LIGNIN-BASED POLYURETHANE ELASTOMERS

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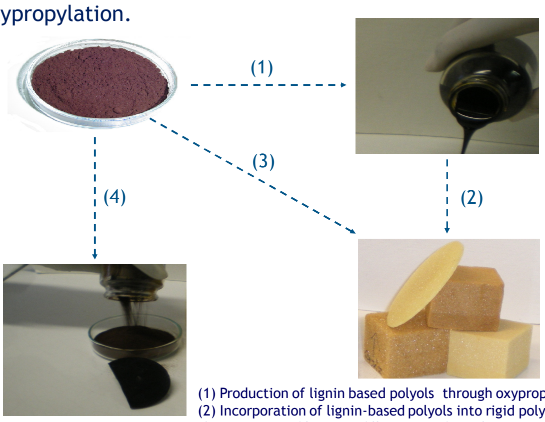
•••• • OBJECTIVES • ••••

Evaluate the suitability of use lignin as such to produce elastomeric polyurethanes.

•••• • 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.

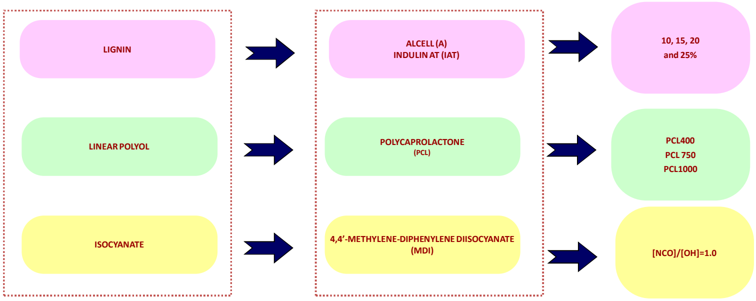


(1) Production of lignin based polyols through oxypropylation
(2) Incorporation of lignin-based polyols into rigid polyurethane foams (RPU)
(3) Direct use of lignin as filler in RPU formulations
(4) Direct use of lignin as macromonomer in elastomer formulations

Different approaches for lignin incorporation in polyurethane materials

•••• • CHEMICAL SYSTEM AND FORMULATIONS • ••••

Lignin-based polyurethanes were synthesized in bulk at 80 ºC using a three-component system.

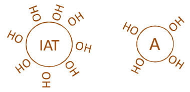


LIGNIN → ALCELL (A)
INDULIN AT (IAT) → 10, 15, 20 and 25%

LINEAR POLYOL → POLYCAPROLACTONE (PCL) → PCL400, PCL 750, PCL1000

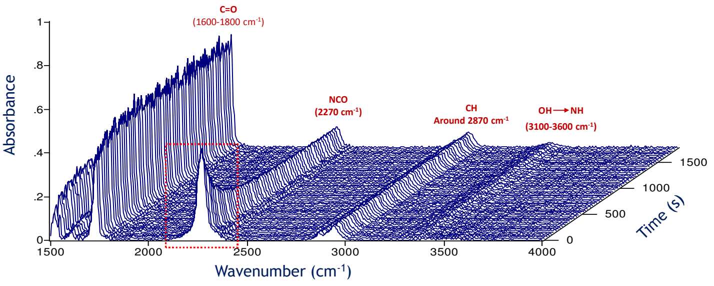
ISOCYANATE → 4,4'-METHYLENE-DIPHENYLENE DIISOCYANATE (MDI) → [NCO]/[OH]=1.0

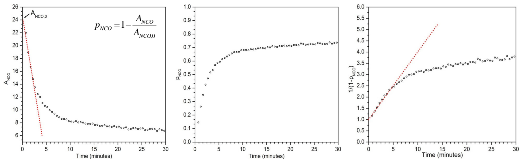
<u>Alcell lignin versus Indulin AT:</u>
Molecular weight: 760 *versus* 1079
Total hydroxyl content: 5.26 *versus* 6.99 mmol OH/g
Aliphatic hydroxyl content: 1.10 *versus* 2.34 mmol OH/g
OH functionality: 4 *versus* 8



•••• • SYNTHESIS MONITORING• ••••

Synthesis monitoring was done by FTIR-ATR at 80 ºC during 30 minutes.





