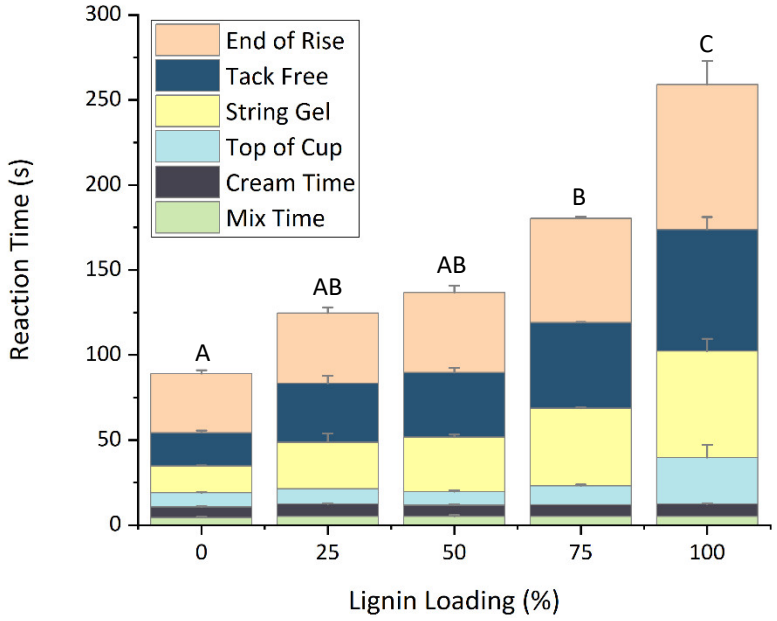


Figure 2. Foaming kinetics of control and lignin-based foams

After the foaming reaction characterization, foams were evaluated for apparent density (Table 4). The apparent density of rigid foams is known to have a logarithmic correlation affecting most other foam properties outside the 30-60 kg/m^3 low-density range.[13,51,53,54] The densities of lignin-based foams ranged from 41-54 kg/m^3 (Table 4), successfully falling within the low-density foam range, making the effect of density on foam properties insignificant. The increased density, compared to the control (35 kg/m^3), in lignin-based foams is likely caused by the use of solid lignin, which can delay foaming times (Figure 2), increase polyol blend viscosity (Table 3), and increase the degree of foam crosslinking.[8–10,19,52] Even so, all lignin-based foams had suitable apparent densities for rigid insulation and structural applications indicated by ASTM D7425 and E1730.[55,56]

The thermal conductivity of rigid PUR and PUR/PIR foams depends on various factors, including cell morphology, closed-cell content, and the type of blowing agent(s) used.[57,58] In general, smaller, more closed, and homogenous cells create foams with lower thermal

conductivities.[4] Blowing agent choice also affects thermal conductivity; for example, the thermal conductivity of air (0.0249 W/m·K) is higher than carbon dioxide (0.0153 W/m·K) and n-pentane (0.0137 W/m·K) measured at 10°C.[4] Low thermal conductivity in rigid foams ensures the foam will act as a good insulator and should be below 0.257 W/m·K.[56] All foams met minimum requirements for thermal conductivity and closed cell content (Table 4) based on ASTM E1730-15[56] and D7425[55], respectively.

Table 4. Measured Foam Properties

Lignin (%)	Apparent Density (kg/m^3)	Thermal Conductivity (W/m·K)	Closed Cell Content (%)
0%	35 ± 1^{a}	0.021 ± 0.01^{a}	98.01 ± 0.8^{a}
25%	41 ± 2^{ab}	0.022 ± 0.01^{ab}	97.92 ± 0.4^{ab}
50%	44 ± 4^{bc}	0.025 ± 0.01^{bc}	97.75 ± 0.6^{b}
75%	47 ± 2^{cd}	0.027 ± 0.01^{cd}	94.18 ± 0.7^{c}
100%	54 ± 2^{d}	0.033 ± 0.02^{d}	91.18 ± 0.4^{d}
Standard	30-60[45]	<0.257[56]	>90[59]

*Values with the same letter are not significantly different ($p < 0.05$)

Although the thermal conductivity of foams increased with lignin addition, they still fell significantly below the standard insulation requirements by a wide margin (~95% lower than required).[56] Compared to other studies, the thermal conductivities of control and lignin-based PUR/PIR foams (Table 4) were comparable to oxypropylated lignin[19] and liquefied biomass-based[60] rigid foams. The oxypropylated lignin polyols used varying amounts of lignin/propylene

oxide/catalyst (30/70/2 or 20/80/5) to replace 50% and 100% of petrochemical polyol in rigid PUR foam.[19] The resultant foams had extremely low densities (18-25 kg/m^3) and used the same blowing agent as our formulation, the oxypropylated lignin-based rigid PUR foams had slightly lower thermal conductivities (~0.029 W/m·K)[19] than unmodified lignin-based PUR/PIR foams (~0.033 W/m·K, Table 4). Researchers[60] also used liquefied marine biomass at 20 and 30% petrochemical polyol replacements for use in low-density rigid PUR/PIR foam;. However, the densities of those foams were higher (~50 kg/m^3), and foam thermal conductivities (~0.03 W/m·K)[60] were similar to the oxypropylated lignin-based PUR foams.[19] The thermal conductivity properties of the unmodified lignin-based PUR/PIR foams in this study compared to the previous studies[19,60] are likely due to increased closed cell content, but neither study measured nor reported those values. A reported knowledge gap for lignin-based rigid foams is the lack of foam testing based on industrial requirements.[12,61] Researchers should incorporate a more comprehensive array of tests to ensure that formulated foams will be suitable for industrial applications.

