Paper 062

Effect of Benzyl Chloride in the Chemical Modification of Cellulose From Sugarcane Bagasse

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Abstract: *The effect of benzyl chloride in the chemical modification of cellulose from sugarcane bagasse was studied. After pretreatment with aqueous NaOH, the cellulose was submitted to benzylation at 110°C using different benzyl chloride amount. The efficiency of reaction was evaluated by the weight variation as a function of the reagents volumes and infrared analysis. The weight increase was observed for all samples, reaching 85%, evidenced the benzyl groups incorporation. Spectra analysis showed evidences that the chemical modification occurred for different amount of benzyl chloride added. Estimative of degree of substitution showed that benzylation is favorable with the small amount of reagent (8-12 mL).*

Keywords: *Cellulose from sugarcane bagasse; benzylation; FTIR; weight variation.*

Introduction

Vegetable fillers/fibers, like sawdust, wood flour, sisal, and bagasse or cellulose from their lignocellulosic materials, are utilized because of their low density, coupled to their relatively good mechanical properties and reactive surface. Nevertheless, the main drawbacks of using such fibers in composites is their hygroscopicity and the difficulties in achieving acceptable dispersion levels in a polymeric matrix [1]. The sugarcane bagasse is an agro-industrial residue very abundant in Brazil and its surplus can be used in more than 40 different applications [2]. An interesting application is the chemical modification of cellulose from sugarcane bagasse inserting new properties in this material, especially hydrophobic characteristics, being the cellulose able to be incorporated into polymers as reinforcement [3].

Cellulose is very susceptible and reactive at chemistry reactions due to the presence of hydroxyl groups [4]. Three hydroxyl groups in glucose unit can be partially or completely replaced by other functional groups: one at the primary carbon and two at the secondary carbons [4, 5]. In this work, the etherification with benzyl chloride will be performed (Figure 1). The pretreatment with aqueous NaOH is necessary to activate the hydroxyl groups, transforming them in alkoxides to facilitate the reaction [6].

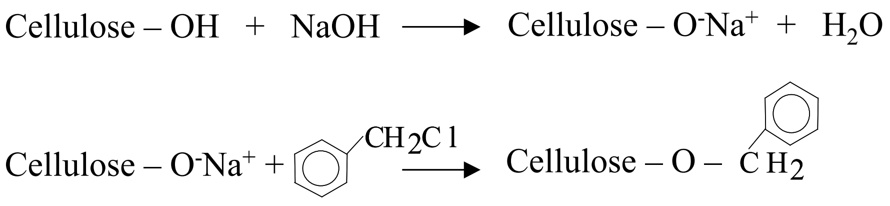

Figure 1. Schematic reactions of cellulose from sugarcane bagasse chemically modified by benzylation.

The efficiency of the reactions was accompanied by weight variation: benzyl groups substitute the hydrogen from OH group and the weight differences between the initial and final polymer were calculated. The infrared spectroscopy has been used specially to determine possible modifications in the lignocelullosic materials [7]. In this work the characteristics of the resulting materials were studied by FTIR spectra

Experimental

Origin of Materials

Cellulose from sugarcane bagasse was obtained by NaOH pulping process. This method was established by Luz [7] utilizing 16 % active Na_2O and 0.15 % of AQ at 170°C for 3.5 h, with sugarcane bagasse:liquor ratio of 6:1 (v/w). After washed, the cellulosic fibers were disaggregated in a disaggregate equipment with 1500 rpm (15 g of fiber and 2 L of water by 5 min at room temperature). The fibers were classified in classifier equipment with sieve of 0.15 mm. The chemical composition of cellulose from sugarcane bagasse was as follows: cellulose (83.1 %), polyoses (4.9 %), total lignin (8.4 %) and ash (1.1 %) [7].

Benzylation

Two g of dried cellulose from sugarcane bagasse were introduced into a 500-mL round flask and the bagasse was mixed with 35 mL of aqueous NaOH (40 % w/v). The temperature was raised 110°C and different amount of benzyl chloride were added (6, 8, 12 and 15 mL) and the reaction was allowed to proceed for 3 h. After reaction, the excess of benzyl chloride and salt were removed by extensive washing of benzylated materials with ethanol and water, respectively. The material was filtered under vacuum, dried at room temperature for 24 h and in oven at 110°C until constant mass. A blank was made without benzyl chloride for 3 h.

The weight gain was evaluated for all reactions according to equation 1, where M_c is the cellulose mass in respect to blank and M_{cb} is the final mass of benzylated cellulose.

$$\% \text{ Weight gain} = \frac{M_{cb}\,M_C}{M_C}.100 \quad \text{equation 1}$$

The estimative of degree of substitution (DS) concerning 1, 2 and 3 OH groups was calculated using the equation 2. Considering that the theoretical molar weight of glucose unit is 161.13 g.mol^{-1}, and substituint group (benzyl), 91.05 g.mol^{-1}, the percentage of hydrogen substituted for one, two or three OH group is 56.9, 114.5 and 172.8 %, respectively, thus, the DS can be calculated in respect to percentage of one hydrogen substituted (56.9 %) as reported in equation 2.

$$DS= \frac{\%\text{Weight gain}}{56.9\%} \quad \text{equation 2}$$

Characterization of the Reaction Products by FTIR Spectra

Samples of modified materials were analyzed by infrared in a spectrometer with Fourier Transformer. The samples (2 mg) were ground with KBr (200 mg) and pellets were obtained. The spectra were recorded in a Perkin Elmer Spectrometer in the 400-4000 cm^{-1} region, with 16 scans and 4 cm^{-1} resolution.

