RIGID POLYURETHANE FOAMS FROM LIGNIN-BASED POLYOLS

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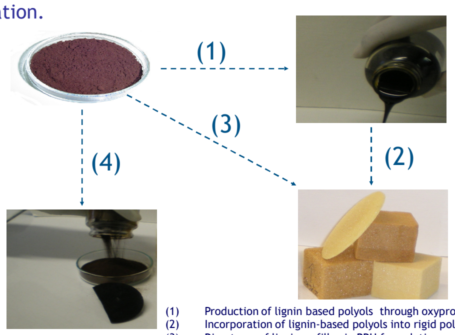
•••• • OBJECTIVES • ••••

Evaluate the suitability of use lignin-based polyols, obtained by oxypropylation, to produce rigid polyurethane (RPU) foams.

•••• • LIGNIN AS A RAW-MATERIAL FOR POLYURETHANES • ••••

The utilization of lignin in polyurethane synthesis often follows two global approaches: (i) the direct utilization without any preliminary chemical modification, alone or in combination with other polyols or, (ii) by making hydroxyl functions more readily available by chemical modification, such as oxypropylation.



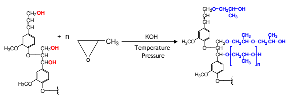
(1) Production of lignin based polyols through oxypropylation
(2) Incorporation of lignin-based polyols into rigid polyurethane foams (RPU)
(3) Direct use of lignin as filler in RPU formulations
(4) Direct use of lignin as macromonomer in elastomer formulations

Different approaches for lignin incorporation in polyurethane materials

•••• • LIGNIN-BASED POLYOLS • ••••

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.

Oxypropylation has been recognized as a viable and promising approach to overcome the technical limitations and constrains imposed by the polymeric nature of lignin. **The high functionality associated to these polyols makes them ideal for the synthesis of RPU foams.**



Schematic representation of lignin oxypropylation reaction.

No purification, concerning homopolymer and catalyst (KOH) presence was performed.

Some properties of the lignin-based produced polyols.

Component		Some Properties		
Lignin based Polyols		I_{OH} (mgKOH/g)	Viscosity (20ºC, Pa.s)	Functionality
20/80/5	Alcell	283	4.0	7.0
	Sarkanda	294	2.7	7.1
	Indulin AT	343	4.3	7.1
	Curan 27-11P	366	4.7	6.4
30/70/2	Alcell	279	49	8.6
	Sarkanda	357	Non-Newtonian	6.1
	Indulin AT	366	66.6	9.0
	Curan 27-11P	462	50.3	7.9

Nomenclature: L/PO/C (ratio between lignin, PO and catalyst content).

•••• • RPU FOAM PREPARATION • ••••

1. The polyol or polyol mixture in combination with 10% (w/w) of glycerol, surfactant (SR-321 NIAX) (2% w/w), water (2% w/w) and a catalyst combination (2% w/w of equal amounts of DMCHA and NIAX) were mixed during 1 minute.
2. *n*-pentane was added (20% w/w) and the mixture was stirred during 30 s.
3. Polymeric isocyanate (MDI) was added and the mixture vigorously stirred until the foam started to grow.
4. 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 and the **content of lignin- based polyols varied between 0-100% (w/w).**

•••• • FOAM CHARACTERIZATION • ••••

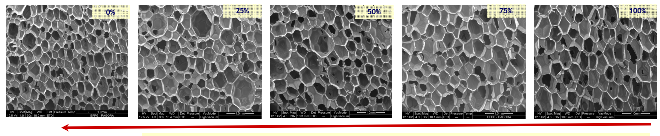
Density, mechanical properties, conductivity and morphology were determined and compared to a reference RPU foam based on a typical commercial polyol.

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

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

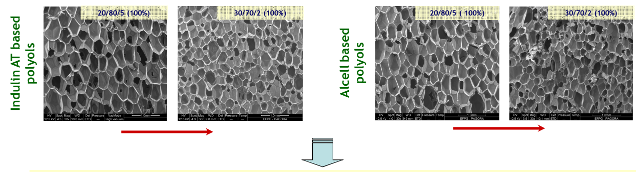
Morphological analysis
Scanning electronic microscopy (SEM)

Effect of lignin content on cells size and geometry (20/80/5 Alcell based polyol)



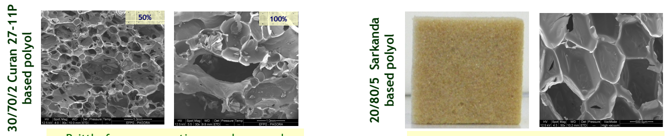
Smaller and less elongated cells with the decrease of lignin based polyols content.

Effect of polyol formulation on cells size and geometry



Smaller and less elongated cells obtained when the 30/70/2 lignin based polyol formulation was used.

Not suitable polyol formulations



Brittle foams presenting very large and undefined cells.

Brittle foams presenting very large cells.

•••• • CONCLUSIONS • ••••

- Alcell and Indulin AT based polyols and 20/80/5 Curan 27-11P based polyol seem to be a good alternative to conventional polyols used in RPU formulations;
- Insulating properties of lignin based RPU foams were, for most of the cases, superior to those of the reference foam;
- RPU foams produced with 30/70/2 Alcell and Indulin AT based polyols (greater quantity of lignin is effectively introduced), exhibited properties superior to those obtained with its counterpart 20/80/5 based polyols, mainly in which to density and compressive modulus;
- The preparation of RPU foams with 30/70/2 Sarkanda based polyol was not possible due to the complex rheological properties presented by this polyol;
- Sarkanda based polyols and 30/70/2 Curan 27-11P based polyol were found to be unsuitable for RPU formulations;
- Further optimization seems to be necessary in order to improve mechanical properties of lignin based RPU foams and fully verify the suitability of using Sarkanda based polyols and 30/70/2 Curan 27-11P based polyol in RPU foam formulations.

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