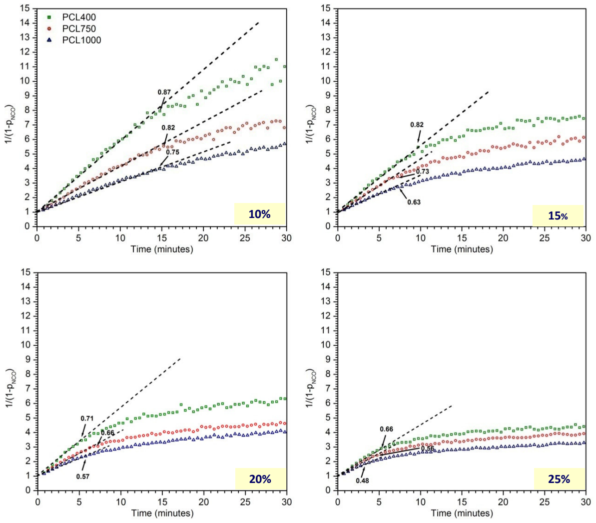
Decay of isocyanate absorbance (A_{NCO}) with time.

Corresponding isocyanate conversion (p_{NCO}) curve with time.

Corresponding second order plot.

<u>Acknowledgments:</u> Meadwestvaco and Solvay Interox for providing Indulin AT and PCLs, respectively. To Dr. Jairo Lora and Prof. Dimitry Evtuguin, for providing us the Alcell lignin and facilities for VPO tests, respectively. Financial support from French-Portuguese Programme (F13/06 and F32/08) and FCT (SFRH/BD/18415/2004) are acknowledged.

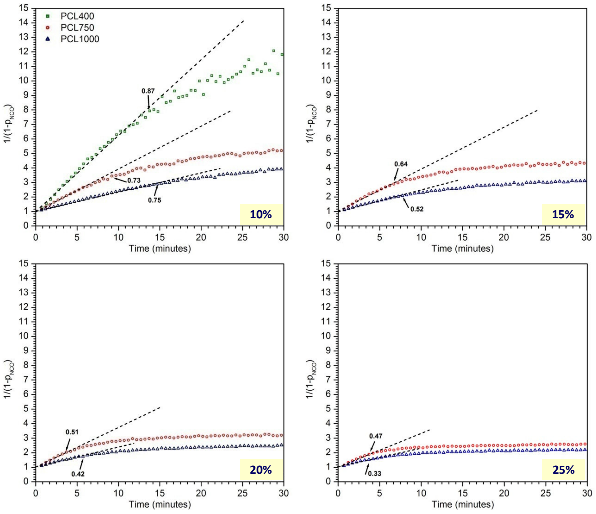
•••• • ALCELL EXPERIMENTS • ••••



Effect of PCL molecular weight for a fixed lignin content ([NCO]/[OH]=1)

- Domain of validity decreases with both increase of PCL molecular weight and increase of lignin content.
- Negative deviation for all experiments. More pronounced as the lignin content increases.

•••• • INDULIN AT EXPERIMENTS • ••••



Effect of PCL molecular weight for a fixed lignin content ([NCO]/[OH]=1)

- For PCL400 and lignin contents > 10% a prompt "solidification" of the reactive mixture occurs.
- Domain of validity decreases with both increase of PCL molecular weight and increase of lignin content.
- Negative deviation more pronounced comparatively to Alcell experiments.

For low lignin contents, the experimental data generally fitted well a global second order kinetic model. After the region of linearity, a negative deviation was always noticed and found to be more pronounced with the increase of lignin content and PCL molecular weight. The negative deviation can be assigned to an effective network formation that hinders the reaction between hydroxyl and isocyanate groups. Moreover, the complex lignin architecture, the lack of reactivity of its phenolic hydroxyl groups and a rapid increase of medium viscosity also contributes to this effect.

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●●●● ● LIGNIN-BASED POLYURETHANES CHARACTERIZATION ● ●●●●

In order to inspect the effect of PCL molecular weight, lignin content and type on lignin-based polyurethane properties, several samples were synthesized and analyzed by modulated DSC and by DMA and subjected to swelling tests in DMF.

