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## Unusual extraction and characterization of nanocrystalline cellulose from cellulose derivatives

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### ABSTRACT

Unlike many nanomaterials, nanocrystalline cellulose (CNC) is not synthesized from molecular or atomic components but rather extracted from naturally occurring cellulose. Undoubtedly, the exploitation of CNCs will become a bridge between nanoscience and natural resource products, which could play a major role in reviving the forest industry. In this work, CNC was successfully extracted from unusual sources, hydroxypropyl methylcellulose (HPMC) and carboxymethylcellulose (CMC). The extracted crystallites were purified and further characterized by Fourier transform infrared (FTIR), scanning electron microscopy (SEM), X-ray powder diffraction (XRD) and dynamic light scattering (DLS). The average size of the CNCs extracted from HPMC and CMC was found to be less (and with lower zeta potential) than the ones extracted from microcrystalline cellulose (MCC). On the other hand, FTIR and XRD revealed that native HPMC and CMC are unexpectedly highly crystalline and hence can be used as a source for CNCs.

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### 1. Introduction

Cellulose, which can be obtained from many sources such as wood pulp, cotton, ramie, and bacteria, is the most abundant and renewable biopolymer resource available today in nature. This polymer organizes in a rather dense and highly hierarchical fashion where an extended intra- and intermolecular network of hydrogen bonds and Van der Waals interactions are believed to constitute the basis of cohesion between cellulose molecules [1–8]. Within the cellulose fibrils there are regions where the cellulose chains are arranged in highly ordered structures – crystallites – and regions that are disordered – amorphous – [9]. The latter regions act as structural defects and can be easily accessed and removed/dissolved by treating the biopolymer with harsh acid conditions. The resulting product is the recalcitrant individual needle-like crystallites of cellulose chains which are commonly called nanocrystals (CNCs). Other related but not necessarily synonymous terminologies are often found in literature such as whiskers, microcrystalline cellulose and cellulose crystallites [10]. In the recent years, CNCs have been realized as a new class of nanomaterials attracting immense interest from both research scientists and industrialists. Compared to cellulose fibers,

CNCs possess many advantages, such as nanoscale dimension, high specific strength and modulus, high surface area, and unique optical properties. These unmatched physico-chemical properties and the apparent lack of environmental constraints enable the use of CNCs in a wide range of potential applications such as a reinforcing agent in nanocomposites, coatings, textiles, aerospace and many others [9,11–13]. The morphology and properties of CNCs are strongly dependent on the source of the original cellulose, extraction procedure and their parameters [14,15]. Therefore, for an efficient comparison and development of these resources, the isolation and further analysis of CNCs from different cellulosic resources are particularly relevant and almost required [13,16,17]. CNCs have been isolated from a variety of sources such as vegetable sources, cotton, wood pulp [14,18] and agricultural byproducts, such as soy hulls [17], corn cob [13] and rice husk [19], and animal sources such as tunicates and bacteria [20–24].

In this work, the cellulose derivatives hydroxypropyl methylcellulose (HPMC) and carboxymethyl cellulose (CMC) were chosen as possible sources of CNCs. The HPMC is one of the most commonly used hydrophilic biodegradable polymers for controlled release formulations since it works as a pH-independent gelling agent. On the other hand, CMC finds applications in medicine, paints, detergents and in the food domain. Both cellulose derivatives share some useful characteristics such as the high viscosity at low concentrations and defoaming,

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surfactant and bulking abilities [25]. In general, cellulose derivatives result from the non-homogeneous substitution of the hydroxyl groups in each anhydroglucose ring by other functional groups. During this process, a decrease in the crystallinity of the substance is expected to occur and therefore, at a first glance, one could argue that cellulose derivatives are not an obvious choice as a source of CNCs. However, despite the fact that hydroxypropyl and methyl groups (in HPMC) and carboxylate groups (in CMC) have replaced the hydroxyls, the crystallinity of both derivatives was here found to be unexpectedly high and thus the extraction of CNCs appears as a viable process. To our knowledge, CNCs have never been extracted from cellulose derivatives and therefore we here report the initial results regarding their extraction and characterization. Scanning electron microscopy (SEM) and dynamic light scattering (DLS) were used to study the morphology while FTIR and X-ray diffraction were further used to infer about more detailed molecular information of the extracted CNCs.

## 2. Experimental

### 2.1. Materials

Microcrystalline cellulose (MCC) (Avicel PH-101, degree of polymerization ca. 260), carboxymethyl cellulose (CMC) ( $M_w = 7 \times 10^5$  Da, degree of substitution of 0.9), and sulfuric acid (98% purity ACS reagent), were obtained from Sigma-Aldrich. Hydroxypropyl methylcellulose (HPMC, Methocel® K15M Premium), 19–24% methoxyl and 7–12% hydroxypropyl,  $M_w = 4.3 \times 10^5$  Da, was purchased from Dow Chemical Company and was used without further purification. Dialysis bags (molecular weight cutoff 2000, Cellu Sep H1) were purchased from Orange Scientific. All samples were prepared using deionized water. The CNCs were extracted according to the procedure outlined below.

