

Energy requirements for the disintegration of cellulose fibers into cellulose nanofibers

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Abstract Cellulose nanofibers have a bright future ahead as components of nano-engineered materials, as they are an abundant, renewable and sustainable resource with outstanding mechanical properties. However, before considering real-world applications, an efficient and energetically friendly production process needs to be developed that overcomes the extensive energy consumption of shear-based existing processes. This paper analyses how the charge content influences the mechanical energy that is needed to disintegrate a cellulose fiber. The introduction of charge groups (carboxylate) is achieved through periodate oxidation followed by chlorite oxidation reactions, carried out to different extents. Modified samples are then subjected to different levels of controlled mechanical energy and the yields of three different fractions, separated by size, are obtained. The process produces highly functionalized cellulose nanofibers based almost exclusively on chemical reactions, thus avoiding the use of intensive

mechanical energy in the process and consequently reducing drastically the energy consumption.

Keywords Cellulose nanofibers · Mechanical energy · Disintegration · Pulp · Periodate

Introduction

From the most basic to the most advanced use, cellulose seems always to be one step ahead of any other material, be it natural or synthetic. Besides being the most abundant biopolymer on earth, as well as being renewable, biodegradable and carbon-neutral, cellulose has unique properties that have been crucial for the existence of life on earth. It has served mankind as the primary source of heat, clothes and building material, to cite the most relevant ones. Because of its proven record of applications, it is not surprising that the use of cellulose nanostructures, especially cellulose nanofibers (CNF) or nanofibrils, promises to play an essential role in the development of the next generation high-tech nanostructured materials.

The cellulose fiber wall, with a typical diameter (d) ranging 15–35 μm , is a compounded material mainly composed of cellulose microfibrils (d \sim 40–100 nm), arranged in different orientations, embedded in a polymeric network of hemicelluloses, pectins and lignins (Somerville et al. 2004), with the percentage of each

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constituent varying in the radial direction through well defined layers. The microfibrils themselves are composed of several nanofibrils ($d \sim 2\text{--}10$ nm) made of crystalline and amorphous domains. Whether these domains are arranged in an alternating configuration or a core–shell distribution (Ding and Himmel 2006) is still an open question, although traditionally the first possibility has been the most widely accepted (Habibi et al. 2010). Finally, the number of cellulose polymeric chains that builds up one nanofibril is also a matter of discussion, but lately a molecular model consisting of a 36-glucan-chain elementary fibril forming both crystalline and subcrystalline structures is being preferentially considered (Ding and Himmel 2006; Gross and Chu 2010). However, cellulose nanofibrils from different sources are known to have different diameters and thus a different number of elementary chains associated with them.

CNF are then the primary complete building entities in the hierarchy of plants. From the point of view of materials science, their fibrillar shape of small diameter and very high aspect ratio makes them ideal to be used as reinforcing elements, but by themselves they are also ideal to form strong and transparent films (Henriksson et al. 2008; Siro and Plackett 2010; Saito et al. 2009) that can compete with polymeric ones. However, there are still two major problems that require solution before considering real-world applications for the CNF (Hubbe et al. 2008; Siro and Plackett 2010): first, finding an efficient and energetically favourable way to isolate them. Because neighbouring nanofibrils are either chemically cross-linked (Somerville et al. 2004) or physically entangled by single-chain polysaccharides (Keckes et al. 2003), it seems that their isolation always requires a considerable amount of shear, i.e. mechanical action, regardless of the type of pretreatment. So far, existing methods (Henriksson et al. 2007; Herrick et al. 1983; Hubbe et al. 2008; Isogai et al. 2011; Siro and Plackett 2010; Turbak et al. 1983) make use of a considerable amount of mechanical energy to disrupt the fiber wall, a process that, in addition to other environmental implications, requires a high energy input and high cost. The second step to be mastered has to do with the problem of dispersing hydrophilic CNF into hydrophobic media, e.g. polymeric matrices. Despite several strategies that have been developed to minimize this effect, such as grafting hydrophobes onto them (Siro and Plackett 2010) or coating them with surfactants (Heux et al. 2000), the high crystallinity is often an issue since it limits reactivity. It is very likely

that without fully addressing these two features, CNF will have a hard time to find their way out of the laboratories and into the factories.

In recent years, the use of enzymatic or chemical pretreatments on cellulose fibers has become popular with the aim of reducing the amount of mechanical energy required to liberate the nanostructures. The enzymatic route typically involves mixtures of various cellulases which are able to partially digest both the crystalline and amorphous regions (Paakko et al. 2007; Henriksson et al. 2007) facilitating the subsequent mechanical disintegration of the fibers. Alternatively, the introduction of carboxylate groups (COO) onto the surface of the nanofibrils leads under mild alkaline conditions to the appearance of repulsive forces that also weaken the structure. In this direction the preferred pathway is the 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) radical-mediated oxidation with hypochlorite and chlorite salts as the most common oxidizing agents (Iwamoto et al. 2010; Saito et al. 2009, 2010; Fukuzumi et al. 2009; Siro and Plackett 2010; Isogai et al. 2011), by which one of the three hydroxyl groups in the accessible glucose units of cellulose is converted to a carboxylic group. The use of such nitroxyl radicals and nitrosonium salts as an oxidative route to transform hydroxyl functions into carboxyl and/or aldehyde groups is disclosed elsewhere (Bobbitt and Flores 1988; Chang and Robyt 1996).

