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Development of Rigid Polyurethane Foams Based on Kraft Lignin Polyol Obtained by Oxyalkylation Using Propylene Carbonate

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Abstract: This study aimed to develop new rigid polyurethane foams (RPUFs) for thermal insulation based on kraft lignin, the main by-product of the pulp and paper industry. Crude lignin-based polyol (LBP) was obtained via the oxyalkylation of kraft lignin using propylene carbonate (PC). A design of experiments (DoE) was used to evaluate the effect of the isocyanate (NCO)-to-hydroxyl (OH)-group's ratio, the content of crude LBP, the blowing agent (BA), and catalyst on the thermal conductivity and density of RPUFs. Statistical analysis revealed that the increase in crude LBP and BA content in the formulation decreases the thermal conductivity and density of the foams. In addition, the fact that LBP is a viscous polyol containing PC-oligomers appears to affect the cellular structure of RPUFs, and consequently reduces their mechanical and thermal properties. The main novelty of this study consisted in the careful optimization of the formulation, namely, with regard to the type of blowing agent and with the high content of crude LBP obtained from the oxyalkylation of LignoBoost kraft lignin without purification to obtain good quality RPUF that meets market requirements for insulation materials.

Keywords: lignin-based polyol; polyether polyol; oxyalkylation; polyurethane foam; insulation material; design of experiments

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1. Introduction

Rigid polyurethane foams (RPUFs) are one of the most efficient high-performance insulation materials used in the construction industry and refrigerators [1,2]. Compared with other thermal insulation materials such as expanded polystyrene, mineral wool, cork, softwood, fireboard, and concrete blocks, RPUFs have outstanding properties including low thermal conductivity, lightweight, high mechanical resistance, and low moisture permeability, allowing effective energy savings with minimal wall thickness [3]. For these reasons, the foam market has grown over the years [4]. RPUFs are cellular thermoset plastics obtained by the expansion of a blowing agent (BA) concomitant with the reaction of a polyol with a polyisocyanate, generally derived from petroleum, a non-renewable resource. However, the increase in petroleum and natural gas costs, and concerns associated with climate change, are motivating researchers to develop products derived from renewable resources. While the development of non-isocyanate PU is still at an early stage [5], the development of bio-based polyols is already a recognized trend, especially those obtained from vegetable oils [6,7].

Among the several renewable raw materials that can be used to produce polyols, lignin is the most abundant aromatic polymer in nature. At an industrial level, the pulp and paper industry extracts 50–70 million tons of lignin annually from black liquor, which is mainly burned for energy generation [8]. However, several technologies have been developed to recover powdered lignin from kraft cooking liquors, namely, the LignoBoost™ and

LignoForce™ processes [9,10], thus opening a way to use it in value-added applications. One of these applications is the production of polymeric materials such as polyurethanes (PU) using lignin as a macropolyol. Although lignin is rich in hydroxyl groups (OH), its direct use as a macropolyol to produce PU involves challenges such as low reactivity towards isocyanate groups due to the steric constraints, recalcitrance, yielding products with less desirable performance, and low miscibility with other polyether petrochemical polyols due to its intrinsic characteristics [11]. One strategy to overcome these limitations is to liquefy lignin via oxyalkylation using propylene oxide (PO), which allows obtaining polyether polyols with properties comparable to conventional polyether polyols [12–14]. The drawback of this strategy is that PO presents a low boiling point and high vapor pressure, which makes it potentially explosive, requiring the use of pressurized reactors. An alternative to PO is the use of cyclic carbonates such as propylene carbonate (PC), ethylene carbonate, and glycerol carbonate, which have a high boiling point and low vapor pressure and are therefore a safer alternative for the oxyalkylation of lignin [15,16]. Recently, it was proposed to optimize the oxyalkylation of lignin kraft LignoBoost using PC without any purification in order to produce a crude lignin-based polyol (LBP) with a hydroxyl number (I_{OH}) and viscosity suitable for use in the production of RPUF and adhesives [17]. The mechanisms involved in the reaction of PC with lignins, considering lignins as a polyphenol, are comparable to the ring-opening polymerization reactions of oxiranes with lignins (e.g., PO). As illustrated in Figure 1, the structures obtained are similar. Once the OH groups of lignin have been activated by base catalysts, the oxyalkylation reaction occurs via ring-opening the cyclic carbonate. Concomitantly, PC can react with both types of OH groups: while the reaction involving aliphatic OH groups leads to chain extension via transesterification yielding carbonate linkages (Figure 1i), the reaction with phenolic OH groups leads to chain extension affording ether linkages and elimination of carbon dioxide (Figure 1ii). Additionally, side reactions can also occur yielding PC-oligomers.

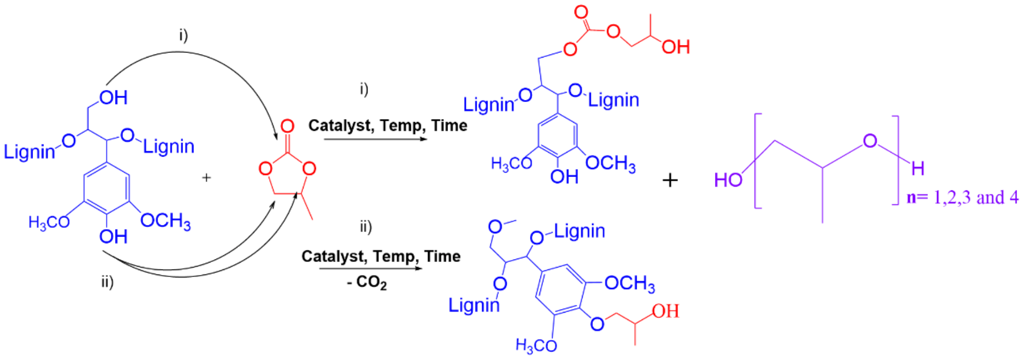


Figure 1. Main synthetic paths involved in lignin oxyalkylation with PC (**i**) reaction with aliphatic OH and (**ii**) reaction with phenolic OH, and representative structure of PC−oligomers formed. Adapted from [18].

