

OXYPROPYLATION OF SODA LIGNIN: CHARACTERIZATION AND APPLICATION IN POLYURETHANE FOAMS PRODUCTION

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Soda lignin precipitated from black liquor of *Stipa tenacissima* L. cooking was converted into polyols by a chain extension reaction with propylene oxide (PO). It was oxypropylated in a batch reactor in the presence of potassium hydroxide (KOH) as a catalyst. The reaction conditions were optimized by modifying the lignin/propylene oxide ratio [L/PO (w/v)], the temperature and the catalyst content. L/PO ratios of 20/80, 30/70 and 40/60 and catalyst contents from 3% to 5% were used. The temperature of the reaction was varied from 120 to 140 °C. The ensuing polyols were characterized by FTIR, ¹H-NMR spectroscopy and size exclusion chromatography. Also, their viscosity and hydroxyl index were determined. A decrease in the molecular weight was observed after the oxypropylation reaction, which was explained by lignin depolymerisation. The viscosity and the hydroxyl index of the polyols ranged from 0.48 to 4.2 Pa.s and 150 to 375, depending on the lignin/PO ratio. Rigid polyurethane foam (RPU) was prepared from the PO extended lignin polyols, and its compressive strength and cell morphology were analysed.

Keywords: lignin, polyol, oxypropylation, rigid polyurethane foam

INTRODUCTION

In Tunisian industry, *Stipa tenacissima* L., the annual alfa plant, is cooked using the soda process and the lignin dissolved in the black liquor is presently burnt for energy recovery purposes. This approach is common for the majority of the alkaline lignin (kraft and soda) produced by the pulp industry, because it has a higher calorific power than that of polysaccharides. In fact, the calorific power of cellulose and hemicelluloses is around 17 MJ/kg, whereas that of lignin is more than 26 MJ/kg.¹ However, this is a rather irrational way of exploiting wood, since lignin is the main source of aromatic structures in vegetal biomass.^{2,3}

Thus, the major part of lignin is a by-product of the pulping and papermaking industrial activity. Its world production is estimated to exceed 50 million tons.³ It is presently not or hardly valorized in the field of chemicals and/or materials. Innovative pulping processes gave rise

to the preparation of new low-molecular weight lignins,^{4,5} readily soluble in common solvents and easily exploitable in the field of organic and macromolecular synthesis.⁴ The chemical structure of lignin is very complex and it has been a matter of extensive studies, including the development of innovative techniques of characterization, in order to ascertain as accurately as possible this complex cross-linked macromolecule.⁶ The chemical modification of the lignin macromolecule is known to improve its reactivity and in some cases, to convert it from solid into liquid state. The most common chemical modification of lignin is its oxypropylation.⁷⁻²⁰ Thus, in previous studies; this method was efficiently applied to convert lignins and other solid residues into liquid viscous polyols by a single-step oxypropylation reaction. The ensuing polyols were recovered from the final reaction medium very simply, since the

process does not require any purification step or separation and removal of solvents, because the used volatile organic compound (propylene oxide) was totally consumed. The oxypropylated lignin fragments constituted interesting macromonomers for the synthesis of polyurethanes.⁷⁻²⁰

Polyurethanes are all around us, playing a vital role in many industries due to their widely ranging mechanical properties and their ability to be relatively easily processed in a variety of forms (flexible and rigid foams, elastomers, adhesives, binders *etc.*). The interested reader can find detailed information about these materials as well as exhaustive data concerning the chemistry and the technology of the polyols used for the preparation of polyurethanes.^{21,22} The use of lignin as a polymeric precursor for the preparation of new high value added products has gained real interest, as witnessed by the increasing number of recent reviews and book chapters.²³⁻²⁶ Several emerging and promising applications have been reported, including bio-based polymeric structures and green hydrogels. The purpose of this work was to contribute to this field by modifying soda-lignin extracted from an annual plant and using the oxypropylated ensuing liquid as a polyol for the preparation of rigid polyurethane foams.