Both enzymatic and chemical modifications allow reducing the disintegration energy of cellulose fibers from somewhere in the order of 100 kWh/kg for unmodified cellulose preparations to as little as 1–2 kWh/kg (Isogai 2009; Siro and Plackett 2010), depending on the extent of the treatment. These new limits are comparable with those required to produce so called mechanical pulps out of wood, which means that are industrially viable. The main drawback of these two approaches, however, is that either they require the input of a substantial amount of energy or they fail to provide reasonable production yields. Another issue, concerning the chemical pretreatments, is that the maximum carboxylic content that can be introduced by means of TEMPO oxidation is limited (in case of TEMPO/NaBr/NaClO around 1.7 mmol/g, i.e. millimoles of COO per gram of dried fibers, and, if TEMPO/NaClO₂/NaClO is used, below 1 mmol/g (Okita et al. 2010; Isogai et al. 2011)). In principle, if one considers that the interior of the crystalline

domains is not accessible, the combination of the amorphous regions and the exterior surfaces of the crystals would still account for more than 3 mmol/g, taking an average degree of crystallinity of 60 % (corresponding to a ECF-bleached pine kraft pulp (Liitia et al. 2003)), assuming that the nanofibrils are composed of 36 cellulose chains in a hexagonal conformation (Ding and Himmel 2006) and considering that only every second glucose unit has the primary hydroxyl pointing out of the crystal. Apparently, diffusion problems prevent taking the modification further toward the theoretical maximum. Other estimations, however, claim that 1.7 mmol/g correspond to the entire surface oxidation of cellulose nanofibrils of wood origin (Okita et al. 2010).

In order to surpass TEMPO moderate oxidation limits, this work uses a different and well studied oxidation route, namely periodate oxidation (Potthast et al. 2009; Potthast et al. 2007; Kim et al. 2000), to produce dialdehyde cellulose, followed by chlorite oxidation to convert aldehydes into carboxylic groups. It has been recently established that periodate oxidation attacks the crystalline domains of CNF already in the early stages of the treatment (Potthast et al. 2009). Such chemical treatment allows reaching carboxylic contents in the order of 6.5 mmol/g (Yang 2011), although in this work only up to 3.5 mmol/g is reported. The paper analyses the relation between the carboxylic content of cellulose fibers and the disintegration energy required to convert them into nanofibrils. It shows that the oxidative treatment ultimately results in the spontaneous liberation of the CNF from the cell wall without the necessity of applying any mechanical energy other than that required to stir fiber suspensions during the chemical treatments. However, the length and especially the crystallinity of the nanostructures are severely affected, which in turn could become beneficial for certain applications such as biofuel production. The study brings some new light in understanding the mechanisms that hold the nanofibrils together inside the fiber cell wall and anticipates the production of CNF exclusively by chemical means by defining a charge threshold beyond which cellulose fibers need no mechanical energy to be disintegrated. Finally, since the process involves the introduction of a large amount of functional groups onto the CNF surfaces, the final product obtained is expected to show a higher reactivity and thus to be more prone to further derivatization than any previous preparation.

Materials and methods

Materials

Unbeaten bleached softwood kraft pulp (SKP), supplied by Domtar Inc. Canada as never-dried pulp, was used as raw material for the chemical treatments. Sodium meta-periodate (NaIO_4 ; Sigma-Aldrich), sodium chloride (NaCl ; ACP Chemicals Inc.), hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$; Sigma-Aldrich), hydrochloric acid (HCl ; ACP Chemicals Inc.), sodium hydroxide (NaOH ; ACP Chemicals Inc.), sodium chlorite (NaClO_2), hydrogen peroxide (H_2O_2 ; Sigma-Aldrich), 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO; Sigma-Aldrich), sodium phosphate buffer, sodium hypochlorite (NaClO), ethanol (ACP Chemicals Inc.) and a mix-bed ion exchange resin (Sigma-Aldrich) were used as received. Double deionized water was used throughout the experimentation, except for the dialysis purification where Milli-Q ultrapure water (Millipore Corp.) was used.

Chemical treatments

Cellulose fibers in the form of pulp suspensions were subjected to two successive chemical treatments, carried out to various extents in order to achieve various degrees of oxidation. Initially, periodate oxidation was carried out in aqueous media using a glass beaker with overhead stirrer, with the following reaction conditions: bleached softwood kraft pulp (3 g), NaIO_4 (1.98 g; 10.75 mmol; 50 mol % based on moles of anhydroglucose in pulp) and NaCl (11.7 g; 1 M based on overall solution) were added to 200 mL water. The beaker was totally covered with aluminium foil before starting the reaction, in order to prevent light from activating side reactions, and the mixture was gently stirred at room temperature. After the desired reaction time, the modified pulp (dialdehyde cellulose) was filtered out and thoroughly washed with deionized water repeatedly. In order to convert aldehyde moieties into carboxylic groups, periodate-oxidized pulp (3.5 g), NaClO_2 (80 % pure; 2.76 g; 24.5 mmol) and H_2O_2 (30 wt.% solution; 2.76 g; 24.5 mmol) were added to 150 mL water. This mixture was stirred at room temperature for 20 h, during which the pH was kept at 5 by drop wise addition of NaOH solution (especially necessary during the first 3 h).

