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Influence of Lignin's pH on Polyurethane Flexible Foam Formation and How to Control It

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Abstract

Low pH of commercial lignins has a catastrophic impact on the polyurethane foaming reactions. Experiments were performed with 10 wt.% of lignin with various pHs in polyols. Virgin lignin (pH 2.5, 35% moisture) has the most negative impact as it reduces the initial foam rising rate by 85% and the foam's final height by 35% as compared to the reference foam, lignin free. Drying of this lignin at 80°C for 12 h can reduce this impact while alkaline treatment to bring the lignin's pH to 6.6 almost cancel it. As revealed by *in situ* dielectric constant measurements, both reactions, gelling via polymerization and blowing via CO_2 degassing, are impacted. *In situ* FTIR analysis of the foaming process demonstrated that blowing reaction is the most pH sensitive. Two methods to counter the pH influence by pH modification were tested and provide interesting results but also significant drawbacks limiting their applicability.

Introduction

PU is probably the most versatile family of polymers on the market today. Since their first introduction in the 40's, PUs have gone through an evolution in their chemistries, properties and applications. As their main chemistry usually relies on the reaction of a polyol and a diisocyanate, the structure of those will drive the architecture and the properties of the final polymer. It can be thermoset (cross-linked chains) or thermoplastic (linear chains), flexible, rigid, elastomeric, viscoelastic, plain or foamed, depending on the components chemical structure. For this reason, PUs are used in various application such as as elastomers, high performance adhesives, surface coatings, synthetic fibres, hard plastic parts, composite matrix, sealants, gaskets, insulation rigid foams, furniture flexible foams, and plenty of other applications.[1]

The chemistry of PUs, which is quite complex, mainly relies on the urethane bond formation. This reaction, exhibited in Figure 1.A, occurs between an isocyanate and a hydroxyl. This reaction is highly exothermic and generally catalysed by a tertiary amine by deprotonation of the hydroxyl (triethylenediamine for example). Using a diol and diisocyanate leads to linear PU linear chain formation, e.g. thermoplastics or elastomers. Using a polyol with functionality of three or more leads to the formation of a three dimensional network, e.g. a thermoset polymer. Most of the diisocyanates used in the industry are aromatic based, allowing good reactivity with polyols, an interesting phase separation behaviour during PU formation and good mechanical properties and chemical resistance for PU. The polyols can be either polyether or polyester based, and are mainly driving the properties. Higher molecular weigth (Mw) polyols

(2 000 g/mol and above) with low functionality (around 3) lead to flexible structures. Lower Mw polyols (around 500 g/mol) with high functionality lead to rigid structures. As moisture is often present in the raw materials and the air, a secondary reaction between isocyanate and water, as shown in Figure 1.B, is also determinant in the polyurethane chemistry. This reaction leads to the formation of a primary amine and carbon dioxide. Then, the primary amine reacts with another isocyanate to form a urea groups. As isocyanate used in PU production are usually bifunctional, this reaction does not lead to the crosslinking but the formation of carbon dioxide promotes a chemical foaming. This reaction is also highly exothermic and usually requires catalysts.[1,2]

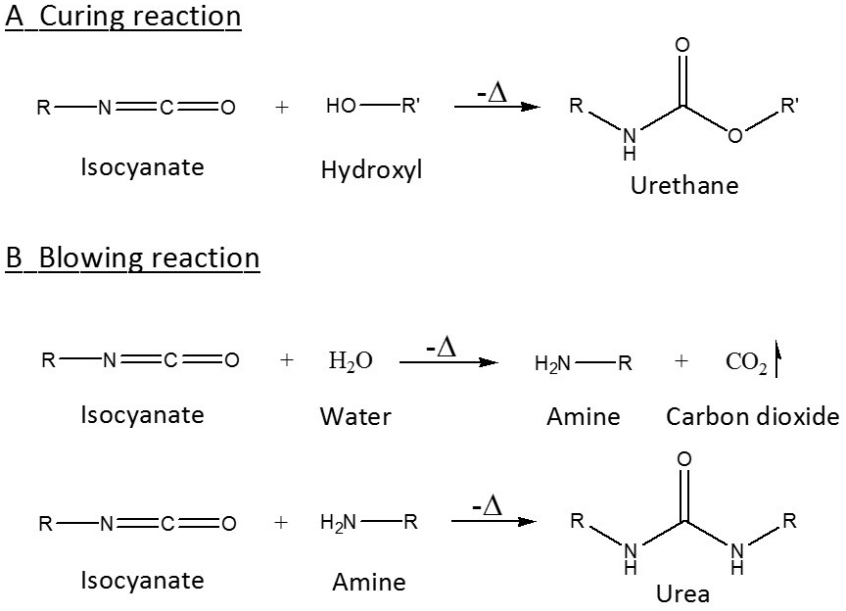

Figure 1: Main chemical reactions involved in PU foam synthesis, A) Curing reaction resulting in urethane linkage and chain extension, and B) Blowing reaction resulting in the formation of carbon dioxide and rising of the foam.

Due to their large consumption in the industry, PUs are an obvious choice for any initiatives trying to reduce the impact of plastic production and end of life on the environment. Those initiatives can focus on the end of life, improving the recycling, developing new depolymerisation approaches[3] or inducing biodegradability[4]. Another way to reduce the environmental footprint would be to change the usual synthesis way, avoiding to use any isocyanate, a potentially toxic family of molecules, made from phosgen[5–8]. Finally, replacing partially petroleum based polyol by bio-based polyol in the PU formulation is already recognized as an efficient approach. This bio-content can be a reacting polyol or an inert filler. Modified vegetable oils (mainly castor oil[9–12] or soybean oil[4,13–16]) are already used to partially replace petroleum based polyols in some applications. They are, in that case, reacting with the isocyanate. Other bio-content have been introduced the same way, as Cardanol (from Cashew nutshells) [17], 3-hydroxy-N,N-bis(2-hydroxyethyl)butanamide (HBHBA, from bacterial fermentation)[18] or heavy oil from biomass liquefaction[5]. In the other hand, various bio-based particles have been introduced as filler, like hazelnut or walnut shells[19], or various wood products[20].

More specifically, components extracted from wood products were the focus of many studies. This includes cellulose[21,22], tannins[6,23–25] and lignin[3,4,28–37,8,38–47,10,48,49,11,12,20,22,26,27]. Cellulose, is the main component of the wood structure and was generally liquefied to enter the polyol phase, using crude glycerol[21] or ethylene carbonate[22]. Tannins, relatively low molecular weight polyphenols usually found in tree barks, were tested as sole polyol[25] or intermediate for the preparation non isocyanate polyurethane[6,23] or part of linear PU structure[24]. Finally, lignin, the second main component of wood, bringing rigidity and rot resistance to the structure, was already the focus of several studies.

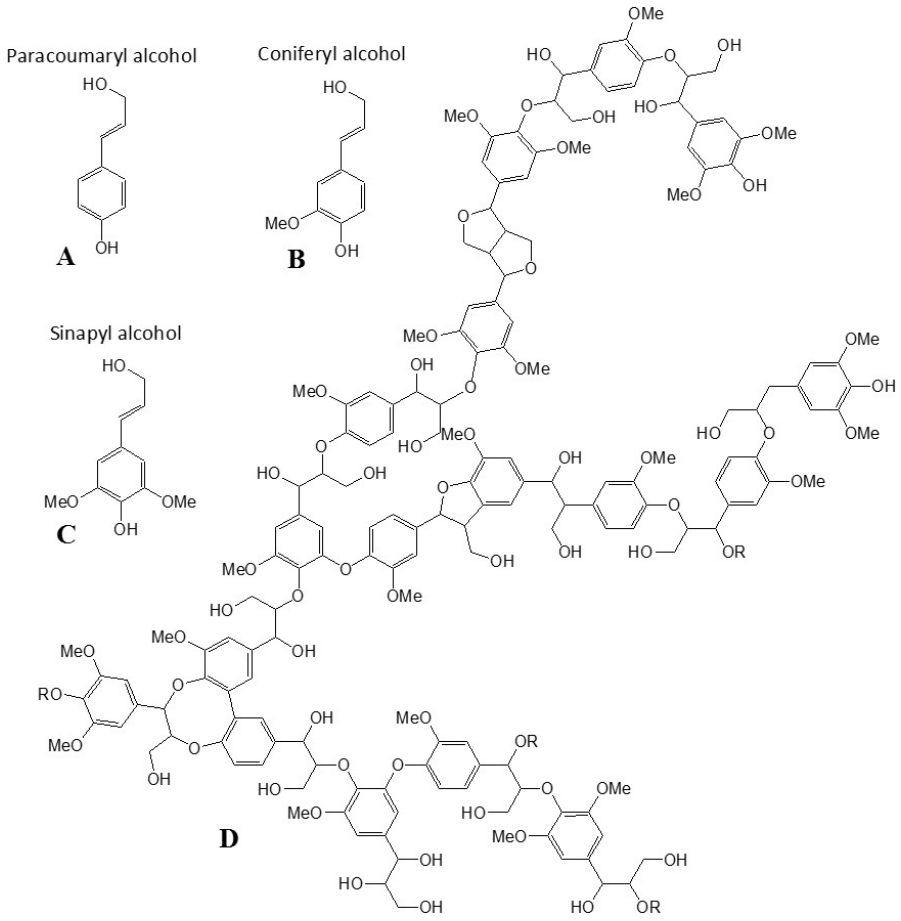

Figure 2: Chemical structure of lignin, including the three main monomers, A) Paracoumaryl alcohol, B) Coniferyl alcohol, C) Sinapyl alcohol, and D) an example of combination.