EXPERIMENTAL

Lignin sample

The lignin used in this study was extracted from black liquor, which in turn was obtained as a by-product from the Tunisian National Society of Cellulose and Paper in Kasserine. Thus, the black liquor of soda cooking of alfa (*Stipa tenassicima* L.) was acidified in order to precipitate the dissolved alkali lignin. The initial pH of the investigated black liquor was 11.6. A quantity of 100 g of this highly viscous liquid was diluted by 500 mL of distilled water and filtered in order to remove suspended solids. A diluted

sulfuric acid solution (0.1 M) was added dropwise to the filtered diluted black liquor until a pH of around 2 was reached, which induced lignin precipitation. The precipitated powder was washed extensively with water, dried at temperatures lower than 40 °C under vacuum and used for further modification. This lignin was fully characterized in a previous study.²⁷ All chemicals, such as potassium hydroxide, deuterated dimethyl sulfoxide-d₆ and propylene oxide, were purchased from Sigma-Aldrich and were used without further purification.

Oxypropylation reaction conditions

A Parr autoclave reactor equipped with a 4842 mechanical stirrer was used to achieve the oxypropylation reaction. The reactor was equipped with adjustable electric heating system. The reactor volume was 450 mL. Different oxypropylation reactions were carried out with a constant volume of propylene oxide of 100 mL. The different concentrations of catalyst and lignin, and the set point temperature of the reactor were varied. The formulation was optimized by modifying the lignin/propylene oxide ratio [L/PO (w/v)], the temperature and the catalyst content. L/PO ratios of 20/80, 30/70 and 40/60 and catalyst contents from 3% to 5% were used. The temperature of the reaction was varied from 120 to 140 °C. Table 1 summarizes the tested formulations and employed reaction conditions.

Lignin, propylene oxide (PO), and KOH were mixed in a glass liner and then sealed in the Parr reactor before heating to 120-140 °C. At first, the pressure gradually rose with increasing temperature, until a maximum value was reached, which depended on the amount of catalyst and L/PO ratio. The manometric pressure increased to a maximum value (P_{max}) and then quickly dropped down to 0 bar (within 4 to 10 minutes), which indicated the completion of the reaction (total consumption of the propylene oxide). When the manometric pressure reached zero, the reactor was cooled under stirring and the ensuing polyols were recovered (Fig. 1).

Table 1
Formulation and operating conditions related to the oxypropylation optimization study

Sample #	Lignin in %	KOH in %	Temperature (°C)		P_{max} (bar)	Time ² (min)
			T_{Set}^1	T_{max}		
Polyol 2	20	5	140	330	40.0	5.0
Polyol 3	20	5	120	218	21.5	9.5
Polyol 4	20	5	130	303	35.0	6.0
Polyol 5	30	3	130	313	39.8	4.5
Polyol 6	30	5	130	280	30.5	9.5
Polyol 7	40	3	130	297	36.5	4.0
Polyol 8	40	5	130	297	35.0	8.5

In all cases 100 g of PO was used; T_{Set}^1 is the reaction initiation temperature; ²The reaction time was counted from the start of the exothermic event to the end of the reaction when the relative pressure returned to 0 bar

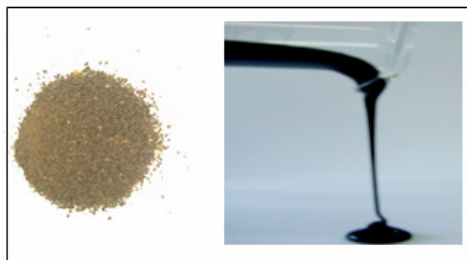


Figure 1: Lignin powder and oxypropylated lignin, respectively

Characterization of oxypropylated lignin

Oxypropylated lignins were characterized by FTIR, $^1\text{H-NMR}$, SEC, viscosity and hydroxyl index. The FTIR spectra were collected on a FTIR BOMEN spectrometer (model MB 104) in the transmittance mode using NaCl crystals. The spectra were recorded between 800 and 4000 cm^{-1} at a resolution of 4 cm^{-1} and co-adding four scans. $^1\text{H-NMR}$ samples were prepared by dissolving 300 mg of oxypropylated lignin in 4 ml of deuterated dimethyl sulfoxide- d_6 (DMSO- d_6 , 99.8%), using a Bruker Avance 400.132 MHz NMR spectrometer with a line width of 4807 Hz , relaxation time for acquisition of 30 s and a pulse of 60° .