The closed-cell content of the foam is crucial in maintaining low thermal conductivity.[4,51] Additionally, closed and more homogenous cells create foams with better mechanical strength and thermal conductivity properties.[51,62,63] The industry-accepted method to measure foam closed cell content uses a gas pycnometer.[64] For lignin-based rigid PUR foams, most researchers have utilized a combination of digital, light, or scanning electron microscopy to estimate closed cell content.[8,65] To have more accurate results, we used a gas pycnometer for closed-cell content analysis (Table 4). All control and lignin-based foams met the minimum 90% closed cell content requirement for thermal insulation,[59] with foams up to 50% lignin loading meeting stricter 95% closed cell content requirements.[56] Even with the decrease in closed cell content with lignin addition, the 100% lignin-

based foam met ASTM requirements and outperformed various biobased polyols reported in the literature.[66–68]

Tu et al.[66] used epoxidized soybean oil to replace 40% of petrochemical polyol in low-density rigid PUR foam but did not meet 90% closed cell content requirements[59] (~87% closed cells). Although lower 10, 20, and 30% soy oil replacements met minimum requirements (~95% closed cells),[66] were all lower than control and lignin-based foams up to 50% lignin loading (Table 4). Unmodified wheat straw lignin and oxypropylated wheat straw lignin polyol were used as 15% filler and 15% polyol replacement, respectively, in rigid PUR foam.[67] Both lignin-based foams had lower closed cell contents (92 ± 3%)[67] than our PUR/PIR control and lignin-based foams (Table 4). Additionally, all foams in this study outperformed oxypropylated tannin as a 75% polyol replacement in rigid PUR/PIR foam (92 ± 2).[68] Though these other studies used either liquefied lignin/biomass[66–68] or lignins with higher hydroxyl contents (8.4[67] compared to 5.8 mmol/g in Table 2), the lower closed cell contents compared to our control and unmodified lignin-based foams (Figure 2) is a combination of high string gel times (>200 s)[67] and end of rise times (100-180 s).[68]

Compression strength has also been reported as a limiting factor for lignin incorporation, along with decreased foam reactivity in lignin-based foams.[12,13] Due to foam anisotropy, the compression strength of foams almost doubles based on testing perpendicular to foam rise compared to parallel.[4,69] Here (Figure 3), we evaluate compression strength perpendicular to foam rise to ensure we meet minimum requirements on the weakest side of the foam. The highest compression strength of control and lignin-based foams was obtained at 50% lignin loading (Figure 3). Although compression strength negatively correlated with lignin loading percentage ($r = -0.6$) as expected due to the use of solid unmodified lignin, all control and lignin-based foams met the minimum

compression strength requirement (>104 kPa) for type 1 rigid foams.[59] Lignin-based foams even outperformed oxypropylated lignin as 100% polyol replacement in low-density rigid PUR foam (90 kPa).[34] A similar result was found with the compression strength of hydroxymethylated lignin used as 2-30% polyol replacement in low-density rigid PUR foam (~40 kPa).[70]

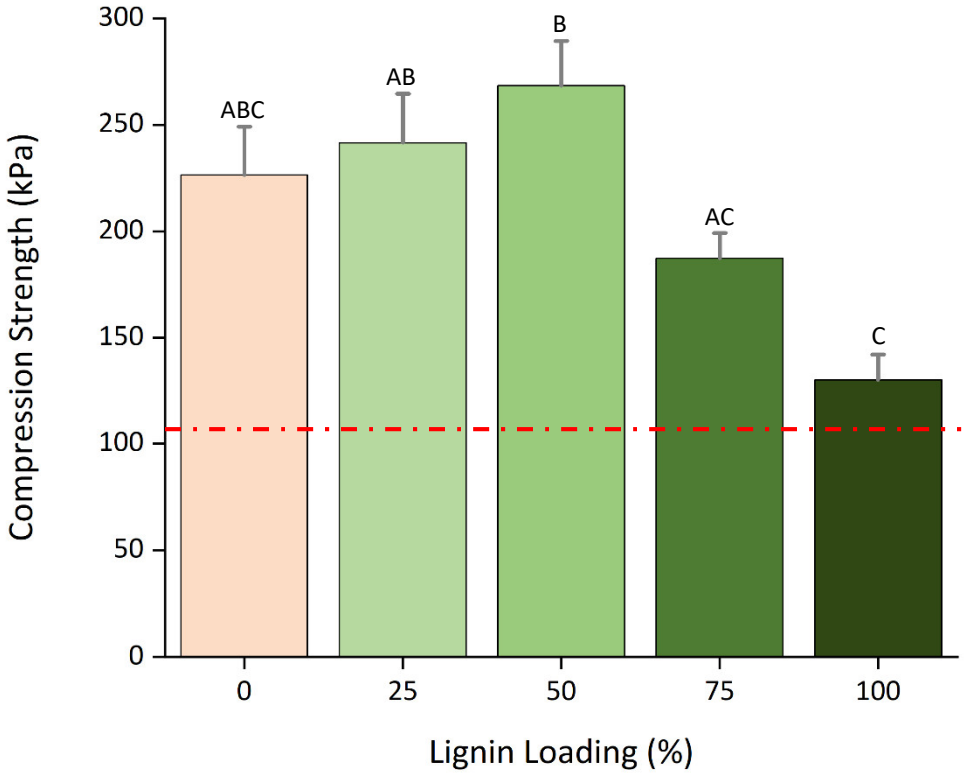


Figure 3. Compression strength of formulated foams. The dashed red line denotes ASTM minimum requirement. Values with the same letter are not significantly different ($p < 0.05$).

