LIGNIN-BASED POLYURETHANE ELASTOMERS

C.A. Cateto[1,3,4], M.F. Barreiro[1], A.E. Rodrigues[b], M.N. Belgacem[3]
[1] Laboratory of Separation and Reaction Engineering (LSRE), Associate Laboratory LSRE/LCM, Polytechnic Institute of Bragança, Campus Santa Apolónia Ap. 1134, 5301-857 Bragança, Portugal,
[2] Laboratory of Separation and Reaction Engineering (LSRE), Associate Laboratory LSRE/LCM, Department of Chemical Engineering, Faculty of Engineering ,University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
[3] Laboratoire de Génie des Procédés Papetiers (UMR 5518 – CNRS), Grenoble INP, Domaine universitaire. BP 65, 38402 St. Martin d´Hères, France
[4] Currently at Institute of Paper Science and Technology, School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332, USA

Abstract
The incorporation of lignin into polymeric materials, directly or after chemical modification, is recognized as one of the most viable approaches to accomplish its valorisation and properly exploit its unique intrinsic properties. In this work polyurethanes with elastomeric properties have been synthesised using a three component system based on lignin, 4,4'-methylene-diphenylene diisocyanate (MDI) and polycaprolactone (PCL). The following variables were studied: the lignin type (Alcell (A) and Indulin AT (IAT)), the PCL molecular weight (400, 750 and 1000) and the lignin content (10, 15, 20 and 25% (w/w)). The results pointed out for effective lignin incorporation into the generated polyurethane network, where Alcell has a predominant role of chain extender and Indulin AT acts more as a crosslinking agent.

Materials and methods
Indulin AT (IAT) is a softwood lignin obtained by the kraft pulping process and Alcell (A), from Repap Enterprises Inc., was extracted from hardwoods by an organosolv process using aqueous ethanol liquor. Comparatively to Indulin AT, Alcell lignin has lower 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) and OH functionality (4 *versus* 7.5) [1]. Lignin-based polyurethanes were synthesised in bulk at 80 ºC ([NCO]/[OH]=1) using a three-component system, consisting of MDI and PCL (PCL400, PCL750 and PCL1000) filled with different amounts of lignin (IAT and A lignins at contents of 10, 15, 20, 25% (w/w)) [2]. Samples were characterized by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) and subjected to swelling tests DMF [3].

Results and discussion
The produced polyurethane elastomers exhibited a behaviour that varied from very flexible to stiff. Moreover, the obtained results have showed that Alcell lignin presents a predominant role of chain extender whereas Indulin AT acts more as an effective cross-linking agent, although both macromolecular structures present functionalities higher than 2 (Figure 1). This observation is consistent with the quite distinct thermo-mechanical behavior exhibited by Indulin AT- and Alcell-based polyurethanes. For a fixed PCL molecular weight, an almost constant storage modulus (E') value, i.e., independent of the used lignin content, was observed for Alcell-based polyurethanes. On contrary, Indulin-based counterparts showed that the E' value increases with increasing lignin content. For both cases the loss tangent (tanδ) shifts towards higher

temperatures and the associated peak become broader as the lignin content increases. This tendency was also confirmed my DSC.

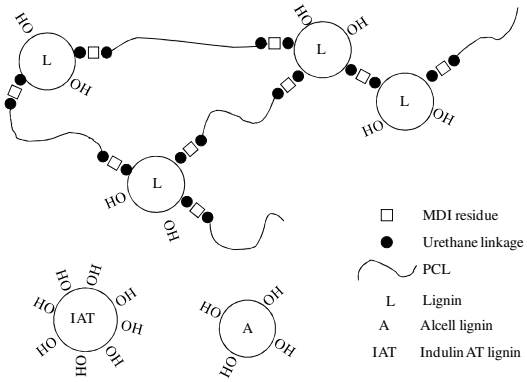

Figure 1. Schematic representation of lignin-based polyurethane networks

The values and tendency of the crosslinking density determined by DMA and swelling tests were found to be in rough agreement. In what concerns Alcell lignin, for a fixed PCL MW (PCL750), both crosslinking density and sol fraction were almost constant, i.e., independent of the lignin content. For a fixed lignin content (25%), crosslinking density was almost constant but an apparent abnormal high sol fraction was determined for the sample A(PCL400/1/25). For samples based on Indulin AT, and for a fixed PCL MW (PCL750), both crosslinking density and sol fraction increase with increasing lignin content. For a fixed lignin content (25%) an increase of crosslinking density was observed as the MW increases and an abnormal high sol fraction was observed for the sample IAT(PCL1000/1/25) (sample with the higher crosslinking density). These apparently contradictory results to the established structure-properties relationships can be explained take into account the structural differences between the two studied lignins and the used PCL molecular weight.

Conclusions

In this work lignin-based polyurethane networks based on two distinct lignins (Alcell and Indulin AT) have been synthesized and characterized. Results pointed out for effective lignin incorporation into the generated polyurethane network.

Acknowledgments

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.

References

1. Cateto, C A, Barreiro, M F, Rodrigues, A E, Brochier-Salon, M C, Thielemans, W, Belgacem,M N (2008): *Lignins as macromonomers for polyurethane synthesis: A comparative study on hydroxyl group determination*. J. Appl. Polym. Sci. 109:5, p. 3008.
2. Cateto, C A, Barreiro, M F, Rodrigues, A E (2008): *Monitoring of lignin-based polyurethane synthesis. by FTIR-ATR*, Ind. Crops and Prod., 27, p. 168.
3. Cateto, C A, Barreiro, M F, Rodrigues, A E, Belgacem, *Polyurethanes as a viable route to valorise lignin*. XXI TECNICELPA/VI CIADICYP, Lisbon, Portugal, 2010, O60.