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Lignin-based rigid polyurethane foams with improved biodegradation

Carolina A Cateto[1,2,3], Maria F Barreiro[1], Carolina Ottati[4,5], Mary Lopretti[4,5], Alírio E Rodrigues[2] and Mohamed N Belgacem[3]

Abstract

Rigid polyurethane (RPU) foams have been synthesized using lignin-based polyols obtained by oxypropylation of four distinct lignins (Alcell, Indulin AT, Curan 27-11P, and Sarkanda). Polyol formulations with two lignin/propylene oxide/catalyst content (L/PO/C) ratios were chosen (30/70/2 and 20/80/5). RPU foams have been prepared with a polyol component that incorporates the lignin-based one at contents ranging from 25 to 100%. A 100% commercial polyol-based (Lupranol® 3323) RPU foam was also prepared and used as the reference. RPU foams were characterized in terms of density, compressive modulus, and conductivity. Cell morphology and size estimation were accessed by scanning electron microscopy. Moreover, biodegradation of the Alcell- and Indulin AT-based foams was evaluated using respirometry tests in liquid and solid media. The Alcell- and Indulin AT-based polyols together with the 20/80/5 Curan 27-11P-based one led to RPU foams with properties quite similar to those of the reference homolog. Biodegradation seems to be, particularly, favored if using Indulin AT-based polyols mixed with Lupranol® 3323.

Keywords

Lignins, oxypropylation, rigid polyurethane foams, biodegradation

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Introduction

Polyurethanes are considered as one of the most versatile polymeric materials offering a wide range of products with applications in diverse sectors. Rigid polyurethane (RPU) foams belong to this class of products and represent a highly versatile and commercially important category of expanded materials. This is greatly due to their outstanding thermal insulating properties resulting from a combination of blowing agent properties as well as the cell size and morphology of the final foam. In fact, the thermal insulation performance of RPU foams is known to be higher than those of other insulating materials, such as expanded polystyrene, mineral wool, cork, softwood, fireboard, concrete blocks, and bricks. These materials, although less expensive than RPU foams, require a larger amount (thickness) of material to reach the same insulation performance.[1,2] Moreover, RPU foams constitute attractive choices in various industrial applications due to their high mechanical strength, their strong adhesive propensity, and, above all, their easy processing.[1]

The use of renewable raw materials can positively contribute to a sustainable development providing a platform capable of substituting, at least partially, the existing petroleum-based counterparts. Hopefully, these raw materials will enable the design of novel bio-based products that can compete, or even surpass, the existing petroleum-based ones. These bio-based products will present a strong eco-friendly connotation, a very desirable property for consumers, therefore contributing to their attractiveness and valorization. In addition to non-food plant oils, other interesting renewable raw materials for polymer synthesis include polysaccharides, proteins, tannins, and lignin.[3–6]

Lignin can be described as a biopolymer possessing a complex tridimensional polyphenolic structure. Its enormous natural abundance is of the same order of magnitude as that of cellulose and chitin.[4] In addition to lignins originating from traditional pulping operations (kraft, soda, and sulfite), representing an amount estimated to be over 70 million tons per year, large amounts of novel lignins can be predicted in a near future resulting from various biorefinery operations. Presently, less than 2% recovered traditional lignins are exploited as a chemical product. In this context, recent projections predict that the production of ethanol from lignocellulosic biomass can generate at least 1.1 million tons of lignin per year evidencing the need of proper exploitation of lignin through more noble applications than fuel.[7]

The incorporation of lignin into several polymeric systems has been already demonstrated in applications such as wood panel products, biodispersants, polyurethanes, and epoxy resins.[8–11] In particular, the use of lignin in polyurethane synthesis, directly or after chemical modification, has been highlighted by several research groups.[10–12] Among other possible transformation processes, oxypropylation has been recognized as a viable and promising approach to overcome the technical limitations and constrains imposed by the polymeric nature of lignin.[12–16] By means of oxypropylation, the hydroxyl groups, in particular the phenolic ones hardly accessible because entrapped inside the molecule are liberated from steric and/or electronic constrains. Moreover, such chain extension reaction leads to the formation of lignin-based liquid polyols; thanks to the introduction of multiple ether moieties.

