The International Lignin Institute

Bringing Lignin Back to the Headlines
Priority Research and New Approaches

PROCEEDINGS

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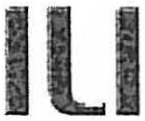

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MONITORING OF LIGNIN-BASED POLYURETHANE SYNTHESIS BY FTIR-ATR

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ABSTRACT. FTIR (Fourier Transform Infrared Spectroscopy), working in ATR (Attenuated Total Reflectance) mode was applied to study the formation of lignin-based polyurethanes. Although some studies related to the use of lignins in polyurethane synthesis, are available in literature, still persist a gap for a systematic study of this kind of systems involving the measurement of kinetic data, optimization and modelling of the process. This methodology allows the test of different formulations at a scale of 3-5 grams, considering several process variables: temperature, NCO/OH ratio, type and MW of the polyol, type of isocyanate, type and weight content of lignin. This work aims to describe the methodology used to perform the FTIR experiments by presenting a case study.

I. INTRODUCTION

The synthesis of polymeric materials, from renewable raw materials, has been subject of research in the last decades. Many biomass components, such as, cellulose, quitin, suberine, have been used in a variety of applications (Gandini and Belgacem, 1998; Meister et al., 1992). Lignin is among these biomass components and has been the material of choice for several research groups (see Glasser and Sarkanen, 1989 and Hu, 2002). The studied applications include the production of polyols, polyurethanes, acrylics, epoxyds and phenolic resins. The promoting factors for the utilization of lignin as raw material for polymeric synthesis can be summarized as follows: (1) Renewable and abundant raw material source: it constitutes about 15-30% of the wood and 12-20% of the annual plants; (2) Material with intrinsic biodegradability. It is expected that this property will be transmitted to polymers where lignin is incorporated; (3) Presence of various reactive points that can be used in wide range of chemical reactions; (4) By-product of the pulp industry, available in large quantities (estimated in 7 million tons per year).

The lignin potential for polymeric applications have come to be disclosed in last the 50 years; however, only now starts to be considered as a viable and economically competitive material for some companies (see, for example, Granit-SA and Meadwestvaco). According to Gandini (Gandini, 2000) much work still remains to be done in this field in terms of both the optimization of the systems already investigated and the search for new ones. This will be achieved by means of basic, technological and economical research.

FTIR is a widely used technique for polymer characterization and to monitor the polymerization process (see for example, Elwell et al., 1996, Hua and Dubé, 2001). The objective of this work is to apply the technique of FTIR in the ATR mode, previously developed to study segmented polyurethanes (Barreiro, 2000) to the formation of lignin based polyurethanes. Our first approach uses lignin as a macromonomer and a linear polyol in the initial formulation, providing flexibility and enabling polymerization in bulk.

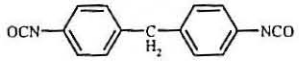
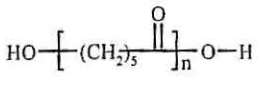
II. EXPERIMENTAL

Materials and formulations

The lignin-based polyurethanes have been prepared starting with 4,4'-methylene-diphenylene diisocyanate (MDI), polycaprolactone diol (PCL) of three different average molecular weights (400, 750 and 1000) and a commercial lignin (Indulin AT from Meadwestvaco) at different weight contents (10, 15, 20 and 25 %). The characteristics of the chemicals used in the formulations are shown in table 1. The polycaprolactones, supplied by Solvay Interox (Cheshire, UK) and lignin were degassed overnight under vacuum at 70 °C. The MDI (Aldrich) was purified by heating at 60 °C and filtered through a heated filter just prior to use. Its purity was determined by the standard di-n-butylamine titration and found to be over 99.5%.

Reaction conditions (temperature of 80 °C and a NCO/OH ratio of 1) were chosen in order to avoid chemical reticulation due to isocyanate secondary reactions.

Table 1. Summary of polyol, lignin and isocyanate characteristics

Designation	Molecular weight	Structural formula	OH or NCO content (mmol/g)
MDI	250		8.000
PCL1000	1000		1.996
PCL750	750		2.674
PCL400	400		4.991
INDULIN-AT *	--	--	Phenolic: 2.413 Total: 4.370

* Characterization performed by CERIDE (Santa Fé, Argentina)

FTIR experiments

The infrared studies were done on a FTIR Bomen (Model MB104) working in the ATR mode. The ATR accessory (Graseby Specac) was equipped with a heater controller and a silicon crystal, a material optically denser than the polyurethane. In order to obtain a more stable background the ATR optics was continuously purged with nitrogen during the FTIR experiments.