However, the production of RPUF using bio-based polyether polyols obtained by oxyalkylation with cyclic carbonates is still little explored. Some examples include the work of Zhang et al. [19], who evaluated the effect of oxyalkylation conditions of lignin with ethylene carbonate (EC) and polyethylene glycol (PEG) on the density and compressive strength of RPUF. However, their effect on thermal conductivity was not considered. Duval et al. [20] produced RPUF using up to 25% of crude lignin-based polyol obtained from oxyalkylation with EC and PEG. The obtained RPUFs had more than 90% closed cells and a thermal conductivity value of approximately 0.0250 W/m·K, suitable for thermal insulation applications. Furthermore, using the crude polyol allowed reducing 75% of the catalyst in the RPUF formulation, since the catalyst used in the oxyalkylation of lignin can be used to catalyze the production of RPUF.

Despite the mentioned examples, obtaining RPUF, especially bio-based RPUF, with the appropriate properties for thermal insulation application can be a challenge. Besides the polyol and polyisocyanate, the BA, surfactants, catalysts, and other additives are crucial to obtain a good cellular structure and control the properties of foams [1]. In fact, there is a direct relationship between the formulation and several properties of RPUF, since the type and quantity of components of the formulation affect the foaming process and, consequently, the cellular structure and resulting properties of RPUF [21,22]. For example, the NCO/OH ratio has a major influence on the chemical architecture of foams and their mechanical properties. Since, RPUF is a crosslinked network structure formed between the polyol and polyisocyanate containing entrapped gas inside, the characteristics of the polyol, such as I_{OH}, molecular weight, viscosity, and type of OH groups, also affect the chemical architecture of foams and their properties [23]. Furthermore, regardless of the type of BA, a large amount of gas can be produced, which is responsible for the cellular structure of RPUF. Indeed, it is worth noting that the entrapped gas in RPUF corresponds to 95–97% of its volume and is responsible for more than 50% of thermal conductivity [24]. The chemical nature of the gas and its thermal conductivity is dependent on the type of BA which are classified either as chemical or as physical blowing agents, depending on the process involved in the formation of the aforementioned gas. Typically, water is a common chemical BA which, upon reaction with isocyanate groups, generates CO_2 responsible for the foam expansion. On the other hand, *n*-pentane is a typical example of a physical BA which evaporates, as a result of the temperature rise associated with the reaction between the isocyanate groups and OH groups of the polyol, resulting in foam expansion [25]. In turn, while the cell growth can be controlled using catalysts, cell formation is stabilized using surfactants. The complexity of formulations to produce RPUF derived from a bio-based polyol and their impact on the thermal conductivity, density, and mechanical properties has been widely discussed in the literature. Gama et al. [26,27] evaluated the effect of formulations on the properties of RPUF for thermal insulation using unrefined crude glycerol and polyol obtained from the liquefaction of coffee ground. For RPUFs produced using 100% of crude glycerol, the statistical analysis showed that the amount of BA and surfactant have a major impact on their density and thermal conductivity. The amount of BA and surfactant also affected the density of RPUFs formulated using the liquefied coffee ground, and the statistical analysis allowed the optimization of the formulation to obtain RPUF with suitable properties for thermal insulation. Kurańska et al. [28] showed that the amount of bio-based polyols in the formulation had a significant impact on the density and morphology of RPUF; however, using an adequate formulation, it was possible to obtain RPUF with low thermal conductivity (approximately 0.0230 W/m·K). Another study using palm kernel-based polyester polyol showed that the increase in polyol content in the formulation decreases the mechanical properties and increases the thermal conductivity of RPUF [29]. These examples clearly demonstrate that the formulation of RPUF is very complex, requiring a systematic study for each new system to yield foams with the properties required by the market. Therefore, a study of the formulation of RPUF using crude polyol obtained via the oxyalkylation of lignin using PC is required, as no previous study has been reported so far.

In this work, the main objective was to develop RPUF derived from LBP with the required properties for thermal insulation applications. For that purpose, the NCO/OH ratio and the amount of crude LBP, BA, and catalyst on the thermal conductivity and density of RPUFs were evaluated using a DoE. The mechanical properties and thermal stability of lignin-based RPUF were also examined and compared with those of an RPUF prepared using a conventional polyether polyol.

2. Materials and Methods

2.1. Materials

For the synthesis of LBP, LignoBoost kraft lignin (KL), propylene carbonate (PC), and a catalyst 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were used. The KL obtained from kraft pulping of Eucalyptus globulus was kindly supplied by a Portuguese pulp and paper mill. PC was purchased from Acros Organics Comp. and was used without any further purification. DBU was supplied by Aldrich Chemical Comp. and was used as received.

For the formulation of RPUFs, Alcupol R®-2510, supplied by Repsol, was used as a polyether polyol. The LBP was obtained via the oxyalkylation of KL as described below. The polymeric isocyanate Voranate M229 MDI with an NCO content of 31.1% and viscosity of 0.19 Pa. s was supplied by Dow Chemicals. The catalyst used in this work was Dabco® 33-LV (33 wt. % solution of triethylenediamine in dipropylene glycol) supplied by EVONIK. The surfactant was a polyether-modified polysiloxane, Tegostab® B8404, supplied by EVONIK. Water was used as a blowing agent, and upon reaction with isocyanate affords CO_2.

