

Cateto, C., Barreiro, M.F., Rodrigues A., **"Study of the formation of lignin-based polyurethanes,"** XIX Encontro Nacional da Sociedade Portuguesa de Química, Coimbra, Portugal, 15-17 April (2004) (*poster*).

KIXSPQ

PLENÁRIA PRÉMIO FERREIRA DA SILVA

MACROCICLOS NATURAIS E AFINS: DA SÍNTESE E REACTIVIDADE ÀS APLICAÇÕES

José A. S. Cavaleiro

Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal

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 os 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.

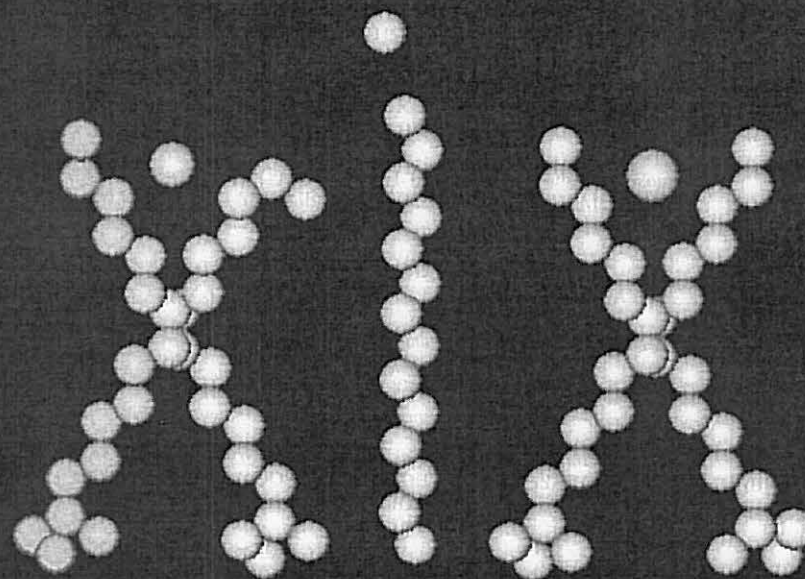
Agradecimentos

Agradece-se a todas as entidades financiadoras que têm permitido a realização, ao longo dos anos em Aveiro, dos estudos referidos (especialmente os então INIC e JNICT, a Universidade de Aveiro e a Fundação para a Ciência e Tecnologia). Agradece-se igualmente a colaboração dada por todos os co-autores das publicações resultantes dos estudos efectuados.

COMUNICAÇÕES EM PAINEL

Sessão de Painéis I (pares)

Sessão de Painéis II (ímpares)