Lignin and PCL were weighed in an analytical balance in the desired proportions and the mixture was homogenized by stirring. Then, the molten MDI was added by volume in one portion and the reactive species were thoroughly mixed together during 30 seconds and rapidly transferred to the ATR cell. Time zero of the reaction was taken as the addition moment of the MDI. The maximum elapsed time between MDI addition and the acquisition of the first scan was one minute. Three scans per spectrum were taken at a resolution of 4 cm^{-1} and the experiment was programmed to record a spectrum every 30 seconds during 30 minutes. A background file was always collected prior to the execution of a FTIR experiment. GRAMS/32 software (Galatic Industries) was employed for data acquisition and subsequent data analysis. Figure 1 shows a typical plot of a FTIR experiment.

III. RESULTS AND DISCUSSION

Analysis of the FTIR experiments

The decay in the isocyanate absorbance during the polymerization can be taken as a measure of the reduction in the isocyanate concentration. The areas under the absorbance peaks were calculated with baseline corrections using GRAMS/32 software. When needed, to compensate for thickness changes during polymerization, a ratio was taken between the absorbance of the isocyanate group and that of an internal standard, i.e., a group whose concentration does not change during the reaction course. In this study, the absorbance corresponding to the CH_2 stretching region was used. Figure 2 shows the data extracted from a FTIR experiment and the corresponding calculated isocyanate conversion curve. All the experiments were done in triplicate (Figure 3).

Figures 4 and 5 show some of the results extracted from the data obtained with the FTIR experiments. The results represented in Figure 4 confirm that, for the system PCL, lignin and MDI, lignin was incorporated in the final polyurethane by chemical reaction with isocyanates. Depending on the molecular weight of the PCL and lignin content, the chemical reaction mostly follows a global second order kinetics (Figure 5).

Figure 1. Typical three-dimensional plot of a FTIR experiment.

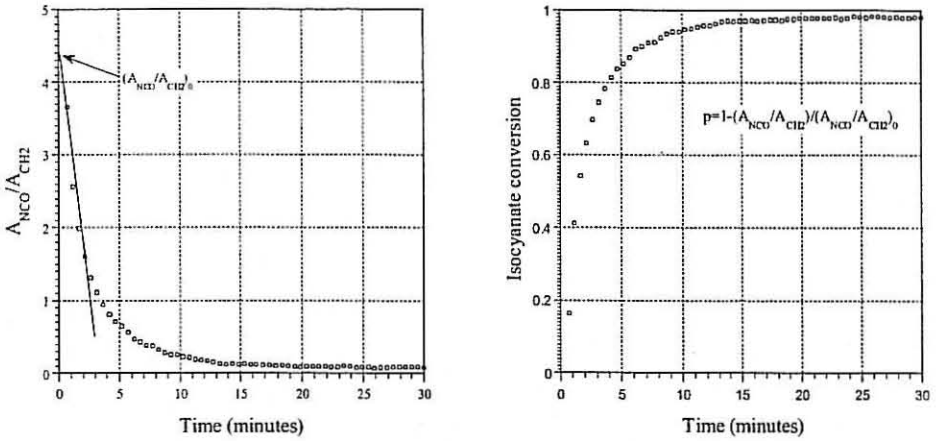


Figure 2. Decay in the relative absorbance (A_{NCO}/ A_{CH2}) (a) and the corresponding calculated isocyanate conversion (b) (A_{NCO} is the integrated absorbance for the isocyanate group, A_{CH2} is the integrated absorbance for the CH_2 group and $(A_{NCO}/ A_{CH2})_0$ is the relative absorbance extrapolated for time zero).