2.2. LBP Production from Oxyalkylation with Propylene Carbonate

KL (6.96 mmol of total OH groups, 1 equivalent molar), PC (5.5 eq. molar), and DBU (0.1 eq. molar) were placed in a 300 cm^3 stainless steel vessel (PARR, model 4566) equipped with an independent controller (PARR, model 4842), stirring (200 rpm), heating resistance (1000 W), internal water-cooling system, and temperature sensor. The mixture was stirred at 180 °C for 2.0 h under N_2 atmosphere. Next, the crude LBP (i.e., without any further purification) was cooled to room temperature and dried in a vacuum oven at 30 °C for several days until constant weight. The characterization of crude LBP, which consists of PC-modified lignin and PC-oligomers, was conducted according to the procedure described elsewhere [17]. The basic characteristics of crude LBP and a conventional polyol are presented in Table 1.

Table 1. Basic characteristics of lignin and polyols.

Properties	Kraft Lignin	Conventional Polyol	Crude LBP
Type		Aliphatic polyether	Aromatic polyether
I_{OH}, mg KOH/g	311	250	257
Viscosity, Pa·s	-	0.25	5.3
Mw, g/mol	1415	670	1760

2.3. RPUFs Formulations

The RPUFs were prepared by mixing different amounts of LBP, BA, catalyst, and fixed content of surfactant (2%) in a paper cup. The obtained mixture was homogenized using an IKA Ost Basic mixer with rotating blades for approximately 20 s at 900 rpm (component A). The pMDI (component B) was blended with component A in specific amounts to ensure different NCO/OH ratios (1.1, 1.2, and 1.3) during 20 s at 900 rpm. Note that the amounts of water present in the polyols were subtracted from the amounts of blowing agent added to give the appropriate NCO/OH. The RPUFs were formed under free-rising conditions. Besides the formulations using LBP, for comparison purposes, one foam was prepared using a conventional polyol (RPUF-conv polyol).

2.4. RPUFs Characterization

The thermal conductivity was determined at room temperature using a thermal analyzer (C-therm®) employing the transient plane source (TPS) method with a one-sided interfacial stainless steel sensor that applies a momentary constant heat source to the samples for 5 s. Five measurements were made for each sample.

The foams were cut in the form of a cube ($1 \times 1 \times 1$ cm^3) and weighted to determine the apparent density knowing the weight of the foams and their volume. The density values were averaged from the determination for 10 samples of each foam.

Fourier transform infrared (FTIR) spectra were recorded on a FTIR System Spectrum BX (PerkinElmer, Waltham, MA, USA) coupled with a universal ATR sampling accessory, from 4000 to 500 cm^{-1} by accumulating 64 scans with a resolution of 4 cm^{-1}.

The surface morphology of foams was assessed using a SU-70 (Hitachi, Tokyo, Japan) scanning electron microscope (SEM). The foams were covered with gold to avoid electrostatic charging during the examination and analyzed using an accelerating voltage of 15.0 kV. The SEM images were recorded along the direction of foam rise and the software Image J was used to calculate the average cell size.

The mechanical tests were performed using an Instron 5966 universal testing machine equipped with a 1 kN load cell according to the ISO 844:2014 standard. The foams were placed between the two parallel plates and compressed at 10 mm/min up to 30% deformation. The analysis was performed along the direction of foaming and the values presented correspond to the average of five specimens.

Thermogravimetric analysis (TGA) was performed to evaluate the thermal stability of the foams using a SET-SYS Evolution 1750 thermogravimetric analyzer (Setaram, Caluire, France) from room temperature up to 800 °C, at a heating rate of 10 °C/min and under oxygen flux (200 mL/min).

2.5. Statistical Analysis

In this study, the DoE was conducted using the Box–Behnken design to evaluate the effects of the NCO/OH ratio and the amounts of LBP, BA, and catalyst on the thermal conductivity and density of RPUFs. To build the matrix of the Box–Behnken design, the experimental ranges of process variables (i.e., the levels) were based on values available in the literature, as well as on the experience of our research group, and are summarized in Table 2. The design was built using JMP Statistical Software, with an analysis of variance (ANOVA) performed to evaluate the significance of the effects of the independent variables and their interaction on the responses at a 95% confidence level, as well as to develop the predicted models for responses (prediction profiler).

Table 2. Process variables and levels for the Box–Behnken design.

Process Variables	**Levels**		
	1	**2**	**3**
NCO/OH ratio (NCO)	1.1	1.2	1.3
Lignin-based polyol (LBP), %	25	62.5	100
Blowing agent (BA), %	1.5	2.5	3.5
Catalyst (CAT), %	0	0.5	1.0
Responses			
Thermal conductivity, W/m·K			
Density, kg/m^3			

1: low level; 2: intermediate level; 3: high level.