Molecular weight distribution (MWD) and average molecular weights (M_n and M_w) were determined by size exclusion chromatography on a Viscotek GPCmax apparatus (VE 2001), equipped with Dual-Angle Light Scattering (DALS) detector (Viscotek 270) and Refractive Index (RI) detector (Viscotek VE3580). Two columns were used in-series (Varian PolarGel-M column, $300\times 7.5\text{ mm}$), preceded by a guard column (PolarGel-M Guard). These columns are specialized for lignin and lignin derivatives analysis in the appropriate range of molar mass. Chromatographic conditions were the following: eluent flow rate of 1 mL/min , the column temperature of $75\text{ }^\circ\text{C}$, RI detector temperature of $35\text{ }^\circ\text{C}$, injection volume of $100\text{ }\mu\text{L}$. The eluent used was DMAC/LiCl (0.5% by weight). The DMAC and LiCl should be kept separately under dry atmosphere prior to eluent preparation. Quantification was based on standard PMMA calibration ($\log M$ vs. retention volume), which was found very linear on the full range of molar mass studied.

The viscosity was measured at $25\text{ }^\circ\text{C}$. The shear flow measurements were performed using cone-plate

geometry (Anton Paar, physical MCR301 viscometers).

Before determining the hydroxyl number of our polyols, their alkalinity in mg of KOH/g was established. In this context, 10 g of the polyol sample was weighed in a flask and 50 mL of ethanol:water solution ($1:1$ (v/v)) was added. The mixture was stirred until the polyol sample was completely dissolved and the pH was measured. The recorded pH was found to be basic. This solution was then titrated with a 0.1 N HCl solution, which provides a first value corresponding to the alkalinity of the polyols.

The hydroxyl number is determined according to the protocol described in ASTM D1638. The basic principle of this standard assay is to acetylate the oxypropylated lignin and a reference “blank” solution. Back-titration of the excess of acetic anhydride in the two solutions is used to measure the hydroxyl number, calculated from the difference between the NaOH volume required for the titration of the blank and that required for the polyol sample. The acetylation reagent must be prepared one day before the reaction, as a mixture of 127 mL of acetic anhydride with 1000 ml of pyridine and 16 g of imidazole added as a catalyst. To 35 mL of this solution, 1 g of oxypropylated lignin is added. The solutions are maintained at a temperature of $105\text{ }^\circ\text{C}$ under reflux. After 1 hour , the solutions are cooled and the excess of acetic anhydride is titrated by a 0.5 M sodium hydroxide solution.

DSC measurements were carried out using Differential Scanning Calorimetry (DSC Q100 device from TA instrument). The heating rate was $10\text{ }^\circ\text{C/min}$ for the testing temperature range of $-100\text{ }^\circ\text{C}$ to $200\text{ }^\circ\text{C}$. These measurements were carried out at least in duplicate.

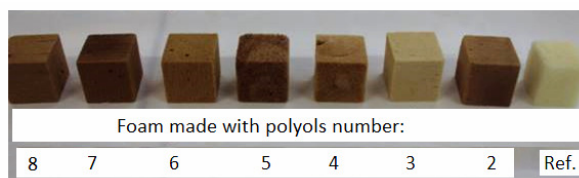


Figure 2: RPU foams produced with lignin-based polyols (Ref.: Reference commercial foam)

Table 2
Typical formulations of polyurethane rigid foams

Raw materials	Material name	Chemical composition	Mass (g)
Polyol blend/ oxypropylated lignin	DALTOFOAM TD 43204	DALTOFOAM TD 43204	20
Surfactant	Dabco DC 5604	Dabco DC 5604	0.4
Catalyst 1	DMCHA	N,N-Dimethylcyclohexylamine	0.15
Catalyst 2	NIAX	Bis[2-(N,N-dimethylamino)ethyl]ether	0.15
Foaming agent	Distilled water	H ₂ O	0.4
Co-crosslinking agent	Glycerol	Glycerol	2.0
Isocyanate	SUPRASEC® 5025	Isocyanic acid polymethylene polyphenylene ester	39.5