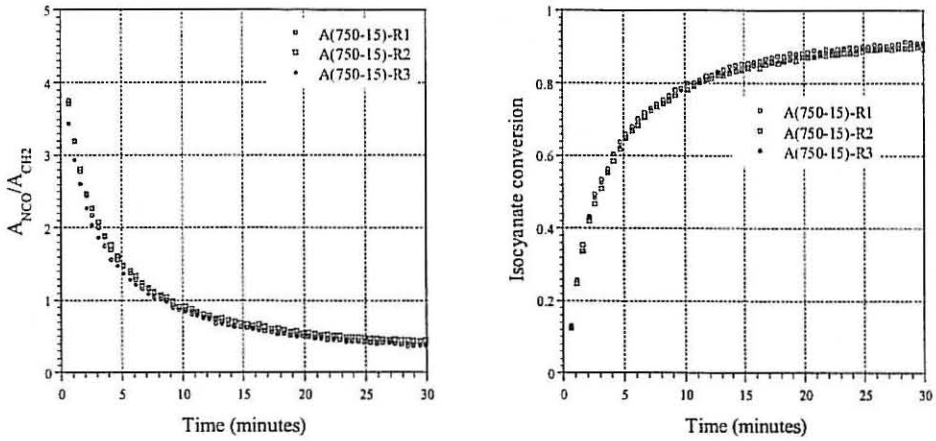


Figure 3. Plot showing the three replicas of the experiment performed with PCL750, Indulin AT (weight content of 15%) and MDI. The final conversion was 0.9020±0.0110.

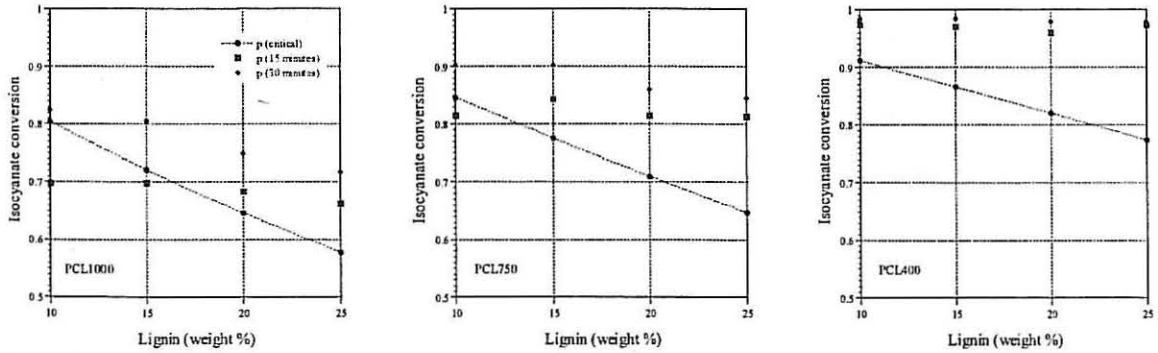


Figure 4. Comparison between critical and experimental isocyanate conversion (critical isocyanate conversion (p(critical)) was defined as the conversion corresponding to the consumption of all OH from PCL).

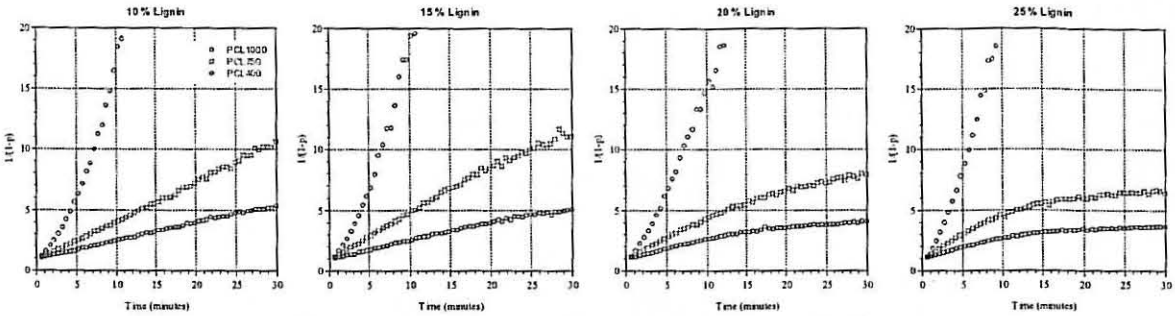


Figure 5. Global second order plots for the reaction of PCL, lignin and MDI.

IV. CONCLUSIONS AND FUTURE WORK

- FTIR-ATR was successfully applied to the study of lignin based polyurethanes. Several process variables could be studied in a simple way, providing a valuable tool to optimize a formulation.
- FTIR-ATR could also be useful to access fundamental kinetic data. It is our objective to continue this study by using model systems to access lignin hydroxyl reactivity, a key feature to model the polymerization process.
- The quality of the results obtained through the application of the FTIR-ATR technique will benefit from a careful lignin characterization in what concerns hydroxyl content, molecular weight and polydispersity. It is our objective to acquire abilities in this field. Previous studies, concerning the hydroxyl determination by acetylation procedures under a wide range of conditions (temperature, composition of the acetylation reagent, presence of a catalyst and drying process of the acetylated samples), point out for an incomplete reaction, leading to an underestimated hydroxyl determination.

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