The following properties have been determined: Glass transition temperature - Tg (determined both by DMA and DSC); Storage modulus - E´ (determined by DMA) ; Crosslinking density (determined both based on DMA data and swelling tests) and sol fraction (determined based on swelling tests).

Crosslinking density:

DMA

$$\frac{E'}{3} = \nu_e RT$$

- *E'* is the storage modulus, in Pa (rubbery plateu)
- ν_e is the crosslinking density, in mol/cm^3
- *R* is the molar gas constant, in J/K.mol
- *T* is the temperature, in K

Swelling

$$\frac{\nu_C}{V_0} = \frac{-2(\nu + \chi\nu^2 + \ln(1-\nu))}{V_1(2\nu^{1/3} - \nu)}$$

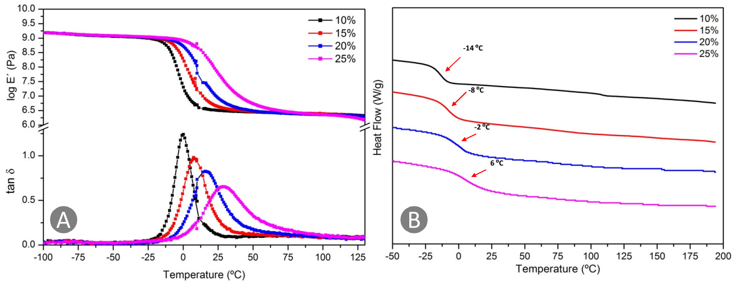
$$\nu = \frac{V_0}{V_\infty}$$

- ν_c is the effective number of crosslinked chains, in moles
- V_0 is the volume of dry polymer, in cm^3
- V_∞ is the volume of the swollen gel at equilibrium, in cm^3
- χ is the polymer-solvent interaction parameter
- V_1 is the molar volume of the solvent, in cm^3/mol

Sol fraction: $\text{sol fraction } (\%, \text{w/w}) = \frac{W_0 - W_D}{W_0} \times 100$

- W_0 is the initial weight of polymer
- W_D is the dry weight of extracted polymer
- χ=0.40 (Yoshida et al., 1987) (chemical system based on PEG, MDI and a kraft lignin).

●●●● ● ALCELL-BASED POLYURETHANES ● ●●●●



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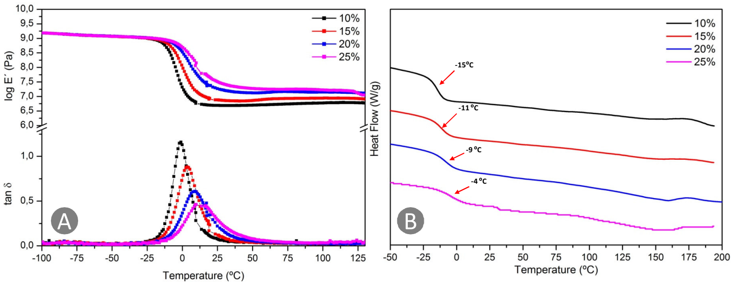
Sample	ν_e ×10^{-3} mol/cm^3		sol fraction (%, w/w)
	DMA	Swelling	
A(PCL750/1/10)	0.28	0.19	8.5
A(PCL750/1/15)	0.28	0.24	8.5
A(PCL750/1/20)	0.26	0.33	8.2
A(PCL750/1/25)	0.28	0.27	8.6
A(PCL400/1/25)	0.33	0.30	12.0
A(PCL750/1/25)	0.28	0.27	8.6
A(PCL1000/1/25)	0.30	0.40	8.0

A. Storage modulus (E´) and loss tan (tan δ) / B. DSC traces with Tg assigned
C. Crosslinking density and sol fraction

- As the lignin content increase, the maximum of tan δ (Tg) shifts towards higher temperatures and the peak become broader. This tendency was also confirmed by DSC analysis.
- Storage modulus (E´) at the rubbery plateau remains approximately constant with both the increase of lignin content and increase of PCL MW (data not shown).
- Crosslink density and sol fraction data show a similar trend. Nevertheless, the sol fraction of A(PCL400/1/25) polyurethane was an exception to the expected tendency, showing an apparently abnormal high value.