Most of the studies devoted to the use of lignin-based polyols obtained by oxypropylation lay on the synthesis of RPU foams. This tendency is a result of the high functionality associated to these bio-based polyols making them ideal for that purpose.[14–16] Moreover, some of these studies pointed out that lignin-based RPU foams could present insulating properties, dimensional stability, and an accelerated aging behavior very similar to those derived from commercial counterparts. Furthermore, the intrinsic properties of lignin are expected to contribute to an improvement of moisture and flame resistance, which are very desirable properties for various applications.[17] More recently, it has also been reported that the incorporation of lignin at amounts lower than 10% (w/w) are able to increase biodegradability of commonly used polyurethanes.[18,19] These factors, jointly with a lack of industrial use of these lignin-based polyols, give emphasis to the need of further research in this domain highlighting aspects such as lignin sources, synthesis procedures, and properties of the generated lignin-based RPU foams.

This work aims to evaluate the suitability of using lignin-based polyols prepared from four technical lignins (Alcell, Indulin AT, Curan 27-11P, and Sarkanda) to produce RPU foams. Density, mechanical properties, conductivity, and cell morphology of the generated RPU foams were determined and compared with a reference (RPU foam prepared with a typical commercial polyol–Lupranol® 3323). Biodegradation was evaluated against *Penicillium chrysogenum*, *Phanerochaete chrysosporium*, *Trametes versicolor*, *Trichoderma harzianum*, and *Trichoderma reesei* fungi, which are reported in the literature as lignin-degrading microorganisms.[20,21]

Materials and methods

Materials

The lignin-based polyols were obtained from the oxypropylation of four technical lignins (Alcell, Indulin AT, Curan 27-11P, and Sarkanda) with a formulation deduced from an optimization study, as described elsewhere.[13] The technical lignins used represent three different pulp processes (Kraft, Soda, and Organosolv) and various vegetal species (softwood, hardwood, and non-wood). Indulin AT and Curan 27-11P (commercialized in the alkali form) are softwood lignins obtained by the Kraft pulping process and were kindly supplied by MeadWestvaco (Glen Allen, VA) and BorregaardLignoTech (Sarpsborg, Norway), respectively. Sarkanda lignin was purchased from Granit SA (Lausanne, Switzerland). It is a non-wood lignin obtained from a soda pulping-precipitation process, patented by Granit SA. Alcell lignin of Repap Enterprises Inc. (Stamford, CT) was extracted from a mixture of hardwoods (maple, birch, and poplar) by an organosolv process using aqueous ethanol. Lignin-based materials were fully characterized in a previous work.[22] The following terminology is used to identify the lignin-based polyol: L/PO/C (ratio between lignin and propylene oxide and catalyst content, v/w/%, w/w). Catalyst content is expressed on a free PO basis. Commercial polyether polyol based on sorbitol (Lupranol® 3323), PMDI (polymeric 4,4'-methylene-diphenyl isocyanate (MDI)) with a functionality of 2.7, silicone surfactant (SR-321 NIAX), and catalysts (NIAX-A1 and DMCHA) were kindly supplied by Elastogran-BASF (France). Glycerol (co-crosslinking agent) and *n*-pentane (physical blowing agent) were commercial products purchased from Aldrich. A summary of the lignin-based polyols and Lupranol® 3323 technical properties (hydroxyl number (I_{OH}), viscosity (μ), and homopolymer content) are presented in Table 1. Homopolymer content refers to polypropylene oxide (PPO) resulting from PO homopolymerization. In fact, during the oxypropylation reaction and in the presence of traces of water, some PO molecules undergo hydrolysis yielding 1,2-propylene glycol, which in turn reacts with PO (present in excess) to form PPO. This fraction is usually left in the final mixture and quantified.

RPU foam formulation and synthesis procedure

A typical RPU foam formulation includes a polyol (lignin-based polyol alone or mixed with 25, 50, and 75% of Lupranol® 3323) combined with 10% (w/w) of glycerol (a co-crosslinking agent). The following terminology is used to identify the polyol composition: LP/CP (ratio between lignin-based polyol and commercial polyol, w/w). For each lignin-based polyol, four LP/CP ratios have been used

Table 1. Some properties of the polyols used in the synthesis of RPU foams.