Determination of aldehyde and carboxylate content

The aldehyde content of the dialdehyde cellulose produced by the periodate oxidation reaction was determined using the hydroxylamine-hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) titration method, by which the HCl released from its reaction with aldehydes is back-titrated with a NaOH solution of known concentration. More specifically, a water suspension of periodate-oxidized cellulose fibers (20 mL; 0.65 g dry basis) was mixed with 40 mL of isopropanol, making a final proportion of isopropanol/water of 2/1 v/v, and the mixture was sufficiently stirred to prepare a well-dispersed slurry. The pH of the mixture was then adjusted to 2–3 by adding a few drops of concentrated HCl and then carefully adjusted to 3.5 with NaOH 0.1 N. 10 mL of 10 wt.% $\text{NH}_2\text{OH}\cdot\text{HCl}$ solution was added to this mixture, allowing it to react for 10 min. Finally, the HCl released from the reaction was titrated with 0.5 N NaOH solution until pH 3.5 was reached again. The aldehyde content was then calculated using the following equation:

$$A_{\text{ald}} = V_{\text{NaOH}} \cdot N / w_{\text{cell}}$$

Here A_{ald} is the aldehyde content (mmol/g cellulose), V_{NaOH} the volume of NaOH (mL) consumed in the titration, N is the normality of the NaOH (eq/L) and w_{cell} the weight of dry cellulose (g) initially suspended.

The carboxylate content of the samples was determined by conductometric titration. To a 120 mL of 0.02 wt.% water suspension of the cellulosic product (20.4 mg dry basis) 2.5 mL of a 0.02 M NaCl solution was added and the mixture was gently stirred. Then 0.1 M HCl was slowly added to the mixture to set the pH value in the range of 2.5–3.0. Using an 836 Titrand titrator (Metrohm, Switzerland) a 0.005 M NaOH solution was added at a rate of 0.05 mL/min until the mixture had reached pH 11. The carboxylate content of the sample was determined from the conductivity curves using the following equation:

$$[\text{COO}] = V_{\text{NaOH}} \cdot M_{\text{NaOH}} / w_{\text{cell}}$$

Here $[\text{COO}]$ is the carboxylate content in mmol per gram cellulose, V_{NaOH} is the volume of NaOH (mL) required for the deprotonation of carboxylic groups, M_{NaOH} is the normality of NaOH (eq/L) and w_{cell} is the amount of dry cellulose product initially used (g).

Disintegration process

Two different devices were used in the disintegration process: a domestic blender (Braun hand held blender, type 4191) and a double-cylinder type homogenizer (Brinkmann Polytron homogenizer PT-35/4), which were always used in combination with a stirring plate to keep the pulp suspensions homogeneously dispersed.

These systems were initially characterized in order to have control over their mechanical action and energy consumption. First, to obtain a reliable measurement of the amount of electrical energy consumed by each set up, an ammeter was connected in series with the stirring plate and the mixer, and a data logging program was run on a computer connected to them. Assuming that the voltage remained constant, the electrical energy was calculated using Ohm's Law:

$$E_e = V \cdot I \cdot t$$

where E_e is electrical energy (J), V is voltage (V), I is current (A) and t is time (s). The electrical input was recorded at different settings over time periods that would be used later for the experimentation and the most stable one, showing a linear consumption with a squared regression factor higher than 0.99, was chosen for each device.

The second part of the characterization attempted to approximate the amount of mechanical action that is actually exerted by each device and which obviously differs from the electrical input; in our approach we correlate this parameter to the thermal energy that such mechanical action releases. With that aim we carried out a Joule experiment, following the idea that the energy transferred to the water in the form of kinetic energy must be dissipated by viscous forces and transformed into thermal energy. We used a thermocouple to measure the increase in temperature of 250 mL of water caused by the blender and the homogenizer at the predefined settings; the water was contained in a glass beaker insulated with a Styrofoam home-made shell. The mass and specific heats of the water and the glass allows the calculation of the thermal energy released:

$$E_t = [m \cdot c \cdot \Delta T]_w + [m \cdot c \cdot \Delta T]_g$$

where E_t is the thermal energy (J), m is the mass (kg), c is the specific heat (J/kg °C), ΔT is the temperature difference (°C), and the sub-indices w and g stand for

“water” and “glass”, respectively. From the characterization of both disintegration equipments we defined an efficiency parameter for each device, as follows:

$$\text{Efficiency}(\%) = 100 \cdot E_t(\text{J})/E_c(\text{J})$$

This characterization was meant to provide a fair approximation rather than an accurate determination.

Having characterized the equipments, the disintegration experiments were performed on 40 mL of 0.25 wt.% modified pulp suspensions at the preselected settings for different amounts of time. Each processing time corresponded to a given electricity consumption and thermal energy released, which we used as a measure of the amount of mechanical energy applied (Thermal Energy \approx Mechanical Energy).

Isolation

The following process was used to isolate the different cellulosic fractions after the reactions and the mechanical treatments were completed: a filtration at atmospheric pressure through a 20 μm -pore size nylon cloth was carried out to separate out the macroscopic fraction composed of non-disintegrated fibers still maintaining their original size; the resulting suspension was vacuum-filtered through a surface-hydrophilized polytetrafluoroethylene (PTFE) membrane with 0.1 μm pore size (Advantec Tokyo, Japan), which caused the retention of the CNF; finally, the resulting filtrate containing mainly dissolved cellulose derivatives was oven dried. Each fraction was weighted and a mass balance was calculated.