The horizontal burn flammability test was used to determine the foams' flammability rating (HF1 and HF2).[45] This test can ensure the safety of products by elucidating the relative burn rate, time, and extent of the burn.[45,71] Longer flame times to the 25 mm mark and lower values for burn time, percent loss, and burn length indicate better fire behavior.[45] On average, the flame did not reach

the 25 mm burn mark for lignin-based foams and had significantly shorter burn times than the control (Table 5). The flame time to the 25 mm mark had a positive correlation (r = 0.7) with the percentage of lignin loading and significantly increased compared to the control (Figure 4). Burn time after flame removal decreased by over 72% in 100% lignin-based foams compared to the control. All burn time values for control and lignin-based foams were below 30 s, meeting the HF1 fire characterization.[45] The weight change and burn length of lignin-based foams, compared to the control, decreased by over 24% and 55%, respectively. All specimens had less than 60 mm burn length and did not ignite the cotton indicator, meeting the HF1 material classification.[45] In general, lignin has been reported to increase the char yield of rigid PUR foams (analyzed via thermal gravimetric analysis at 10°C/min) due to its aromatic structure and creating an insulation layer to further prevent the spread of flame.[8]

Table 5. Fire Behavior of Foam

Lignin (%)	Flame time to 25 mm mark (s)	Burn Time After Flame Removal (s)	Percent Weight Loss (%)	Burn Length (mm)
0%	5 ± 1^{a}	4.6 ± 0.5^{a}	-5.6 ± 0.6^{a}	35 ± 14^{a}
25%	18 ± 9^{a}	2.2 ± 0.3^{b}	-4.5 ± 0.7^{ab}	22 ± 8^{a}
50%	19 ± 10^{a}	1.6 ± 0.8^{b}	-4.3 ± 0.6^{ab}	20 ± 9^{a}
75%	b**	1.3 ± 0.6^{b}	-4.1 ± 0.5^{ab}	17 ± 5^{a}
100%	b**	1.3 ± 0.3^{b}	-3.7 ± 0.6^{b}	15 ± 4^{a}

*Values with the same letter are not significantly different ($p < 0.05$)

**Flame removed after 30 seconds because flame did not reach 25 mm mark

Though fire properties in rigid foam are generally enhanced via the use of reactive flame retardants, active flame retardants, or flame-retardant coatings, [72] higher density foams and the use of PUR/PIR over PUR formulations will increase fire retardant behavior due to a more compact burn layer[73] and the presence of more thermally stable polyisocyanurate bonds,[4] respectively. Since all of our foams were within the low-density range for rigid polyurethane foams (30-60 kg/m^3), the effects of density should not be significant.[13,51] This is confirmed by the low correlations between apparent density and fire properties: burn time after flame removal ($r = -0.3$), percent weight loss ($r = 0.5$), and burn length ($r = -0.5$). The addition of unmodified kraft lignin as a polyol replacement and its ability to function as a flame retardant further increases the value proposition of lignin for use in rigid PUR and PUR/PIR foams.

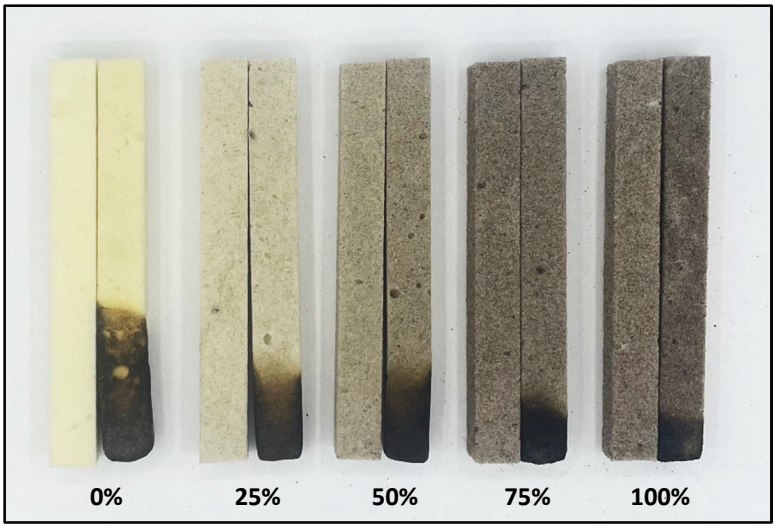
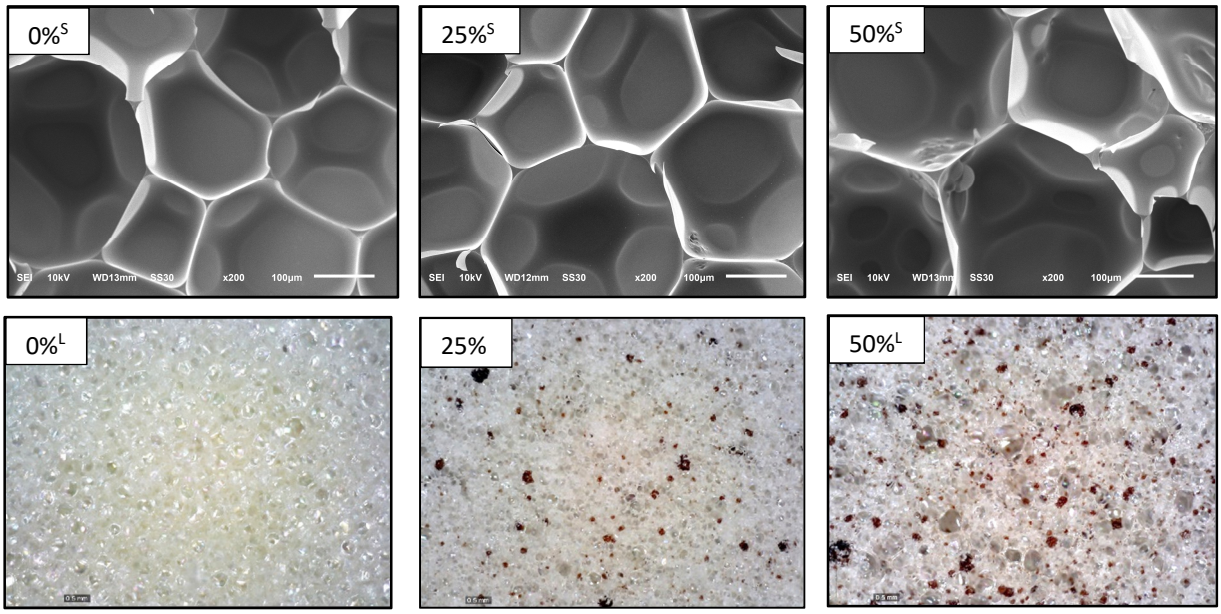


Figure 4. Charring of control and lignin-based foams. Uncharred samples are on the left, and charred samples are on the right.

