Changes of crystallinity index and crystallite size in cotton cellulose nanoparticles obtained by ball milling

Josué David Hernández-Varela
Departamento de Ingeniería Bioquímica, ENCB
Instituto Politécnico Nacional
Mexico City, México.
jherandezv1717@alumno.ipn.mx

José Jorge Chanona-Pérez
Departamento de Ingeniería Bioquímica, ENCB
Instituto Politécnico Nacional
Mexico City, Mexico.
jorge.chanona@hotmail.com

Silvia L. Villaseñor-Altamirano
Departamento de Ingeniería Bioquímica, ENCB
Instituto Politécnico Nacional
Mexico City, Mexico.
sleticia.altamirano@hotmail.com

Claudia Mendoza-Martínez
Departamento de Ingeniería Bioquímica, ENCB
Instituto Politécnico Nacional
Mexico City, México.
cla_isminaluna@hotmail.com

Felipe Cervantes Sodi
Departamento de Física y Matemáticas, Universidad Iberoamericana,
Mexico City, Mexico.
Felipe.cervantes@ibero.mx

Abstract—Crystallinity (CI) and crystallite size (Dhkl) of cellulose nanoparticles obtained from commercial cellulose (cotton) have been evaluated after a ball milling by the deconvolution method. Ball milling was used to achieve cellulose nanoparticles based on the values of crystallite size previously reported. Variations in the CI were found in a range from 88% to 45%. Crystallite sizes were evaluated in an initial value from 4.99 nm that decrease until 1.41 nm by ball milling. A clear dependency of CI and D_hkl was found since ball milling decrease the CI until a re-agglomeration of the samples is found. Results for D_hkl reveals that cotton cellulose is a soft material easy to grind into nanoparticles in a heterogenous way as authors reported before. Cross-contamination due to higher quantities of silicon oxide was found after two-hour milling. This study presents an insight into the behavior of cellulose nanoparticles using ball milling and the selection of a time in which non-cross contamination or re-agglomerations have been found.

Keywords—cellulose, nanoparticles, ball milling, crystallinity, crystallite size, cotton.

I. INTRODUCTION

Cellulose and its nano-derivatives (nanoparticles, nano-crystals, nanowhiskers, etc) are considered an abundant organic polymer, with a huge range of potential applications for the development of biocomposites [1], [2]. There have only been a few reports published on obtaining cellulose nanoparticles (CNP), by physical treatments. Usually, to obtain CNP chemical methods has been used [3]–[5]; however, these methods have drawbacks due to the costs, the uses of chemical polluting solutions, and lower recovery yields [6], [7]. In opposition, ball milling emerges as a low cost, easy and rapid technology to obtain nanosized cellulosic material [1]. The yields using the ball milling process are higher when initial material is grinder into a powder form, in which the nanowhiskers and nanoparticles are separated from the initial material [1], [6], [8]. An important characteristic is found since the ball milling process causes changes in the crystallinity index (CI) of the samples, due to the size reduction of the structure of cellulose at the nanoscale [5], [9]. This behavior is noticed in the crystallite size (Dhkl), which is the small portion of the polymer molecule in which crystal lattices are reduced by physical treatments [10]. Ball milling produces higher yields of CNP with higher hydrophilicity [11] and shows increased density and tensile strength [12].

These characteristics are valuable for CNP to be used as reinforcing material [13], nanoporous membranes [14], agar-based films [2], and novel antimicrobial film [15]. On the other hand, the extensive use of microscopy and spectroscopy techniques allows characterized samples and provide important results to be discussed [9], [16]. Microscopy techniques as Scanning Electron Microscopy (SEM) permits to find nanosized materials and evaluated the agglomeration behavior of these materials when ball milling is applied [17]. Besides FTIR and XRD allows to corroborate the presence of cellulosic material and verify the purity of samples when ball milling is used. The authors reported important cross-contamination of samples when agate ball and agate containers for ball milling are used [5], [18]. This study evaluated the changes in the CI and D_hkl of cotton cellulose after ball milling and provide a valuable result to choose a time of milling in which a lower crystallite size and less cross-contamination are found, to use this nanosized cellulosic material in diverse applications.

