Preparation of High Thermal and Mechanical Resistant Cellulose Nanocrystals (CNCs) using Alkaline Hydrolysis Agent

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Introdução

Cellulose, the most abundant organic compound on earth, is a classical example of a natural source to produce organic nanoreinforcement elements called Cellulose nanocrystals (*CNCs*), or cellulose nanowhiskers (*CNWs*). Compared with inorganic fillers, the main advantages of using *CNCs* to formulate biobased nanocomposites include their renewable nature, low cost, low density, high specific mechanical properties, and nonabrasive nature, which allows easy processability. Besides these characteristics, *CNCs* could find economical interest because they can be prepared from a large variety of natural sources including agricultural residue such as sugar cane bagasse, rice hulls, and maize straw. In this context, *CNCs* appear as an alternative way to prepare new ecologically friendly biobased nanocomposites. They are highly crystalline rod-shaped nanoparticles that can be obtained from different cellulose sources through a hydrochloric or sulfuric acid hydrolysis.[1,2] The discovery of the acid cellulose hydrolysis generating *CNCs* is assigned to Ranby[3] and since then acidic medium is the methodology normally used to prepare *CNCs*. To the best of our knowledge there is no report on using only alkaline medium to prepare *CNCs.* The preparation of *CNCs* described herein, is through a selective and controlled reaction of cellulose with benzyltrimethyl ammonium hydroxide (**BzTMAH**), specifically involving the breakdown of beta-4-O-glycosidic linkage from only the amorphous regions of cellulose through the interaction with the lipophilic part of the benzylic moiety. Thus, the more crystalline, more hydrophilic and less lipophilic regions of the cellulose might not be attacked, leaving the crystalline parts of cellulose, the *CNCs*, intact. For comparison purposes, tetramethyl ammonium hydroxide (TMAH) was also used.

Resultados e Discussão

In all tests using TMAH, the CNCs were not obtained, and only the base adsorption seemed to occur. However, the investigation with **BzTMAH** shows itself very promising since the CNC can be prepared through a simple, efficient and reproducible novel alkaline hydrolysis route. After many experiments, the best methodology used was the following: 0.75 g of cellulose (50mg/L) in an aqueous medium 40% solution of **BzTMAH** was stirred at 60 ^{o}C for 24h, followed by centrifugation and washing with distilled water until pH neutralization and dispersion. Figure 1a shows typical flow birefringence found in the CNC suspensions at 4% (w/w) concentration, observed between two crossed polarizers. This birefringence indicates the presence of isolated cellulose nanocrystals in the dispersion. Thermogravimetric analysis (TGA / DTG) (Figure 1b) showed higher thermal stability of the nanoparticles obtained from alkaline hydrolysis (363 ºC) than the nanocrystals obtained from the traditional method (acid hydrolysis, 274 °C). TEM images (Figure 2) show elongated nanoparticles with length and diameter of 145 and 5 nm, respectively.

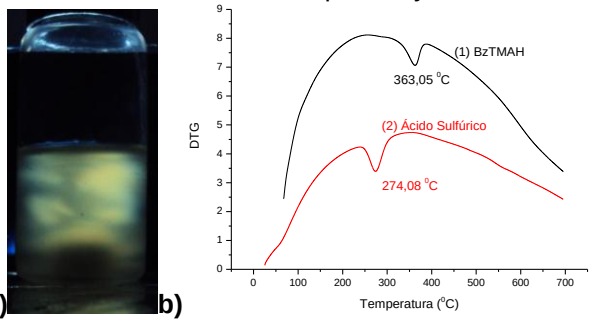

Figure 1. a) NCC dispersion at 4% (w/w) concentration, observed between crossed polarizers; **b)** DTG analysis comparison to NCCs by (1) **BzTMAH** and (2) sulfuric acid

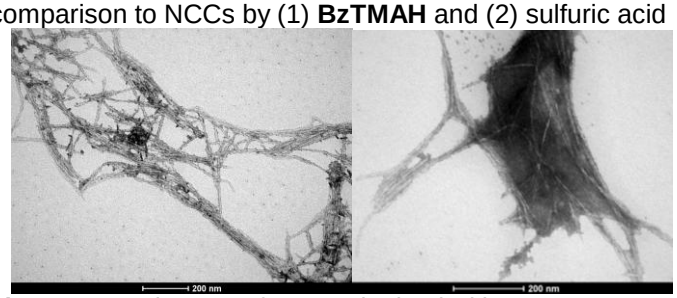

Figura 2.MET images of NCCs obtained with **BzTMAH**

Conclusões

A new method to prepare CNCs from cellulose sources using an alkaline medium was discovered.[4]

Agradecimentos

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[1] Jiang, L.; Morelius, E.; Zhang, J.; Wolcott, M.; Holbery, J. *J. Compos. Mater.* **2008**, *42*, 2629.
[2] Podsiadlo, P.; S. Y. Choi; B. Shim; J. Lee; M. Cuddihy; N. A. Kotov; *Biomacromolecules*, **2005**, *6*, 2914.
[3] Ranby, B.G. *Discussions of the Faraday Society*, **1951**, *11*,158.
[4] INPI BR1020130223735, 02/09/2013