Film characterization

Cellulose nanofibrils obtained in the form of films and oven dried at 60 $^{\circ}\text{C}$ for 8 h were characterized by X-ray diffraction (XRD) analysis and atomic force microscopy (AFM). The XRD measurements were performed on a Bruker D8 Discover two dimensional diffractometer with VANTEC 2D detector and $\text{CuK}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). Diffractograms were acquired with a 2θ (Bragg angle) range of 12.5–32.5 $^{\circ}$ at a scan rate of 0.005 $^{\circ}$ /s. A crystallinity index (CI) was calculated empirically (Segal et al. 1959) as $100 \times (I_{18^{\circ}} - I_{18^{\circ}})/I_{\text{max}}$, where I_{max} is the maximum intensity of the 002 lattice diffraction and $I_{18^{\circ}}$ the intensity recorded at that particular angle, both in arbitrary units.

The surface morphology of the films was examined by AFM. The images were acquired with a MFP-3D atomic force microscope (Asylum Research, Santa Barbara, CA) on the films glued to a glass slide with double-sided tape. The experiments were conducted in tapping mode using silicon cantilevers (Nanoworld) with force constant 42 N/m, tip length 125 μm , tip radius 8 nm or less and resonance frequencies 320 kHz. Similar AFM conditions were employed to measure CNF that had been liberated from those films by magnetic stirring in water for 5 days.

Results and discussion

Figure 1 illustrates the effect of carboxylate concentration on the energy required to disintegrate cellulose fibers by plotting some of the limits reported in the literature and recalculating others from the experimental details provided there. The references to the disintegration energy in most of the works are often very vague and rarely contain a production yield associated to it, but similar limits appear repeatedly in one form or the other in patents and scientific papers

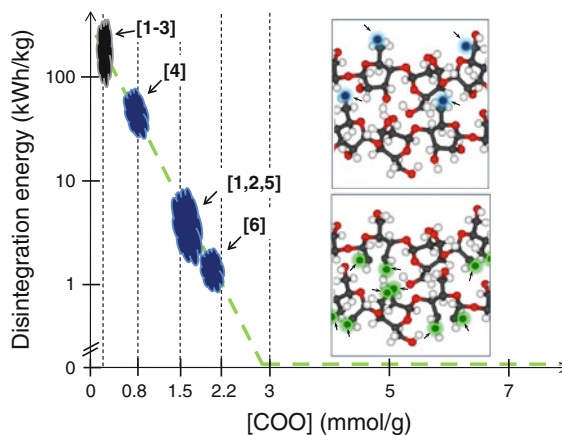


Fig. 1 Estimates of the energy required to disintegrate cellulose fibers into cellulose nanofibrils according to data available in the literature (1 Siro and Plackett 2010, 2 Isogai 2009, 3 Turbak et al. 1983, 4 Saito et al. 2009, 5 Engelhardt et al. 2009, 6 Saito et al. 2008). *Cloud shapes* represent unmodified (lowest COO content) and TEMPO-oxidized wood cellulose fibers. The *green dashed line* shows how, apparently, the disintegration energy would approach zero energy at $[\text{COO}] \sim 3 \text{ mmol/g}$. The *arrows* in the *insets* illustrate the carboxylation of primary (*blue dots*) or secondary (*green dots*) hydroxyl groups achieved respectively through TEMPO or Periodate + Chlorite oxidations, and the different charge densities that result in each case. (Color figure online)

(Engelhardt et al. 2009; Isogai 2009; Saito et al. 2009, 2008; Siro and Plackett 2010; Turbak et al. 1983). What these publications do not tackle, however, is a complete analysis of how the energy required to disintegrate a fiber is affected by the charge content, and more importantly, how the combination of these two parameters affects the production yield and the associated mechanisms.

Mechanically fibrillated cellulose, with or without pretreatment, has been extensively studied for the last two decades. Figure 2 shows atomic force microscopy (AFM) images of two different nanofibrillar cellulose preparations. Figure 2a corresponds to CNF extracted from coir (*Cocos nucifera*) fibers after being disintegrated exclusively by mechanical action (20 passes in Niro Soavi high pressure homogenizer with 500 bar pressure drop (Tejado et al. 2006)). The image shows the intrinsic limitations of this technique: damaging of the nanofibrils and difficulty to totally disintegrate the cellulose fibers (Siro and Plackett 2010; Henriksson et al. 2007). Figure 2b shows CNF isolated from softwood kraft pulp after TEMPO/NaClO/NaClO₂ treatment ([COO] = 0.8 mmol/g) following a previous work (Saito et al. 2009); oxidized fibers were disintegrated in a domestic blender (Waring Commercial Blender, Model 51BL31) for 15 min and then sonicated (Vibra-Cell, Sonics & Materials Inc.) for 5 min before imaging. Nanofibrils look much longer and better dispersed than in the previous case.

The chemistry used in the present work for the introduction of charges on cellulose fibers is

schematically shown in Fig. 3. Compared to TEMPO-mediated oxidation it allows the introduction of a larger amount of carboxylic groups and consequently the study of the effect of the charge content on the disintegration energy through a wider range, including the limit where, according to Fig. 1, the energy is expected to approach zero. Four samples with different carboxylate content (1.0, 2.0, 2.5 and 3.5 mmol/g, obtained from conductometric titrations) were used for this study.