II. MATERIALS AND METHODS

A. Materials

Microcrystalline powder of cotton cellulose referred as commercial cellulose (C) was purchase from Sigma-Aldrich (cod. 435236, St. Louis, MO, USA) with a particle size of 51 μm and free of humidity.

B. Ball milling to obtain cellulose nanoparticles (CNP)

Commercial cellulose (C) was pulverized until cellulose nanoparticles (CNP) using a high-energy planetary micro mill PULVERISETTE 7 (Fritsch GmBH, Idar-Oberstein, Germany) as Hernández-Varela et al. [18] reported. Dry milling at different times (0 min, 60 min, 120 min, 180 min, 240 min) with a ratio of 1:72 (g material/no* balls) was performed using an initial quantity of 2 g. CNP of samples at different times were evaluated in an initial value from 4.99 nm that decrease until 1.41 nm by ball milling. A clear dependency of CI and Dhkl was found since ball milling decrease the CI until a re-agglomeration of the samples is found. Results for Dhkl reveals that cotton cellulose is a soft material easy to grind into nanoparticles in a heterogenous way as authors reported before. Cross-contamination due to higher quantities of silicon oxide was found after two-hour milling. This study presents an insight into the behavior of cellulose nanoparticles using ball milling and the selection of a time in which non-cross contamination or re-agglomerations have been found.

C. Scanning electron microscopy of milled samples

Scanning Electron Microscopy (SEM) images of the commercial cellulose at different times of milling were obtained using a SEM microscopy (SU3500, Hitachi Co., Ltd., Matsuda, Japan). Samples were put in aluminum holders with carbon tape and powders were stick on the surface. Then, samples were coated with a thin gold layer (<5 nm) using a
sputter-coated (SPI suppliers, USA). Samples were observed using a secondary electron (SE) detector, 10 kV acceleration voltage, and 6.7 mm of work distance. Images were acquired in TIFF format with a resolution of 800 x 600 pixels. The elemental composition of samples was acquired using an Energy Dispersive Spectroscopy (EDS) detector coupled to the SEM and the intensity of the signal (cps) was recorded in a range of 0-15 keV. The presence of Si (%) was obtained from the data acquired in the equipment and used for discussion.

D. FTIR of cellulose nanoparticles

The powders of CNP before and after the ball milling were analyzed using a FTIR spectrometer (Nicolet 8700, Thermo Scientific, Waltham, MA, USA). A scan rate of 4 scans per minute over wavenumber ranging between 400 and 4000 cm\(^{-1}\) was used to obtain the FTIR spectra.

E. XRD of cellulose nanoparticles

Powders of CNP from ball milling samples at different times were used to perform an XRD analysis. Patterns were acquired with a diffractometer (D8 ADVANCE, Bruker, USA), Cu K\(\alpha\) radiation source at 40 kV, scans from 2\(\theta\)=10 to 50\(^{\circ}\), at 0.4 s/step. Then, patterns were corrected in a baseline using the Origin Pro software version 9.6.5.1 (OriginLab Corporation, USA). Five crystalline peaks around (TT0) at 14\(^{\circ}\), (110) at 15\(^{\circ}\), (021) at 20\(^{\circ}\), (200) at 22\(^{\circ}\), and (040) at 34\(^{\circ}\) were selected for the initial sample and for the milled powders, only the crystalline peak 200 shifted to the left in lower values (\(\approx 20^{\circ}\)) were selected. Processed patterns were used to calculate the crystalline index (CI, %) using the Seagal method reported by Kathirselvam et al. (2019) using the following Eq. (1):

\[
CI(\%) = \frac{(I_a - I_c)}{I_a} \times 100
\]

where \(I_a\) is the intensity of peak in the amorphous contribution (2\(\theta\)=18\(^{\circ}\)) and \(I_c\) is the intensity for the crystalline peak contributions for time 0 (2\(\theta\)=22\(^{\circ}\)) and for the crystalline contribution in the rest of the times (2\(\theta\)=20\(^{\circ}\)). Additionally, to corroborate the presence of other crystalline compounds, the DIFFRAC.EVA software (V5.1, Bruker, USA) was used to assign the peaks [20].