Synthesis of rigid polyurethane foams (RPU)

The foams were obtained by the free rise method at room temperature.^{11,13} Typical formulations are presented in Table 2. All the starting chemicals were mixed (except the isocyanate), in a plastic container for 1 minute. Then the isocyanate was added and mechanically stirred with a high-speed stirrer. The system was further mixed and then the foam was allowed to freely rise (Fig. 2).

Characterization techniques of rigid polyurethane foams (RPU)

All foams were left at room temperature for at least 48 hours before testing. The foams obtained were characterized for their density (ρ), compressive modulus (E), morphology (SEM) and chemical functionalization (FTIR).

Foam density was determined according to the ASTM D1622 standard method. Cubic specimens with approximate dimensions of 40×40×40 mm³ (width × length × thickness) were cut and conditioned during 24 hours at 23 °C. The samples were then weighed and their exact dimensions were measured. Apparent density was obtained by simply calculating the ratio between the weight and the volume for each specimen. The compressive strength was measured using an Instron instrument (model 5985) in the foam rise direction using sample dimensions of 40×40×20 mm³. The samples were placed between two parallel plates and the force required to compress the foam was measured at the rate of 10 mm/min.

The scanning electron microscopy used to characterize foam morphology was a Zeiss ULTRA55 Scanning Electron Microscope (SEM) with an acceleration voltage of 12.5 kV. Small specimens were cut from the foam samples, and then the surface and cross section were studied.

RESULTS AND DISCUSSION

Oxypropylation

Several series of samples were synthesized with various L/PO ratios, catalyst contents and temperature. The terminology used to identify the

samples is expressed as L/PO/C (ratio between lignin and PO, followed by catalyst content). A typical oxypropylation reaction could occur under the following conditions: L/PO 20/80, a catalyst of 5% and a temperature of 140 °C. In such a case, the temperature gradually increases with time to reach the targeted value (T = 140 °C). At this temperature, the pressure increases rapidly to reach a P_{max} of 40 bar and decreases relatively fast to 5 bar. The temperature rises rapidly to a T_{max} of 330 °C and then drops more slowly to room temperature (Fig. 3). When the pressure starts to decrease, the temperature reaches its maximum value. This reflects the total consumption of propylene oxide. These features are very similar for all the tested oxypropylation reactions.

The FTIR and NMR spectra were performed for all the samples and showed that the samples displayed the same resonances. We have chosen to present only one sample (taken as an example), but all the sample spectra are similar. Figure 4 illustrates the FTIR spectra of the original and oxypropylated lignins (20/80/5, taken as an example). As seen from these spectra, there was a substantial increase in the bands at 2870-2970 cm⁻¹, attributed to the C-H stretching modes of the aliphatic CH₃, CH₂ and CH groups and in the bands at 1100 cm⁻¹, associated with the presence of C-O-C associated with ether moieties, and an increase in the band at 1371 cm⁻¹, confirming the introduction of CH₃ groups and ether groups and the reduction in the intensity of the carbonyl peak at 1680 cm⁻¹. The regions where the main evolution was observed were highlighted in the FTIR spectra.

The ¹H NMR spectra confirmed the occurrence of oxypropylation by the emergence of peaks around 1 ppm, corresponding to CH₃ of poly(propylene oxide) (PPO) grafts and the change in intensity and shape of the region

between 3 and 4 ppm attributed to CH and CH₂ groups (PPO units), respectively. The peak observed at 4.5 ppm corresponds to the OH groups of the polyol mixture, but also is most

probably due to the presence of some moisture traces (Fig. 5).