Lignin is a natural polyol found in the wood structure, acting as binder and protecting sheath around the cellulose and hemicellulose fibrils. The lignin architecture and composition can vary depending on various factors, including the wood essence or the tree part. There is no defined primary structure, the architecture relies on three monolignol monomers, Paracoumaryl alcohol (Figure 2. A.), Coniferyl alcohol (Figure 2. B.) and Sinapyl alcohol (Figure 2. C.). They are incorporated in the lignin as *p*-hydroxyphenyl, guaiacyl and syringyl units respectively. The ratio of each unit depends on the wood essence. To complete the picture, most of the aromatic ring units are methoxylated and the molecule is crosslinked to reach a significant, but non homogeneous, molecular weight (up to 10 000 g/mol). An example of structure is proposed in Figure 2. D.[26,48,50,51]

Most of commercially available lignins are currently produced by the pulp and paper industry and is mostly a byproduct of the pulp production. Several techniques exist to remove the lignin. The four main families are the sulfite pulping, the soda process, the Kraft process and organosolv. The sulfite pulping uses sulfuric acid to extract the lignin. This process tends to well remove the lignin, but the acidity tends to damage the cellulose fibers more than other processes. The extracted product, called lignosulfonate, is a relatively low degraded lignin with low level of sulfonation, thus allowing good water solubility. Kraft process uses sodium hydroxide and sodium sulfide to separate the lignin from the hemicellulose and cellulose, and partially depolymerized it. At a certain point, lignin becomes soluble in the basic solution, to form the black liquor. It is then precipitated by acidification using sulfuric acid, then rinsed and dried. The Kraft lignin is more degraded than the one obtained from the sulfite process, leading to lower Mw, but is not sulfonated. On the other hand, due to the final precipitation step with acid, this lignin, even after washing, is still very acidic. Finally, organolv process relies on the use of organic solvent to solubilize the hemicellulose and lignin. The solvents involved are acetone, methanol, ethanol, butanol, ethylene glycol, formic acid and acetic acid. The lignin endures a hydrolytic cleavage above the boiling temperature of the mix until the resulting fragment are soluble in the mixture. The lignin is collected by acidification of the medium and flotation. The organosolv lignins are usually more hydrophobic than the other lignins, are relatively acidic (pH around 4) and confined in well-defined particles. This process has a lower environmental impact compared to the previous ones because of the very little chemical used and the fact that solvent can be easily recycled by distillation, however, it is more expensive. [52,53]

As a non-food grade source, a natural polyol, a potential low density filler, and a cheap resource largely available, lignin is an obvious choice as an additive or reactant in polyurethane chemistry. During the last decade, a lot of studies focused on this matter. Several options were already tested, using lignosulfonate[39,54], Kraft lignin[3,8,10,11,32,33], soda lignin or organosol lignin[28]. The approaches include the liquefaction into a polyol[22,30,32,44] (mainly polyethylene glycol, ethylene carbonate or glycerol, sometime microwaves assisted[12,31,36,37]), the functionalization[38,40,46,49,55], the depolymerization[3], the oxypropylation[12] or the introduction as filler[20,34]. The final product can be a film[11,40,43], an elastomer[27,45], a rigid foam[3,4,10,20,32,35,36,42,45,54] or a flexible foam[12,31,33,34,37,38,41,45]. If some of those studies were really promising, none of those technologies actually reached yet the market, as they all include some road blocks. The main ones are the cost and the consistency. Although lignin is cheap, intensive chemical process applied on it tends to rise the final cost to a level which becomes discouraging for the industry. In addition, as a by-products in pulping processes lignin quality is not taken cared leading to the lack of consistency which is very important for the industry.

For those reasons, it seems that limited modifications should be applied to lignin. So, as a starting point, the use as filler seems to be the most appropriate. Unfortunately, even then, some commercial lignins affect negatively the polyurethane chemistry and this issue has not been well addressed in the literature. As a number of commercial crude lignins are only available with low pH, due to the final steps of the extraction processes, and as this pH is also quite variant from batch to batch, knowing exactly how it could impact the reactions and how to eventually counteracting it, is crucial. This is the primary purpose of this study.

Experimental part

Materials

Three petroleum based polyols were used during this study, Multranol 9139 (6000 g/mol, propylene oxide-based triol, 26-30 mg KOH/g, 1050-1250 mPa.s, Covestro), Multranol 9190 (4000 g/mol, propylene oxide-based diol modified with ethylene oxide, 26-30 mg KOH/g, Covestro) and Jeffol G31-28 (6000 g/mol, propylene oxide-based triol ethylene oxide tipped, 28 mg KOH/g, 1175 mPa.s, Huntsman). The catalysts including the TegoAmin 33 (Triethylenediamine based, gelling reaction) and TegoAmin BDE (Bis(2-(Dimethylamino)ethyl)ether based, blowing reaction) were provided by Evonik Industries. The surfactant TegoStab B8727 LF2 (silicon surfactant) was also obtained from Evonik Industries. The isocyanate Suprasec 7507 (MDI based diisocyanate) was supplied by Huntsman. Biochoice Lignin (Kraft lignin from softwood) was kindly provided by Domtar. This lignin has a humidity level of 35% in normal conditions (as mentioned by the provider in the Safety Data Sheet, and verified by drying a sample on a balance) and a pH of 2.5. The average particle size is between 0.5 and 1 µm, as measured by scanning electron microscopy. Most of the particles are aggregated in larger clusters. Dried Biochoice Lignin was produced simply by drying the Biochoice lignin at 80°C overnight.

Lignin pH Measurement and pH Modification

The pH of the lignin was measured by the following process. Lignin was dispersed mechanically in distilled water at a ratio of 20% in weight. The mixing was maintained for 5 min before measuring the mix's pH using a Mettler-Toledo pHmeter. Variation of the pH was carried out by addition of 2 wt.% NaOH solution to the lignin suspension in water (20 Wt.%) while stirring until reaching the target pH of 4, 4.5, 6 and 6.6. The stirring was maintained until the pH stayed unchanged for at least 30 min (stabilization).The lignin was then centrifuged and dried.

Foaming Process

First, the lignin (10% of the total initial formulation weight) was introduced in the polyols and exposed to 1500 RPM mechanical mixing for 5 min. Then, catalysts, surfactant and water (chemical blowing agent) were added before additional 2 min 1500 RPM mechanical mixing. The mix was then let to rest for 5 min before the addition of the isocyanate and the final mixing of 15 s at 1500 RPM. The mixing sequence was systematically the same. The foaming was performed by hand pouring the mixture into a disposable cardboard cup to allow free rising. The isocyanate index (percentage of isocyanate reactive sites compared to the polyol reactive sites) was fixed at 105, to eventually allow reactivity between the lignin and the diisocyanate.

	Weigth g				
	Reference Foam	Virgin Lignin Foam	Dried Lignin Foam	*pH-Mod-Lignin Foam	NaOH-Treated Lignin Foam
Multranol 9139	22.5	22.5	22.5	22.5	22.5
Multranol 9190	7.5	7.5	7.5	7.5	7.5
TegoAmin 33	0.1	0.1	0.1	0.1	0.1
TegoAmin BDE	0.1	0.1	0.1	0.1	0.1
TegoStab B8727 LF2	0.15	0.15	0.15	0.15	0.15
Water	1	1	1	1	
Commercial Biochoice Lignin		5.7			
Dried Biochoice Lignin			5.7		5.7
*pH modified Biochoice Lignin				5.7	
NaOH 10%					1
Suprasec 7507	20	20	20	20	20

Table 1: Flexible foam formulation used during this study for the all the tests but the FTIR analysis.

	Weigth g			
	Reference Foam	Virgin Lignin Foam	Dried Lignin Foam	*pH-Mod-Lignin Foam
Jeffol G31-28	30	30	30	30
TegoAmin 33	0.1	0.1	0.1	0.1
TegoAmin BDE	0.1	0.1	0.1	0.1
TegoStab B8727 LF2	0.15	0.15	0.15	0.15
Water	1	1	1	1
Commercial Biochoice Lignin		5.7		
Dried Biochoice Lignin			5.7	
*pH modified Biochoice Lignin				5.7
Suprasec 7507	20	20	20	20

Table 2: Flexible foam formulation used for the FTIR analysis. The polyol phase was modified, removing the diol, to simplify spectra analysis.