Polyol				
L/PO/C ratio (w/v/%,w/w)	Lignin (*)	I_{OH} (mg KOH/g)	μ (20°C, Pa.s)	Homopolymer content (%, w/w)
20/80/5	Alcell	291.6	4.02	43.7
	Sarkanda	319.0	2.73	44.5
	Indulin AT	326.2	4.34	36.7
	Curan 27-11P	366.1	4.66	46.4
30/70/2	Alcell	279.7	48.96	29.5
	Sarkanda	322.8	43.40	27.0
	Indulin AT	348.8	66.56	24.2
	Curan 27-11P	428.1	50.25	28.2
Lupranol 3323		340.0	3.50 (25°C)	(na)

*Alcell and Indulin AT have an average functionality of 4 and 7.5, respectively. Functionality of Sarkanda and Curan 27-11P was not determined due experimental difficulties (solubility problems).[22,25]
na: not applicable.

(100/0, 75/25, 50/50, and 25/75). A 100% Lupranol® 3323-based RPU foam was also prepared to be used as a reference. Additionally, the formulation included a physical blowing agent (*n*-pentane at 20% (w/w)), a catalyst combination (mixture with equal amounts of DMCHA and NIAX-A1 at 2% (w/w)), a surfactant (SR-321 NIAX at 2% (w/w)), and water at 2% (w/w). Blowing agent, catalyst, surfactant, and water weight contents were determined with respect to polyol total weight. PMDI was added at a NCO/OH ratio of 1.1.

RPU foams synthesis procedure comprised the following steps: (1) the polyol combined with the co-crosslinking agent was stirred together with the surfactant and the catalyst mixture, during 60 s, (2) the physical blowing agent was added and the mixture stirred during more 30 s, and (3) the isocyanate was added in one portion and the reactive mixture stirred during more 15 s. After foam rise, samples were left to cure during 24 h at room temperature and thereafter stored until characterization.

Characterization of RPU foams

Apparent density was determined according to ASTM D1622 standard method. Cubic specimens with approximate dimensions of 50 × 50 × 50 (width × length × thickness) mm^3 were cut and conditioned during 40 h at 23°C and 50% of relative humidity. The specimens were then weighted and its real dimensions measured. Apparent density for each specimen was obtained as the ratio between the determined weight and the volume.

Compression tests were conducted according to ASTM D1621 standard method using an Instron instrument (model 4501). As for density determination, RPU foams were cut in cubic specimens with dimensions of 50 × 50 × 50 mm^3 and then conditioned during 40 h at 23°C and 50% of humidity. The load was applied at crosshead speed of 5 mm/min until the specimen was compressed to approximately 15% of its original thickness. Measurements were made in perpendicular free-rise direction.

Conductivity measurements were performed according to ASTM C177 standard method using a prototype developed at the Laboratory of Pulp and Paper Science and Graphic Arts (LGP2). Specimens with a diameter of 90 mm and thickness of 4 mm were placed between two plates maintained at different temperatures. Thermal conductivity of the samples was estimated after thermal equilibrium was reached (uniform temperature gradient through the sample), according to Fourier law (equation (1)).

$$\lambda = \frac{q \times l}{2 \times A \times \Delta\theta} \tag{1}$$

where:

λ is the thermal conductivity in W/mK

q is the power in W

l is the thickness in mm
A is the sample area in mm^2
$\Delta\theta$ is the temperature differential between the apparatus plates in K.

Morphological analysis was performed on a Quanta 200 FEI field emission scanning electron microscope (SEM). The samples were cut and gold coated before scanning. The used accelerating voltage was of 12.5 kV. Samples were analyzed both in the free-rise and in the perpendicular free-rise directions. Calculations of cell size were performed using ImageJ software from Broken Symmetry software.

Biodegradation studies were performed both in liquid and solid media. *P. chrysogenum*, *P. chrysosporium*, *T. versicolor*, *T. harzianum*, and *T. reesei* fungi were tested. For liquid media, tests were performed using a nutritive broth (20 g/l of glucose, 3 g/l of yeast extract, and 1% salts) and for solid media using soil with pH of 6–7 and moisture content of 60–65%. Media were inoculated with the desired microorganism and incubation was done at 37°C. Foam samples with 1 × 1 × 1 cm have been used in the two types of assays. After the final period of incubation (30 days for the liquid media and four months for the soil assays), the final samples were washed and weighted to access weight loss. Biodegradation assays have been performed with foam formulations proceeding from 30/70/2 Alcell- and Indulin AT-based polyols using LP/CP ratios of 100/0, 50/50, and 0/100 (reference foam).