### 2.2. Extraction of nanocrystalline cellulose

The extraction procedure of CNCs was based on a previously reported method [26]. Briefly, 5 g of MCC powder was added to a 100 mL sulfuric acid (65 wt.%) aqueous solution. The hydrolysis was carried out during 30 min at 65 °C and afterwards the reaction was quenched by the addition of a large excess of deionized water (250 mL) and the mixture was centrifuged at 3800 rpm for 15 min at room temperature. This centrifugation step was repeated several times before the suspension was dialyzed against distilled water for one week to neutralize the pH of solution and remove undesired salts. The resulting suspension was kept refrigerated for later use. The same procedure was followed for the extraction of CNCs from HPMC and CMC.

### 2.3. Scanning electron microscopy

High resolution (Schottky) Scanning Electron Microscope, equipped with the analytical systems X-ray microanalysis (EDS) and back-scattered electron diffraction pattern analysis (EBSD) was used to observe the morphology and size of the extracted CNCs (model Quanta 400FEG ESEM/EDAX Genesis X4M). Generally, 50  $\mu$ L of a suspension (0.1 wt.% crystals) was dropped onto clean glass lamella followed by drying for 24 h in a kiln and then sputtered with an approximately 6 nm thin Au/Pd film by cathodic pulverization using a SPI Module Sputter Coater before SEM analysis, during 90 s with a current of 15 mA. Starting materials (powders) were deposited directly over the carbon tape on the support and sputtered following the procedure previously described. The accelerating voltage ranged from 5 to 15 kV.

### 2.4. X-ray diffraction

The X-ray diffraction (XRD) experiments were performed on a Siemens D5000 X-ray diffractometer, capable of identifying crystalline phases down to 3% of the bulk. This equipment consists of a  $\theta/2\theta$

diffraction instrument. A  $\text{CuK}\alpha_1$  is used as radiation source with  $\lambda = 1.54056$  Å, focused by a primary Ge crystal monochromator. The detector is a standard scintillation counter. The Cu tube runs at 40 mA and 40 kV. The cooling is supplied by an internal water-filled recirculation chilling system, running at approximately 16 °C with a flow rate of 4–4.5 L/min. The slit arrangement is a 2 mm pre-sample slit, 2 mm post-sample slit and a 0.2 mm detector slit. The freeze-dried crystals (powder) were placed in a proper support and analyzed.

### 2.5. Fourier transform infrared spectroscopy

The infrared spectra were recorded at 25 °C with an ATR-FTIR spectrophotometer Thermo Nicolet, IR300 (USA), using a universal ATR sampling accessory. FTIR spectral analysis was performed within the wave number range of 400–4000  $\text{cm}^{-1}$ . A total of 256 scans were run to collect each spectrum at a resolution of 1  $\text{cm}^{-1}$  in the transmission mode. The CrI (also referred to as “lateral order index”—LOI) was estimated from the ratio between the absorption band at 1430  $\text{cm}^{-1}$  and the absorption band at 890  $\text{cm}^{-1}$  [27,28]. Additionally, the “total crystallinity index” (TCI) was estimated from the ratio between the bands at 1370  $\text{cm}^{-1}$  and 2900  $\text{cm}^{-1}$  [29].

### 2.6. Dynamic light scattering

The potential charges on the surface of CNCs in pure water were measured with a Malvern Zetasizer Nano ZS, while the particle averaged size was determined by photon correlation spectroscopy (PCS) on the same equipment. To avoid excess light scattering in the spectrometer, the samples measured on the Zetasizer Nano ZS were diluted to a final concentration of 1.0 wt.% and an ultrasonic bath was used to facilitate dispersion of the CNCs in water.

## 3. Results and discussion

### 3.1. Microscopy characterization: morphology and zeta potential

The morphology of CNCs can be studied by different methods. The most common and conventional techniques to probe cellulose structure on the nanometer level are atomic force microscopy (AFM) [30] and transmission electron microscopy (TEM) [31]. The latter, among other advantages, can provide high-resolution images of the samples while the former can give topographic profiles of individual cellulose chains down to the atomic level. Besides these techniques, environmental scanning electron microscopy (ESEM) has been successfully applied [32] which, like conventional SEM, is a surface technique offering significant high spatial resolution particularly important for the study of biological samples, such as cellulose.

In Fig. 1, the SEM micrographs of the raw cellulosic materials used in this work are shown.

Coarse particles of different sizes are observed in all celluloses. Additionally, in the CMC case, soft elongated aggregates are also visible. When the dry powders are suspended in water, the crystalline cellulose sample (MCC) presents coarse particles with an average size around 50  $\mu$ m, while the cellulose derivatives (for instance, HPMC) present particles with a smaller average size, i.e. between 2 and 5  $\mu$ m (Fig. 2).

The larger size of the MCC particles might also reflect some aggregation due to their lower solubility in water. On the other hand, the cellulose derivatives are water-soluble and, therefore, individual particles are expected to disperse more efficiently in the solvent.

The SEM micrographs of the CNC suspensions extracted from the cellulose derivatives CMC and HPMC are shown in Fig. 3 (panels c, d and panels e, f, respectively). For comparison, micrographs of the CNCs from the MCC sample are shown on the top of Fig. 3 (panels a and b).

The CNCs from MCC (Fig. 3, a and b) are wider (ca. 200–300 nm) and longer (ca. 1  $\mu$ m) than the CNCs from the cellulose derivatives: CMC (Fig. 3, c and d) shows individual crystallites which are approximately

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