

# Lignin characterization by acetylation procedures

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The synthesis of polymeric materials from renewable raw materials has been subject of research in the last decades. Many biomass components, such as, cellulose, chitin, suberine, have been used in a variety of applications. 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.

Recently, our research group started to be involved in the field of lignin based polyurethane synthesis (Cateto et al., 2004 and Cateto et al., 2005). The typical chemical system studied involves an isocyanate, a commercial lignin and a polyestherdiol. In order to minimize isocyanate secondary reactions, a NCO/OH ratio of 1 and a reaction temperature of 80 °C were mostly used. The course of the polymerization reaction was followed by FTIR working in ATR mode. This methodology provided a way to test different formulations at a scale of 3-5 grams, considering several process variables: temperature, NCO/OH ratio, type and MW of polyol, type of isocyanate, type and weight content of lignin.

To enhance the lignin utilization in polymeric applications there is need to access samples with controlled quality in what concerns purity, chemical composition and properties. This is, in principle, difficult to achieve and could be overcome by a careful sample characterization. In what concerns the utilization of lignin in the polyurethane synthesis, the determination of hydroxyl content, molecular weight and polydispersity are important features.

Several of the methods used for lignin characterization are based in acetylation procedures (see Dence and Lin, 1992). For instance, the total hydroxyl content is usually estimated by a standard process using acetic anhydride-pyridine mixture, followed by back titration of acetic acid with a sodium hydroxide solution. FTIR, <sup>1</sup>H and <sup>13</sup>C NMR analysis are most often based in acetylated samples and, even the GPC molecular weight determination uses acetylation, in order to enhance solubility and to avoid association effects of lignin molecules.

The objective of this work is to examine the reliability of some typical lignin acetylation procedures. Briefly, the lignin samples were acetylated using an acetic anhydride-pyridine mixture and the recovered acetylated lignin samples were analysed by FTIR using KBr pellets. Several variables were studied, namely reaction time and temperature, composition of the acetylation reagent, presence of a catalyst and drying process of the acetylated samples. The experimental conditions used are summarized in Table 1. For all the conditions studied, the obtained results pointed out for an incomplete lignin acetylation (see Figure 1), meaning that an accurate lignin characterization is difficult to achieve when based on acetylation procedures. This observation is in accordance with recent published works (see for example Gosselink et al., 2004) and justifies the lack of agreement among some published experimental results concerning interlaboratory analysis.

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Table 1. Resume of the acetylation procedures.

Sample	Lignin (g)	Catalyst (g)	Acetylation Reagent Acetic Acid: Pyridine	Temperature	Reaction Time (min)	Drying	
01	1.5010	-	88:12	Heat under reflux	60	At 60 °C until constant weight	
02	1.5010	-			120		
03	1.5000	-			180		
04	1.5014	-			15	Freeze drying	
05	1.5013	-			30		
06	1.5033	-			45		
07	1.5004	-			60		
08	1.5011	0.7999			88:12		60
09	1.5002	0.8001			88:12		120
10	1.5011	0.8001			88:12		180
11	1.5000	-			80:20		60
12	1.0009	-	50:50	Room Temperature	24 hours		

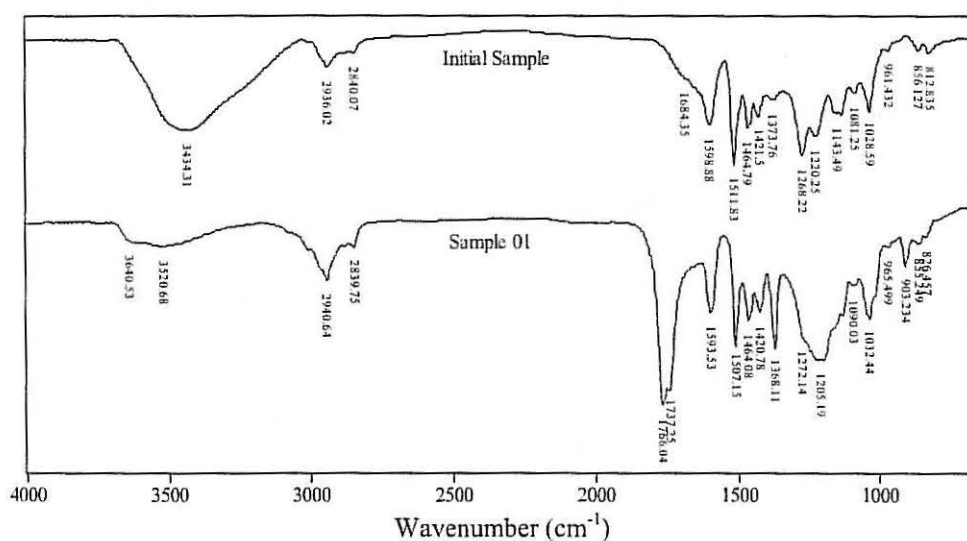


Figure 1. FTIR spectra of a lignin sample: before and after acetylation (sample 01).

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