Results and discussion

RPU foams prepared with the lignin-based polyol formulation 20/80/5

Table 2 presents a summary of the characterization data (density (ρ), conductivity (λ), compressive modulus (E), and average size cell) obtained for the RPU foams prepared with the 20/80/5 lignin-based polyols. For comparison purposes, the properties of the reference foam prepared with 100% Lupranol® 3323 polyol are also presented in Table 2 and its micrographs are shown in Figure 1. As can be observed, RPU foams that incorporate lignin-based polyols exhibit both compressive modulus and density values lower than those of the reference foam (31.10 kg/m^3 and 30.3 mW/mK, respectively). However, RPU foams based on Alcell and Indulin AT polyols presented compressive modulus and density values higher than those based on Sarkanda and Curan 27-11P homologs. Sarkanda-based RPU foams presented very large cells with a heterogeneous size distribution and were brittle (Figure 2). This behavior, possibly ascribed to the lignin origin (Sarkanda is a non-wood lignin, whereas the other ones are wood lignins), was more noticed as the lignin content increased.

RPU foams produced with 100% lignin-based polyols (polyol formulation 100/0) presented the lowest conductivity values. SEM analyses revealed that these foams have hexagonal cells with a well-defined shape, however quite elongated. Moreover, they presented a more homogeneous size distribution when

Table 2. Density, thermal conductivity, compressive modulus, and average cell size of RPU foams obtained from 20/80/5 polyols.

Lignin	Polyol (LP/CP, w/w)	ρ (kg/m^3)	λ (mW/mK)	E (MPa)	Average cell size (mm)
Alcell	100/0	20.87	26.7	2.53	0.67
	75/25	20.18	30.7	3.00	0.52
	50/50	23.92	30.5	3.27	0.47
	25/75	24.99	28.8	3.41	0.48
Sarkanda	100/0	20.76	29.1	1.82	1.13
	75/25	21.25	31.7	2.07	1.11
	50/50	22.34	30.9	2.17	0.66
	25/75	24.51	30.0	2.79	0.47
Indulin AT	100/0	19.21	26.8	2.60	0.52
	75/25	20.26	29.4	2.37	0.50
	50/50	22.43	32.9	2.42	0.48
	25/75	25.78	30.7	2.93	0.46
Curan 27-11P	100/0	18.48	30.0	2.46	0.59
	75/25	17.81	31.5	2.28	0.56
	50/50	19.42	31.3	2.72	0.47
	25/75	21.86	32.1	2.07	0.63
Reference foam	0/100	31.10	30.3	4.58	0.44

A 100% Lupranol 3323-based foam is presented as reference.

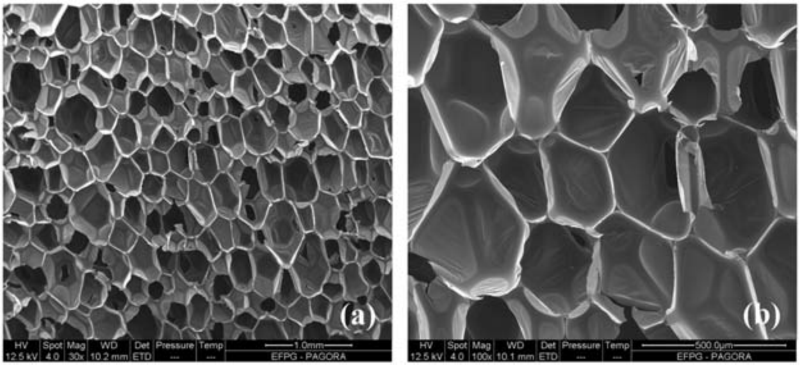

Figure 1. RPU reference foam SEM micrograph (free-rise direction) obtained at different magnifications: (a) 30X and (b) 100X.