F. Deconvolution analysis in XRD patterns of CNP

Diffractograms of CNP at different times were used to calculate the crystallite size \(D_{hkl}\), nm. The deconvolution method was used to fit a Gaussian function of the crystalline peak at 2\(\theta\)=22\(^{\circ}\) before ball milling, and 2\(\theta\)=20\(^{\circ}\) after each time of milling. XRD patterns were analyzed using the XRD software. The crystallite size was calculated using the Scherrer’s equation (2):

\[
D_{hkl} = \frac{(K \cdot \lambda)}{\beta \cos \theta}
\]

where \(K\) is Scherrer’s constant (0.89), \(\lambda\) is the wavelength of radiation (0.15418 nm) and \(\beta\) is the full width at half maximum (FWHM) in radians of the deconvoluted crystalline peak at the crystallographic planes (200) with \(\theta\) in radians, obtained with Origin Pro software [19].

Fig. 1. (a) FTIR spectra and (b) XRD pattern of commercial cellulose of initial and milled samples.

III. RESULTS AND DISCUSSION

Since a commercial sample (cellulose from cotton) is used for analysis, the microscopic analysis is overcome. But it is well-known that spectroscopy analyses (FTIR and XRD) are an effective and complementary method to know the chemical structure of samples, since the elucidation on chemical composition, molecular conformation, and patterns of formation of hydrogen bridges in the purified cellulose is made [21], [22].

Fig. 1a and 1b, show the FTIR spectra and XRD pattern for commercial cellulose of initial and milled samples, respectively. Fig. 1a shown a FTIR spectra with a characteristic tendency of the samples in the initial (0 min) and final milling (240 min). The highest intensity peak can be observed between 3400 and 3200 cm\(^{-1}\) which is due to the O-H stretching vibration of the hydrogen-bond hydroxyl group of cellulose [23]. The bands approximately to 2880 cm\(^{-1}\) are attributed to the asymmetric stretch of the C-H group present in cellulose [21], [24]. In all spectra, the peaks close to 1640 cm\(^{-1}\) and 2125 cm\(^{-1}\) can be attributed to the water absorbed by the cellulose in the isolation process that became less present at the end of the milling [25]. Two other peaks at ~1100 cm\(^{-1}\) and ~880 cm\(^{-1}\) were associated with C-O stretching and C-H oscillating vibrations of cellulose,
which appeared in all spectra [26]. Finally, under 500 cm⁻¹, other bands with unknown intensity are found. This region knows as the fingerprint region is present due to the halogen compounds (C-X) from the sample [27].

Fig. 1b shown the XRD patterns for the samples before and after the milling experiment. Crystalline cellulose (0 min) was confirmed by the presence of four peaks showed at 2θ=15° (110), 16.4° (110), 22.6° (200), and 34.7° (040), typically for type I cellulose [28]. A higher value for CI is found in cotton cellulose (88%) without milling. A notable decrease in the intensity of the main crystalline plane and the value of CI is observed [1], [29]. The high energy milling increases the content of amorphous cellulose and induced a reduction of particle size [24] as the milled spectrum is shown in Fig. 1b. The CI in the milled sample decreases drastically (Table 1) until a lower value of 34% in the sample at 120 min milled. The ball milling technique is a well-known technique in which the morphology of cellulose is change, making small semispherical particles due to the mechanical stress promoted inside of the equipment [9]. Also, ball milling provokes cross-contamination of the samples due to the strong interaction between the sample and the bowl walls/milling balls [5]. In this case, a peak around 2θ=26.7° was assigned to cross-contamination by SiO₂ from the agate balls used to milling the samples [18]. The authors reported a gradual increase of SiO₂ from 120 min to 240 min (Fig. 1b, stars). To corroborate this peak, an assignment with the XRD pattern library of the instrument was made. The crystallographic pattern for SiO₂ (COD=1011159) coincides with the signal obtained in the pattern. Hernández-Varela et al. [18] explain that friction and energy employed in the milling are responsible for the cross-contamination by SiO₂ at large milling times. These results prove that nanosized material before 120 min of milling is adequate to obtain CNP without excessive cross-contamination.