Foam Rising Measurement

Foam rising was recorded using a Foamat system from Format Messtechnik. The mix was performed in disposable cups, at ambient temperature. The mixing time was fixed at 15 s and the recording time was up to 10 min. The data were analysed using the FOAM software. The reported and analysed data in this

study are the maximum height (mm), the final height (mm) and the maximum foaming velocity (mm/s). These are presented in details in the results section and are the basis of the following discussion. In addition, rise time (s), gel time (s), shrinkage (%) and density (kg/m^3) were also recorded. The data were gathered in Table 3.

	Rise Time	Gel Time	Shrinkage	Density
	s	s	%	kg/m^3
Reference Foam	64 ± 5	115 ± 12	7 ± 2	54 ± 2
Virgin Lignin Foam	116 ± 8	440 ±35	60 ± 14	166 ± 12
Dried Lignin Foam	164 ± 11	350 ± 25	9 ±3	78 ± 4
pH 4.0 Mod Lignin Foam	165 ± 9	275 ±17	8 ± 3	80 ± 4
pH 4.5 Mod Lignin Foam	95 ± 7	151 ± 12	7 ± 2	75 ± 5
pH 6.0 Mod Lignin Foam	84 ± 8	135 ± 13	6 ± 4	74 ± 3
pH 6.6 Mod Lignin Foam	80 ± 10	128 ± 26	8 ± 3	72 ± 3
NaOH-Treated Lignin 0h Foam	71 ± 5	182 ± 15	44 ± 9	130 ± 11
NaOH-Treated Lignin 2h Foam	74 ± 7	184 ± 21	30 ± 17	110 ± 9
NaOH-Treated Lignin 6h Foam	88 ± 11	225 ± 12	19 ± 3	97 ± 7
NaOH-Treated Lignin 24h Foam	85 ± 9	230 ± 18	10 ± 2	90 ± 6
NaOH-Treated Lignin 48h Foam	80 ± 12	305 ± 27	33 ± 6	125 ± 11

Table 3: Rise time, gel time, shrinkage and density of the foam produced during this study.

Foam Curing Measurement

Foam curing was recorded using a SubCase system from Format Messtechnik, relying on the dielectric constant of the foam. The mix was performed at ambient temperature. The mixing time was fixed at 15 s and the recording time was up to 10 min. The data were analysed using the SUBCASE software. The reported data in this study are the pot life time (90% of maximum D, Dielectric displacement), the curing time (25% of minimum D', derivative of Dielectric displacement) and the foam temperature.

Fourier Transform Infrared (FTIR)

FTIR analysis was performed using a Nicolet iS50R FT-IR from ThermoScientific, equipped with a DTGS detector and a Polaris Infra-Red source. Static spectra were acquired on MIRacle diamond ATR from PIKE, 64 scans at a resolution of 4 nm. Series were acquired on a Golden Gate diamond ATR from Specac, 8 scan per spectrum at a resolution of 4 nm. The spectra were analysed using OMNIC software from ThermoScientific. Initial isocyanate consumption % was calculated by measuring the reduction of the isocyanate band (2270 cm^{-1}) during the first minute of reaction. Carbonyl bands, 1730 cm^{-1} (free urethane), 1710 cm^{-1} (hydrogen bounded urethane) and 1670 cm^{-1} (urea), formation rates were calculated by measuring their corresponding band intensity evolution during the first minute of reaction. All the spectra were normalized using the 1600 cm-1 asorption band, corresponding to the isocyanate aromatic rings.

Scanning Electron Microscopy

Scanning Electron Microscopy was performed on a Hitachi S-4700 microscope. The foam samples were razor blade prepared and platinum coated prior to observation. Measurements on the micrographs were performed using the ImageJ software from National Institutes of Health (open source).

Results

Lignin Influence on Foaming

The first step of this study was the assessment of the commercial virgin lignin influence on blowing and gelling chemistry. To do so, free rising experiments were performed with various lignins, virgin lignin as received (pH 2.5), dried lignin (similar pH) and pH modified lignin (pH 6.6, dried) and compared to a reference lignin free foam. The formulation was kept exactly the same for all the foams, and the amount of lignin added represent 10% of the total weight.

Figure 3. A. shows the maximum rising velocity recorded during the foaming. This rise roughly happens during the first minute of the process due to the formation of CO_2 and slowdowns as there is less isocyanate available for this formation and also due to cell coalescence. Although, the rise is mostly the result of the carbon dioxide degassing during the isocyanate reaction with water it also requires some viscosity build-up through polymerization (to restrain the cell coalescence). Lignins negatively impact this rise. Interestingly, the negative impact varies a lot depending on the lignin type. The most significant impact comes from the Virgin Lignin. In that case, the velocity is drastically reduced by 85% as compared to that of the reference foam. Just by drying the lignin, this impact is reduced to 50%, and by modifying the pH (6.6), to 30%.

As shown in figure 3. B., a similar impact can be observed on the maximum and final height of the foam. Maximum height represents the height at which there is no further increase. It can be speculate that the foam reaches a temporary equilibrium between the formation of CO_2, the growth of the cell by exotherm created by the chemical reactions involved in the process and the cell collapse. The final height represents the volume taken by the foam after complete reaction (blowing and gelling). This height is systematically lower as cell collapse and cell shrinking due to the temperature decrease surpass the cell growth. The final height of the foam is reduced by 35% in presence of Virgin Lignin, 15% in presence of Dried Lignin, 7% in presence of pH modified Lignin. In addition, the observe relapse is significantly more important in the case of the Virgin Lignin (30%) than in the case of Dried Lignin (5%), pH modified Lignin (7%) or the reference foam (4%).

Such evolution of the reactivity shows the following points:

- A low pH tends to slowdown the foaming process, which involves urea formation and carbon dioxide degassing and also urethane formation (polymerization).
- Crosslinking, due to urethane formation, may also be negatively impacted by the pH, as relapse is also increased.
- Humidity in the lignin may promote the protonic exchange and amplifies the previous effects.

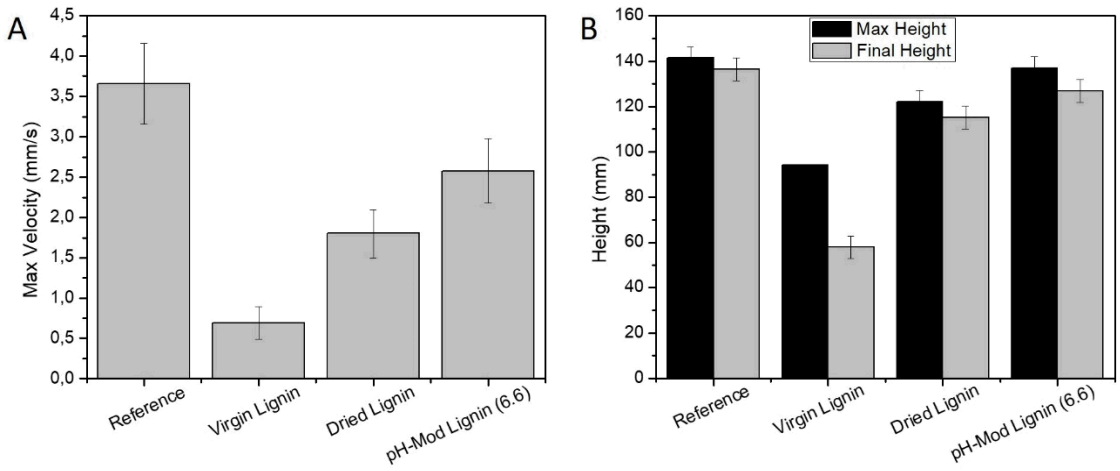

Figure 3: Foaming properties of Reference (no lignin), Virgin Lignin based, Dried Lignin based and pH-Modified Liginin based (pH 6.6) foams. A) Maximum foaming velocity, B) Maximum and final foaming height.

Lignin Influence on Gelling

Figure 4 focuses on the gelling properties of the foams, that is to say, the PU polymerization reaction. Pot life and Curing time are obtained by measurement of the dielectric constant of the sample and are presented in figure 4. A. Pot life is defined as the time at which the dielectric displacement D drops by 10 % (90% of maximum D), when the rise of viscosity is significantly too high for pre-reaction handling (good mixing). Curing time is defined as the time at which D' (derivative of D) reaches 25% of its minimal value. This curing time is supposed to represent the moment at which the foam approaches its final form by polymerization. Interestingly, those two parameters are greatly impacted by the addition of Virgin Lignin (they are roughly multiplied by 4) while Dried Lignin does not seem to disturb so much the polymerization. Pot life only increases by 10% and curing time by 30% compared to the reference foam, without lignin. Even more interesting, pH modified Lignin (6.6) do not have any significant effect.

As the blowing and gelling reactions are both exothermic, the temperature is expected to significantly rise during the process. Similar assessment can be performed by analysing the foam temperature. At similar volume of the material mixtures prior to foaming, the maximum internal temperature for those foams is presented in Fig 4. B. A rise of almost 30 °C is observed in the reference foam (from 20 to approximatively 50 °C). The addition of Virgin Lignin clearly limits this temperature rise, only 20 °C, demonstrating that the reactivity is reduced. Again, the negative impact on reactivity is diminished with Dried Lignin (25 °C) and cancelled with pH corrected Lignin.