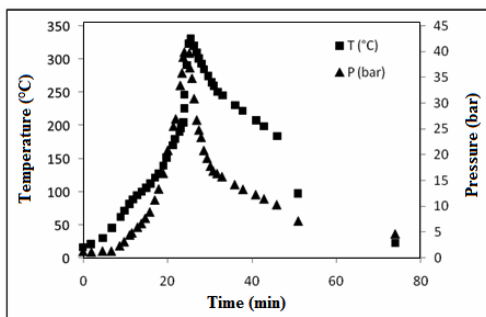


Figure 3: Temperature and pressure evolution as a function of reaction time for L/PO: 20/80, 5% KOH and temperature 140 °C

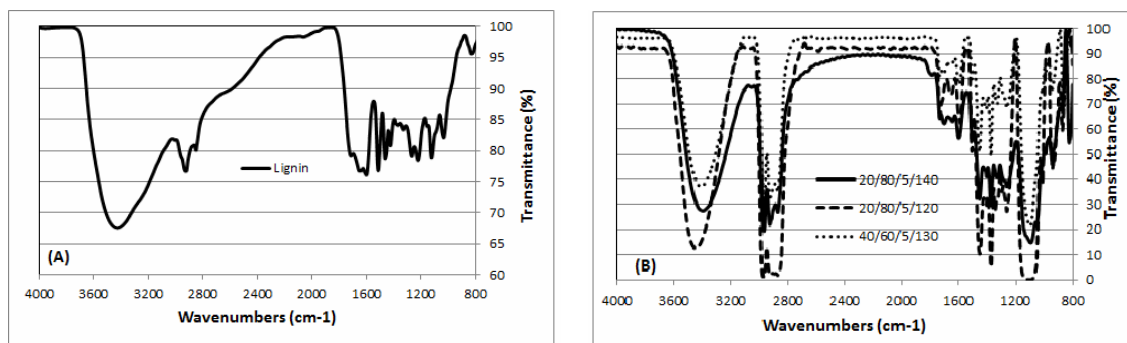


Figure 4: FTIR spectra of: (A) original and (B) oxypropylated lignins

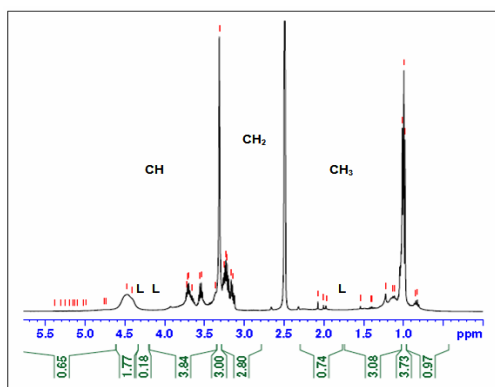


Figure 5: ¹H NMR spectrum of oxypropylated lignin (20/80/5 at 140 °C) taken as an example (L – lignin)

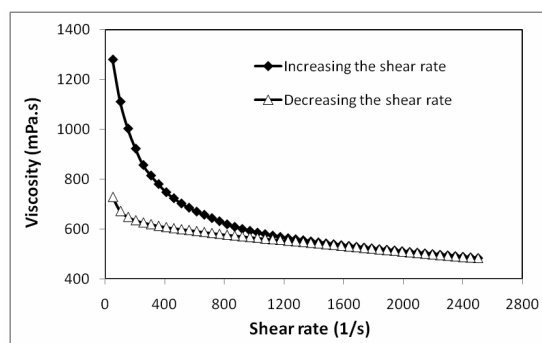


Figure 6: Viscosity vs shear rate for oxypropylated lignin (L/PO 20/80, 5% KOH at 140 °C) taken as an example

A typical viscosity *versus* shear rate curve is given in Figure 6. It shows that oxypropylated lignin displays a non-Newtonian fluid behavior. Since the viscosity decreases with increasing shear rate, the polyol can be considered a shear-thinning fluid. The apparent viscosity of this fluid at 2500 s⁻¹ is around 0.5 Pa.s. Moreover, when

observing the two cycles (increasing and decreasing the shear rate), the tested polyols showed a clear hysteresis, which is indicative of a thixotropic behavior. This reduction of viscosity with increasing shear rate is due to disentanglements and to molecular alignments of the polymer chains in the direction of flow. The

thixotropic character indicates that the polyol built up a network held by entanglement and hydrogen bonding among hydroxyl groups, which is progressively broken down under increasing shear rate. However, the network rebuilding is not instantaneous and the rearrangement of the chains takes time to restore the network structure. The rheological behavior of the polyol could be fitted with a power law equation as follows:

$$\sigma = K \cdot \dot{\gamma}^n \quad (1)$$

where σ is the shear stress (in Pa), K is the consistency (in Pa.s⁻ⁿ), $\dot{\gamma}$ the shear rate (in s⁻¹) and n the fluidity index (dimensionless parameter indicating the sensitivity of the fluid to shear rate).