3. Results

3.1. Study of the Effect of the Formulation on the Thermal Conductivity and Density of RPUFs

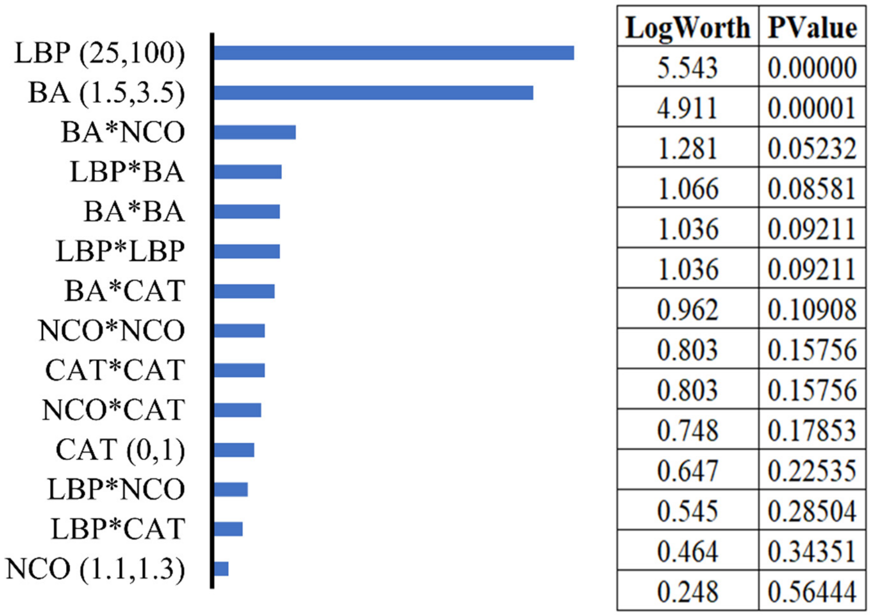
A statistical analysis was applied to obtain a better understanding of the effect of the NCO/OH ratio, LBP, BA, and catalyst content on the thermal conductivity and density of RPUFs. The experimental data for thermal conductivity and density are presented in Table 3. From the results obtained, it can be observed that the RPUF produced with crude LBP showed thermal conductivity values ranging from 0.0380 to 0.0430 W/m·K and density values varying between 21.7 and 42.6 kg/m^3.

The data were analyzed using the main effects and interaction effects of process variables on the responses hierarchically (multiple linear regression function) to evaluate the relationship between the responses and the process variables. The Pareto chart depicted in Figure 2, adapted from JMP software, shows the p-values < 0.05. As can be observed, only the LBP and BA variables significantly affect the responses. In turn, the catalyst, NCO index, and the interaction of process variables do not seem to affect the responses. From the ANOVA results (Table 4), the two models proved to be significant and to adequately represent the experimental data with predicted data at a 95% significance level (p-value < 0.05). Thus, a prediction profiler (Figure 3) was developed from the predicted models, showing the responses behavior as a function of each process variable.

Table 3. Experimental data for thermal conductivity and apparent density.

Run	Process Variables				Responses	
	LBP (%)	BA (%)	NCO/OH Ratio	CAT (%)	* Thermal Conductivity (W/m·K)	* Density (kg/m^3)
1	100	2.5	1.3	0.5	0.0396	25.6
2	25	1.5	1.2	0.5	0.0430	42.6
3	62.5	1.5	1.3	0.5	0.0410	33.6
4	25	3.5	1.2	0.5	0.0380	29.4
5	25	2.5	1.2	0.5	0.0400	34.7
6	25	2.5	1.2	0	0.0400	34.7
7	62.5	3.5	1.3	1.0	0.0380	24.9
8	100	2.5	1.2	0.5	0.0390	18.7
9	62.5	3.5	1.2	1.0	0.0390	25.5
10	62.5	3.5	1.1	1.0	0.0380	22.5
11	100	3.5	1.2	0.5	0.0360	21.7
12	62.5	2.5	1.3	0.5	0.0390	26.2
13	62.5	1.5	1.2	0	0.0420	34.9
14	100	2.5	1.2	0	0.0400	23.6
15	62.5	2.5	1.1	0	0.0390	23.8
16	62.5	2.5	1.2	1.0	0.0390	26.9
17	62.5	1.5	1.1	0.5	0.0420	41.9
18	62.5	1.5	1.2	0.5	0.0410	29.2
19	100	2.5	1.1	1.0	0.0400	21.7
20	62.5	3.5	1.2	0.5	0.0380	22.6
21	62.5	2.5	1.1	0	0.0390	29.0
22	100	1.5	1.2	0	0.0400	25.6
23	25	2.5	1.3	0.5	0.0410	35.9
24	25	2.5	1.1	0.5	0.0400	30.3
25	62.5	2.5	1.2	0.5	0.0430	30.4
26	62.5	2.5	1.2	0.5	0.0410	28.0
27	62.5	2.5	1.3	1.0	0.0380	28.1

* Average values.



LogWorth	PValue
5.543	0.00000
4.911	0.00001
1.281	0.05232
1.066	0.08581
1.036	0.09211
1.036	0.09211
0.962	0.10908
0.803	0.15756
0.803	0.15756
0.748	0.17853
0.647	0.22535
0.545	0.28504
0.464	0.34351
0.248	0.56444

Figure 2. Pareto chart of the main effects obtained from the Box–Behnken design.

Table 4. ANOVA results for the regression models for thermal conductivity and density.

Source	Responses					
	Thermal Conductivity			Density		
	DF	SS	MS	DF	SS	MS
Model	8	4.82×10^{-5}	6.023×10^{-6}	8	812.4	101.5
Error	18	1.45×10^{-5}	8.086×10^{-7}	18	125.3	6.96
Total	26	6.27×10^{-5}		26	937.6	
F ratio		7.45			14.6	
p value		0.0002			2.033×10^{-6}	
R^2		0.768			0.866	
R^2 adjusted		0.664			0.807	
Mean of response		0.0394			28.60	

DF: Degrees of freedom; SS: Sum of squares; MS: Mean of squares.

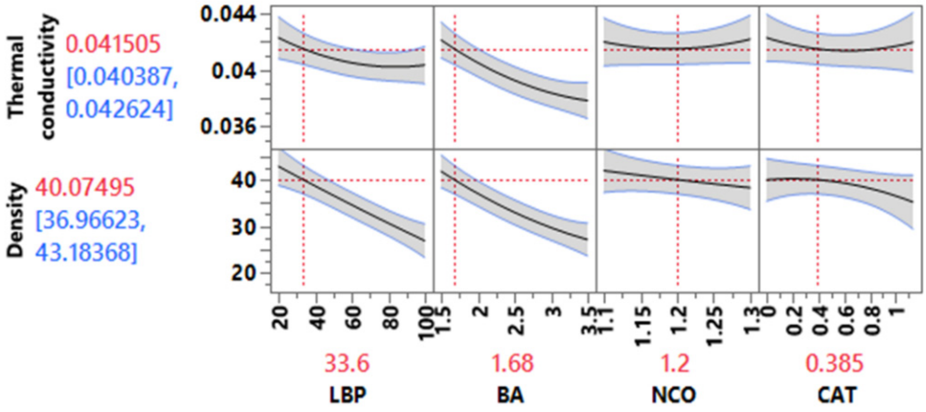


Figure 3. Prediction profiler for thermal conductivity and density.