So, similarly to the foaming, the gelling reaction is impacted by the presence of acid in lignin, but the humidity trapped into the lignin seems to aggravate this influence.

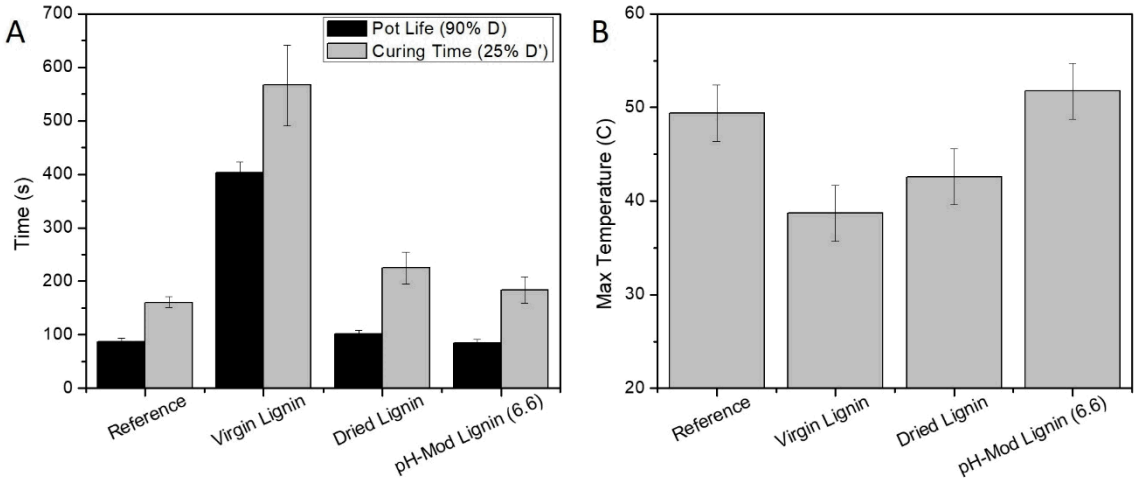

Figure 4: Gelling characteristics of Reference (no lignin), Virgin Lignin based, Dried Lignin based and pH modified Lignin based (pH 6.6) foams. A) Pot life and curing time, B) Maximum recorded temperature.

FTIR Static Analysis

Figure 5 shows FTIR spectra of the lignins and the resulting foams. Figure 5. A represents the Dried Lignin and the pH modified lignin (pH 6.6). The area between 2500 and 2000 cm^{-1}, mostly noise due to the cut-off of the diamond ATR was removed for clarity. The attribution can be described as follow[51]:

- The broad band between 3680 and 3100 cm^{-1} can be assigned to O-H hydroxyls, including aliphatic and phenolic ones.
- The bands comprised between 3000 and 2800 cm^{-1} correspond to the C-H of the lignin skeleton.
- The band at 1705 cm^{-1} belongs to C=O stretching in carbonyl/carboxyl.
- The bands at 1600, 1515 and 1426 cm^{-1} belong to the aromatic skeleton.
- The band at 1462 cm^{-1} corresponds to the C-H deformation combined with the aromatic vibration.
- The following set of bands: 1270 cm^{-1} (G ring and C=O stretch), 1140 cm^{-1} (C-H in plane deformation), 854 and 817 cm^{-1} (C-H out of plane deformation) are characteristic of the guaiacyl unit (from coniferyl alcohol monomer). This lignin is from softwood southern pine species so the guaiacyl unit is the predominant composition.
- The 1370 cm^{-1} band belongs to OH and aliphatic C-H in methyl groups.
- The 1215 cm^{-1} band originated from the superposition of C-C, C-O and C=O stretching bands.

The comparison between the spectra of the Dried Lignins before and after the pH correction shows no difference. They are perfectly superimposable. This demonstrate that the correction does not modifies the structure of the lignin nor removes specific content (such as a lower molecular weight lignin portion or other compositions presented in lignin) but only modifies the pH.

Figure 5. B. shows the spectra of reference foams obtained from the two polyol formulations used in this study (Jeffol and Multranol mix) and a Multranol based foam including 10 % of Virgin Lignin. The attribution can be described as follow:

- The 3480 cm^{-1} band belongs to O-H stretching.

- The two superposed bands centered at 3300 cm^{-1} belong to the urea and urethane N-H groups stretching.
- Asymmetric and symmetric C-H stretching vibrations of the CH_2 backbone are visible at 2970 and 2870 cm^{-1} respectively.
- A small band at 2260 cm^{-1} resulting from remaining N=C=O.
- The 1740-1640 cm^{-1} massive gathers all the C=O stretching (1730 cm^{-1} free urethane, 1710 cm^{-1} hydrogen bonded urethane, 1670 cm^{-1} urea).
- The 1600 cm^{-1} band corresponds to the aromatic rings of the isocyanate part.
- The 1510 cm^{-1} band belongs to N-H deformation.
- The 1535 cm^{-1} band is an aggregation of the C-N stretching and N-H bending vibrations.
- The 1410 cm^{-1} is another C-N stretching vibration band.
- Finally, the 1090 cm^{-1} band is an aggregation of all the C-O-C stretching vibrations in the network.

Looking at the comparison of the three spectra, it is clear that they are really similar due to the very similar structure of the two polyol mix (propylene oxide based, low functionality polyols), the final structure of the two systems being almost identical at this scale. Also, the fact that the lignin itself is not visible in those spectra shows that, there is no real miscibility between the lignin and the polyurethane system. The lignin barely reacts and is mainly a filler, being encapsulated in the polyurethane. If any reaction happened between the lignin and the isocyanate, this only occurred at the surface of the encapsulated lignin particles, and is not detectable by infrared. The impact on reactivity cannot be linked to any replacement of polyol by lignin, but only interferences as demonstrated earlier.

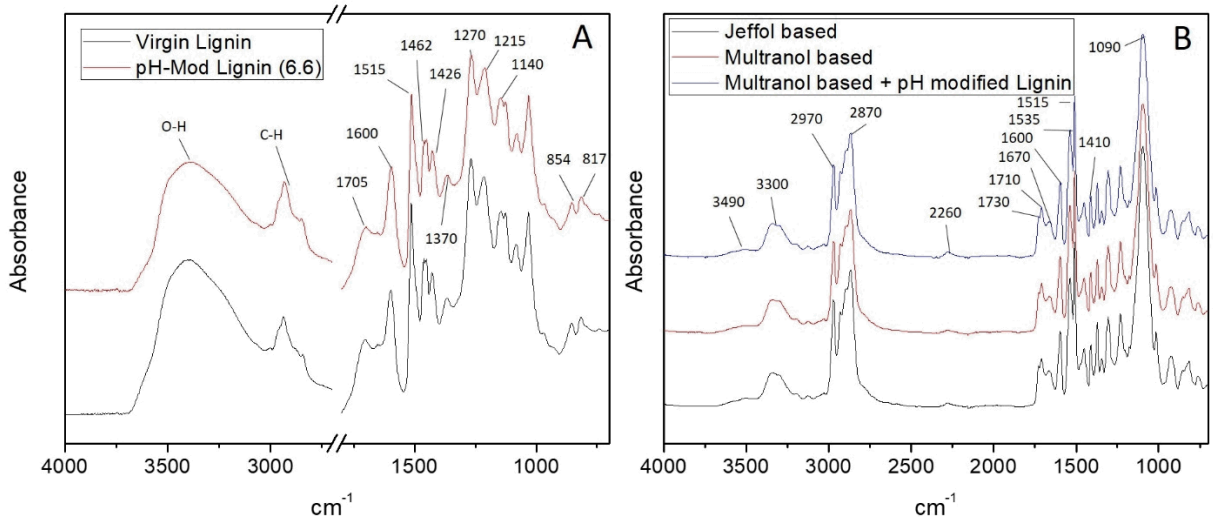

Figure 5: Absorbance FTIR spectra of A) Dried Lignin and pH modified Lignin (pH 6.6), and B) Jeffol G31-28 based, Multranol (9138 and 9190) based, and Multranol (9138 and 9190) and pH modified Lignin based foams.

FTIR Dynamic Analysis

Finally, Figure 6 focuses on the detailed reactivity during the foams formation observed *in situ* by FTIR. In this part of the study, the formulation of the polyol phase was slightly modified. Initially, the combination of the two polyols was selected to be representative of an industrial formulation, in which the triol

(Multranol 9139) creates the network and the diol (Multranol 9190) introduces more flexibility while also reducing the polyol phase viscosity (two important factors when introducing lignin). Unfortunately, The two types of hydroxyls (from the triol and diol), not having exactly the same FTIR signature, tended to broaden the bands and to make the interpretation more difficult. So the polyol phase chemistry was modified by removing the diol to simplify the FTIR analysis. The triol used is in this part (Jeffol 31-28) is similar to the triol used in the rest of the study (Multranol 9139), and the isocyanate index (isocyanate-hydroxyl ratio) remains unchanged.