For non-Newtonian fluids, the viscosity can be given at a given shear rate (arbitrary choice or at a shear rate close to that reached in the targeted application). Here, the apparent viscosity of the tested fluids is given at a shear rate value of 2500 s⁻¹, as summarized in Table 3. From these data, several conclusions could be drawn:^{9,11,16}

- Increasing the reaction temperature decreases the viscosity of the ensuing polyol. This is probably due to a higher reaction extent, as expected from higher reaction temperature.
- Increasing the L/PO ratio yields an increase of the viscosity, as well as T_{\max} and P_{\max} . This expected result is due to higher exothermal events during the reaction.
- Decreasing the catalyst quantity increases the viscosity of the oxypropylated lignin. This result could be correlated to the oxypropylation reaction rate. Thus, the

higher the catalyst content, the higher is the reaction rate and consequently the lower is the viscosity.

- As expected, increasing the catalyst quantity decreases the reaction time.
- The glass transition temperature decreases with the increase of the reaction extent, which is also in agreement with the involved reactions. In fact, increasing the extent of the oxypropylation reaction increases the number of ether groups. These chemical groups have very low cohesive energy, which makes them flow. The higher the number of ether groups, the lower the cohesive forces and consequently the lower the glass transition.
- The hydroxyl index of the prepared polyols is relatively high and is within the typical values known for polyols used to prepare rigid polyurethane foams.

Figure 7 allows a comparison of the molecular weight distributions between unreacted lignin and oxypropylated lignins. Only 3 oxypropylated lignins have been represented, chosen as representative of the range of variation of molecular weights. The untreated lignin is characterized by a quite broad distribution in the high molecular weight region and smaller peaks are representative of lignin monomers and oligomers. M_n , M_w , M_{peak} and polydispersity index were calculated to be 1730 Da, 12.8 kDa, 10 kDa and 7.4, respectively, and the longest chains are found to have a molecular weight of 90 kDa, corresponding to a degree of polymerization of about 500.

Table 3
Polyol characteristics (hydroxyl number, viscosity, average-molecular weights, polydispersity index and T_g)

Sample #	Viscosity (at 20 °C in Pa.s)	I _{OH} (mg KOH/g polyol)	M _n (Da)	M _w (Da)	M _{peak} (Da)	PI (ad)	T _g (°C)
Lignin	-	-	1730	12800	10000	7.4	
Polyol 2	0.5	252	--	--	--	--	-41
Polyol 3	2.5	272	337	1420	1600	4.2	-55
Polyol 4	0.7	289	270	1140	1250	4.2	-42
Polyol 5	1.9	149	356	2460	2500	6.9	-58
Polyol 6	3.3	224	451	6420	4000	14.2	-56
Polyol 7	2.5	373	439	7690	3500	17.5	-57
Polyol 8	4.2	289	401	3660	4000	9.1	-56

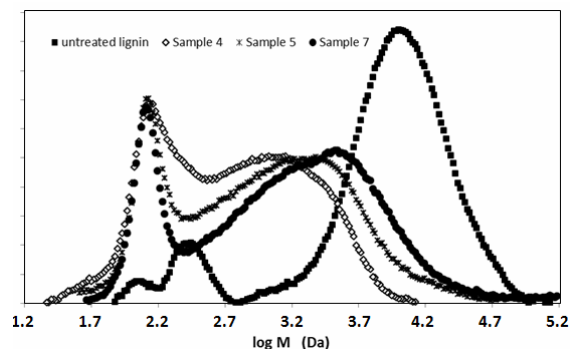


Figure 7: Comparison of molar mass distribution of untreated lignin and oxypropylated lignin (samples 4, 5 and 7 chosen as representative of the range of molar mass)