Scanning electron and digital light microscope images (Figure 5) showed an increase in cell diameter and perimeter (Figure 6) with lignin addition ($r = 1$). Up to 50% loading, no significant

difference was found for lignin-based foams compared to the control for cell perimeter and diameter, while the cell strut width showed no significant difference from the control at any lignin loading percentage. Overall, the cell diameter of our control and lignin-based foams (~0.2 mm) were smaller than previous studies using 0-6% lignin loading in low-density rigid PUR foam (~0.5 mm).[52] All cell size results were comparable to other biobased polyols used in low-density rigid PUR/PIR foam formulations,[60] our previous research,[13] and ASTM specifications.[74]



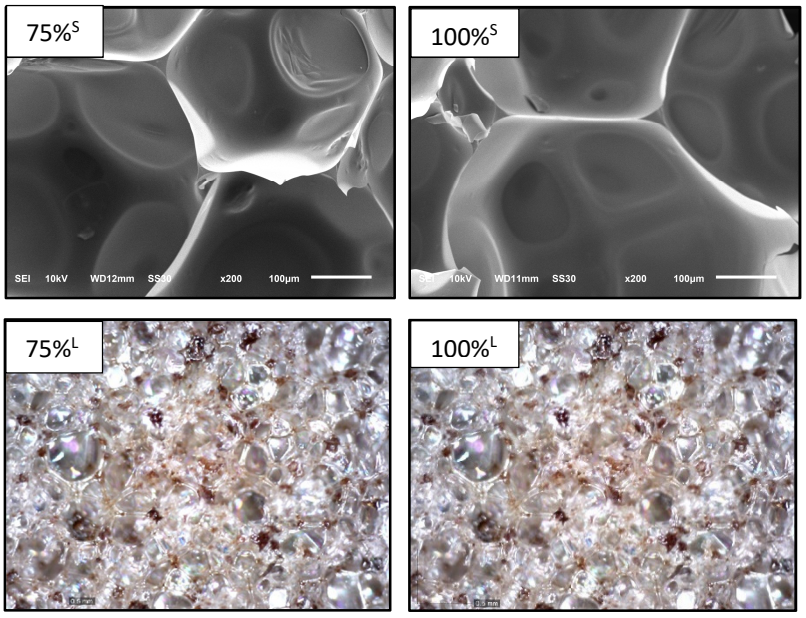


Figure 5. Scanning electron microscope[S] and digital light microscope[L] images of formulated foams.

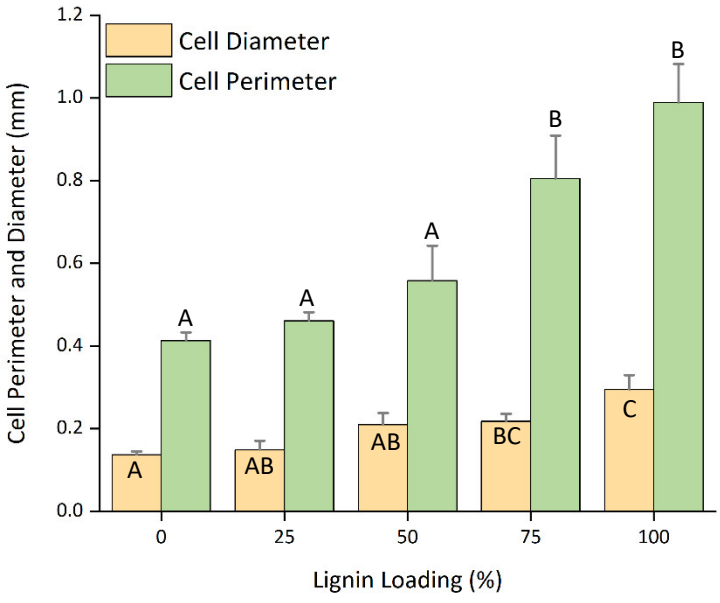


Figure 6. Cell Sizes of Formulated Foams. Values with the same letter are not significantly different ($p < 0.05$). All cell strut widths were within 0.05 ± 0.01 mm.

CONCLUSIONS

This study is the first to demonstrate the complete substitution of petrochemical polyols with unmodified commercially available solid lignin in low-density rigid polyurethane /polyisocyanurate foams. Kraft softwood lignin was incorporated into the foam by gradually replacing 0-100% of petroleum-based polyol in 25% increments. All lignin-based foams outperformed the control in burn time by over 56% while still meeting the minimum ASTM-required closed-cell content, compression strength, and thermal conductivity for rigid foam applications. This work shows the feasibility of using unmodified commercial lignin to fully replace fossil fuel-based polyols when formulating low-density rigid polyurethane/ polyisocyanurate foams that meet the standard requirements for type 1 insulation applications. This represents a significant step towards using more sustainable foams with superior fire performance for building construction applications. In addition, this creates a value-added opportunity for lignin as an underutilized portion of the biomass. Future research should focus on optimizing lignin-based foams for industrial scale-up and tuning lignin properties such as hydroxyl content and molecular weight to further enhance and evaluate their effects on foam properties.

AUTHOR INFORMATION

Corresponding Author

*Mojgan Nejad

nejad@msu.edu

AUTHOR CONTRIBUTIONS

C.H.: Data curation, formal analysis, investigation, methodology, validation, visualization, and writing original draft; M.N.: Conceptualization, funding acquisition, methodology, project administration, resources, supervision, validation, visualization, and writing and editing. All authors have read and agreed to the published version of the manuscript.

FUNDING SOURCES

This material is based upon work supported by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) under the Bioenergy Technology Office, Award Number DE-EE0008502; Grant Case 48166 of the 21st Century Jobs Trust Fund received through the MSF from the State of Michigan (MTRAC); and the USDA National Institute of Food and Agriculture, McIntire Stennis, 1021850.

ACKNOWLEDGMENT

Special thanks to Huntsman; Dr. Sachi Singh for his invaluable technical advice and thermal conductivity analysis; Saeid Nikafshar for his support in lignin characterization; Alex Bakke, and Laura Mihlbachler for assisting with foam characterization**.**

ABBREVIATIONS

PUR, polyurethane; PIR, polyisocyanurate; PUR/PIR, polyurethane/polyisocyanurate; PMDI, polymeric methylene diphenyl diisocyanate.