Two aspects are analysed, the isocyanate consumption and the urethane/urea bonds formation. The first one, isocyanate consumption, is presented in figure 6. A. and is expressed as % loss per min. This value is obtained by calculating the decrease of the isocyanate band (2270 cm-1) during the first minute of reaction, as the consumption is linear on this range of time (the drop in isocyanate concentration starting to slow down the reactivity after 1 min). This consumption can either fuel the urethane formation (reaction with polyol), the urea formation (reaction with water) or both. Without the presence of lignin, the average value is above 25%. Similar value is obtained with a pH modified Lignin. However, this value drops below 20% with Dried Lignin (pH 2.5), and reaches 5% with Virgin Lignin, indicating the general reactivity of the isocyanate is hindered in the presence of virgin and dried acidic lignin.

Figure 6. B. exhibits the intensity growth rate of the 1730, 1710 and 1670 cm^{-1} absorption bands (respectively free urethane, hydrogen bonded urethane and urea) during the first minute. Two details can be noted. First, the addition of pH modified Lignin tends to slightly increase the amount of free urethane bounds but to reduce the amount of hydrogen bounded urethane bounds. This can be speculated that if this lignin has only a low impact on the reactivity in that case, the structure of the crosslinked network is disturbed (less internal phase separation), which will greatly impact the final properties (stiffer foam). Second, but more spectacular, the Virgin Lignin (35% of water content) reduces significantly the urethane formation as well as inhibits the urea and CO_2 formation. Thus, the biggest impact of the acidity in lignin is definitively on slowing down the blowing process.

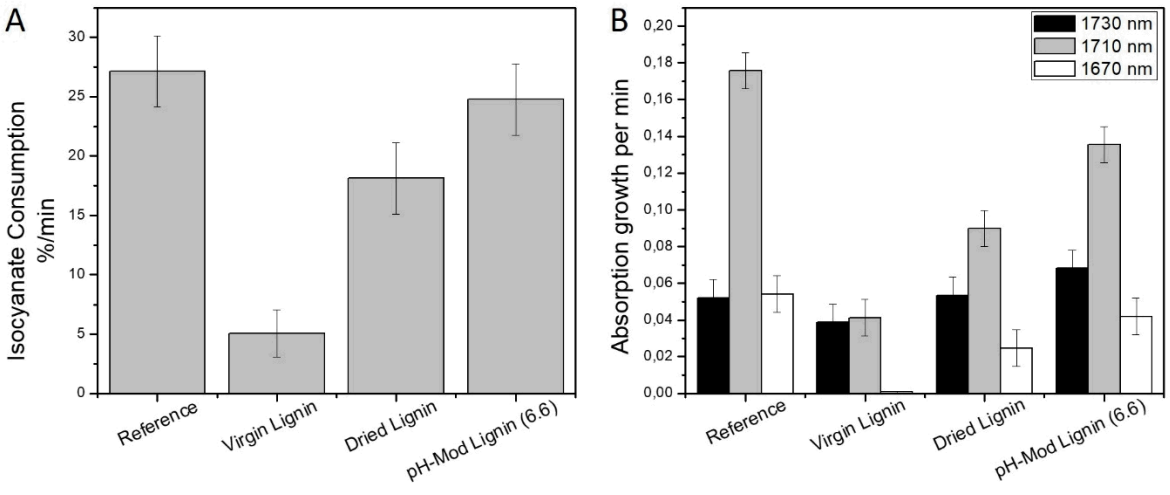

Figure 6: FTIR reactivity analysis. A) Isocyanate consumption (%/min) calculated by the decrease of the isocyanate band (2270 cm^{-1}) during the first reaction minute, B) Formation rate of the carbonyl bands (1730, 1710 and 1670 cm^{-1}) calculated by the bands absorption rise during the first reaction minute.

Foam Microstructure

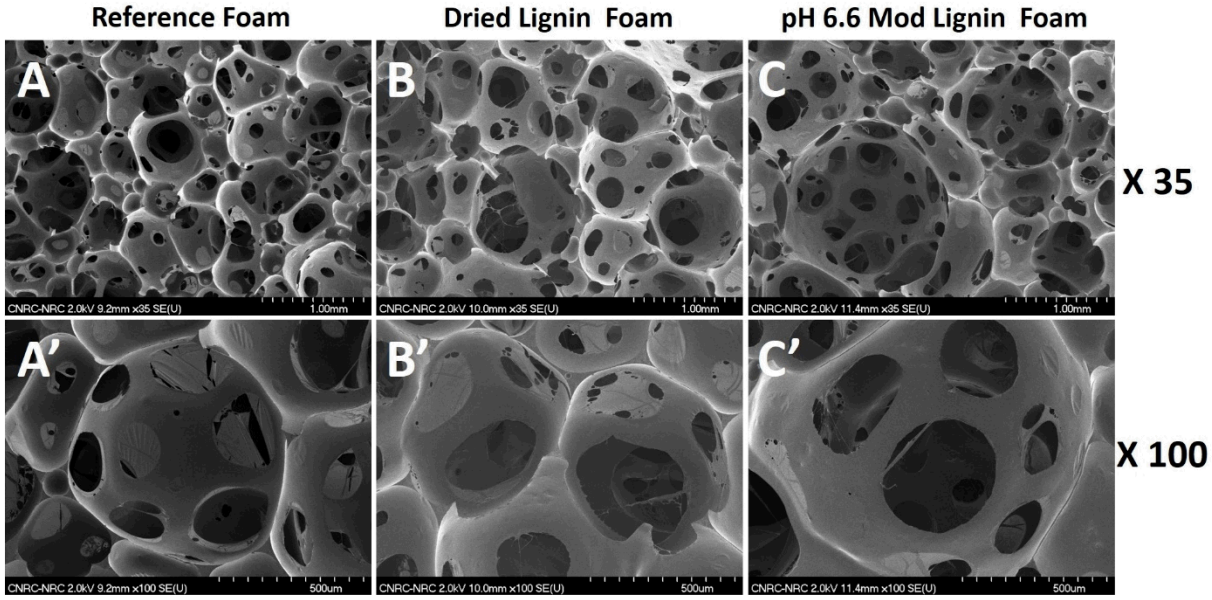

Figure 7: Scanning Electron Microscopy micrographs of Reference Foam (A, A'), Dried Lignin Foam (B, B') and pH 6.6 Mod Lignin Foam (C, C'), acquired at 35X (A, B, C) and 100X (A', B', C') magnification.

Figure 7 exhibits scanning electron microscopy pictures obtained from Reference Foam, Dried Lignin Foam and pH 6.6 Mod Lignin Foam. Comparison of 35x magnification micrographs shows very similar cellular structures for all foams. General cell sizes stay very close (610 µm for Reference Foam, 750 µm for Dried Lignin Foam and 730 µm for pH 6.6 Mod Lignin Foam). The main difference is the homogeneity of the cells, the standard deviation being doubled by the presence of lignin (from 105 µm for Reference Foam to 195 µm for Dried Lignin Foam and 250 µm for pH 6.6 Mod Lignin Foam). This could be explained by two phenomena, cell walls collapsing during early stage of foaming caused by the presence of lignin particles and delaying of the cell nucleation step. The lower reactivity of the foaming will enlarge the cell nucleation widow, allowing the cohabitation of cells with more varied "ages".

100x magnification micrographs show that the fine structure of the cell is not affected by the lignin presence. As observed by static FTIR, the lignin is not present at the surface. The lignin particles are barely visible, encapsulated in the cured resin, mostly in the network nods.

Preliminary pH Correction

Previous results demonstrated that bringing lignin close to pH neutral can limit its negative impact on the polyurethane reactivity. To better understand this improvement, foams were produced using dried lignin of various controlled pH, from 2.5 (initial virgin lignin) to 4, 4.5, 6 and 6.6. The foaming was recorded using Foamat system and the curves are reported in Figure 8. To begin, at very low pH (2.5), the lignin has various negative impact. First, its presences delayed the foaming for 30 s, while the reference foams without any delay. Second, the blowing speed is slowed down in comparison to the reference, as visible by the initial slope of the curve. Then, the foam cannot reach the same height as the reference (max of 115 mm, against 140 mm). Finally, the foam completely collapses as the polymerization is not advanced enough to prevent the cell coalescence during the degassing. Increasing the pH to 4 reduces the initial

delay and the collapse, but neither the maximum height nor foaming speed are improved. At a pH of 4.5, initial delay is eliminated while the maximum height is significantly increased and the foaming speed improved. Above pH 4.5, results are not modified except the foaming speed continues to increase slowly. So, the breaking point at which the pH has a catastrophic impact on the foaming is below 4.5.

It can be noted that as the formulation was not modified in that case, the foams including lignin never reach the same height or foaming speed as the reference. This is due to variations of the medium viscosity and accessibility of the reacting sites. The resulting foams are denser and stiffer. The formulation can be optimized by modifying the catalysts, surfactants and foaming agent mixture to readjust the foaming process in order to reach similar density and properties. However, this is not part of this study.