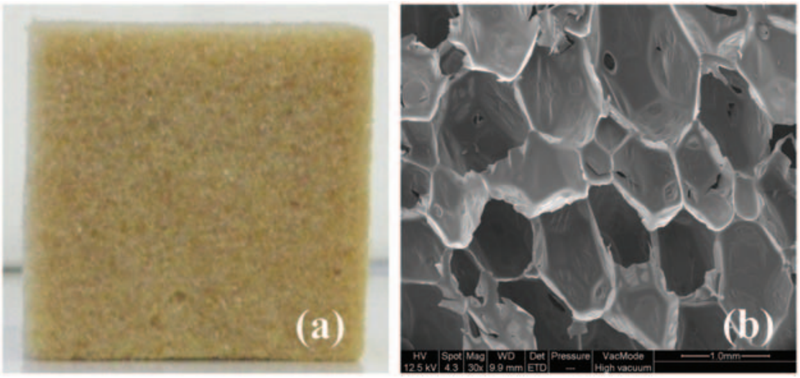

Figure 2. Sarkanda-based RPU foam with a 100/0 polyol composition. (a) Sample foam and (b) SEM micrograph taken in free-rise direction (50X magnification).

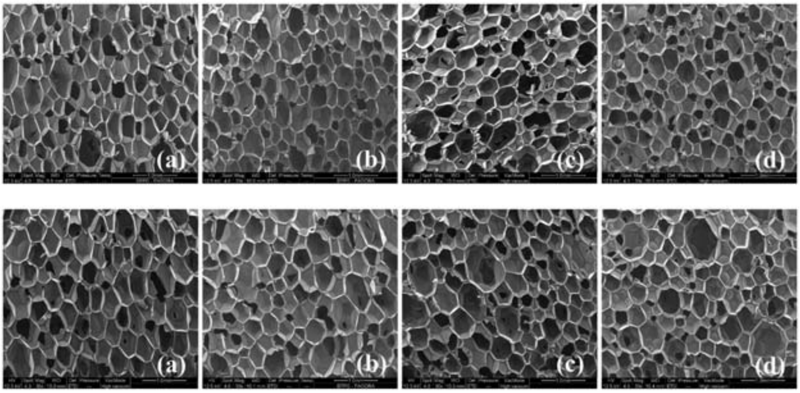

Figure 3. SEM micrographs of RPU foams produced from Alcell (first series) and Indulin AT (second series) 20/80/5 lignin-based polyols. Polyol composition of (a) 100/0, (b) 75/25 (c) 50/50, and (d) 25/75 20/80/5 lignin-based polyols. Free-rise direction and magnification of 30X.

compared with foams prepared with lower lignin-based polyol content (75/25, 50/50, and 25/75 polyol formulations). The observed elongate shape can thus explain the low compressive modulus obtained for foams based on this formulation. In a general way, SEM micrographs show that cells tend to become smaller and less elongate as the lignin-based polyol content decrease, i.e., as the commercial polyol content increases. This behavior can explain the observed density and compressive modulus increase as the lignin-based polyol content decreases. Density is known to increase as cell size decreases, which influences mechanical properties.[23] Nevertheless, this hypothesis is only true for cells with similar wall thickness. Figure 3 shows SEM micrographs obtained for foams containing 25, 50, 75, and

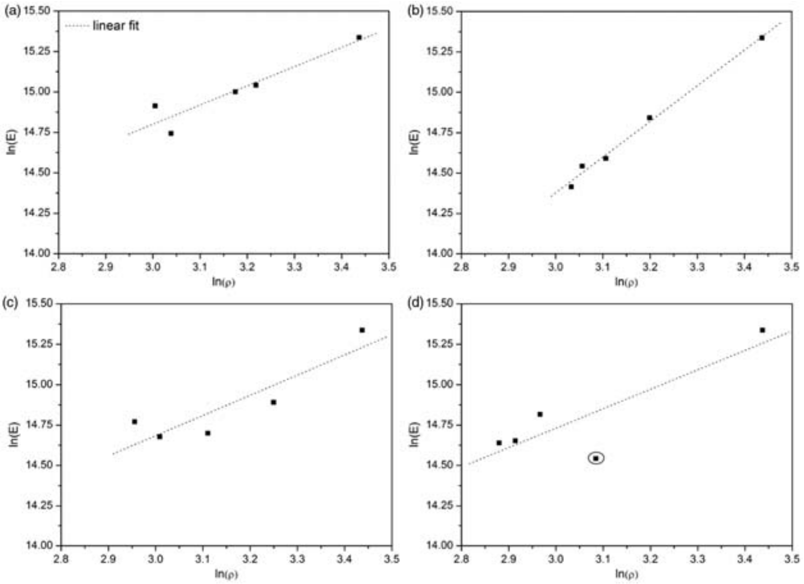

Figure 4. Relationship between compressive modulus and density of RPU foams produced with (a) Alcell, (b) Sarkanda, (c) Indulin AT, and (d) Curan 27-11P 20/80/5 lignin-based polyols.

