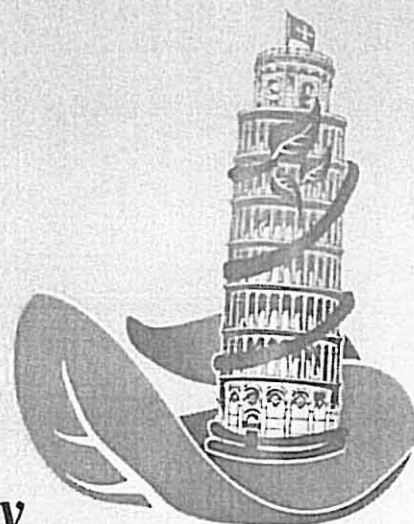


4th Workshop

Green Chemistry and Nanotechnologies in Polymer Chemistry

4-6 September 2013 – Pisa, Italy



Organised by

*Department of Civil and Industrial Engineering,
University of Pisa*

Institute for Composite and Biomedical Materials, CNR

National Interuniversity Consortium of Materials Science and Technology, INSTM



OFFICIAL PROGRAM

Wednesday, 04.09.2013

17.00-19.00 Registration

19.00-21.00 Welcome Reception

Thursday, 05.09.2013

8.30-13.00 Registration

9.00-9.20 Welcome and Opening

Session A - Green Chemistry

09:20 **Matjaž Kunaver**
CO01 Biomass waste - A source of raw materials

09:40 **Mikelis Kirpluks**
CO02 High Density Rigid Polyurethane Foams from Renewable Materials for Automotive Application

10:00 **Claudia Crestini**
CO03 Ultrasound assisted production of biocompatible lignin core-shell micro/nanocapsules for storage and delivery of hydrophobic molecules

10:20 **Aiga Paberza**
CO04 Flammability and thermal properties of rigid polyurethane foams obtained from oxypropylated lignin

10:40 **Tomáš Vlček**
CO05 Coatings with enhanced properties and prolonged lifetime

11.00-11.30 Coffee break

11:30 **Aleksandra Gawelczyk**
CO06 Depolymerization of polycarbonate by castor and rapeseed oils

11:50 **Anda Fridrihsone**
CO07 Post curing kinetics of VOC-free, 100 % solids, spray-applied polyurethane coatings from rapeseed oil polyols

12:10 **Hilda Gómez Bernal**
CO08 Corn stover valorization to high energy furan liquids by microwave assisted autohydrolysis

12:30 **Datta Janusz**
CO09 Thermo dynamical and mechanical characterization of polyurethanes synthesized using glycolysates intermediates

12:50 **M. Filomena Barreiro**
CO10 Chemical modification as a strategy to modulate properties of oxypropylated products

13.10-14.00 Lunch

14.00-15.00 Poster session.

Session B – Nanotechnologies

15:00 **Ivan Kelnar**
CO11 Effect of chitin nanofibrils/ plasticizer combination on mechanical behaviour of chitosan-matrix films

15:20 **PierFrancesco Morganti**
CO12 Chitin nanofibrils: a multifunctional biomaterial of marine origin

15:40 **Jana Mikešová**
CO13 Rheological properties of chitosan solutions filled with chitin nanofibrils

16:00 **Galina Tishchenko**
CO14 Biodegradable composite films from chitosan and chitin nanofibrils



ORAL



CHEMICAL MODIFICATION AS A STRATEGY TO MODULATE PROPERTIES OF OXYPROPYLATED PRODUCTS

Mariana Barbosa^a, Marina Matos^b, M. Filomena Barreiro^{a,*}, and Alessandro Gandini^{b,#}

^a *Laboratory of Separation and Reaction Engineering (LSRE), Associate Laboratory LSRE/LCM, Polytechnic Institute of Bragança, Campus Santa Apolónia Ap. 1134, 5301-857 Bragança, Portugal - ^b CICECO and Chemistry Department, University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal - [#]Presently at Instituto de Química de São Carlos - São Paulo University, Brasil - *00351273303089, 00351273313951, barreiro@ipb.pt*

Concept and objectives

Nowadays a great interest is devoted to the production and use of biobased products. The main scope of the oxypropylation process is to obtain polyols, in the form of viscous liquids, which can be interesting comonomers to produce polyurethanes and polyesters. Due to the high hydroxyl content of natural polymers (suitable substrates to be oxypropylated), the generated polyols are multifunctional, hence most adequate to be used in rigid polyurethane foam formulations. Additionally, their properties can be modulated through chemical modification, thus opening new avenues for their exploitation.

Following that strategy, an oxypropylated product (I_{OH} of 350) used as a model polyol, was modified by reacting it with a mixture containing phenyl isocyanate (PI) and toluene diisocyanate (TDI) at PI/TDI molar ratios of 100/0, 80/20, 50/50, 20/80 and 0/100. This chemical system was chosen in order to guarantee a homogeneous medium during the course of the reaction. Syntheses were performed in dichloromethane solution at room temperature under nitrogen, using DBTDL as catalyst, with a reaction time of 6 hours.

Kinetics was followed by FTIR in transmittance mode using a liquid cell equipped with NaCl windows. For that purpose, sample aliquots were taken from the reaction medium at time intervals of 10 minutes during the first hour, 30 minutes during the second hour and at one hour intervals until the end of the reaction. After the established reaction time of 6 hours, residual isocyanates were neutralized with methanol and the final product purified, dried and characterized by FTIR and DSC.

Results and Discussion

Figure 1 shows a typical plot of a FTIR experiment. Quantification of the isocyanate group conversion was

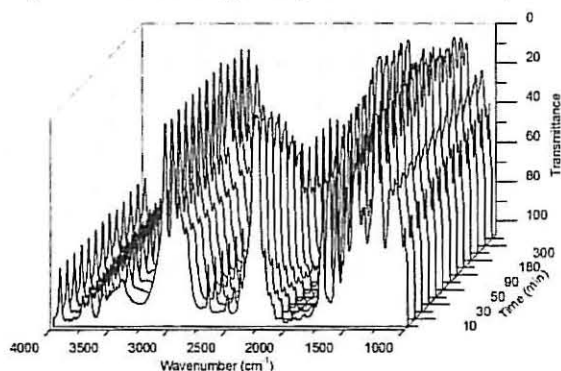


Figure 1. Typical FTIR plot.

estimated from the isocyanate absorption band (2270 cm^{-1}) intensity decay. It was observed that as the PI/TDI molar ratio decreased, i.e. as the content of the difunctional monomer increased, the final isocyanate conversion (time = 360 min) decreased and the polymer Tg shifted towards higher values, thus corroborating an increase in the crosslink density. An increase of crosslinking density introduces restrictions on the molecular motion lowering NCO conversion and increasing the Tg value. In fact the produced polyurethanes changed from a highly viscous liquid (PI/TDI=100/0 and 80/20) to stiff solids (PI/TDI=50/50, 20/80 and 0/100). In conclusion, the strategy used in this work demonstrates a way to modulate the final properties of the oxypropylated products.

Aknowledgments

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