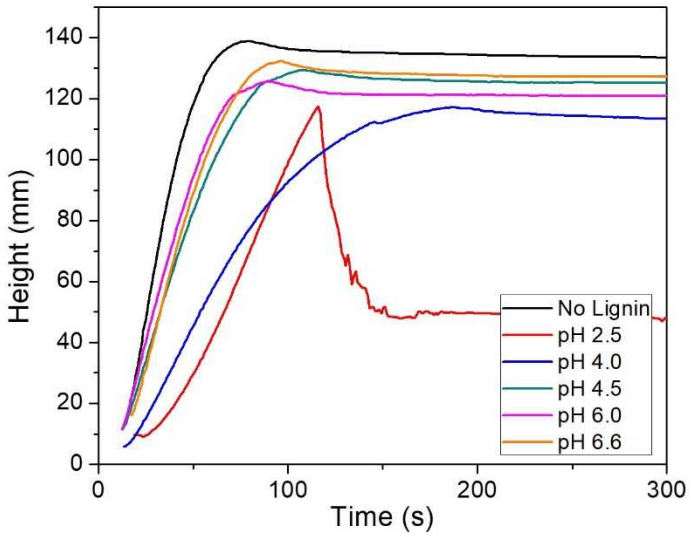

Figure 8: Foam rising of flexible foams with preliminary pH correction. The foam formulations are similar in every cases. Reference foam contains no lignin, while the lignin foams containing 10 wt.% of dried lignin with pH=2.5, pH = 4, pH = 4.5, pH = 6 and pH = 6.6 foams.

Polyol Phase pH Correction

The pH of the lignin is a drawback from the extraction process. A low pH is used to precipitate the lignin during the black liquor treatment step in the pulp and paper industry, and obtained by using sulfuric acid. The unpurified Kraft lignins often have this low pH. Performing the correction on a lignin requires to disperse it in water and to adjust the pH with a basic chemical (like sodium hydroxide). Then, the lignin has to be dried again. When pH above 4 lignin has more affinity with water so it leads to lower yield. This is a time and energy consuming and expensive process which will dramatically increase the price of the lignin, making it a less attractive filler.

A better option would be to perform the pH adjustment directly in the foam preparation step. The chemical foaming process offers a great opportunity, as it uses water as foaming agent via its reaction with isocyanate. This water, usually of neutral pH, could be used as a media for pH adjustment. A simple way to do so would be to replace this neutral water by a sodium hydroxide basic solution. This approach was tested and the results are exposed in Figure 9. This graph exposes the growing of the foam along the

reaction. The Virgin Lignin curve is the base foam produced with Virgin Lignin and water. In all the other curves, the water was replaced by a 10% NaOH solution. The difference between the curves is the exposure time allowed the interaction between the basic solution and all the foam ingredients except isocyanate. The polyol, the lignin and the solution were mixed together in a mechanical mixer and let to set for 0, 2, 6, 24 and 48 h prior to foaming.

As expected, this modification improves the reaction, but not as efficiently as the pH adjustment in aqueous solution described above. With water, the foaming is slow and the foam completely collapses. With the use of NaOH solution at 0 h, the foaming is accelerated (change in the initial slope), but the foam still exhibit a retraction close to a complete collapse. After 2 h, the foaming is similar, but the retraction is reduced. Increasing the exposure time will have two effects, slowing down the reaction, and reducing the regression (higher foam), with a maximum at 24 h. At 48 h, the retraction is increased again, close to a collapse.

The behavior observed can be explained by the fact that as the complete process relies on both the urea reaction (isocyanate and water, leading to forming CO_2 and foaming) and the urethane reaction (isocyanate and polyol, leading to polymerization and crosslinking). Both reaction are deactivated by the presence of acid in the lignin as discussed earlier. Adding the sodium hydroxide solution will help both reactions, but not at the same rate. Urea formation is the first to be reactivated. The rising is observed, but the crosslinking is still too slow to prevent the cell collapse. Increasing the exposure time to the sodium hydroxide slowly improves the crosslinking because it provides more time for alkali to neutralize the acid in lignin, but another phenomenon tends to promote collapsing. Two possibilities were identified. First, the sodium hydroxide could be damaging the polyol phase, by reducing the molecular weight through hydrolysis (polypropylene oxide based, sensitive to basic solution). This would tend to reduce the overall viscosity of the foaming thus facilitating the cell collapse. This impact would become predominant for longer NaOH exposure. Second possibility, the lignin slowly solubilizes in the aqueous solution (at pH of 7 and above, lignin is water soluble). In this situation, the physical chemistry of the whole medium would be modified, as the solubilized lignin phase, highly hydrophilic, would not be miscible with the hydrophobic polyol phase. The reactivity of the system would be then disturbed.

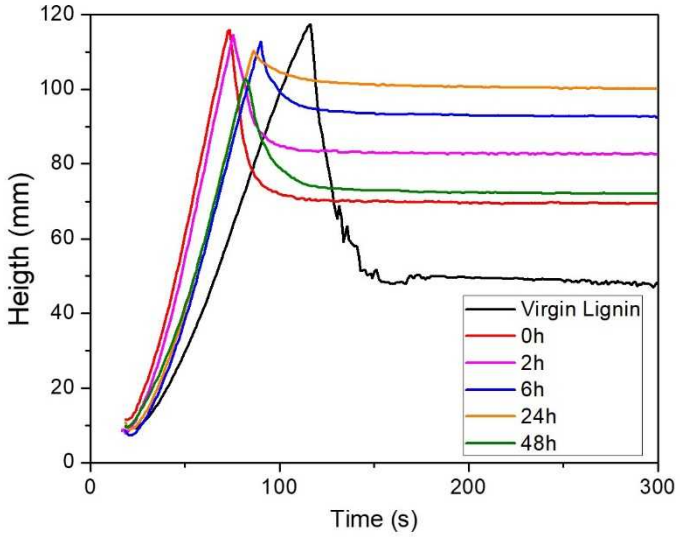

Figure 9: Impact of NaOH as pH correction in situ. Reference foam contains water as blowing agent, while other foams contain 10% NaOH solution as blowing agent. Exposition time allowed to interact between blowing agent and polyol phase varies from 0 h (immediate foaming) and 48 h.

Discussion

To summarize

The core information which can be extracted from the results are the following:

Direct impact of the lignin:

- Interaction with catalysts, water and possibly surfactant thus hindering the interactions between reactive sites.
- Modification of the internal phase separation of the network (switch from hydrogen bounded urethanes to free urethanes, as shown by *in situ* FTIR results).
- Possible water absorption into lignin during the mix, thus resulting in less water available for reaction with the isocyanate → limiting the foaming.

Impact of lignin pH:

- Slowing down of both blowing and gelling reactions.
- More significant impact on urea formation (blowing).
- Acceptable reactivity for pH of 4.5 and above.
- Direct aqueous correction using sodium hydroxide first restore the blowing reaction, then the gelling reaction.

Impact of humidity

- Greatly promotes the pH impact, catastrophically reducing the blowing and gelling reactions.

Mechanism of Deactivation

In light of the results described above a simple mechanism for the deactivation can be proposed. This mechanism is directly linked to the catalysis of the reactions. For this reason, the catalysis mechanisms has to be explained first.

In the present study, both reactions, gelling and blowing, are catalysed by tertiary amine molecules. The exact behavior of each catalyst is little bit different, but their general purpose is to form a complex with a potential nucleophilic reagent, which could be the polyol or the water. The catalyst itself interacts with the terminal hydrogen, unbalancing the O-H covalent bound. The oxygen is then made more nucleophilic and reaches for the carbon of the isocyanate function. The triethylenediamine, with a very characteristic cage like structure, mainly targets the terminal hydroxyls of the polyol. As soon as the nucleophilic attack is completed, the catalyst returns the trapped hydrogen to the resulting secondary amine, finally completing the urethane bound formation. In the other hand, the Bis(2-(Dimethylamino)ethyl)ether, almost exclusively targets the water molecules. This is due to the specific shape of this catalyst, able to complex the water molecules, one hydrogen being trapped by the amine terminated “moving arms” and the other hydrogen forming a hydrogen bound with the central oxygen of the catalyst. The complex, exhibiting a highly nucleophilic oxygen, then reacts with the isocyanate, but the resulting molecule not being stable, the carbon dioxide is release and a highly reactive primary amine is formed. The primary amine, being naturally very nucleophilic, reacts with another isocyanate to form a urea bound (with possible support of the catalysts in the medium).[2,56,57] The mechanisms are schematized in Figure 10. This catalyst combination was selected as it is representative of industrial application, but also because it separates the two reactions relatively well. Each catalyst targeting mainly one kind of molecule. Other combinations exist, including the synergetic effect of amine and tin catalyst, but as they are less selective, the mechanism would have been more difficult to analyse.