100% of Alcell- and Indulin AT-based polyols. As can be observed, cells of very large size were often detected leading to overall heterogeneous structures in terms of cell size distribution. This heterogeneity can explain why no consistent relationship between conductivity and lignin-based polyol content was observed.

The relationship between density and compressive modulus is described in polyurethane foam literature according to the power-law presented in equation (2).

$$E = A \times \rho^n \tag{2}$$

where:

E is the compressive modulus, in MPa
A is a constant
ρ is the density, in kg/m^3
n is the density exponent.

Figure 4 shows the linear plot derived from equation (2) (ln(E) versus ln(ρ)) for RPU foams produced with lignin-based polyols. As can be observed, a good correlation was found for foams produced with Alcell- and Sarkanda-based polyols presenting correlation coefficients of 0.94 and 0.99, respectively. For foams produced with Indulin AT- and Curan 27-11P-based polyols, lower correlation coefficients were obtained, i.e., 0.90 and 0.85, respectively. The poor correlation obtained for Curan 27-11P polyol-based foams can be due to the apparently

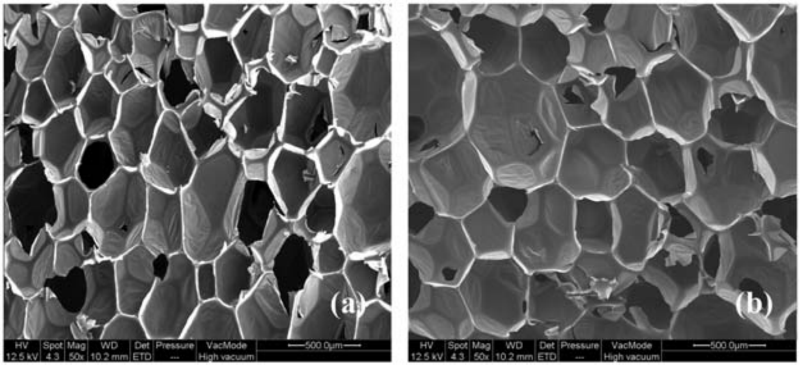

Figure 5. SEM micrographs of RPU foams produced with a polyol composition of: (a) 50% and (b) 25% of 20/80/5 Curan 27-11P-based polyol (free-rise direction, magnification of 50X).

abnormal result achieved for the foam with a polyol content of 25%. SEM analysis showed that this foam presented larger cells comparatively with those produced with other contents of Curan 27-11P-based polyol (Figure 5). When this value is removed, a correlation coefficient of 0.99 is obtained. The calculated density exponent values were approximately constant for foams produced with Alcell, Indulin AT and Curan 27-11P polyols, respectively, 1.18, 1.25, and 1.20. For Sarkanda polyol-based foams, the density exponent value was found to be superior (2.2). According to the literature, n values are usually comprised between 1.0 and 2.0.[24]

The obtained results for compressive modulus were quite intriguing since due to the aromatic nature of the used polyols, together with its high functionality, an increasing value as a direct consequence of the lignin-based polyol content increase was expected. Nevertheless, it is important to notice that the KOH used in the oxypropylation process was left in the polyol mixture, thus contributing as an additional catalyst when lignin-based polyols are used. This result can also be explained by the molecular architecture of these polyols, characterized by the presence of quite long PPO grafts that can impart some degree of flexibility to the final products.

A global inspection of the results obtained with the 20/80/5 polyol-based formulations indicated that the ones derived from Alcell, Indulin AT, and Curan 27-11P lignins produced foams with properties quite comparable with the reference foam. Sarkanda-based polyols seem to be inadequate for RPU foams formulations, at least for the chemical system used in this work.