REFERENCES

(1) Cao, H.; Liu, R.; Li, B.; Wu, Y.; Wang, K.; Yang, Y.; Li, A.; Zhuang, Y.; Cai, D.; Qin, P. Biobased Rigid Polyurethane Foam Using Gradient Acid Precipitated Lignin from the Black Liquor: Revealing the Relationship between Lignin Structural Features and Polyurethane Performances. *Ind. Crops Prod.* **2022**, *177* (August 2021), 114480. https://doi.org/10.1016/j.indcrop.2021.114480.

(2) Mahmood, N.; Yuan, Z.; Schmidt, J.; Xu, C. (Charles). Preparation of Bio-Based Rigid Polyurethane Foam Using Hydrolytically Depolymerized Kraft Lignin via Direct Replacement or Oxypropylation. *Eur. Polym. J.* **2015**, *68*, 1–9. https://doi.org/10.1016/j.eurpolymj.2015.04.030.

(3) Rahman, M. M.; Rabbani, M. M.; Saha, J. K. Polyurethane and Its Derivatives. In *Functional Polymers, Polymers and Polymeric Composites: A Reference Series*; 2019; pp 225–240. https://doi.org/10.1007/978-3-319-95987-0_7.

(4) Randall, D.; Lee, S. *The Polyurethanes Book*; Huntsman Polyurethanes Distributed by John Wiley & Sons: Everberg, Belgium, 2002.

(5) Freedonia Focus Reports. *Polyurethane : United States*; 2016.

(6) Zhao, J. R.; Zheng, R.; Tang, J.; Sun, H. J.; Wang, J. A Mini-Review on Building Insulation Materials from Perspective of Plastic Pollution: Current Issues and Natural Fibres as a Possible Solution. *J. Hazard. Mater.* **2022**, 129449. https://doi.org/10.1016/J.JHAZMAT.2022.129449.

(7) Dessbesell, L.; Yuan, Z.; Hamilton, S.; Leitch, M.; Pulkki, R.; Xu, C. C. Bio-Based

Polymers Production in a Kraft Lignin Biorefinery: Techno-Economic Assessment. *Biofuels, Bioprod. Biorefining* **2018**, *12* (2), 239–250. https://doi.org/10.1002/BBB.1834.

(8) Luo, S.; Gao, L.; Guo, W. Effect of Incorporation of Lignin as Bio-Polyol on the Performance of Rigid Lightweight Wood–Polyurethane Composite Foams. *J. Wood Sci.* **2020**, *66* (1), 1–10. https://doi.org/10.1186/s10086-020-01872-5.

(9) Mahmood, N.; Yuan, Z.; Schmidt, J.; Tymchyshyn, M.; Xu, C. (Charles). Hydrolytic Liquefaction of Hydrolysis Lignin for the Preparation of Bio-Based Rigid Polyurethane Foam. *Green Chem.* **2016**, *18* (8), 2385–2398. https://doi.org/10.1039/C5GC02876K.

(10) Han, Y. M.; Qin, T. F.; Chu, F. X. Preparation and Properties of Polyurethane Heat Insulating Building Materials Based on Lignin. *Appl. Mech. Mater.* **2012**, *193–194*, 505–508. https://doi.org/10.4028/www.scientific.net/AMM.193-194.505.

(11) Luo, X.; Xiao, Y.; Wu, Q.; Zeng, J. Development of High-Performance Biodegradable Rigid Polyurethane Foams Using All Bioresource-Based Polyols: Lignin and Soy Oil-Derived Polyols. *Int. J. Biol. Macromol.* **2018**, *115*, 786–791. https://doi.org/10.1016/j.ijbiomac.2018.04.126.

(12) Alinejad, M.; Henry, C.; Nikafshar, S.; Gondaliya, A.; Bagheri, S.; Chen, N.; Singh, S. K.; Hodge, D. B.; Nejad, M. Lignin-Based Polyurethanes: Opportunities for Bio-Based Foams, Elastomers, Coatings and Adhesives. *Polymers*. Multidisciplinary Digital Publishing Institute July 18, 2019, pp 1–21. https://doi.org/10.3390/polym11071202.

(13) Henry, C.; Gondaliya, A.; Thies, M.; Nejad, M. Studying the Suitability of Nineteen Lignins as Partial Polyol Replacement in Rigid Polyurethane / Polyisocyanurate Foam. *Mol. 2022,*

Vol. 27, Page 2535 **2022**, *27* (8), 2535. https://doi.org/10.3390/molecules27082535.

(14) Liu, Z.-M. M.; Fei, Y. U.; Fang, G.-Z. Z.; Yang, H.-J. J.; Yu, F.; Fang, G.-Z. Z.; Yang, H.-J. J.; Fei, Y. U.; Fang, G.-Z. Z.; Yang, H.-J. J.; Yu, F.; Fang, G.-Z. Z.; Yang, H.-J. J. Performance Characterization of Rigid Polyurethane Foam with Refined Alkali Lignin and Modified Alkali Lignin. *J. For. Res.* **2009**, *20* (2), 161–164. https://doi.org/10.1007/s11676-009-0028-9.

(15) Pan, X.; Saddler, J. N. Effect of Replacing Polyol by Organosolv and Kraft Lignin on the Property and Structure of Rigid Polyurethane Foam. *Biotechnol. Biofuels* **2013**, *6* (1), 12. https://doi.org/10.1186/1754-6834-6-12.

(16) Xue, B.-L.; Wen, J.-L.; Sun, R.-C. Lignin-Based Rigid Polyurethane Foam Reinforced with Pulp Fiber: Synthesis and Characterization. *ACS Sustain. Chem. Eng.* **2014**, *2* (6), 1474–1480. https://doi.org/10.1021/sc5001226.