The four modified cellulose samples were subjected to mechanical treatments of different intensities, by varying the amount of time, with either a domestic blender or a homogenizer and the electrical energy consumed during each treatment was recorded. The characterization of both disintegration equipments showed that the efficiency (see section “Disintegration process”) was around 27 % for the domestic blender but only about 9 % for the homogenizer at the selected settings. According to our measurements, that means that the homogenizer wastes most of the electricity consumed in internal processes and heat released from the engine, and only around 10 % is actually taken into the suspension. On the other hand, the domestic blender transfers more than one fourth of the electricity into the pulp preparations being thus much more efficient for this application. As expected, after applying the efficiency correction factor, the thermal energy input for the blender and the homogenizer fell into a comparable range (1.9 and 2.4 kJ/min, resp.) despite having very disparate electric consumptions

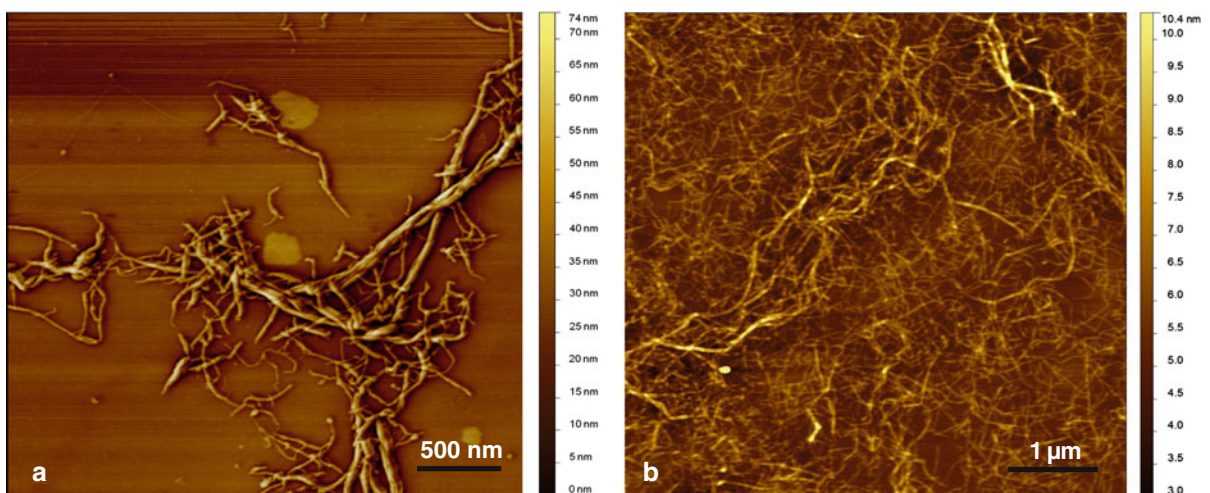


Fig. 2 AFM images of cellulose nanofibrils from **a** coir, after intensive mechanical homogenization (Tejado et al. 2006), and **b** TEMPO-oxidized softwood kraft pulp after disintegration with a domestic blender followed by sonication

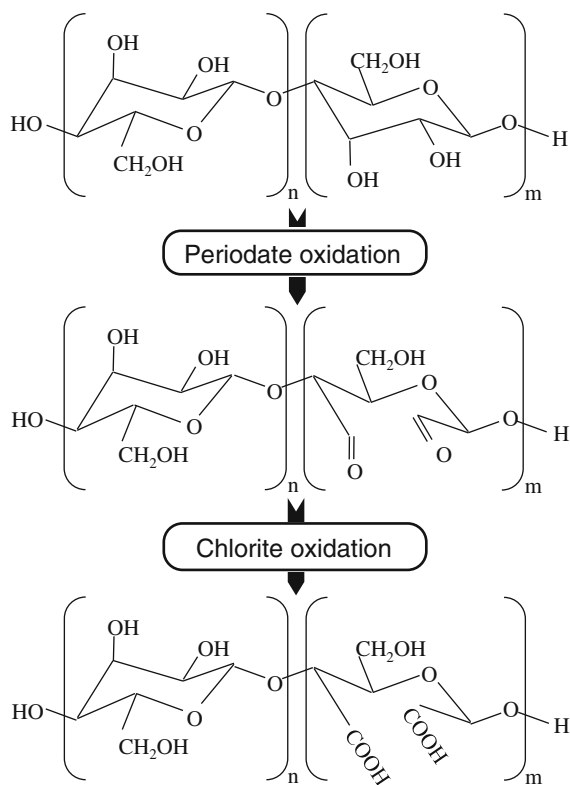


Fig. 3 Scheme of the periodate oxidation + chlorite oxidation mechanism

(7.2 and 26.0 kJ/min, resp.). This agreement actually proves the reliability of the energy measurements since, as will be seen later, the mass yields for all three cellulosic fractions fit perfectly with the thermal energy recorded regardless the type of device used.

