

Lignin-based polyurethane materials

Carolina Cateto^{1,2,3}, Filomena Barreiro^{1*}, Alírio E. Rodrigues², Naceur Belgacem³

¹LSRE - Laboratory of Separation and Reaction Engineering, Instituto Politécnico de Bragança, Campus de Santa Apolónia, Ap 1134, 5301-857 Bragança, Portugal

²LSRE - Laboratory of Separation and Reaction Engineering, Faculdade de Engenharia da Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

³Matériaux Polymères, École Française de Papeterie et des Industries Graphiques (EFPG-INPG), BP 65, 38402 St. Martin d'Hères, France

Keywords: Lignin, Polyurethanes, Bio-based, Added-value

Lignin is defined as a random, amorphous three-dimensional polymeric network, which does not possess a uniform, homogenous, well defined structure with well established repeating units. Commercially available lignins are, most often, Kraft or lignosulfonates associated to the corresponding most commonly used industrial processes for wood delignification and fibres isolation (Kraft and sulphite, respectively). These lignins are largely used in dispersing and binding applications and a small part is employed in the production of specially chemicals like vanillin and dimethylsulfoxide (Gosselink et al., 2004). Recently, sulphur-free lignins are becoming an emerging class of lignin products, partly motivated by environmental policies, but also, by less capital intensive associated technologies. They could be obtained from three main sources: (i) biomass conversion technologies – biorefineries; (ii) solvent pulping – organosolv processes; and (iii) soda pulping of alternative biomass resources, such as agricultural harvesting residues and non-wood fibre crops (Lora and Glasser, 2002).

The utilization of lignin as a macromonomer in polyurethane synthesis often follows two global approaches: (i) the direct utilization of lignin without any preliminary chemical modification, alone or in combination with other polyols (Thring et al., 1997, Evtuguin et al., 1998, Cateto et al., 2008) or, (ii) by making hydroxyl functions more readily available by chemical modification, such as esterification and etherification reactions (Glasser, 1989, Gandini et al., 2002, Nadji et al., 2005).

The four technical lignins used in this work represent three different pulping processes (Kraft, Soda and Organosolv) and different botanic origins, i.e., softwood, hardwood and non-wood lignin types. Indulin AT and Curan 27-11P (commercialized in the alkali form) are softwood lignins obtained by the Kraft pulping process and were supplied by MeadWestvaco and BorregaardLignoTech, respectively, whereas Sarkanda lignin was supplied by Granit SA. The latter is a non-wood lignin obtained from a soda pulping-precipitation process, patented by Granit SA. Alcell lignin of Repap Enterprises Inc. is extracted from mixed hardwoods (maple, birch and poplar) by an organosolv process using aqueous ethanol. A summary of the performed characterization is shown in Table 1.

In the present work we have studied the two previously described global approaches. The first one involved the direct use lignin as a co-monomer in combination with a linear polycaprolactone (PCL). PCL was introduced into the formulation to provide flexibility and enable polymerization in bulk. The produced polyurethanes have properties that vary from very flexible to very hard materials depending on the amount of lignin effectively incorporated, and according to the molecular weight of the used PCL. For the formulations studied, the success of lignin incorporation by chemical reaction with the isocyanates (formation of urethane linkages) was noticeable. In the second approach lignin was oxypropylated and the ensuing polyols used for rigid polyurethane foams preparation, alone or in combination with other commercial

* Corresponding author. Tel + 351-273 303 089. E-mail: barreiro@ipb.pt

polyether-polyols. The produced foams have shown mechanical strength and conductivity similar, or even superior, to those of foams produced with commercial polyols alone. Examples of the produced materials are shown in Figure 1.

Table 1. Properties of the technical lignins used in this work

Lignin Sample	Total OH (mmol/g)	Phenolic OH (mmol/g)	COOH (mmol/g)	Ash content (% w/w)
Alcell	5.26	3.81	0.23	0.05
Sarkanda	5.26	2.41	0.62	3.26
Indulin AT	6.99	3.95	0.39	3.06
Curan 27-11P	6.21	3.63	0.47	17.0

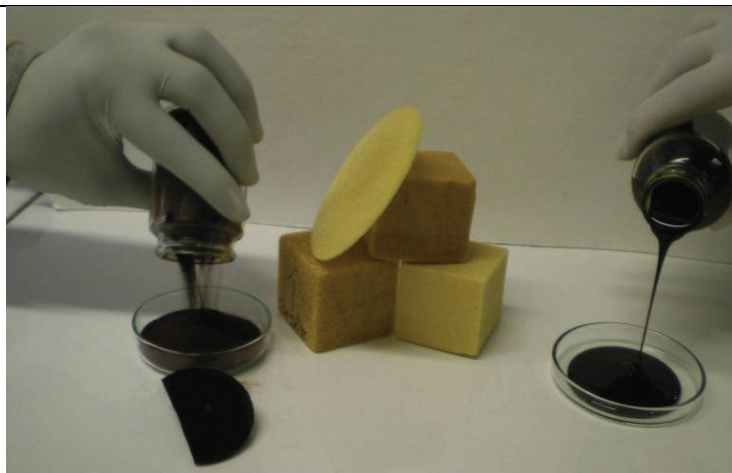


Figure 1. Original lignin and examples of the produced materials.

Acknowledgements

The authors wish to thank Meadwestvaco, Borregaard LignoTech and Granite SA for the kind gift of lignin samples. Alcell lignin of Repap Enterprises Inc. was offered by Dr. Jairo Lora, to whom we are indebted. Financial support from FCT (grant SFRH/BD/18415/2004) and French-Portuguese Scientific Cooperation Programme (F-32/08) are also acknowledged.

References

- Cateto, C.A., Barreiro, M.F., Rodrigues, A.E., (2008). *Monitoring of lignin-based polyurethane synthesis by FTIR-ATR. Ind. Crops and Prod.*, 27, 168-174.
- Evtuguin, D.V., Andreolety, J.P. and Gandini, A., (1998). *Polyurethanes Based on Oxygen-Organosolv Lignin. Eur. Polym. J.*, 34, 1163-1169.
- Glasser, W.G., (1989). *Novel structural materials from lignin*. In: Kennedy, J.F., Phillips, G.O., Williams, P.A. (Eds), *Wood Processing and Utilization*. Ellis Hordwood Limited Publishers, Chichester, 163-173.
- Gosselink, R.J.A., Jong, E. de, Guran, B. and Abächerli, A., (2004). *Co-ordination network for lignin—standardisation, production and applications adapted to market requirements (EUROLIGNIN), Ind. Crops and Prod.* 20, 121-129.
- Gandini, A., Belgacem M.N., Guo, Zhao-Xio and Montanari, S., (2002). *Lignins as a macromonomers for polyester and polyurethanes*. In: Hu, Thomas Q. (Ed.), *Chemical Modification, Properties and Usage of Lignin*, Kluwer Academic/Plenum Publishers, 57-80.
- Lora, J.H. and Glasser, W.G., (2002). *Recent Industrial Applications of Lignin: A Sustainable Alternative to Nonrenewable Materials, Journal of Polymers and the Environment.* 10, 39-48.
- Nadji, H., Bruzzèse, C., Belgacem, M.N., Benaboura, A., Gandini, A., (2005). *Oxypropylation of Lignins and Preparation of Rigid Polyurethane Foams from the Ensuing Polyols, Macromol. Mater. Eng.*, 209, 1009-1016.
- Thring, R.W., Vanderlaan, M.N., Griffing, S.L. (1997). *Polyurethanes from Alcell®. Biomass and Bionergy*, 13, 125-132.