QM#3- <u>A. Barros-Timmons</u> , A. C. Esteves e T. Trindade SÍNTESE DE NANOCOMPÓSITOS FUNCIONAIS POR POLIMERIZAÇÃO EM EMULSÃO E EM MINI-EMULSÃO.....	283
QM#4- <u>Mariana Beija</u> , Paula Relógio, P. Brogueira, M. A. Gonçalves da Silva, J. P. S. Farinha, J. M. G. Martinho FILMES FINOS DE POLIDIMETILACRILAMIDA HIDROFOBICAMENTE MODIFICADA.....	284
QM#5- <u>J. Branquinho</u> , M. Figueiredo, J. A. C. Alves, M. H. Gil DESENVOLVIMENTO DE MICROPARTÍCULAS PARA MODIFICAÇÃO DE SUPERFÍCIES.....	285
QM#6- <u>P. Ferreira</u> , R. Pereira, J. C. Bordado, M. H. Gil, DESENVOLVIMENTO DE NOVOS ADESIVOS CIRÚRGICOS DE BASE POLIURETANA.....	286
QM#7- <u>Carolina Cateto</u> , Filomena Barreiro, Alfrío Rodrigues STUDY OF THE FORMATION OF LIGNIN-BASED POLYURETHANES.....	287
QM#8- <u>Anselmo M. Elias</u> , M. Elisabeth Elias and Victor M. Oliveira POLY(<i>p</i> -PHENYLENE) SYNTHESIS IN IONIC LIQUIDS.....	288
QM#9- <u>Telma Encarnação</u> , Ricardo Valente, Hugh D. Burrows, David Palomar and Maria José Tapia COMPLEXATION OF TRIVALENT LANTHANIDE IONS WITH ON POLY(ACRYLIC ACID) AND POLY(METHACRYLIC ACID) IN AQUEOUS SOLUTION.....	289
QM#10- A. S. N. Pontes, A. P. M. Tavares, J. Gamelas, A. Gaspar, <u>D. V. Evtuguin</u> , A. M. R. B. Xavier APLICAÇÃO DO SISTEMA LACASE-MEDIADOR NO BRANQUEAMENTO DE PASTA KRAFT.....	290
QM#11- L. Ardasheva, <u>C. Freire</u> and A. R. Hillman EPR CHARACTERIZATION OF POLYMERIC FILMS BASED ON PALLADIUM(II) <i>SALÉN</i> COMPLEXES.....	291
QM#12- <u>Sandra Gago</u> , Yanmei Zhang, José A. Fernandes, Ana Santos, Martyn Pillinger, Anabela A. Valente, Teresa M. Santos, Paulo Ribeiro-Claro, Fritz E. Kühn, Isabel S. Gonçalves MANGANESE(II) COMPLEX SUPPORTED ON MCM-41: AN INITIATOR MODEL FOR POLYMERIZATION IN HETEROGENEOUS PHASE.....	292
QM#13- Ana Catarina Trindade, <u>Maria Helena Godinho</u> , João Luís Figueirinhas SYNTHESIS AND CHARACTERISATION OF NEW ANISOTROPIC URETHANE/UREA BASED ELASTOMERS.....	293
QM#14- Sonia Dapía, <u>Beatriz Gullón</u> , Valentín Santos, J. Carlos Parajó KINETIC STUDY OF CELLULOSE CARBOXYMETHYLATION.....	294
QM#15- <u>S. Lisboa</u> , D. Evtuguin e C. Pascoal Neto CARACTERIZAÇÃO DE GLUCURONOXILANAS PRECIPITADAS DO LICOR NEGRO DO COZIMENTO KRAFT DO <i>Eucalyptus globulus</i>	295

QM#16- <u>I. Maia e Silva</u> , L. Ferreira, Rui Carvalho, M. H. Gil CARACTERIZAÇÃO E PREPARAÇÃO DE HIDROGEIS A PARTIR DE DEXTRANO OXIDADO.....	296
QM#17- <u>C. Molina</u> , L. D. Carlos, R. R. Gonçalves, S. J. L. Ribeiro, Y. Messaddeq, P. J. Moreira, O. Soppera, A. P. Leite, P. V. S. Marques, V. de Zéa Bermudez PLANAR AND UV WRITTEN CHANNEL OPTICAL WAVEGUIDES PREPARED WITH ORGANIC-INORGANIC SOL-GEL SILOXANE-POLY(OXYETHYLENE) MATERIALS.....	297
QM#18- A. Charas, <u>J. Morgado</u> , J. M. G. Martinho, L. Alcácer SÍNTESE E CARACTERIZAÇÃO DE UM POLIFLUORENO ELECTROLUMINESCENTE E FOTOACTIVO.....	298
QM#19- <u>M. L. Pinto</u> , J. Pires, A. P. Carvalho, M. B. de Carvalho, J. C. Bordado ESPUMAS DE POLIURETANO PARA SUPORTE DE MATERIAS ADSORVENTES.....	299
QM#20- <u>Carla Santos</u> , Patrícia Seabra, Ivonne Delgadillo, J. A. Lopes da Silva MEMBRANAS DE QUITOSANO E INTERACÇÕES COM A ÁGUA- EFEITO DO GRAU DE ACETILAÇÃO DO BIOPOLÍMERO.....	300
QM#21- Sonia Dapía, Susana Alvarez, <u>Valentín Santos</u> , J. Carlos Parajó. CELLULOSE CARBOXYMETHYLATION BY SEQUENTIAL ADDITIONS OF MONOCHLOROACETIC ACID.....	301
QM#22- <u>J. M. G. Sarraguça</u> and A. A. C. C. Pais ION CONDENSATION AND POLYELECTROLYTE FOLDING.....	302
QM#23- <u>S. Sequeira</u> , Inês Portugal, D. Evtuguine SÍNTESE E CARACTERIZAÇÃO DE MATERIAIS HÍBRIDOS CELULOSE/SÍLICA PREPARADOS PELO MÉTODO SOL-GEL.....	303
QM#24- <u>Abílio J.F.N. Sobral</u> , Artur J.M. Valente, Alfonso Jiménez, Ana R. Gaspar, Ana R.C.B. Oliveira, Ramon S. I. Iborra, Vitor M.M. Lobo CARACTERIZAÇÃO E TRANSPORTE DE ELECTRÓLITOS NÃO-ASSOCIADOS EM POLIACRILAMIDAS CONTENDO <i>meso</i> -OCTAMETIL-PORFIRINOGENIO.....	304
QM#25- <u>Andreia F. Sousa</u> and Alberto A. C. C. Pais SIMULATION OF TRANSFECTION PROCESSES.....	305
QM#26- <u>A. J. M. Valente</u> , H. D. Burrows, A. Ya. Polishchuk, C. P. Domingues, C. E. C. Zeferino, M. G. Miguel, V. M. M. Lobo CARACTERIZAÇÃO E TRANSPORTE DE DODECILSULFATO DE SÓDIO EM MISTURAS POLIMÉRICAS DE POLIANILINA E ACETATO DE CELULOSE.....	306
QM#27- A. J. M. Valente, H. D. Burrows, <u>C. J. S. Dinis</u> , I. A. L. Salada, M. G. Miguel, V. M. M. Lobo TRANSPORTE E <i>SWELLING</i> DE ELECTRÓLITOS NÃO-ASSOCIADOS E TENSIOACTIVOS IÓNICOS EM POLIACRILAMIDA MODIFICADA COM β -CICLODEXTRINA.....	307
QM#28- <u>Carlos Vila</u> , Rosana Pérez, Valentín Santos, J. Carlos Parajó MANUFACTURE OR CELLULOSE WITH LOW POLYMERISATION DEGREE BY AUTOHYDROLYSIS.....	308