Unfortunately, those nucleophilic catalysts can be sensitive to the overall pH of the medium. The presence of protons of H_2SO_4 (a strong Brønsted-Lowry acid) in the lignin interact with water to form hydronium ions (H_3O^+). Those ions can be trapped by the catalysts, but the resulting complex is paradoxically more stable than the ones made with polyol or water, and don’t seek the reaction with the isocyanate (excess of proton killing nucleophilic reactions). The same situation can happen with the polyols. But, as the water itself is poorly miscible with the polyols (hydrophobic), the protonation of the polyol hydroxyls is slower than the protonation of water. That is probably why the foaming reaction, which depends on the interaction with water, is more affected than the gelling reaction. For the same reason, this is why, when mixed with sodium hydroxide, the foaming reaction correction is almost instantaneous (immediate pH correction in the aqueous phase), when the gelling reaction correction (deprotonation of the polyol hydroxides) requires more time.

Other hypotheses could be 1) catalysts migration into the lignin particles, reducing their efficiency for the reactions of isocyanate and/or 2) lignin has aliphatic hydrocarbon that can interact with surfactant that reduces its efficiency in preventing bubble collapse.

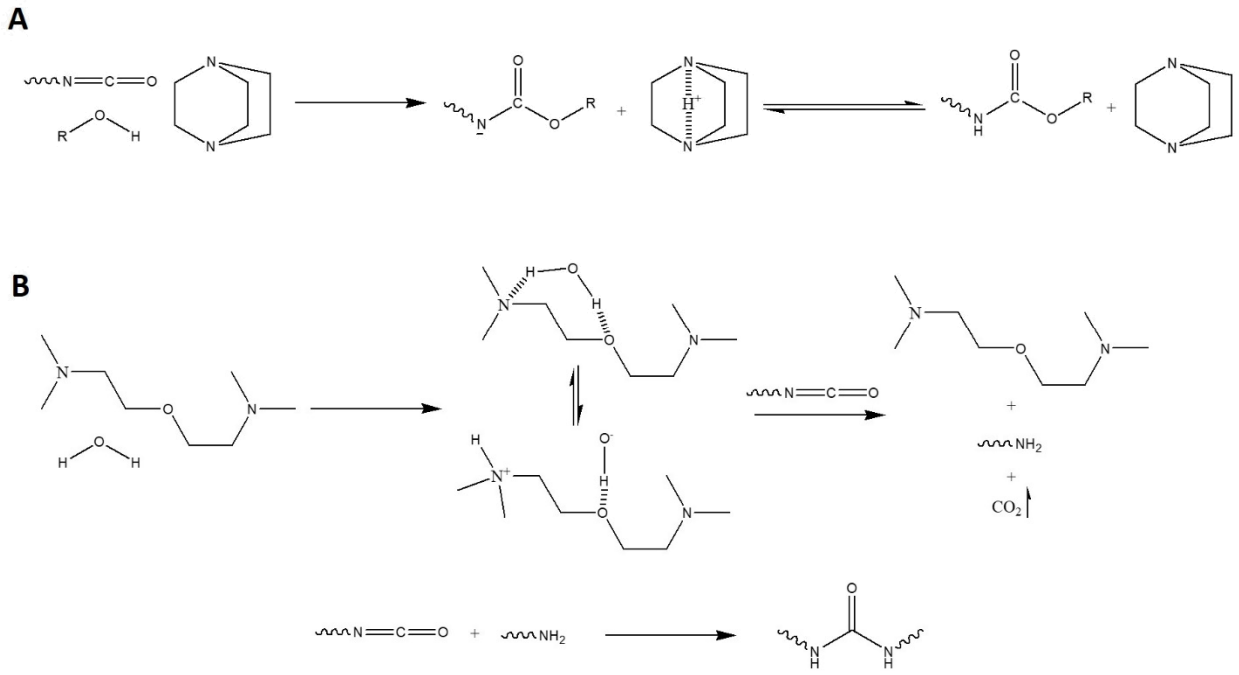

Figure 10: Mechanisms of catalysis of A) Triethylenediamine for urethane formation; B) Bis(2-(Dimethylamino)ethyl)ether for the urea formation.

Influence of Mositure

One of the most surprising observation is the fact that humid lignin (35 % of humidity) is spectacularly more damaging for the reactions than dried lignin, even without pH correction. This is unexpected for three reasons. First, the water in lignin should feed the reaction with isocyanate to form CO_2 and urea. So, introducing a moist lignin should accelerate this reaction. Second, the more water we have in the lignin powder, the less pure lignin is introduced (as the lignin is introduced by weight, including the water). Finally, a dried lignin should absorb the water, limiting its reaction with the isocyanate, a behaviour that moist lignin should less exhibit. But surprisingly, the exact contrary is observed.

The proposed explanation is relatively simple. When a dried lignin dispersed in the polyol is in contact with water, this one will be absorbed and not released until saturation of the lignin. The acidity trapped in the lignin is still confined in it, as the lignin is not soluble in the polyol directly and the water getting in is not able to get out. On the other hand, at 35% of moisture, the lignin is at an equilibrium. When an already water saturated lignin introduced in the polyol is in contact with water, this one can exchange with the highly acidic water already trapped inside. In that case, the acidity of the lignin can propagate quickly in the mix and disturb the reactivity. This is why humidity, when combined with acidic lignin (synergic effect), is the most challenging factor for the foam production.

Correcting the pH

Two approaches were proposed in this study to modify the lignin pH. The first one, quite efficient, requires an additional preliminary process. The lignin has to be submerged in water, the pH of the solution adjusted with sodium hydroxide, then the lignin is extracted and dried. The final results shows that for lignin treated that way, most of the negative impact are corrected. Only few adaptations of the formulation (addition

of more water to counteract the lignin absorption during the mix) would be required to obtain an optimal foam. Unfortunately, such a pre-treatment is unlikely to be performed in the industry, as already explained.

Unfortunately, the direct NaOH treatment using the water intended to act as blowing agent as a media for sodium hydroxide is not as efficient. If the correction of the blowing reaction is clear and almost instantaneous, the one of the gelling requires a long exposure time (24h). In addition, a too long exposure time results in a new unexpected collapsing behavior. Other approaches could be imagined, as the introduction of a dried alkaline agent in the lignin powder which would dissolve in contact with water to equilibrate the pH from the lignin. Such experiments were tried without any conclusive results yet. Further studied will be done in that way. Another option would be the use a direct process prior to the introduction, preferably continuous and not in any wet condition (water or solvent).

Conclusion

Introduction of lignin in flexible foams is a great opportunity to introduce a renewable content in an unfortunately still 100% petroleum based commodity product. If the specific chemistry of the lignin opens a lot of options for modifications, depolymerisation or functionalization, such chemistry is too expensive for the industry. However, even not miscible in most of the flexible foams polyols, the lignin particles are still finely dispersible and can be used as efficient fillers. The main issue with this appealing option is the reaction disturbance brought by the lignin acidity.

The present study worked on unveiling the exact impact of this acidity on the two main reactions involved in flexible foams formation. The mechanism of the catalysts deactivation was elucidated, and the aggravating action of the lignin moisture was identified. Relying on the present analysis, various options can be proposed to further improve the production of lignin based flexible foams. The most obvious one, already tested and approved in this study, is the drying of the lignin, which avoid the synergic impact of pH and moisture. Then, knowing that dried lignin will greatly absorb the added water, increasing the amount of this blowing agent should compensate. Other catalyst combinations, less selective to specific reactions, i.e. amine with tin catalysts, could also be tested.

Finally, new cost-effective options have to be developed to reduce the acidity of the lignin. The two approaches described in the present study did not fulfill all the requirements in terms of cost-effectiveness and practical operation. A preliminary treatment in suspension in water is efficient, but not adapted to the production model. The simple pH modification through the added water is more adapted, but not as efficient and more complex to control. Regarding the production model, the best approaches would be either a dry additive premixed with the lignin powder which would be activated in contact with water, or a simple preliminary treatment, preferably in dry state, applicable by the resin provider or the foam producers. Such options will be tested in future work.

Acknowledgments

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Bibliography

1. Ionescu, M. *Chemistry and Technology of Polyols for Polyurethane*; RAPRA Technology Ltd, **2005**; Vol. 2.

2. Humbert, H. H.; Zimmerman, R. L.; Walker, M. In *Catalysts in Polyurethane Foams: A One-day Seminar*; RAPRA Technology Ltd, **1997**; pp 1.

3. Mahmood, N.; Yuan, Z.; Schmidt, J.; Xu, C. *Renew. Sustain. Energy Rev.* **2016**, *60*, 317.

4. Luo, X.; Xiao, Y.; Wu, Q.; Zeng, J. *Int. J. Biol. Macromol.* **2018**, *115*, 786.

5. Zou, X.; Qin, T.; Wang, Y.; Huang, L.; Han, Y.; Li, Y. *Bioresour. Technol.* **2012**, *114*, 654.

6. Thébault, M.; Pizzi, A.; Dumarçay, S.; Gerardin, P.; Fredon, E.; Delmotte, L. *Ind. Crops Prod.* **2014**, *59*, 329.

7. Blattmann, H.; Lauth, M.; Mülhaupt, R. *Macromol. Mater. Eng.* **2016**, *301*, 944.

8. Santiago-Medina, F. J.; Basso, M. C.; Pizzi, A.; Delmotte, L. *J. Renew. Mater.* **2018**, *6*, 413.

9. Lee, Y. J.; Park, C. K.; Kim, S. H. *Polym. Compos.* **2016**, *2016*, 1.

10. Carriço, C. S.; Fraga, T.; Pasa, V. M. D. *Eur. Polym. J.* **2016**, *85*, 53.

11. Tavares, L. B.; Boas, C. V.; Schleder, G. R.; Nacas, A. M.; Rosa, D. S.; Santos, D. J. *Express Polym. Lett.* **2016**, *10*, 927.

