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MACROCICLOS NATURAIS E AFINS: DA SÍNTESE E REACTIVIDADE ÀS APLICAÇÕES

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Em cada organismo vivo têm lugar, a cada momento, funções vitais que envolvem a acção de muitos compostos. Muitos grupos de investigação centraram, desde há várias décadas, as respectivas actividades científicas nesses compostos, através da realização de estudos de caracterização físico-química, de elucidação dos processos de biossíntese e modos de acção e metabolismo e do estabelecimento de metodologias de síntese para oa mesmos. Outros investigadores, sobretudo em décadas mais recentes, têm considerado nos seus estudos a procura de possíveis aplicações, quer para derivados de muitos compostos naturais, quer para análogos obtidos em processos de síntese relativamente simples.

Estudos realizados na Universidade de Aveiro, sobretudo nos últimos quinze anos, têm tido como objectivos principais os seguintes: procura de novos e melhores métodos de síntese para certos compostos de tipos porfirínico e polifenólico; estudo da reactividade desses compostos em transformações de ciclo-adição; avaliação, através de colaborações interdisciplinares, de propriedades biológicas dos novos derivados e procura de aplicações medicinais (p.e. no tratamento de neoplasias e como agentes antivirais e antibacterianos), catalíticas e outras para os mesmos; caracterização de produtos de origem vegetal e suas transformações de catálise oxidativa em derivados de valor acrescentado. Serão apresentados na presente palestra os resultados mais significativos obtidos em tais estudos.

Agradecimentos

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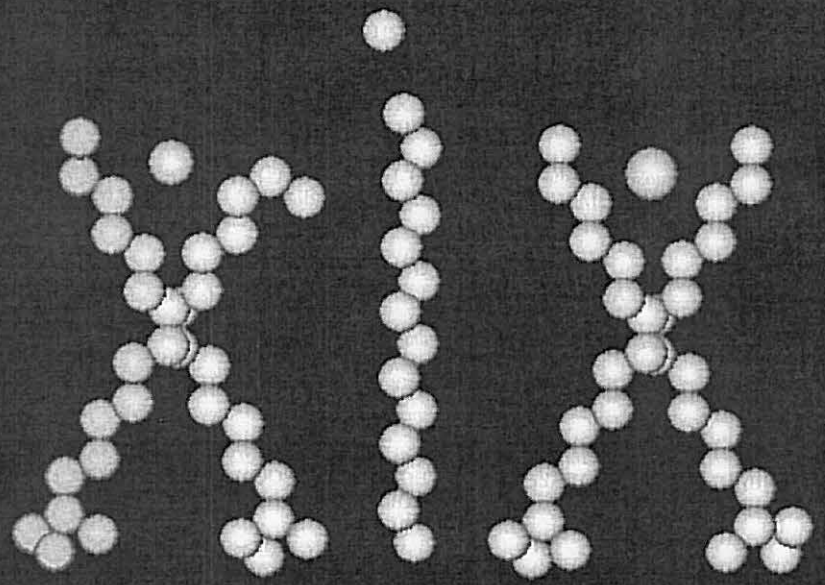
COMUNICAÇÕES EM PAINEL

Sessão de Painéis I (pares)

Sessão de Painéis II (ímpares)



Study of the formation of lignin-based polyurethanes

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Introduction:

The synthesis of polymers from biomass components has attracted considerable interest in recent years. Lignin, the second most abundant biopolymer, only after cellulose, is among these biomass components. It has a polyphenolic structure with several available reaction groups: carbonyl, carboxyl and hydroxyl groups. The presence of hydroxyl groups (aliphatic and aromatic) allows its use (direct or after minor derivatization) as the polyol component in polyurethane formulations.

The polyurethane samples have been prepared starting with 4,4'-methylene-diphenylene isocyanate (MDI), policaprolactonediol (PCL) of three different average molecular weights (1000, 750 and 400) and a commercial lignin (Indulin AT from Westvaco) at different weight contents (10, 15, 20 and 25%). PCL was chosen because of its favorable miscibility characteristics and biodegradability. Stoichiometric conditions (NCO/OH=1) were used for all formulations.

Reaction conditions (temperature and NCO/OH ratio) were chosen in order to avoid chemical reticulation due to isocyanate secondary reactions. In that way, we will expected a three dimensional network as a direct consequence of lignin incorporation.

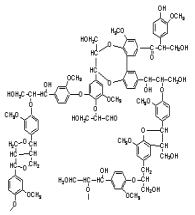
FTIR experiments:

Lignin and PCL were weighed in an analytical balance in the desired proportions and the mixture was homogenized by stirring. Then, molten MDI was added by volume in one portion and the reactive species were thoroughly mixed during 30 seconds and rapidly transferred to the ATR cell. Time zero of the reaction was taken as the moment of the addition of the diisocyanate. The maximum elapsed time between MDI addition and acquisition of the first scan was one minute.