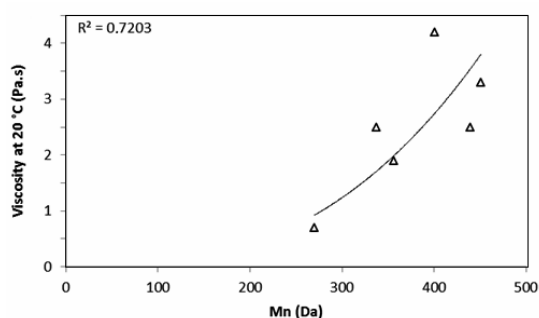


Figure 8: Viscosity vs M_n (number-average molecular mass) for different samples of oxypropylated lignins

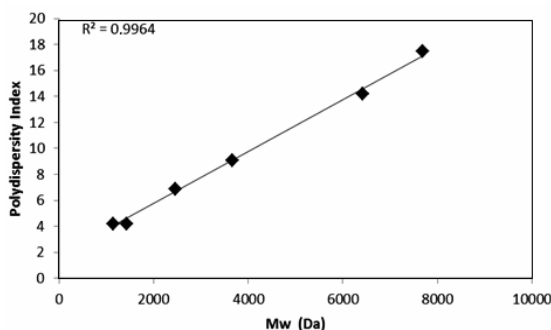


Figure 9: Variation of polydispersity index (PI) as function of the weight-average molecular weight (M_w)

Unlike the untreated lignin, oxypropylated lignins are characterized by much lower molecular weights and a large population of very small molecules ($M < 200$ Da). Therefore, it appears that lignin depolymerisation during oxypropylation is quite severe, and it masks the observation of molecular extension during the reaction. Lignin degradation is due to the fragility of the different kinds of aryl-alkyl ether linkage of the lignin polymer, when they are elevated at high temperature.

The data in Table 3 show that among the three measured properties of the oxypropylated lignins (viscosity, I_{OH} and T_g), the only one that presents a certain correlation with the sample molecular weight is the viscosity. Indeed, Figure 8 shows that the viscosity tends to increase non-linearly with M_n , the number-average molecular weight. The correlation with M_w , the weight-average molecular weight, was found significantly lower with a R^2 value of only 0.43. It is thus quite clear that the viscosity of the polymer is more affected by the abundance of small chains in the polymer, and also possibly, by the presence of oligomeric homopolymer chains (POP: poly(propylene oxide)), which also grow up during the reaction.

Figure 9 shows that an excellent correlation exists between the polydispersity index (PI) and M_w , which can be justified by the small variation of M_n by comparison with the variation of M_w . Actually, the very high increase of the polydispersity index with chain length may have several origins, namely: (i) the high temperature may induce self-condensation reactions (or even cross-linking); (ii) the amount of the homopolymer (POP: poly(propylene oxide)) can vary from one reaction to another.

Finally, by comparing the data in Tables 1 and 3, it may be concluded that the percentage of lignin in the polymer is the single parameter that affects its molecular weight. The higher the percentage of lignin, the higher is the molecular weight. Variations were quite important since the longest chains in samples 5 to 7 attained molecular weight values in the range of 40 - 60 kDa, and about 10 kDa in samples 3 and 4.

Rigid polyurethane foams

The physical characteristic of the prepared foams were summarized in Table 4. The data show a broad evolution in properties according to the extension degree of the polyol used, with

density ranging between 40 and 70 kg/m³, an average cell size in the range of 0.4 to 0.8 mm and

a compression modulus ranging from 0.1 to 8.7 MPa.

