RIGID POLYURETHANE FOAMS FROM LIGNIN BASED-POLYOLS

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ABSTRACT

Rigid polyurethane (RPU) foams were synthesized using lignin-based polyols obtained by an oxypropylation process. Alcell, Indulin AT, Curan 27-11P and Sarkanda lignins have been oxypropylated using formulations deduced from an optimization study with Alcell. L/PO/C (ratio between lignin, PO and catalyst content) of 30/70/2 and 20/80/5 were used to obtain the desired polyols.
The resulting RPU foams were characterized in terms of density, mechanical properties, conductivity and morphology. All Sarkanda lignin based polyols and the 30/70/2 Curan 27-11P polyol were found inadequate for RPU formulations. Alcell and Indulin AT based polyols and the 20/80/5 Curan 27-11P polyol resulted in RPU foams with properties very similar to those obtained from conventional commercial polyols. RPU foams produced with the 30/70/2 Alcell and the 30/70/2 Indulin AT polyols exhibited improved properties compared with those from 20/80/5 based formulations.

1 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. Due their excellent insulation and mechanical properties they are widely used in construction, automotive, freeze industry and nautical applications.
Nowadays, due to economical and environmental concerns, the utilization and development of low-cost polyols from abundant and renewable biomass resources has gained an increasing attention in polyurethane industry. Lignin is among these biomass resources, and its application as a macromonomer in polyurethane synthesis, has been the subject of study of several research groups [1-2].
Oxypropylation has been recognized as a viable and promising approach to overcome the technical limitations and constrains imposed by the polymeric nature of lignin when directly used as a macromonomer for synthesis purposes. 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 polyol, thanks to the introduction of multiple ether moieties.
The high functionality associated to these polyols makes them ideal for the synthesis of RPU foams. Several studies revealed that RPU foams obtained from lignin based polyols present insulating properties, dimensional stability and accelerated ageing behaviour very similar to those prepared with commercial polyols [2-3]. Moreover, the intrinsic properties of lignin will also contribute to an improvement of moisture and flame resistance [4]. These results were quite motivating, giving emphasis to the need of further research in this domain allowing lignin valorisation through its incorporation in a polymeric material.
This work aims to evaluate the suitability of two lignin-based formulations (20/80/5 and 30/70/2) to produce RPU foams. Density, mechanical properties, conductivity and morphology of lignin based RPU foams were determined and compared to reference RPU foam based on a typical commercial polyol.

2 EXPERIMENTAL

2.1 Materials The lignin based polyols used in this work were obtained from the oxypropylation of four technical lignins (Alcell, Indulin AT, Curan 27-11P and Sarkanda) as described elsewhere [4]. The following terminology will be used to identify the polyol formulations used in this work: L/PO/C (ratio between lignin, PO and catalyst content). The commercial polyether polyol (Lupranol® 3323), polymeric MDI (PMDI with a functionality of 2.7), silicone surfactant (SR-321 NIAX) and the catalysts NIAX and DMCHA were kindly supplied by Elastogran-BASF (France). Glycerol and *n*-pentane were commercially obtained.

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2.2 Foam Preparation Polyurethane foams were prepared by initially mixing, during 1 minute, the polyol or polyol mixture in combination with 10% w/w of glycerol with the surfactant (2% w/w), water (2% w/w) and a catalyst combination (2% w/w of equal amounts of DMCHA and NIAX). Thereafter, *n*-pentane was added (20% w/w) and the mixture was stirred during 30 s. Finally, the polymeric isocyanate was added and the resulting mixture was vigorously stirred until foam started to grow. Foams were left to cure during 24 hours at room temperature. The weight percentage of glycerol, surfactant, water, catalysts and, *n*-pentane are giving relatively to total weight of the polyol. The isocyanate/hydroxyl (NCO/OH) ratio was of 1.1.

2.3 Foam Characterization For density and compression tests, foams were cut into cube specimens of 50×50×50 mm^3 dimensions and thereafter conditioned during 40 hours at 23ºC and 50% of humidity.
The densities of the foams were determined according to ASTM D1622 standard method. The specimens were weighted and its dimensions measured. Density was calculated by dividing the mass and volume obtained for each specimen.
Compression test were conducted according to ASTM D1621 standard. Measurements were performed using Instrom model 4501 equipment in the direction perpendicular to foam growth. A load was applied at crosshead speed of 5 mm/min until the specimen was compressed to approximately 15% of its original thickness.
Conductivity measurements were conducted according to ASTM C177 standard. Specimens with a diameter of 90 mm and thickness of 4 mm were cut and placed in an apparatus developed to measure the thermal conductivity of isolating materials. This apparatus consist in two plates maintained at different temperatures. The thermal conductivity of the samples was determined when the thermal equilibrium was reached and a uniform temperature gradient thought the sample was establish.
The morphology analysis of RPU foams 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 and the sample was observed both in the free-rise direction and free-rise perpendicular direction.