12. Bernardini, J.; Cinelli, P.; Anguillesi, I.; Coltelli, M. B.; Lazzeri, A. *Eur. Polym. J.* **2015**, *64*, 147.

13. Ji, D.; Fang, Z.; He, W.; Luo, Z.; Jiang, X.; Wang, T.; Guo, K. *Ind. Crops Prod.* **2015**, *74*, 76.

14. Hou, C.; Czubernat, K.; Jin, S. Y.; Altenhof, W.; Maeva, E.; Seviaryna, I.; Bandyopadhyay-Ghosh, S.; Sain, M.; Gu, R. *Int. J. Fatigue* **2014**, *59*, 76.

15. Campanella, A.; Bonnaillie, L. M.; Wool, R. P. *J. Appl. Polym. Sci.* **2009**, *112*, 2567.

16. Zhang, L.; Jeon, H. K.; Malsam, J.; Herrington, R.; Macosko, C. W. *Polymer (Guildf).* **2007**, *48*, 6656.

17. Huo, S.; Wu, G.; Chen, J.; Liu, G.; Kong, Z. *Korean J. Chem. Eng.* **2016**, *33*, 1088.

18. Lan, Z.; Daga, R.; Whitehouse, R.; McCarthy, S.; Schmidt, D. *Polymer (Guildf).* **2014**, *55*, 2635.

19. Bryśkiewicz, A.; Zieleniewska, M.; Przyjemska, K.; Chojnacki, P.; Ryszkowska, J. *Polym. Degrad. Stab.* **2016**, *132*, 32.

20. de Avila Delucis, R.; Magalhães, W. L. E.; Petzhold, C. L.; Amico, S. C. *J. Appl. Polym. Sci.* **2018**, *135*, 1.

21. Kosmela, P.; Hejna, A.; Formela, K.; Haponiuk, J. T.; Piszczyk, Ł. *Cellulose* **2016**, *23*, 2929.

22. Yamada, T.; Ono, H. *Bioresour. Technol.* **1999**, *70*, 61.

23. Thébault, M.; Pizzi, A.; Essawy, H. A.; Barhoum, A.; Van Assche, G. *Eur. Polym. J.* **2015**, *67*, 513.

24. Peng, Y.; Zheng, Z.; Sun, P.; Wang, X.; Zhang, T. *New J. Chem.* **2013**, *37*, 729.

25. García, D. E.; Glasser, W. G.; Pizzi, A.; Paczkowski, S.; Laborie, M. P. *Eur. Polym. J.* **2015**, *67*, 152.

26. Rajesh Banu, J.; Kavitha, S.; Yukesh Kannah, R.; Poornima Devi, T.; Gunasekaran, M.; Kim, S.-H.;

Kumar, G. *Bioresour. Technol.* **2019**, *290*, 121790.

27. Li, H.; Sun, J. T.; Wang, C.; Liu, S.; Yuan, D.; Zhou, X.; Tan, J.; Stubbs, L.; He, C. *ACS Sustain. Chem. Eng.* **2017**, *5*, 7942.
28. Arshanitsa, A.; Krumina, L.; Telysheva, G.; Dizhbite, T. *Ind. Crops Prod.* **2016**, *92*, 1.
29. Faruk, O.; Sain, M.; Farnood, R.; Pan, Y.; Xiao, H. *J. Polym. Environ.* **2014**, *22*, 279.
30. Jin, Y.; Ruan, X.; Cheng, X.; Lü, Q. *Bioresour. Technol.* **2011**, *102*, 3581.
31. Cinelli, P.; Anguillesi, I.; Lazzeri, A. *Eur. Polym. J.* **2013**, *49*, 1174.
32. Li, H. Q.; Shao, Q.; Luo, H.; Xu, J. *J. Appl. Polym. Sci.* **2016**, *133*, 1.
33. Jeong, H.; Park, J.; Kim, S.; Lee, J.; Ahn, N. *Fibers Polym.* **2013**, *14*, 1301.
34. Santos, O. S. H.; Coelho da Silva, M.; Silva, V. R.; Mussel, W. N.; Yoshida, M. I. *J. Hazard. Mater.* **2017**, *324*, 406.
35. Hayati, A. N.; Evans, D. A. C.; Laycock, B.; Martin, D. J.; Annamalai, P. K. *Ind. Crops Prod.* **2018**, *117*, 149.
36. Huang, X.; De Hoop, C. F.; Xie, J.; Hse, C. Y.; Qi, J.; Hu, T. *Int. J. Polym. Sci.* **2017**, *2017*.
37. Bernardini, J.; Anguillesi, I.; Coltelli, M. B.; Cinelli, P.; Lazzeri, A. Optimizing the lignin based synthesis of flexible polyurethane foams employing reactive liquefying agents. *Polym. Int.* **2015**, *64*, 1235–1244.
38. Gómez-Fernández, S.; Ugarte, L.; Calvo-Correas, T.; Peña-Rodríguez, C.; Corcuera, M. A.; Eceiza, A. *Ind. Crops Prod.* **2017**, *100*, 51.
39. Wysocka, K.; Szymona, K.; McDonald, A. G.; Maminski, M. *BioResources* **2016**, *11*, 7355.
40. Zhang, Y.; Yan, R.; Ngo, T. dung; Zhao, Q.; Duan, J.; Du, X.; Wang, Y.; Liu, B.; Sun, Z.; Hu, W.; Xie, H. *Eur. Polym. J.* **2019**, *117*, 114.
41. Zhu, S.; Chen, K.; Xu, J.; Li, J.; Mo, L. *RSC Adv.* **2018**, *8*, 15754.
42. Hatakeyama, H.; Hatakeyama, T. Advances of polyurethane foams derived from lignin. *J. Renew. Mater.* **2013**, *1*, 113–123.
43. Zhang, Y.; Wang, J.; Fang, X.; Liao, J.; Zhou, X.; Zhou, S.; Bai, F.; Peng, S. *Polymer (Guildf).* **2019**, *178*, 121572.
44. Muller, L. C.; Marx, S.; Vosloo, H. C. M. *J. Renew. Mater.* **2017**, *5*, 67.
45. Alinejad, M.; Henry, C.; Nikafshar, S.; Gondaliya, A.; Bagheri, S.; Chen, N.; Singh, S. K.; Hodge, D. B.; Nejad, M. *Polymers (Basel).* **2019**, *11*, 1202.
46. Kühnel, I.; Saake, B.; Lehnen, R. *Macromol. Chem. Phys.* **2018**, *219*, 1.
47. Ilmiati, S.; Haris Mustafa, J.; Yaumal, A.; Hanum, F.; Chalid, M. *IOP Conf. Ser. Mater. Sci. Eng.* **2017**, *223*.
48. Lang, J. M.; Shrestha, U. M.; Dadmun, M. *Front. Energy Res.* **2018**, *6*, 1.

49. Gómez-Jiménez-Aberasturi, O.; Ochoa-Gómez, J. R. *J. Chem. Technol. Biotechnol.* **2017**, *92*, 705.

50. Laurichesse, S.; Avérous, L. *Prog. Polym. Sci.* **2014**, *39*, 1266.

51. Boeriu, C. G.; Bravo, D.; Gosselink, R. J. A.; Van Dam, J. E. G. *Ind. Crops Prod.* **2004**, *20*, 205.

52. Sjöström, E. *Wood Chemistry, Fundamenytals and Applications, Second Edition*; Elsevier, **1993**.

53. Sarkanen, K. V.; Tillman, D. A. In *Progress in biomass conversion*; Press, A., Ed.; **2012**; Vol. 2, pp 127.

54. Merle, J.; Birot, M.; Deleuze, H.; Mitterer, C.; Carré, H.; Bouhtoury, F. C. El *Mater. Des.* **2016**, *91*, 186.

55. Zhu, H.; Peng, Z.; Chen, Y.; Li, G.; Wang, L.; Tang, Y.; Pang, R.; Khan, Z. U. H.; Wan, P. *RSC Adv.* **2014**, *4*, 55271.

56. Moore, J. A.; Carraher, C. E. In *Modification of Polymers*; Springer US: Boston, MA, **1983**; pp 1.

57. Liu, G. Experimental and Prediction Approaches to Determine Dissociation Constants (pK a) of Amines A Thesis Submitted to the Faculty of Graduate Studies and Research In Partial Fulfillment of the Requirements For the Degree of Master of Applied Science in Proc, University of Regina, **2018**.