The effect of the mechanical action on the yield of non-disintegrated cellulose fibers, dissolved carboxylated cellulose and cellulose nanofibrils, respectively, is shown in Fig. 4a–c for the four different samples. Data obtained with the blender and the homogenizer are mixed without specifically mentioning their origin. Figure 4a shows that the amount of non-disintegrated fibers decreases with increasing carboxylate content at a given energy level, and also with increasing energy at a given concentration. This is exactly the kind of behaviour that is expected, as the charge groups create repulsion between the nanofibrils, thus weakening the macrostructure, and the mechanical action separates them physically. It is remarkable to see that already at 1 mmol/g only about 55 wt.% gets caught on the 20 μm pores while the rest

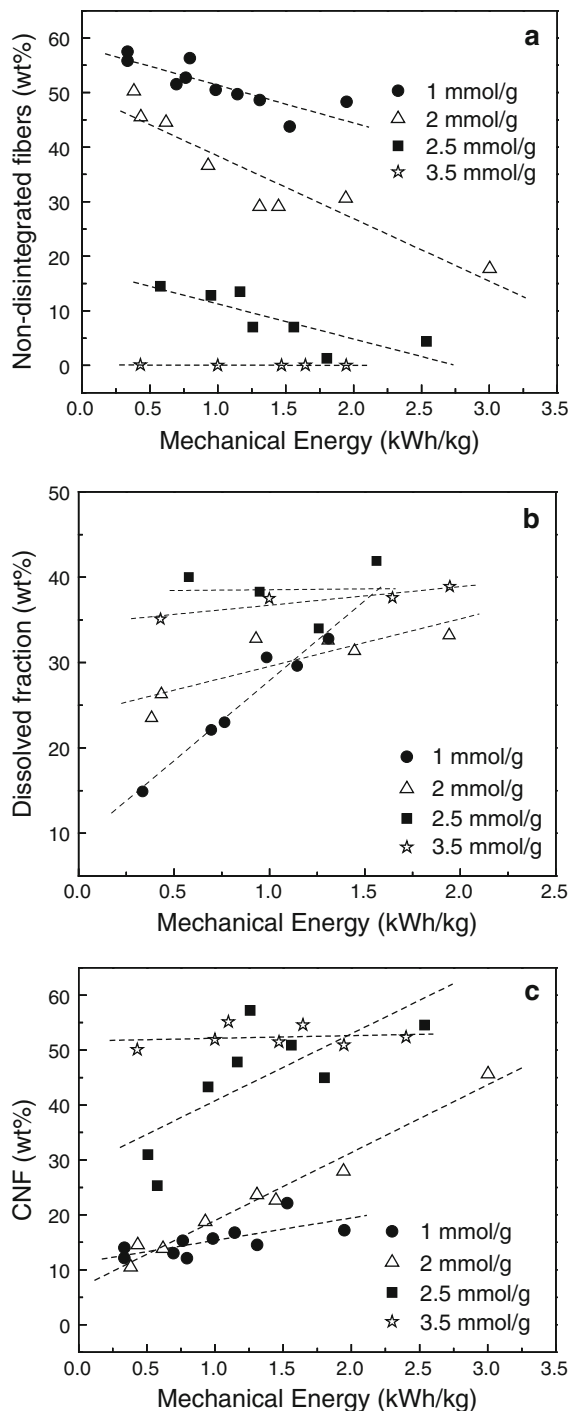


Fig. 4 Yield of **a** non-disintegrated fibers (wt%), **b** dissolved fraction and **c** cellulose nanofibrils, as a function of Mechanical Energy (kWh/kg) applied to the suspension of modified cellulose fibers having different concentrations of carboxylic groups. Dashed lines are guide to the eye only

passes through. Maybe more interesting is to note that at 3.5 mmol/g such amount gets close to zero, even at the minimum energy level tested. Such observation strongly supports the prediction highlighted in Fig. 1, which shows that, above certain charge content, cellulose fibers need almost no energy to get disintegrated. Indeed, according to present results, the threshold value may well lay around 3 mmol/g as suggested from that graph.

Figure 4b shows the cellulose fraction that passed through the 0.1 μm pore size filter and which we generally correlate with dissolved carboxylated cellulose. The trend is the opposite than that for the non-disintegrated fibers, with the yield being favoured by both carboxylate content and energy applied. In this case both the 3.5 and 2.5 mmol/g samples show an almost constant yield, ranging from 35 to 40 wt.%, while the less charged samples seem to approach this value as the energy is increased. These results suggest that the liberation of the CNF is driven by the dissolution of large cellulose fractions. The chemical treatment would preferentially oxidize the amorphous domains, as they are more accessible and thus more reactive, which would get released by a solvating force upon reaching a certain charge concentration. That would cause the spontaneous liberation of the CNF, a mechanism illustrated in Fig. 5.

Finally Fig. 4c shows the evolution for the CNF fraction. As a general rule, the yield follows the same

trend observed in Fig. 4b and increases with increasing carboxylate content for a given energy level and with increasing energy input for a given charge content. However, for a carboxylate concentration of 3.5 mmol/g a plateau value is observed regardless the amount of energy applied, suggesting that the maximum possible yield has been reached and, again, that the energy applied has played little or no role on it. The same plateau, in the range 50–60 wt.%, is reached for the 2.5 mmol/g sample after applying 1.25 kWh/kg. A similar plateau value has been recently observed by other authors upon the study of different catalysts as potential TEMPO substitutes (Iwamoto et al. 2010). The authors also relate the yield to the charge content and obtain similar maxima. Although not calculated specifically, the disintegration specifications (domestic blender, 5 min) suggest that the amount of mechanical energy applied in those cases is several times greater than the highest level used in our study. Nevertheless, other studies using the TEMPO route (Isogai et al. 2011) claim that up to 95 % of the original cellulose can be converted into CNF if enough energy is applied.