Chemical system

Chemical	OH or NCO content (mol/g)
Indulin AT (*)	Phenolic - 2.42×10^{-3} Total - 4.37×10^{-3}
MDI	0.008
PCL (**)	PCL1000 - 1.996×10^{-3} PCL750 - 2.674×10^{-3} PCL400- 4.991×10^{-3}

(*) Characterization performed by CERIDE (Santa-Fé, Argentina)
(**) Values supplied by Solvay Interox

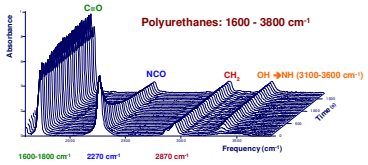


Simplified structure of lignin. The whole molecule is a complex, three-dimensional framework containing thousands of phenyl-propane units.

The course of the polymerization reaction was followed by FTIR, working in the ATR mode. The optics of the ATR cell was continuously purged with nitrogen to eliminate the CO_2 interference. Each experiment was done in triplicate.

The decay in the isocyanate absorbance was measured during 30 minutes at a temperature of 80ºC. Three scans per spectrum were taken at a resolution 4 cm^{-1}. Each spectrum was recorded at 30 seconds intervals during 30 minutes. GRAMS/32 software was used for data acquisition and subsequent data analysis.

FTIR Bomen (Model MB104) working in ATR mode



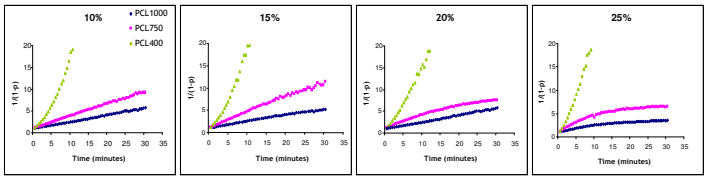
Typical three-dimensional plot of an FTIR experiment

Isocyanate conversion (p_{NCO}) was calculated from the following expression:

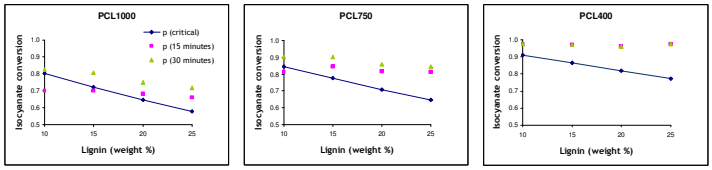
$$p = 1 - \frac{A_{NCO}/A_{CH_2}}{A_{NCO_0}/A_{(CH_2)_0}}$$

- A_{NCO} is the integrated absorbance for the isocyanate group and A_{NCO_0} is the integrated absorbance corresponding to the initial isocyanate concentration.
- A_{CH_2} was used to compensate volume changes during the course of polymerization reaction.

FTIR results:



Preliminary studies of reaction kinetics.



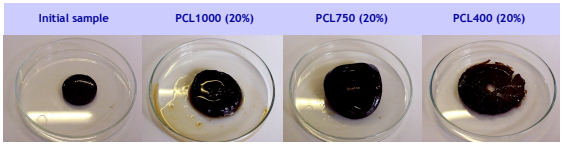
p (critical) was defined as the conversion corresponding to the consumption of all OH from PCL.

Comparison between the critical and experimental isocyanate conversion.

Swelling and extraction studies:

Swelling studies:

The swelling experiments were done in DMF during 3 days at ambient temperature.



Effect of the molecular weight of the PCL

Extraction studies:

The polyurethane samples were extracted with dioxane in a soxlhet during 12 hours and dried at 60 ºC. Then, they were stored in a dessicator until a constant weight was achieved. The yield of the insoluble polymer was calculated with respect to the initial weight of the sample.

Conclusions:

- The studies performed in this work confirm that lignin was incorporate in the final three-component polyurethane by chemical reaction with isocyanates – formation of urethane linkages. Final conversion, determined experimentally by FTIR, was always greater than the defined critical conversion.
- Swelling and extraction tests confirm that the final samples correspond to a chemically reticulated structure:
  - For the same series, the increasing of lignin content corresponds to a increase in the yield of extraction and a decrease in the final swelling volume.
  - For the same lignin content, the maximum yield of extraction corresponds to the samples with PCL750 and the minimum to the samples with PCL400.
- Depending on the molecular weight of the PCL and lignin content, the chemical reaction mostly follows a global second order kinetics. A better understanding of the kinetics of this kind of systems will be the subject of our future work.
- The work presented here is indented to be a starting point in a more wide research in this new challenging field of biopolymers from biomass. We go on studying other chemical systems by varying the source of lignin, type of polyol and isocyanate.

Acknowledgements:

- To Solvay Interox (Cheshire, UK) for supplying us with samples of PCL1000, PCL750 and PCL400.
- To Meadwestvaco (South Carolina, USA) for supplying us with samples of INDULIN AT.
- To Dra. Susana Gervasio from CERIDE (Santa-Fé, Argentina) for the lignin characterization.