RPU foams prepared with the lignin-based polyol formulation 30/70/2

The reactive mixtures prepared with the 30/70/2 Sarkanda based polyol were heterogeneous and no RPU foams were produced. This was attributed to the non-Newtonian behavior presented by this polyol. Foams produced with

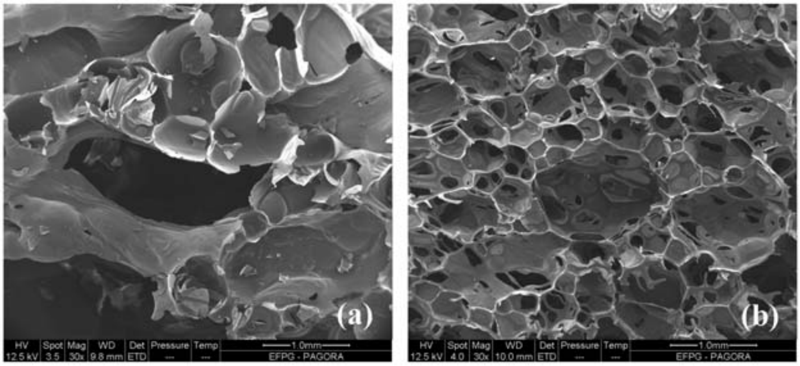

Figure 6. SEM micrographs obtained for RPU foams containing (a) 100% and (b) 50% of 30/70/2 Curan 27-11P-based polyol (free-rise direction, magnification of 30X).

Table 3. Density, thermal conductivity, compressive modulus, and average cell size of RPU foams obtained from 30/70/2 polyols.

Lignin	Polyol (LP/CP, w/w)	ρ (kg/m^3)	λ (mW/mK)	E (MPa)	Average cell size (mm)
Alcell	100/0	22.3	25.7	3.1	0.36
	50/50	25.1	26.9	3.0	0.37
Indulin AT	100/0	23.1	27.4	4.0	0.37
	50/50	23.7	29.1	3.6	0.40
Curan 27-11P	100/0		Very brittle foams		
	50/50				
Reference foam	0/100	31.10	30.3	4.58	0.44

A 100% Lupranol 3323-based foam is presented as reference.

Curan 27-11P-based polyol were generally brittle. Moreover, SEM analysis revealed foams with no defined cells for a content of 100% (Figure 6(a)), and foams with irregular cell size and quite deteriorated cells for a content of 50% (Figure 6(b)). Therefore, this polyol formulation seems to be unsuitable for RPU synthesis, at least this is valid for the chemical system used in this work.

The properties of the RPU foams produced with Alcell- and Indulin AT 30/70/2-based polyols are summarized in Table 3. Comparatively to those obtained with 20/80/5 polyols, these RPU foams exhibited both higher density and compressive modulus. Moreover, the achieved values are closer to those of the reference RPU foam. In what concerns conductivity values they were inferior to those of the reference foam as well as to those produced with the 20/80/5 polyols, i.e. foams produced with 30/70/2 present better insulation properties. Only foams prepared

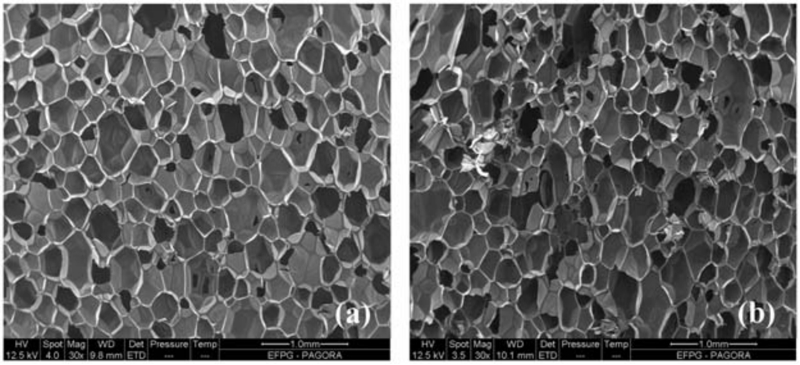

Figure 7. RPU foams prepared with 100% of (a) Alcell- and (b) Indulin AT 30/70/2-based polyols (free-rise direction, magnification of 30X).

with 100% Indulin AT 30/70/2 polyol presented conductivities slightly superior (therefore are inferior), to those of its counterpart obtained with Indulin AT 20/80/5 polyol.

Properties improvement exhibited by RPU foams produced with 30/70/2 polyols (Alcell- and Indulin AT-based) could be related to cell size distribution that includes, predominantly, small size cells, as illustrated by Figure 7. In addition, this polyol formulation presents a higher lignin content, a lower homopolymer content, and a lower catalyst content, comparatively to 20/80/5 polyol formulation. These factors contribute to increment crosslinking density thus improving mechanical properties. In conclusion, for RPU foam production purposes, both for Alcell and Indulin AT, the polyol formulation 30/70/2 seems to be a better choice than the formulation 20/80/5. This is in fact quite encouraging since when using this polyol formulation a greater quantity of lignin is effectively introduced in the final polymeric materials.