3 RESULTS AND DISCUSSION

Lignin based polyols obtained from four technical lignins, without any type of purification in which regards homopolymer and catalyst (KOH) contents, were used to produce RPU foams. Several RPU foams were prepared by varying the lignin based polyol content from 0 to 100% (w/w).
For Sarkanda lignin 30/70/2 polyols, the generated mixtures were heterogeneous and no RPU foams were produced. Moreover, RPU foams produced with 20/80/5 polyol were very brittle, showing very large cells and consequently poor mechanical properties. Similar properties were also presented for the RPU foams prepared with 30/70/2 Curan 27-11P-based polyols. Beyond the conditions used in this study, the 30/70/2 Curan 27-11P polyol and Sarkanda lignin-based polyols seem to be not adequate for RPU foams formulations.
Alcell and Indulin AT based polyols and 20/80/5 Curan 27-11P polyol results in RPU foams with properties very similar to that obtained from typical commercial polyols. The density, thermal conductivity and compressive modulus of some of these foams are summarized in Table 2. The properties of the RPU foams produced with the commercial polyol are also shown as a reference.
The data from Table 2 shows that the lowest conductivity values are obtained when RPU foams are produced with 100% lignin based polyols. Moreover, morphological analyses also revealed that these foams present cells with a well defined hexagonal geometry and with quite homogeneous sizes (see Fig. 1). However, the density and compressive modulus of lignin-based RPU foams showed to be always lower to that of reference RPU foam.
Alcell and Indulin AT foams obtained with 30/70/2 polyols, in which a greater quantity of lignin is effectively introduced, exhibited properties slighter higher than those obtained with 20/80/5 polyols, mainly with respects to density and compressive modulus, which have been found to be closer to that of the reference RPU foam.

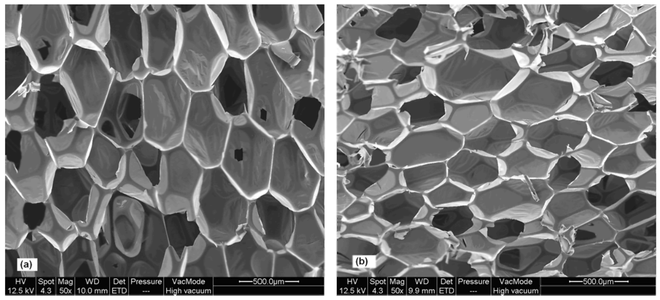

Figure 1 Scanning electron micrographs obtained for RPUs foams containing 100% w/w of 20/80/5 polyol (a) Alcell and (b) Indulin AT.

L/PO/C (w/v/(%w/w))	Lignin sample/ % Lignin polyol (w/w)	Density (Kg/m^3)	Conductivity (mW/mK)	Compressive Modulus (MPa)
30/70/2	Alcell/100	22.3	25.7	3.1
	Alcell/50	25.1	26.9	3.0
	Indulin AT/100	23.1	27.4	4.0
	Indulin AT/50	23.7	29.1	3.6
20/80/5	Alcell/100	20.9	26.7	2.5
	Alcell/50	23.9	30.5	3.3
	Indulin AT/100	19.2	26.8	2.6
	Indulin AT/50	22.4	32.9	2.4
	Curan 27-11P/100	18.4	28.5	2.3
	Curan 27-11P/50	19.4	31.3	2.7
Reference Foam (100% commercial polyol)		31.10	30.3	4.6

Table 1 Density, thermal conductivity and compressive modulus of some RPU foams.

3 CONCLUSIONS

RPU foams were prepared by using two formulations of lignin-based polyols (20/80/5 and 30/70/2) obtained from the oxypropylation of four technical lignins (Alcell, Indulin AT, Curan 27-11P and Sarkanda). Foams with very poor properties were obtained when 20/80/5 Sarkanda and 30/70/2 Curan 27-11P polyols were used. The utilization of 30/70/2 Sarkanda polyol also presented some difficulties and the preparation of RPU foams was not possible. Alcell and Indulin AT based polyols and the 20/80/5 Curan 27-11P polyol seem to be a good alternative to conventional polyols used in RPU formulations. The RPU foams obtained presented properties close to those found for foams made with commercial polyols. Moreover, insulating properties were, for most of the cases, higher than those corresponding to commercial polyol-based materials. Further optimization seems however to be necessary in order to improve mechanical properties of lignin based RPU foams.

It was also observed that Alcell and Indulin AT 30/70/2 polyols produced foams with properties slighter superior to those of 20/80/5 polyols.

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