(17) Nadji, H.; Bruzzèse, C.; Belgacem, M. N.; Benaboura, A.; Gandini, A. Oxypropylation of Lignins and Preparation of Rigid Polyurethane Foams from the Ensuing Polyols. *Macromol. Mater. Eng.* **2005**, *290* (10), 1009–1016. https://doi.org/10.1002/mame.200500200.

(18) Cateto, C. A.; Barreiro, M. F.; Ottati, C.; Lopretti, M.; Rodrigues, A. E.; Belgacem, M. N. Lignin-Based Rigid Polyurethane Foams with Improved Biodegradation. *J. Cell. Plast.* **2014**, *50* (1), 81–95. https://doi.org/10.1177/0021955X13504774.

(19) Cateto, C.; Barreiro, F.; Rodrigues, A.; Belgacem, N.; D'Amore, A.; Acierno, D.; Grassia, L. Rigid Polyurethane Foams From Lignin Based-Polyols. In *AIP Conference Proceedings*; AIP, 2008; Vol. 1042, pp 243–245. https://doi.org/10.1063/1.2989020.

(20) Li, Y.; Ragauskas, A. J. Ethanol Organosolv Lignin-Based Rigid Polyurethane Foam Reinforced with Cellulose Nanowhiskers. *RSC Adv.* **2012**, *2* (8), 3347–3351. https://doi.org/10.1039/c2ra00646d.

(21) Berrima, B.; Mortha, G.; Boufi, S.; Aloui, E. El; Belgacem, M. N. Oxypropylation of Soda Lignin: Characterization and Application in Polyurethane Foams Production. *Cellul. Chem. Technol.* **2016**, *50* (9), 941–950.

(22) Li, H.; (Charles) Xu, C.; Yuan, Z.; Wei, Q. Synthesis of Bio-Based Polyurethane Foams with Liquefied Wheat Straw: Process Optimization. *Biomass and Bioenergy* **2018**, *111* (February), 134–140. https://doi.org/10.1016/j.biombioe.2018.02.011.

(23) Muller, L. C.; Marx, S.; Vosloo, H. C.; Fosso-Kankeu, E.; Chiyanzu, I.; Cm Vosloo, H.; Fosso-Kankeu, E.; Chiyanzu, I.; Vosloo, H. C.; Fosso-Kankeu, E.; Chiyanzu, I. Rigid Polyurethane Foams from Unrefined Crude Glycerol and Technical Lignins. *Polym. from Renew. Resour.* **2018**, *9* (3–4), 111–132. https://doi.org/10.1177/2041247918803187.

(24) Vale, M.; Mateus, M. M.; Galhano dos Santos, R.; Nieto de Castro, C.; de Schrijver, A.; Bordado, J. C.; Marques, A. C. Replacement of Petroleum-Derived Diols by Sustainable Biopolyols in One Component Polyurethane Foams. *J. Clean. Prod.* **2019**, *212*, 1036–1043. https://doi.org/10.1016/j.jclepro.2018.12.088.

(25) Zhang, J.; Hori, N.; Takemura, A. Influence of NCO/OH Ratio on Preparation of Four Agricultural Wastes Liquefied Polyols Based Polyurethane Foams. *Polym. Degrad. Stab.* **2020**, *179*, 109256. https://doi.org/10.1016/j.polymdegradstab.2020.109256.

(26) Hatakeyama, H.; Kosugi, R.; Hatakeyama, T. Thermal Properties of Lignin-and Molasses-

Based Polyurethane Foams. *J. Therm. Anal. Calorim.* **2008**, *92* (2), 419–424. https://doi.org/10.1007/s10973-007-8963-1.

(27) Seto, C.; Chang, B. P.; Tzoganakis, C.; Mekonnen, T. H. Lignin Derived Nano-Biocarbon and Its Deposition on Polyurethane Foam for Wastewater Dye Adsorption. *Int. J. Biol. Macromol.* **2021**, *185* (July), 629–643. https://doi.org/10.1016/j.ijbiomac.2021.06.185.

(28) Huo, S.-P.; Nie, M.-C.; Kong, Z.-W.; Wu, G.-M.; Chen, J. Crosslinking Kinetics of the Formation of Lignin-Aminated Polyol-Based Polyurethane Foam. *J. Appl. Polym. Sci.* **2012**, *125* (1), 152–157. https://doi.org/10.1002/app.35401.

(29) Wang, R.; Zhou, B.; Zhu, Y.; Wang, Z. Preparation and Characterization of Rigid Polyurethane Foams with Different Loadings of Lignin-Derived Polycarboxylic Acids. *Int. J. Polym. Sci.* **2019**, *2019*, 1–6. https://doi.org/10.1155/2019/3710545.

(30) Xue, B.-L.; Huang, P.-L.; Sun, Y.-C.; Li, X.-P.; Sun, R.-C. Hydrolytic Depolymerization of Corncob Lignin in the View of a Bio-Based Rigid Polyurethane Foam Synthesis. *RSC Adv.* **2017**, *7* (10), 6123–6130. https://doi.org/10.1039/C6RA26318F.

(31) Liu, Z. M.; Yu, F.; Fang, G. Z.; Yang, H. J. Performance Characterization of Rigid Polyurethane Foam with Refined Alkali Lignin and Modified Alkali Lignin. *J. For. Res.* **2009**, *20* (2), 161–164. https://doi.org/10.1007/s11676-009-0028-9.

(32) Yang, L.; Wang, X.; Cui, Y.; Tian, Y.; Chen, H.; Wang, Z. Modification of Renewable Resources-Lignin-by Three Chemical Methods and Its Applications to Polyurethane Foams. *Polym. Adv. Technol.* **2014**, *25* (10), 1089–1098. https://doi.org/10.1002/pat.3356.

(33) Xing, W.; Yuan, H.; Zhang, P.; Yang, H.; Song, L.; Hu, Y. Functionalized Lignin for Halogen-Free Flame Retardant Rigid Polyurethane Foam: Preparation, Thermal Stability, Fire Performance and Mechanical Properties. *J. Polym. Res.* **2013**, *20* (9), 1–12. https://doi.org/10.1007/s10965-013-0234-1.