The CNF fractions, obtained originally as films, were characterized through AFM and XRD. Figure 6 shows images from (a) one of these films, corresponding to $[\text{COO}] = 2.5$ mmol/g sample, and (b) CNF with $[\text{COO}] = 1$ mmol/g after being liberated from the corresponding film. Cellulose nanofibers with

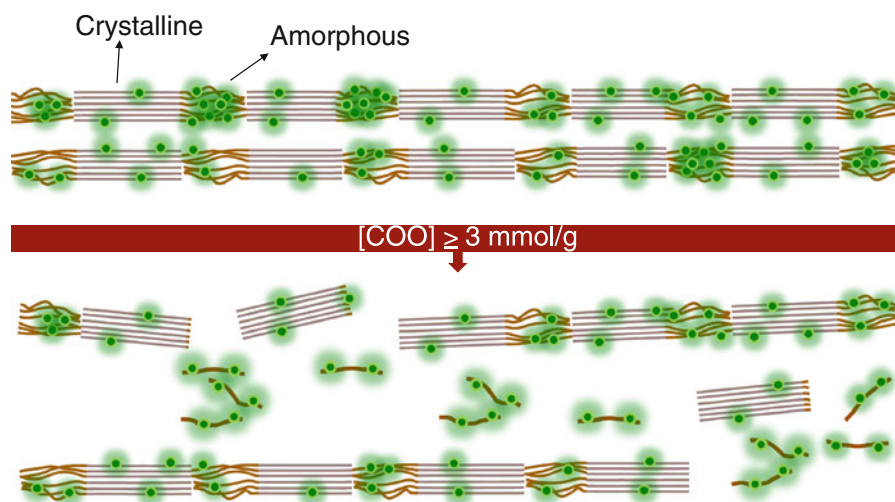


Fig. 5 Suggested mechanism for the liberation of CNF in the absence of mechanical energy. The preferential oxidation of the amorphous domains of cellulose leads, upon surpassing a threshold value, to their solubilisation with the subsequent

liberation of cellulose nanostructures of varying length. Green glossy dots represent (charged) carboxylate groups. This process starts at the readily available surface of the fibers and continues inward (Varma et al. 1997). (Color figure online)

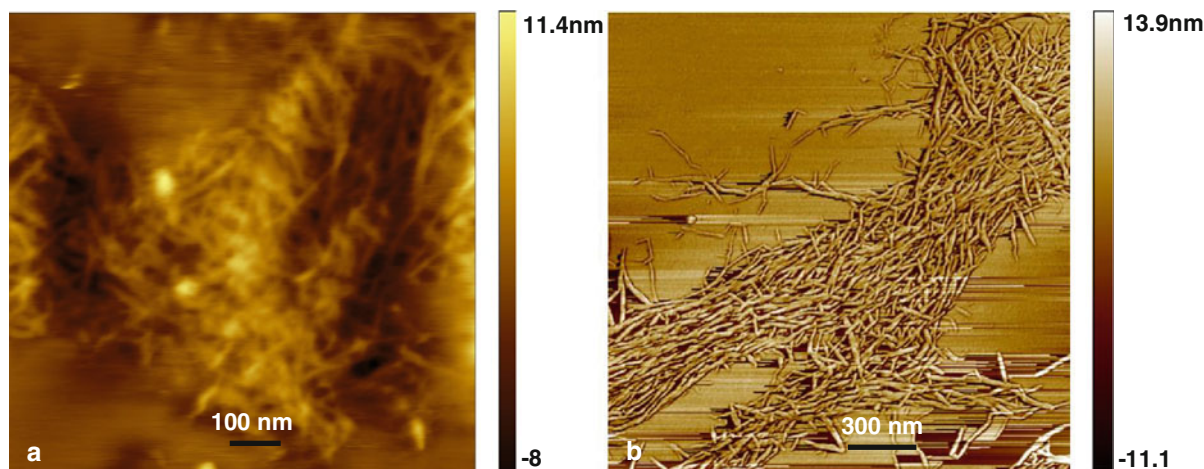


Fig. 6 AFM images of **a** CNF film made of $[\text{COO}] = 2.5$ mmol/g nanofibers and **b** CNF fibers liberated from a CNF film made of $[\text{COO}] = 1$ mmol/g nanofibers

diameters in the order of 10–20 nm are clearly visible in both samples. In addition to CNF, Fig. 6a shows large regions within the film where nanofibers are absent. Those areas could be made of amorphous cellulose, in agreement with previous observations in which cellulose becomes increasingly amorphous with progressive periodate oxidation leading to new cellulose derived products (Varma et al. 1997). Another possibility is the presence of dissolved carboxylated cellulose that had deposited on top of a CNF network during the filtration process, favoured by the blocking of the 0.1 μm pores. Figure 6b shows well defined CNF of varying width, including both individualized nanofibrils and small bundles of them which were never completely disintegrated. Despite these bundles, the degree of isolation of individual CNF achieved is shown to be very high considering the limited mechanical treatment applied, and must be ascribed almost completely to the chemical modification carried out.

In the XRD curves of these films (Fig. 7) a typical X-ray diffraction pattern of oxidized native softwoods is observed in all cases, similar to that shown elsewhere (Okita et al. 2010). The crystallinity indices obtained from these curves (66.2, 68.2, 69.8 and 73.5 %, respectively for 1.0, 2.0, 2.5 and 3.5 mmol/g carboxylate content) also correspond to samples with both crystalline and amorphous parts, instead of a highly crystalline CNF sample as would be expected. It has been reported that periodate oxidation of cellulose leads to a severe loss of crystallinity (Kim

et al. 2000; Hou et al. 2007; Varma et al. 1997), what would explain the low CI values. The increase in CI with increasing charge content could be related to a higher degradation of the more oxidized samples leading to a lower deposition of dissolved carboxylated cellulose onto CNF networks.