Figure 2 shows that the thermal conductivity of RPUF decreases with the increase in LBP content and BA. The reduction of the thermal conductivity of RPUF with an increase of LBP content can be attributed to the moderate viscosity of LPB (5.3 Pa·s), which has a strong impact on foam's morphology. These results are in line with reports on studies of PUFs prepared using bio-based polyols (including lignin-derived polyols) with moderate-to-high viscosity [28,30–32]. Indeed, higher-viscosity polyols are advantageous during nucleation because bubbles tend to be trapped which results in a larger number of cells and a more uniform size distribution.

Likewise, the results obtained for the effect of the BA on the thermal conductivity are also in agreement with several works in the literature. However, it should be noted that the common explanation for the reduction of the thermal conductivity is attributed to the increasing amounts of blowing agent trapped within the foam cells whose thermal conductivity is far lower than that of the PU polymer [27,33–35]. Yet, when the cellular morphology is heterogeneous and the number of closed cells is not high, many other factors can be at stake [36].

As regards the effect of the amount of LBP used on the density, Figure 3 shows that the density decreases with an increase in the amount of LBP. The same observation has been reported in the literature for lignin-derived polyols [20,28]. Yet, Cateto et al. [37], who also used lignin-based polyols, observed the opposite tendency and even succeeded in fitting the data obtained using a power law which is frequently used in the literature to correlate compressive strength and density. Nonetheless, in that very same study, it was shown that a formulation which afforded a foam with larger cells did not follow that trend very closely. In brief, the impact of the amount of LBP on the density, shown in Figure 3, depends on the cellular morphology of the foams which results from a complex combination of variables and not just one.

In what concerns the effect of the BA on the density, it was observed that the density values decreased as the amount of BA used in the formulation increased. This was expected because the water, used as the BA, reacts with isocyanate, producing CO_2, which diffuses into nucleated bubbles aiding the formation of bigger bubbles, ensuring low-density foams. This effect has been widely reported [24,27,35,38].

3.2. Evaluation of the Characteristics of RPUFs Using Different Contents of LBP in the Formulation

Within the 27 bio-based formulations, 3 foams with the best dimensional stability and different amounts of LBP used in the formulations were chosen to evaluate their structural characteristics and thermo-mechanical properties. The RPUF produced using a conventional polyether polyol was used for comparison.

FTIR analysis was used to assess the chemical composition of RPUF produced using the conventional polyether polyol and 25, 62.5, and 100% of LBP, with the spectra obtained shown in Figure 4. All RPUF presented very similar spectra and were typical of PU. The absorption bands for the urethane linkages are mainly characterized by the stretching vibrations of C=O peak at 1700 cm^{-1}, N–H stretching vibration in the range of 3200–3440 cm^{-1}, and N–H bending vibrations with a band at 1510 cm^{-1}. The other characteristic bands at 2860 and 2970 cm^{-1} are associated with alkane C-H stretching vibrations, while the band at 1080 cm^{-1} is associated with the ester C-O-C stretching vibration. Interestingly, the typical free isocyanate (NCO) stretching band at 2270 cm^{-1} was not observed for RPUF produced using LBP. In turn, the spectrum of the RPUF produced using a conventional polyol shows a small band at this wavenumber, indicating that the quantity of isocyanate used was not fully consumed in this case. As the water content of the polyols was taken into consideration to calculate the amount of isocyanate to be used in the formulations, this suggests that the OH groups from LBP are more reactive, possibly due to the presence of residual catalyst and PC-oligomers being thus able to consume the excess of isocyanate. These PC-oligomers result from side reactions that can occur during the oxyalkylation of lignin with PC: besides the main reaction of oxypropylation leading to the alkylation of lignin phenolic groups, the side reaction of aliphatic hydroxyl groups via transesterification with the formation of carbonate linkages can take place as illustrated in Figure 1 [18].