(34) Li, Y.; Ragauskas, A. J. Kraft Lignin-Based Rigid Polyurethane Foam. *J. Wood Chem. Technol.* **2012**, *32* (3), 210–224. https://doi.org/10.1080/02773813.2011.652795.

(35) Saffar, T.; Bouafif, H.; Braghiroli, F. L.; Magdouli, S.; Langlois, A.; Koubaa, A. Production of Bio-Based Polyol from Oxypropylated Pyrolytic Lignin for Rigid Polyurethane Foam Application. *Waste and Biomass Valorization* **2020**, *11* (11), 6411–6427. https://doi.org/10.1007/s12649-019-00876-7.

(36) Miao Wu; Jian-Jun Peng; You-Ming Dong; Jin-Hui Pang; Xue-Ming Zhang. Preparation of Rigid Polyurethane Foam from Lignopolyol Obtained through Mild Oxypropylation. *RSC Adv.* **2022**, *12* (34), 21736–21741. https://doi.org/10.1039/D2RA02895F.

(37) Kalami, S. Development of Biobased Phenolic Adhesives for Engineered Wood Products, Doctor of Philosophy, Mississippi State University, Starkville, MS, USA, 2018. https://doi.org/https://scholarsjunction.msstate.edu/td/1449/.

(38) Argyropoulos, D. S. Quantitative Phosphorus-31 Nmr Analysis of Lignins, a New Tool for the Lignin Chemist. *J. Wood Chem. Technol.* **1994**, *14* (1), 45–63. https://doi.org/10.1080/02773819408003085.

(39) ASTM International. Standard Practice for Polyurethane Raw Materials : Polyurethane Foam Cup Test 1. *ASTM D7487* **2013**, 1–5. https://doi.org/10.1520/D7487-08.

(40) ASTM International. Standard Test Method for Apparent Density of Rigid Cellular Plastics. *ASTM D1622* **2014**, 3–6. https://doi.org/10.1520/D1622-14.2.

(41) ASTM Int. C518-15: Standard Test Method for Steady-State Thermal Transmission Properties by Means of the Heat Flow Meter Apparatus. *ASTM Int.* **2015**, 1–15. https://doi.org/10.1520/C0518-17.2.

(42) ASTM-2856. Standard Test Method for Open-Cell Content of Rigid Cellular Plastics by the Air Pycnometer. *ASTM D6226 − 15* **1998**, *i*, 6. https://doi.org/https://doi.org/10.1520/D6226-15.2.

(43) Micromeritics. Gas Displacement Pycnometer Series. *Accu Pyc ® II Ser.* **2016**, 1–17. https://doi.org/https://www.micromeritics.com/Repository/Files/Calculations_-_AccuPyc_II_Series.pdf.

(44) ASTM International. Standard Test Method for Compressive Properties Of Rigid Cellular Plastics. *ASTM D1621* **2016**, 1–8. https://doi.org/10.1520/D1621-10.2.

(45) ASTM International. Standard Test Method for Horizontal Burning Characteristics of Cellular Polymeric Materials 1. *ASTM D4986* **2018**. https://doi.org/10.1520/D4986-18.

(46) ASTM International. Standard Test Method for Cell Size of Rigid Cellular Plastics 1. *ASTM D3576* **2015**, 1–5. https://doi.org/10.1520/D3576-04R10.2.

(47) Oertel, G.; Abele, L. *Polyurethane Handbook: Chemistry-Raw Materials-Processing-Application-Properties*; Hanser Publishers: Munich Vienna, New York, USA, 1985.

(48) Paberza, A.; Cabulis, U.; Arshanitsa, A. Wheat Straw Lignin as Filler for Rigid

Polyurethane Foams on the Basis of Tall Oil Amide. *Polimery* **2014**, *59* (06), 477–481. https://doi.org/10.14314/polimery.2014.477.

(49) Rogers, K. A.; Cupp, J. N.; Tabor, R. L. Flame Retardant Characteristics of Recycled- and Lignin-Based PET Polyols for Rigid Foam Applications. *Resinate Mater. Group, Inc.* **2017**, 1–15. https://doi.org/https://www.scribd.com/document/371432107/Flame-Retardant-Characteristics-of-Recycled-and-Lignin-Based-PET-Polyols-for-Rigid-Foam-Applications.

(50) Li, H.; Wang, B.; Shui, H.; Wei, Q.; Xu, C. C. Preparation of Bio-Based Polyurethane Hydroponic Foams Using 100% Bio-Polyol Derived from Miscanthus through Organosolv Fractionation. *Ind. Crops Prod.* **2022**, *181*, 114774. https://doi.org/10.1016/j.indcrop.2022.114774.

(51) Woods, G. *The ICI Polyurethanes Book*, 2nd ed.; Published jointly by ICI Polyurethanes and Wiley: Chichester, New York, USA, 1990.

(52) Haridevan, H.; McLaggan, M. S.; Evans, D. A. C.; Martin, D. J.; Seaby, T.; Zhang, Z.; Annamalai, P. K. Dispersion Methodology for Technical Lignin into Polyester Polyol for High-Performance Polyurethane Insulation Foam. *ACS Appl. Polym. Mater.* **2021**, *3* (7), 3528–3537. https://doi.org/10.1021/acsapm.1c00430.

(53) Ashida, K. *Polyurethane and Related Foams: Chemistry and Technology*; Boca raton, FL, USA, 2006.

(54) Szycher, M. *Szycher's Handbook of Polyurethanes*; CRC press, 2013. https://doi.org/10.5860/CHOICE.37-1570.

(55) ASTM International. Standard Specification for Spray Polyurethane Foam Used for Roofing Applications 1. *ASTM D7425/D7425M* **2013**, 7–9. https://doi.org/DOI: 10.1520/D7425_D7425M-13.

(56) ASTM International. Standard Specification for Rigid Foam for Use in Structural Sandwich Panel Cores 1. *ASTM E1730* **1998**, *04*, 4–7. https://doi.org/DOI: 10.1520/E1730-15. 2.