The film characterization, however, confirms that cellulose nanofibrils have been liberated almost in the absence of mechanical treatment; at the same time it suggests that the separation method should be improved in order to have well defined fractions, which will be attempted in future work. The fact that periodate oxidation leads to cellulose degradation could be also related to the decreased CNF yields described before. According to our mass balances, this yield loss is due to the solubilisation of amorphous carboxylated cellulose prior to the liberation of the nanofibrils. Such disintegrating mechanism leads to a reduced CNF production yield but at the same time allows an energetically friendly production. Moreover, the total disintegration of cellulose fibers could find an interesting field of application in biofuel production, where the decreases in crystallinity and polymerization degree of carbohydrates are highly desired, as they favour their digestibility (Mora-Pale et al. 2011).

The practical implications of this work are very interesting. It not only suggests that cellulose nanofibers can be produced almost in the absence of mechanical energy, but also that samples can be prepared in such a way that they need a predefined

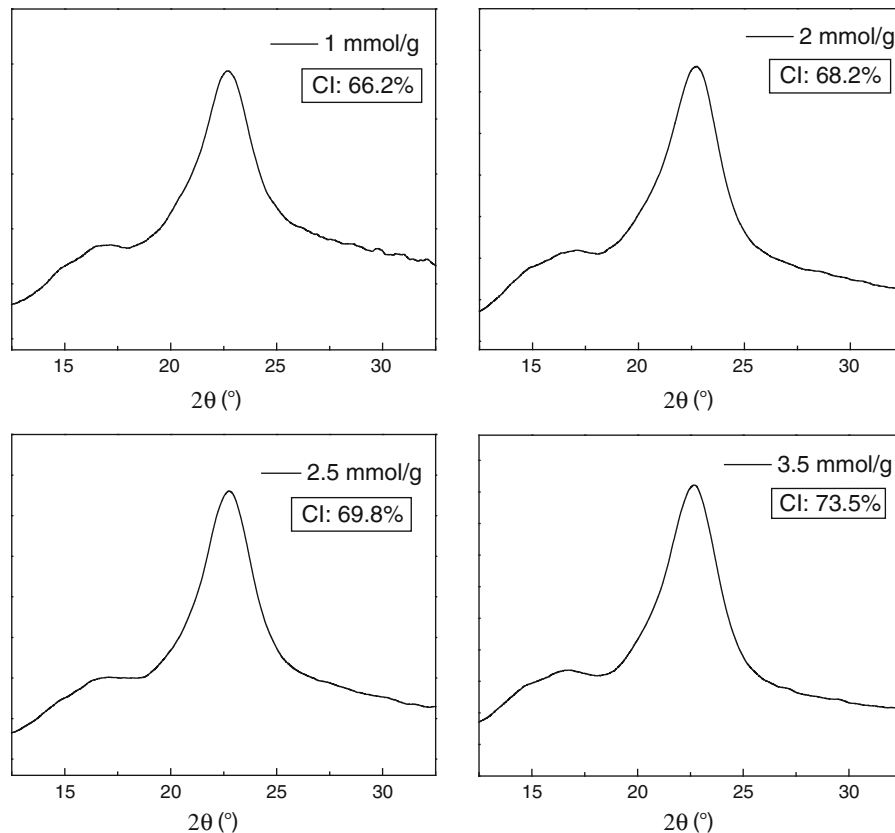


Fig. 7 XRD curves of CNF films obtained at different carboxylate contents (mmol/g). The calculated crystallinity index (%) is shown next to each diffractogram

amount of shear to be torn apart. This would facilitate some problematic aspects related to nanofibrillar cellulose preparations, such as their transportation and elevated viscosity. For example, one big problem that prevents cellulose nanofilms to be produced in a continuous industrial process is the high viscosity that CNF suspensions already show at very low concentrations (Siro and Plackett 2010). This could be avoided by preparing suspensions of modified cellulose fibers (having a viscosity close to that of water), which had been previously oxidized to the extent where they become disintegrated by a precise mechanical energy (Tejado et al. 2011). Using a papermaking machine as an example, that mechanical energy would be the one exerted in the headbox at the time the pulp suspension is delivered onto the forming wire. Before getting to the headbox, no difference with regular pulp suspensions should be encountered, thus no viscosity problems are expected; only upon passing through the slice opening, the fibers would be disintegrated and

deposited on a forming wire as nanofibrils. The same could apply to mixtures of regular and oxidized fibers, where the latter would act as a reinforcing element of paper, or to mixtures of polymer matrices and CNF, which could take advantage of the shear imparted by an extruder or a mixer.

Conclusions

This paper shows that the isolation of cellulose nanofibers can be achieved almost in the absence of mechanical energy if the oxidation is sufficiently high. The mechanism responsible for this “spontaneous” disintegration is shown to be the dissolution of overcharged amorphous domains, which become solubilised upon surpassing a certain charge threshold value set around 3 mmol/g, according to experimental results. A maximum of 50–60 wt.% of the original cellulose is converted into cellulose nanofibers what seems to be a direct

consequence of the chemistry applied (periodate-chlorite oxidations). This study opens up the possibility for the energy-friendly production of cellulose nanofibers.

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