Table 4
Density, average cell size and compressive modulus (E) obtained for RPU based foams

Foam made of	Sample #	Polyol ratios L/PO/%KOH/T°C	Density (kg/m ³)	Average cell size (µm)	E (MPa)
Commercial polyol	Ref.	-	44.9	799	2.5
Polyol 2	2	20/80/5/140	39.9	419	-
Polyol 3	3	20/80/5/120	41.7	312	2.1
Polyol 4	4	20/80/5/130	32.7	453	0.1
Polyol 5	5	30/70/3/130	41.1	586	-
Polyol 6	6	30/70/5/130	54.8	412	5.0
Polyol 7	7	40/60/3/130	69.0	424	7.9
Polyol 8	8	40/60/5/130	71.5	351	8.7

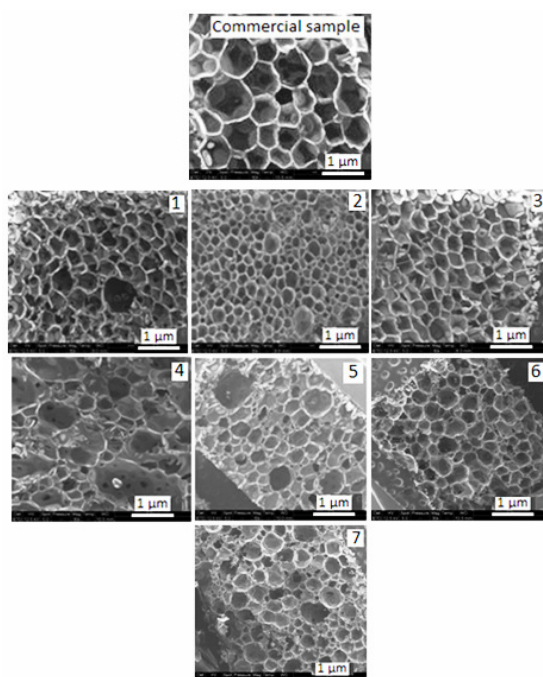


Figure 10: SEM micrographs obtained for commercial RPU foams and RPU foams produced with lignin-based polyols

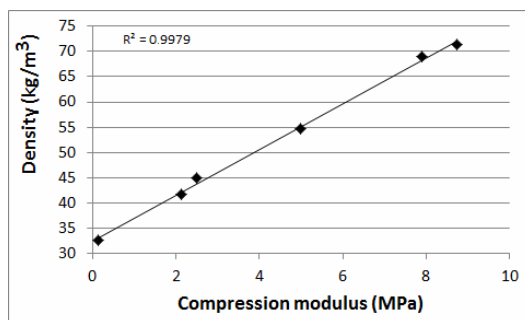


Figure 11: Compression modulus of RPU foams as a function of their density

The average cell size was high for the reference foam sample made of a typical RPU formulation (around 800 μm) and quite similar for most of the other RPU foams prepared in this study (about 400 μm). However, two exceptions can be mentioned for samples #3 and #8, in which the cell size is lower (around 330 μm) and sample #5 for which the average cell size is close to 600 μm . Figure 10 shows the SEM photomicrographs of the RPU foams prepared in this study.

The SEM microphotographs of some foams were analyzed in order to determine the ratio of close/open cells. Thus, foams #3, 6 and 8 were characterized and found that these cellular materials possessed mostly closed cells (85-90% of the cells were closed). This explains the thermal conductivity (λ) performance of these three foams. In fact, all the three foams displayed a value of λ equal to 20-22 mW/m.K, before aging and of 24-28 mW/m.K after one month of natural aging.

The compression modulus was found to increase linearly with the increasing density of the prepared foams, as shown in Figure 11. This is a quite expected result, but it should be pointed out, because the compression resistance of cellular materials is a key issue. RPU foams are mainly used as insulating material for cold room walls to preserve food products. However, in addition to their thermal insulation properties, their resistance to compression is one of the most relevant requirements.

CONCLUSION

Soda lignin from *Stipa tenacissima* L. was converted into liquid polyols by oxypropylation with propylene oxide and potassium hydroxide as a catalyst. The obtained polyols were viscous liquids and possessed relatively high hydroxyl index. These two parameters were close to those of commercial polyols used in a similar context and opened the way of testing them in this field of application. Thus, rigid lignin-based polyurethane foams were elaborated and displayed very promising properties. These materials can be used for thermal and acoustic insulation.

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