Results and Discussion

The insertion of groups with different molecular weight in the cellulose chain increases the polymer molar weight. The differences between molar weight of cellulose (blank) and reaction products allow evaluating the efficiency of cellulose degree of substitution.

Table 1 shows the results of weight variation and the estimative of DS. The weight gain was observed for all reagent volumes added. In the addition of 6 mL of benzyl chloride, the weight gain and DS is observed and the increase of these values reached 85 % and 1.49, respectively, for 8 mL. Above this volume, the weight gain and DS decreased.

Table 1. Weight variation of benzylated materials as a function of the benzyl chloride amount added (values in relation to blank) and estimative of degree of substitution.

Sample[a]	Weight gain (%)	DS
0	0	0.00
6	64	1.12
8	85	1.49
12	80	1.41
15	39	0.69

[a] Numbers correspond to volume in mL of benzyl chloride.

The spectra of benzylated cellulose were evaluated (Figure 2). A decrease in the intensity of O-H bond at 3448 cm^{-1} was verified in the FTIR spectra in different reagent volume, in comparison with the blank. This absorption corresponds to hydroxyl groups forming hydrogen bonding with the groups of water from moisture. After the modification, the hydrogen of OH group is substituted by benzyl groups. Evidences of modifications were: (1) presence of aromatic rings absorptions at 3007-3090 cm^{-1} (characteristic of aromatic C-H bonds), (2) carbon-carbon (C-C) bond, characteristic of axial deformation in aromatic rings at 1606 cm^{-1} and (3) absorption at 641-785 cm^{-1}, strong duplet intensity, characteristic of aromatic ring mono-substituted of benzyl groups.

Table 2 shows the ratios of the intensities of O-H, aromatic ring mono substituted (ARMS) and C-H aromatic bonds in respect to the band 894 -912 cm^{-1}, characteristics of O-C-O bonds in cellulose. A decrease of O-H/O-C-O ratio occurs with the increase of the reagent volume exception for sample with 15 mL of benzyl chloride. The decrease of the intensity of O-H bonds evidenced that the substitution of hydrogen from hydroxyl groups by benzyl groups occurred.

On the other hand the increase of values ARMS/O-C-O and C-H aromatics ratio was verified. Those ARMS/O-C-O and C-H aromatics bonds are present in the aromatic rings introduced in the structure of cellulose reassert the substitution. The ARMS/O-C-O and C-H aromatics ratios reached the maximum values for 12 mL sample and the O-H/O-C-O ratio presented a minimum value for the volume which suggested a high substitution followed by the ethers benzylated with 6 and 8 mL which showed similar ARMS/O-C-O and C-H aromatic ratios, with similar behavior of the weight variation showed in Table 1.

The sample benzylated with 15 mL can be hydrolyzed due to very severe reaction conditions and the great quantity water formed. This is confirmed in higher O-H/O-C-O ratio, the low ARMS/O-C-O and C-H aromatics and weight gain.

Table 2. Band ratios spectra from benzylated materials as a function of benzyl chloride.

Sample [a]	O-H/O-C-O	ARMS/O-C-O	C-H/O-C-O
0	5.02	---	---
6	4.15	2.67	0.61
8	2.77	2.56	0.61
12	2.48	2.91	0.69
15	5.16	2.23	0.55

[a] Numbers correspond to volume in mL of benzyl chloride

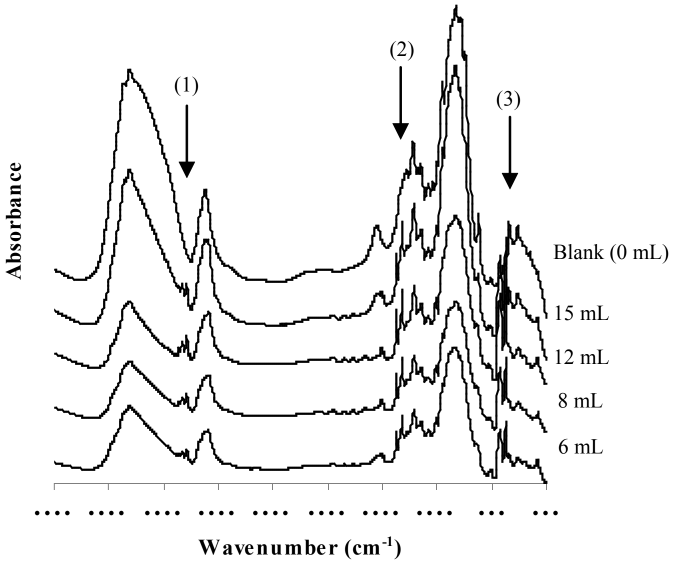

Figure 2. FTIR spectra of benzylated products obtained from various volumes of reagents.

Conclusions

Cellulose from sugarcane bagasse can be chemically modified through benzylation reactions and the changes in the structure may be easily evaluated by infrared analysis. The analysis in the infrared region was very important for the confirmation of chemical reaction. In the benzylation, the chemical modification was supported by reagent amount. The quantification by weight variation considered in this work allows estimating the DS of cellulose. The results suggest that exist a ratio between reagent amount and reaction efficiency and large quantities reagents decrease these efficiency.

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