Tables 4 and 5 show the attained weight loss for samples subjected to biodegradation assays in liquid and solid media, respectively. Biodegradation results based on 30/70/2 polyols have pointed out that RPU foams produced from 100% lignin-based polyol are highly resistant to biodegradation for all the tested microorganisms. This situation changes when a mixed polyol (lignin-based plus commercial) is used, being the results also superior to those obtained with the reference foam. This is particularly valid for Indulin AT-based polyols that have shown this tendency both in liquid and solid media. In solid media, both samples using the mixed polyols based on Alcell or Indulin AT gave quite similar results.

Among the used microorganisms, *P. chrysosporium* and *T. versicolor*, have originated the higher weight loss. These two fungi produce enzymatic extracts rich on lignin peroxidase (Lip), manganese peroxidase (MnOX), and laccase (Lac), three enzymes whose combinatory effect on lignin biodegradation is well known. Lignin biodegradation is favored if an alternate food source is present in the medium and Lupranol® 3323, a sorbitol-based polyol, seems to assume this role.

Table 4. Weight loss (%, w/w) in liquid media for RPU foams obtained from 30/70/2 polyols.

	Alcell		Indulin AT		
	100/0	50/50	100/0	50/50	Reference foam
P. chrysogenum	ND	ND	ND	ND	ND
P. chrysosporium	1	5	ND	18	4
T. versicolor	1	10	1	12	8
T. harzianum	ND	ND	ND	2	ND
T. reesei	ND	1	ND	ND	1

ND: not detected

Table 5. Weight loss (%, w/w) in solid media for RPU foams obtained from 30/70/2 polyols.

	Alcell		Indulin AT		
	100/0	50/50	100/0	50/50	Reference foam
P. chrysogenum	ND	ND	ND	ND	ND
P. chrysosporium	ND	25	ND	25	10
T. versicolor	1	15	1	16	10
T. harzianum	ND	ND	ND	5	ND
T. reesei	ND	10	ND	ND	1

ND: not detected

Comparatively to Alcell, Indulin has both high residual sugars and total hydroxyl contents (with predominance of aliphatic ones), which can also contribute to the higher degradation level of Indulin-AT-based RPU foams.

Conclusions

RPU foams have been prepared using lignin-based polyols obtained by oxypropylation of four technical lignins (Alcell, Indulin AT, Curan 27-11P, and Sarkanda). Two formulations comprising L/PO/C ratios of 20/80/5 and 30/70/2 have been used alone or mixed with a commercial polyol (Lupranol® 3323) at contents of 25, 50, and 75%. Foam formulations using Alcell- and Indulin AT-based polyols, or the 20/80/5 Curan 27-11P one, led to RPU foams with properties quite similar to those of the reference foam. The two Sarkanda-based polyols and the 30/70/2 Curan 27-11P one were found inappropriate. Foams produced with these polyols were quite brittle and, in the case of 30/70/2 Sarkanda polyol, very heterogeneous reactive mixtures were formed hindering foam formulation.

RPU foams produced with Alcell and Indulin AT 30/70/2 polyols exhibited properties superior to those obtained with the corresponding 20/80/5-based polyols. This behavior was associated to: (1) a more prominent presence of lignin and (2) a less pronounced contribution of KOH catalyst in foam formation.

It is worth to note that the drawn conclusions concerning the evaluation of the effect of the polyol type on conductivity and compressive modulus should be taken with care because the density of the reference foam is significantly higher than those made of lignin-based polyol containing formulations. A more comprehensive work will result if density heterogeneity among samples could be minimized.

Among the tested lignin-degrading fungi, biodegradation of lignin-based RPU foams was more evident when using *P. chrysosporium* and *T. versicolor* and formulations using mixed polyols (lignin-based polyol plus Lupranol® 3323, a commercial sorbitol-based polyol). Although the use of 100% of lignin-based polyols is desirable in terms of maximizing the incorporated lignin content, this "symbiotic" effect can provide added-value to this type of products, that can be presented has having improved biodegradation.

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