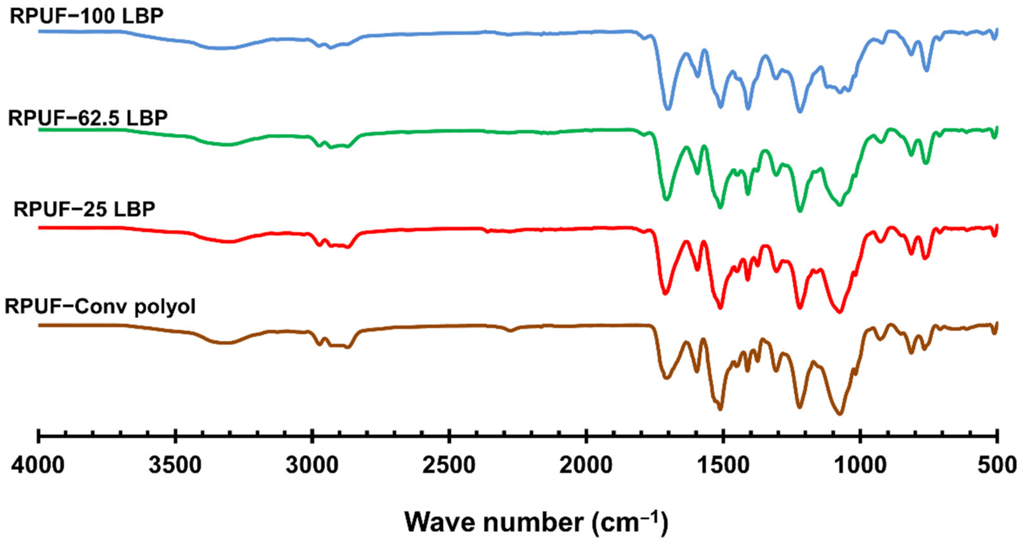


Figure 4. FTIR normalized spectra of RPUF prepared with a conventional polyol (RPUF−Conv polyol), with 25% (RPUF−25 LBP), 62.5% (RPUF−62.5 LBP), and 100% (RPUF−100 LBP) of LBP on the formulation.

The cellular structure was assessed by SEM and representative images are presented in Figure 5, while Table 5 summarizes the results obtained for the average cell size, density, and thermal conductivity, as well as the mechanical properties.

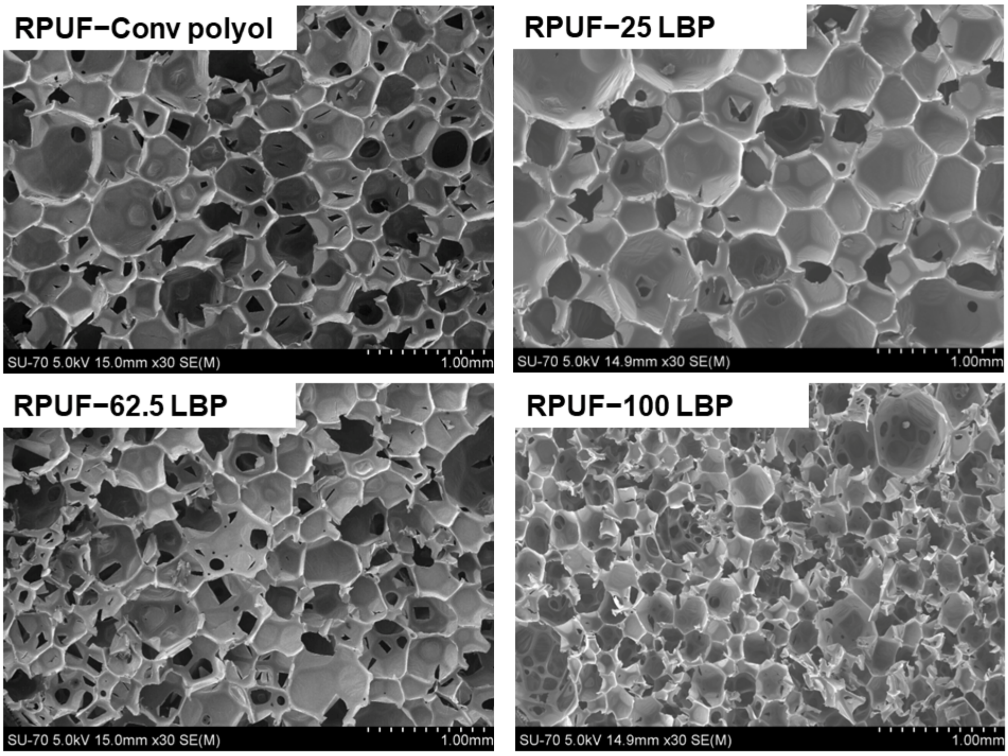


Figure 5. SEM of RPUF prepared with a conventional polyol and different amounts of LBP. Free-rise direction and magnification of 30×.

Table 5. Characteristics of RPUF with different amounts of LBP on the formulation.

Properties	RPUF−Conv Polyol	RPUF-25 LBP	RPUF−62.5 LBP	RPUF-100 LBP
* Formulation	2.5BA/1.0CAT/1.2NCO	3.5BA/0.5CAT/1.2NCO	3.5BA/0.5CAT/1.3NCO	2.5BA/0.5CAT/1.3NCO
Density, kg/m^3	38.5 ± 3.0	29.4 ± 2.0	25.6 ± 2.0	25.6 ± 3.0
Thermal conductivity, W/m·K	$0.0401 \pm 3.3 \times 10^{-4}$	$0.0382 \pm 1.4 \times 10^{-4}$	$0.0385 \pm 2.9 \times 10^{-4}$	$0.0396 \pm 2.3 \times 10^{-4}$
Average cell size, μm	392 ± 128	529 ± 187	377 ± 103	334 ± 100
σ10%, kPa	112 ± 10.5	100 ± 7.4	81.2 ± 8.1	80.0 ± 7.0
Young Modulus, kPa	680 ± 74.8	568 ± 79.6	453 ± 58.9	415 ± 51.9

* Formulation codes: BA (blowing agent), CAT (catalyst), NCO (NCO/OH ratio).

