

## Characterization of nano-scaled cellulose surface area and pore size

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**Statement of Purpose:** As a biocompatible and biodegradable polymer, cellulose has widely been used in implant, drug delivery, tissue scaffolding and engineering. In particular, nano-scaled cellulose particles enable developing engineered systems with enhanced biological and mechanical performance. Quantifying the porous structure of nano-cellulose is fundamental to understanding a wide range of binding interactions in the development of cellulose nanocomposites which may contain various chemical and biological additives. In this area, the use of hydrolyzed nano-dimensional cellulose fibers known as cellulose nanowhiskers (CNWs) has attracted significant interest, yet the porosity and surface area of these materials have not been explored. The objective of this work was to characterize the surface area and porosity of cellulose from different origins (plant/bacterium) and different acid treatments ( $H_2SO_4$ /HCl/ $H_3PO_4$ ) by  $N_2$  sorption technique. The surface morphology and crystal structure of CNWs are determined by FESEM and XRD, respectively. Understanding the surface structure of cellulose materials is fundamental to its application in nanocomposite materials for biomedicine development.

**Methods:** The CNWs were produced from Whatman<sup>TM</sup> CF11 (cotton) cellulose by  $H_2SO_4$  (63.5%, w/w) according to Bondeson *et al.*<sup>1</sup>. The HCl treated CNWs were generated from either CF11 or *Gluconacetobacter xylinus* cellulose by HCl (15%, w/w)<sup>2</sup>. The phosphoric acid swollen cellulose (PASC) was produced according to Hsu and Penner<sup>28</sup> by 87%  $H_3PO_4$  at 0 °C<sup>3</sup>. The  $N_2$  sorption measurements were carried out at 77 K using an Accelerated Surface Area and Porosimetry Analyzer (ASAP 2020; Micromeritics Instrument Corp.). The specific surface area was calculated by BET<sup>4</sup> method from the linear part of the sorption isotherm and the pore size distribution (PSD) of the mesopores and micropores were obtained by BJH<sup>5</sup> and HK<sup>6</sup> methods, respectively. All the samples were degassed at 303.15 K for 240min under vacuum at 10  $\mu$ m Hg prior to the measurements. The XRD patterns were collected on a PANalytical X'Pert Pro MPD (multi-purpose diffractometer) with  $CuK\alpha$  radiation generation. A LEO 1530 (GEMINI) FESEM was used for cellulose morphology observation.

**Results:** Our results showed that CNWs produced from either  $H_2SO_4$  or HCl exhibited significantly increased surface area and porosity as compared to the starting material. In particular, HCl treated CNWs had a larger accessible surface area than  $H_2SO_4$  treated CNWs. Mesopores existed in the CNWs generated by  $H_2SO_4$  hydrolysis, and both mesopores and micropores were observed in CNWs produced by HCl digestion. It was also found that the surface area increased dramatically in phosphoric acid swollen cellulose (PASC) due to an increase in porosity. These results were further confirmed

by field emission scanning electron microscopy (FESEM).

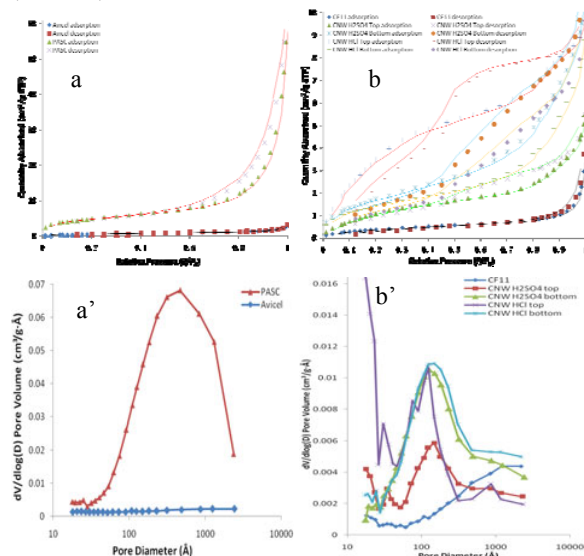


Figure 1.  $N_2$  adsorption & desorption isotherms (a,b) and corresponding pore size distribution of (a',b') cellulose samples (Sample Only; not all the data).

**Conclusions:**  $N_2$  sorption isotherms and FESEM micrographs of cellulose samples formed by different acid treatments and from different origins were analyzed to obtain information about cellulose surface area, pore volume, pore area, PSD and morphology. It is shown that Avicel PH101 and CF11, have the smallest specific surface area and porosity.  $H_3PO_4$  treatment is shown to significantly increase the surface area and porosity; PASC gains more surface area by means of increasing porosity due presumably to an increase in amorphous content and both fibril and bundle disassembly. HCl and  $H_2SO_4$  treatments also result in a significant increase in surface area and porosity. Since these treatments result in increased crystallinity, the increased surface area likely results from fibril and bundle disruption. In addition, new microporosity is observed in HCl treated cellulose. Microporosity is not observed in  $H_2SO_4$  treated cellulose. It is believed sulfate esterification of the cellulose precludes  $N_2$  adsorption in these new pores. Bacterial CNWs from *G. xylinus* show significantly increased porosity comparing to plant originated CNWs. These findings may allow various forms of cellulose to be used more effectively in both scientific and engineering applications.

**References:** (1). Bondeson D. Cellulose 2006;13:171-180. (2). Araki J. Colloids Surf. A: Physicochem. Eng. Aspects. 1998;142:75-82. (3). Hsu JC. J. Nutr. 1989; 119(6):872-878. (4). Brunauer S. J. Am. Chem. Soc. 1938;60:309-319. (5). Barret EP. J. Am. Chem. Soc. 1951;73:373-380. (6). Horvath G. J. Chem. Eng. Jpn. 1983;16:470-475.