●●●● ● INDULIN AT-BASED POLYURETHANES ● ●●●●



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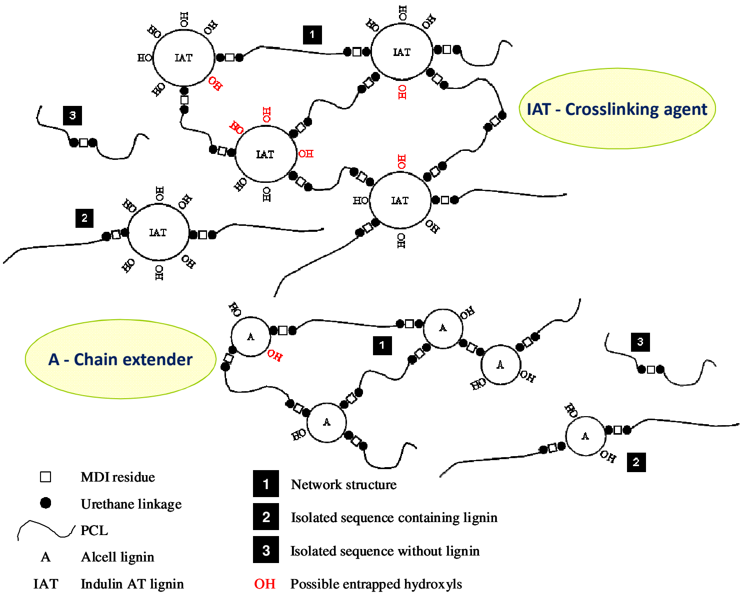
Sample	ν_e ×10^{-3} mol/cm^3		sol fraction (%, w/w)
	DMA	Swelling	
IAT(PCL750/1/10)	0.64	0.25	4.4
IAT(PCL750/1/15)	0.96	0.32	4.9
IAT(PCL750/1/20)	1.59	0.39	6.3
IAT(PCL750/1/25)	1.99	0.14	7.5
IAT(PCL750/1/25)	1.99	0.14	7.5
IAT(PCL1000/1/25)	3.88	2.48	10.1

A. Storage modulus (E´) and loss tan (tan δ) / B. DSC traces with Tg assigned
C. Crosslinking density and sol fraction

- As the lignin content increase, the maximum of tan δ (Tg) shifts towards higher temperatures and the peak become broader. Also confirmed by DSC analysis.
- E´ (rubbery plateau) increases with lignin content increase until a lignin content of 20% (w/w) and with PCL MW (data not shown).
- Crosslink density increases with lignin content increase.
- Sol fraction was always inferior to that of Alcell based polyurethanes counterparts and increases slightly with lignin content increase. An abnormal high value was achieved for the sample IAT (PCL1000/1/25).

●●●● ● LIGNIN-BASED POLYURETHANE NETWORKS ● ●●●●



IAT - Crosslinking agent

A - Chain extender

□	MDI residue
●	Urethane linkage
∼	PCL
A	Alcell lignin
IAT	Indulin AT lignin

1	Network structure
2	Isolated sequence containing lignin
3	Isolated sequence without lignin
OH	Possible entrapped hydroxyls

ALCELL *versus* INDULIN AT

The achieved structure-properties relationships are generally in accordance with published data, nevertheless some change clear cut of tendency was noticed for the samples A(PCL400/1/25) and IAT(PCL1000/1/25). Comparatively to Alcell, Indulin AT has a higher molecular weight and higher hydroxyl content. Moreover, in the network structure Indulin-AT generates larger and stiffer lignin “islands” comparatively to Alcell. In conclusion low molecular weight PCL are, in principle, less efficient in creating three-dimensional polyurethane networks. This effect is highlighted for Alcell lignin that contains lower hydroxyl content. This seems to be the case of A(PCL400/1/25), for which a apparently abnormal high sol fraction was achieved. On the opposite side, high molecular weight polyols increase network formation efficiency. Nevertheless, for very long PCL chains this efficiency decreases mainly due to a dilution effect of the hydroxyl chain-ends. This effect is highlighted for Indulin-AT where the volume of the stiff lignin islands hinders an effective network formation. This seems to be the case of IAT(PCL1000/1/25), for which a apparently abnormal high sol fraction was achieved.