According to Figure 4, it appears that increasing the LBP content in the formulation resulted in a reduction of the average cell size and that the cells gradually became more damaged. Since the viscosity of the crude LBP used in the formulation is moderate (5.3 Pa·s), while it can be an advantage to promote cell nucleation and homogeneous size distribution, the rheology of the foaming process might have been affected, limiting the bubble expansion [30,39]. In fact, this is in agreement with Arbenz et al. [32], who evaluated the properties of rigid foams from alkoxylated glycerol (0.2 Pa·s) and tannin (6.9 Pa·s), with the values of the corresponding average cell size of foams obtained being 440 and 220 μm, respectively. In addition, the RPUF made with 100% of alkoxylated tannin presented slightly lower thermal conductivity. Interestingly, combining the results presented in Figure 3 (regarding the correlation between the amount of LBP, associated with higher viscosity, on the density) with the SEM images (Figure 5) and the apparent density values

(Table 5), it can be inferred that the cellular structure is indeed strongly affected by the viscosity of the polyol. Indeed, the higher the percentage of LBP used in the formulation, the smaller the average cell size, the more heterogeneous the foam cellular structure, and the lower the apparent density. Nevertheless, as mentioned earlier, the cellular morphology results form a very complex combination of factors. While the viscosity of the polyol can limit bubble expansion, as it depends on the kinetics of the gas and gelling reactions, it should be stressed that the LBP used in the present study was not purified, hence, the presence of PC-oligomers and residual catalyst cannot be ignored. The former may limit the crosslinking density of foam and thus reduce the apparent density, while, concomitantly, the latter can accelerate foam expansion, thus promoting the reduction of foams' apparent density. It must also be noted that the expansion of the PU network depends on the reactivity of the polyol with diisocyanate. The higher the reactivity of the polyol, the less time is available for the formation of expanded cells (smaller volume) and the stiffer the cell walls. According to the preliminary evaluation, LBP showed greater reactivity than commercial polyol. Therefore, the decrease in cell dimensions and their damage with the increase in LBP in the RPUF formulation is quite understandable.

As regards the thermal conductivity of these three foams, the effect of the amount of LBP is hardly noticeable, although RPUF−25 LBP and RPUF−62.5 LBP present a thermal conductivity slightly lower, which might be attributed to the fact that the formulations used had a higher amount of BA than RPUF-100 LBP. Nevertheless, considering that the cells are so disrupted, the thermal conductivity is hardly regulated by the lower conductivity of CO_2 (0.0145 W/m·K at 20 °C) trapped in the cells as a result of the reaction between water and isocyanate groups. Instead, atmospheric air (0.0256 W/m·K at 20 °C) must be at equilibrium with the air inside the foams' cells.

It is well recognized that the cellular structure affects the mechanical properties and thermal conductivity of foams [22,40]. Even though the increase in the LBP content had a major impact on the morphology and density of these foams, but hardly any effect on the thermal conductivity, the impact on the mechanical properties was substantial, as can be observed in Table 5 and Figure 6. As can be observed, increasing contents of LBP in the formulation resulted in a reduction of the compressive stress at 10% of strain, the Young's modulus, and of the toughness of these foams. These effects are more pronounced for foams produced using 62.5 and 100% of crude LBP which actually present more cell walls ruptured and lower compression values compared to the foams produced using 25% of LBP and a conventional polyol. Członka et al. [41] and Narine et al. [42] attributed the decrease of mechanical properties to the broken walls of cells of foams, as well as the presence of homopolymer. This may also apply to our results as the cellular structure is considerably disrupted and the crude LBP contains PC-oligomers which, besides limiting the crosslinking density, can also act as a plasticizer, increasing the flexibility of the polymer network countering, to a certain extent, the rigidity conferred by the aromatic structure of lignin [13,22].

Since lignin presents an aromatic structure, it was expected that the use of LBP would lead to an improvement of the thermal stability of the ensuing RPUF [11]. However, the TGA results revealed the opposite tendency. From Figure 7, it can be seen that the thermal stability of foam decreases as the amount of crude LBP increases. The lignin-based RPUFs were thermally stable up to 160–175 °C, while the foam produced using a conventional polyol was thermally stable until 240 °C. In addition, it can be seen that foams produced using 62.5 and 100% of crude LBP start to degrade at lower temperatures but present a slower degradation rate compared with the foam using 25% of crude LBP and a conventional polyol. In fact, analyzing the derivative of the mass loss as a function of temperature, it becomes evident that the rate of degradation of all bio-based RPUF is much lower than that of the foam prepared using the conventional polyol (Figure 7b). This is in fact due to the aromatic structure of the polyol [28,43,44]. Yet, the lower thermal stability of these lignin-based RPUFs can be attributed to the characteristics of the crude LBP. After alkoxylation, the acidic phenolic OHs are replaced by comparatively less acidic secondary aliphatic OHs, which reduce the potential to create strong intramolecular hydrogen bonds and consequently reduce their thermal stability [45–47]. In addition, the presence of PC-oligomers in the crude LBP jeopardizes the thermal stability of the ensuing foams. As they are relatively thermal labile, PC−oligomers contribute to lowering the temperature of thermal degradation. Actually, Figure 7b clearly illustrates this aspect: even though the rate of decomposition is lower for the RPUF prepared using 100% LBP polyol, the maximum rate of degradation occurs at a lower temperature, proving that the higher the number of PC-oligomers present in the formulation, the more thermal labile the foam is.