Study of the formation of lignin-based polyurethanes

Carolina Cateto^{1,2}, Filomena Barreiro^{1,2} & Alírio E. Rodrigues²



(1)
School of Technology and Management
Bragança Polytechnic Institute



(2)
Laboratory of Separation and Reaction Engineering
School of Engineering - University of Porto

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), polycaprolactonediol (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 expect a three dimensional network as a direct consequence of lignin incorporation.

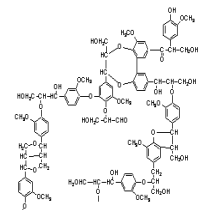
FTIR experiments:

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



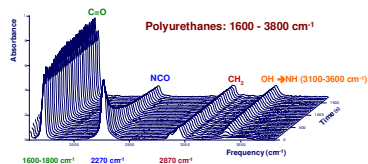
Simplified structure of lignin. The whole molecule is a complex, three-dimensional framework containing thousands of phenyl-propane units.

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 CO₂ interference. Each experiment was done in triplicate.

The decay in the isocyanate absorbance was measured during 30 minutes at a temperature of 80°C. 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



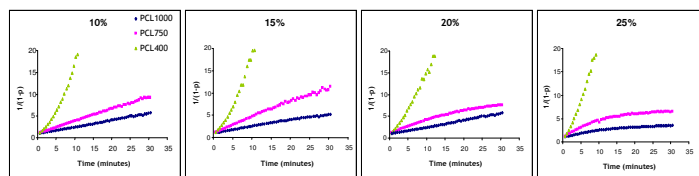
Typical three-dimensional plot of an FTIR experiment

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

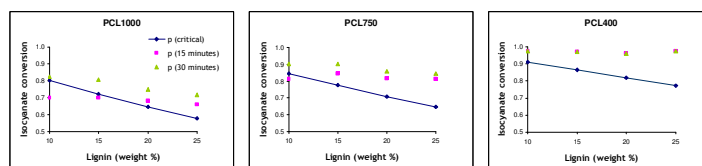
$$p = 1 - \frac{A_{NCO} / A_{CH_2}}{A_{NCO_0} / A_{(CH_2)_0}}$$

• 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.



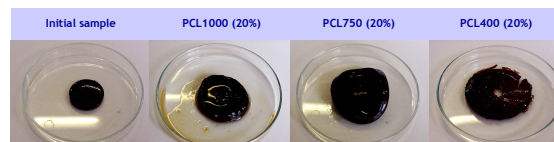
p (critical) was defined as the conversion corresponding to the consumption of all OH from PCL.

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 soxhlet during 12 hours and dried at 60 °C. 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 incorporated 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 an 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 intended 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.