(57) Thirumal, M.; Khastgir, D.; Singha, N. K.; Manjunath, B. S.; Naik, Y. P. Mechanical, Morphological and Thermal Properties of Rigid Polyurethane Foam: Effect of Chain Extender, Polyol and Blowing Agent. *Cell. Polym.* **2009**, *28* (2), 145–158. https://doi.org/10.1177/026248930902800202.

(58) Gao, L.; Zheng, G.; Zhou, Y.; Hu, L.; Feng, G. Improved Mechanical Property, Thermal Performance, Flame Retardancy and Fire Behavior of Lignin-Based Rigid Polyurethane Foam Nanocomposite. *J. Therm. Anal. Calorim.* **2015**, *120* (2), 1311–1325. https://doi.org/10.1007/s10973-015-4434-2.

(59) ASTM International. Standard Specification for Spray-Applied Rigid Cellular Polyurethane Thermal Insulation. *ASTM C1029* **2015**, 1–6. https://doi.org/DOI: 10.1520/C1029-15.

(60) Kosmela, P.; Hejna, A.; Suchorzewski, J.; Piszczyk, Ł.; Haponiuk, J. T. Study on the Structure-Property Dependences of Rigid PUR-PIR Foams Obtained from Marine Biomass-Based Biopolyol. *Materials (Basel).* **2020**, *13* (5), 1257. https://doi.org/10.3390/ma13051257.

(61) Sardon, H.; Mecerreyes, D.; Basterretxea, A.; Avérous, L.; Jehanno, C. From Lab to Market: Current Strategies for the Production of Biobased Polyols. *ACS Sustain. Chem. Eng.* **2021**,

9 (32), 10664–10677. https://doi.org/10.1021/acssuschemeng.1c02361.

(62) Berardi, U. The Impact of Aging and Environmental Conditions on the Effective Thermal Conductivity of Several Foam Materials. *Energy* **2019**, *182*, 777–794. https://doi.org/10.1016/j.energy.2019.06.022.

(63) Biedermann, A.; Kudoke, C.; Merten, A.; Minogue, E.; Rotermund, U.; Seifert, H.; Ebert, H.-P.; Heinemann, U.; Fricke, J. Heat-Transfer Mechanisms in Polyurethane Rigid Foam. *High Temp. Press.* **2001**, *33* (6), 699–706. https://doi.org/10.1068/htwu71.

(64) ASTM International. Standard Test Method for Open Cell Content of Rigid Cellular Plastics 1. *ASTM D6226 − 15* **2015**, 1–7. https://doi.org/10.1520/D6226-15.2.

(65) Flôres, C. C.; Nahra, L. R.; Rodrigues, I. Z. Viscoelastic Polyurethane Foams from Unmodified Kraft Lignin Dispersed into Methoxy Polyethylene Glycol and Palm Kernel Oil as Partial Substitutes of Petroleum-Based Polyols. **2022**, 1–23. https://doi.org/10.21203/rs.3.rs-1171841/v1.

(66) Tu, Y.-C.; Suppes, G. J.; Hsieh, F.-H. Water-Blown Rigid and Flexible Polyurethane Foams Containing Epoxidized Soybean Oil Triglycerides. *J. Appl. Polym. Sci.* **2008**, *109* (1), 537–544. https://doi.org/10.1002/app.28153.

(67) Arshanitsa, A.; Paberza, A.; Vevere, L.; Cabulis, U.; Telysheva, G. Two Approaches for Introduction of Wheat Straw Lignin into Rigid Polyurethane Foams. In *AIP Conference Proceedings*; 2014; Vol. 1593, pp 388–391. https://doi.org/10.1063/1.4873806.

(68) Arbenz, A.; Frache, A.; Cuttica, F.; Avérous, L. Advanced Biobased and Rigid Foams,

Based on Urethane-Modified Isocyanurate from Oxypropylated Gambier Tannin Polyol. *Polym. Degrad. Stab.* **2016**, *132*, 62–68. https://doi.org/10.1016/j.polymdegradstab.2016.03.035.

(69) Andersons, J.; Kirpluks, M.; Stiebra, L.; Cabulis, U. Anisotropy of the Stiffness and Strength of Rigid Low-Density Closed-Cell Polyisocyanurate Foams. *Mater. Des.* **2016**, *92*, 836–845. https://doi.org/10.1016/j.matdes.2015.12.122.

(70) Lee, Y.; Tran, M. H.; Lee, E. Y. Hydroxymethylation of Technical Lignins Obtained from Different Pretreatments for Preparation of High-Performance Rigid Polyurethane Foam. *Eur. J. Wood Wood Prod.* **2022**, No. 0123456789. https://doi.org/10.1007/s00107-022-01845-z.

(71) Ngo, T. Development of Sustainable Flame-Retardant Materials. *Green Mater.* **2019**, *8* (3), 101–122. https://doi.org/10.1680/jgrma.19.00060.

(72) Zhu, M.; Ma, Z.; Liu, L.; Zhang, J.; Huo, S.; Song, P. Recent Advances in Fire-Retardant Rigid Polyurethane Foam. *J. Mater. Sci. Technol.* **2022**, *112*, 315–328. https://doi.org/10.1016/j.jmst.2021.09.062.

(73) Pham, C. T.; Nguyen, B. T. T.; Nguyen, H. T. T.; Kang, S.-J.; Kim, J.; Lee, P.-C.; Hoang, D. Comprehensive Investigation of the Behavior of Polyurethane Foams Based on Conventional Polyol and Oligo-Ester-Ether-Diol from Waste Poly(Ethylene Terephthalate): Fireproof Performances, Thermal Stabilities, and Physicomechanical Properties. *ACS Omega* **2020**, *5* (51), 33053–33063. https://doi.org/10.1021/acsomega.0c04555.

(74) Standard Test Method for Cell Size of Rigid Cellular Plastics 1 This International Standard

Was Developed in Accordance with Internationally Recognized Principles on Standardization Established in the Decision on Principles for the Development of Internat. https://doi.org/10.1520/D6226-15.

"For Table of Contents Only"

Lignin-Based Polyurethane/ Polyisocyanurate Rigid Foam.