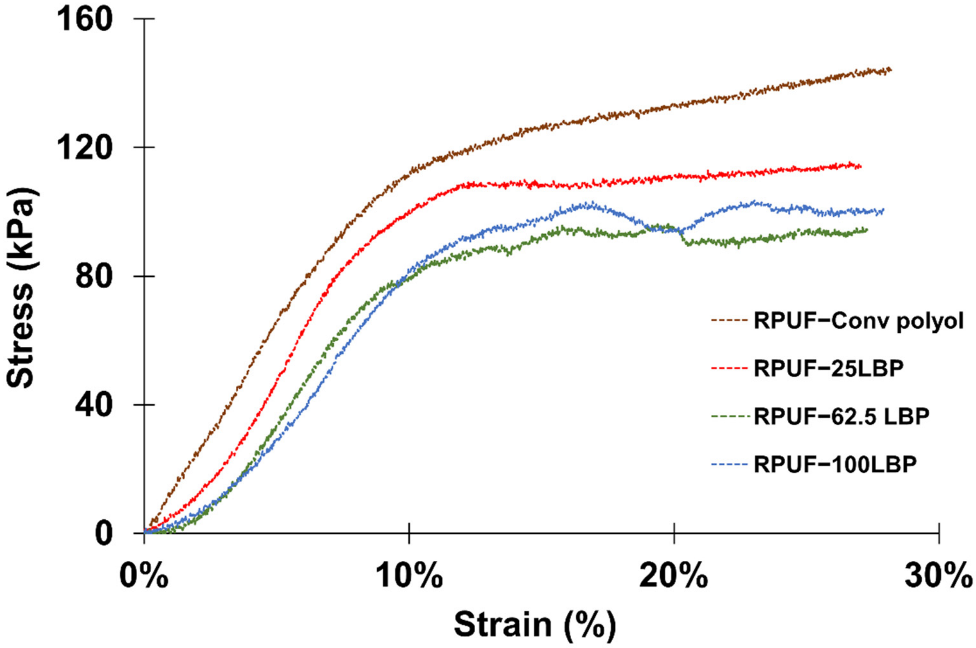


Figure 6. Compressive stress–strain curves of RPUF−Conv polyol, RPUF−25 LBP, RPUF−62.5 LBP, and RPUF−100 LBP.

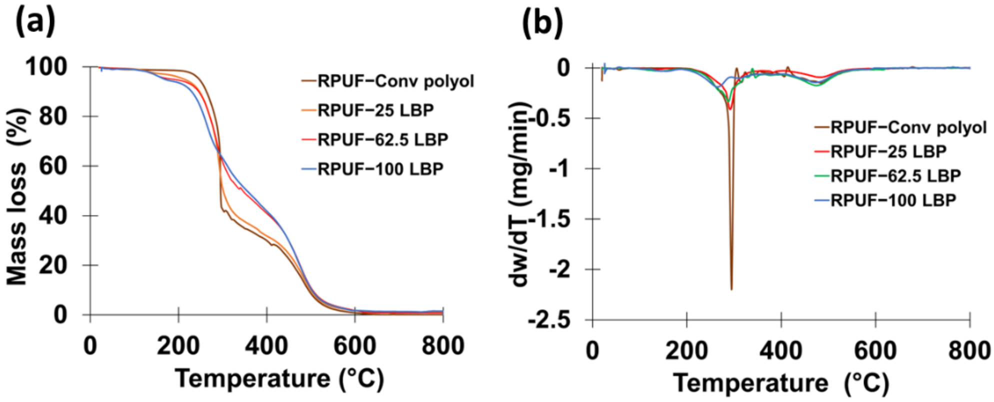


Figure 7. (**a**) TGA curves and (**b**) derivatives of mass loss (dw/dT) of RPUF prepared using different amounts of LBP and a conventional polyol.

Lightweight (25–60 kg/m^3) RPUFs with low thermal conductivity (<0.0300 W/m·K) are usually required for applications as insulation materials. However, from Table 3, even though the apparent density of the foams falls within the range required, the average thermal conductivity obtained is 0.0394 W/m·K, and is thus not suitable for the insulating RPUF market. While various parameters can be associated with the cellular structure, based on the results obtained in the present study, the fact that water was used as a blowing agent is considered the most critical. This is not necessarily due to the fact that the thermal conductivity of CO_2 is not low enough but, more importantly, due to the very exothermic character of the reaction between the isocyanate and water which can lead to cellular disruption as a result of the accelerated foam expansion. Furthermore, this highly exothermic reaction can cause scorching or fire, as well as increase the costs of production because water-blown foams consume more isocyanate [22]. In view of all these problems, an alternative BA should be considered.

Considering that the use of hydrocarbons (HCs), such as *n*-pentane (0.0137 W/m·K at 20 °C), in foams formulations has shown excellent insulating properties [25] on their own or in combination with water, two other formulations of RPUFs were prepared based on the formulations described in run 1 (Table 3). However, instead of using only water as the BA, mixtures of *n*-pentane and water were used: specifically, for RPUF−100 LBP, 7% of *n*-pentane and 2% of water, while for RPUF−100 LBP, 20% of *n*-pentane and 2% of water. The ensuing RPUF presented suitable dimensional stability and the thermal conductivity reduced significantly from 0.0396 W/m·K to 0.0320 and 0.0290 W/m·K for formulations 1 and 2, respectively. These results indicate that tuning the BA composition allows reaching the market requirements for thermal conductivity. However, further studies are necessary because the low polarity of *n*-pentane may limit its solubility in the polyol and other PU raw materials. Hence, the use of appropriate surfactants to improve their solubility may be another process variable to consider [48].

4. Conclusions

In this study, crude LBP was used to produce RPUFs for insulation applications. A DoE was applied to obtain information about the effect of the NCO/OH ratio, LBP, BA, and catalyst content on the thermal conductivity and apparent density of RPUFs. The statistical data analysis revealed that the decrease in the apparent density and the thermal conductivity of foams is significantly affected by the content of crude LBP and BA. Using water as the BA, it was only possible to obtain thermal conductivity values of 0.036 W/m·K, which is slightly higher than those recommended for insulation needs in building construction. Furthermore, the increase of LBP in the formulation jeopardized the mechanical properties and the thermal stability of RPUFs, which may be attributed to the characteristics of crude LBP, namely, the viscosity and the presence of PC-oligomers. Overall, the insulation and other properties of the bio-based RPUFs using crude LBP still need to be improved, by adjusting suitable ingredients in the formulation such as the type of BA and surfactant, as well as their quantities. In fact, preliminary results have shown that the partial replacement of water by *n*-pentane led to a significant reduction of thermal conductivity. To the best of our knowledge, this is the first report regarding the use of significant percentages of unpurified LBP obtained via oxyalkylation of LignoBoost kraft lignin in the production of RPUF.

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