Fig. 2 show the SEM images used for analysis from the samples before and after milling. It is observable that the initial material (Fig. 2a) have bigger sizes (>51 mm) as the supplier report. After 60 min of milling (Fig. 2b), small particles appear but nanoparticles became difficult to found with this resolution. Around 120 min (Fig. 2c) ball milling grinds the material in small pieces, but after 180 min and 240 min (Fig. 2d y 2e), a re-agglomeration of the samples is observed. This behavior is due to the exposition of more defects in the sample, when ball milling exposes -OH groups of the cellulose chain, making more effective the inter and intramolecular hydrogen bonds between the sample [29]. Also, this fact yield CNP with more active sites and capability for interact with other compounds, showing an increase in CI, which indicates the presence of more crystalline material, maybe due to cause by the larges times of milling (240 min) [8].

Using SEM images (Fig. 2) and CI values (Table 1), it is possible to corroborate that ball milling in samples has a variation depending on time and sample. Samples tend to re-agglomerate, decrease their CI, and increase their cross-contamination as authors reported before [1], [8]. In this sense, the presence of cross-contamination is verify using the SEM images when an EDS detector is used.
In Fig. 2, small sections of samples (yellow squares from i to v) were analyzed and values for elemental composition were calculated. The initial samples show a presence of Au around 11% originated for the sputter-coated, as well as C and O originally from the chemical composition of the samples. But a noticeable present of Si from SiO\textsubscript{2} after the first milling is observed (0.52%). Higher values of Si from SiO\textsubscript{2} are found after 120 min (39%) as XRD and FTIR reported before. The presence of Si was evaluated using the intense peak around 1.8 keV that is a characteristic signal from this element in the EDS experiment [30]. It is noticeable that after 120 min of milling, the Si values start to increase until higher values at the end of milling (71%). As was explained before, the ball milling grinds the sample but the stress promotes inside of the apparatus, increasing the interaction sample-ball milling material, provoking cross-contamination [5].

Using the XRD pattern from Fig. 1b, it was possible to calculate the crystallite size (D\textsubscript{hkl}) with the deconvolution method (Fig. 3) using Eq. 2. For time 0 (Fig. 3a) five crystalline peaks were selected, corresponding to the well-known planes propose in the XRD analysis (Fig. 1b). For each milling time (Fig. 3b-3e), three different peaks or contributions were analyzed (15°, 20°, 27°). The main peak associated with the displacement of the plane 200 was selected to calculate the crystallite size.

Table 1 shows the crystallite size values (D\textsubscript{hkl}) obtained for the cellulose nanoparticles. For cotton cellulose, D\textsubscript{hkl} is estimated at around 4.99 nm and it is reduced until 1.41 nm. These values follow the same tendency that [31] reported for cellulose in cotton fibers from 7 nm to 3 nm in ball milling. These initial values are comparable with those obtained for cellulose fibers of Thespesia populnea bark (3.58 nm, Kathirselvam et al., 2019), cellulose from onion skin (2.11 nm, Rhim et al., 2015), ramie (5 nm) and fortisan (4 nm) [32], and several pomaces between 2-3 nm [33]. The values of CI and D\textsubscript{hkl} showed a clear dependency on its reduction values. The authors reported that the reduction of particle size, provoke changes in the size of crystallites, increase the amorphous contribution after each milling time, and finally, a decrease in CI that is related with non-uniform strain into the crystals [19].

Since studies of commercial cellulose (cotton) are widely made, CNPs using ball milling are scarce studies yet. In this case, more advanced microscopy techniques need to be used to achieve a realistic nanoparticle size. Even though, this study reveals an interesting behavior of the formation of crystallite sizes in CNP. As Ling et al. (2019) explain, cellulose fractioning during ball milling occur homogeneous and heterogeneously.

### Table 1. Values of Crystallinity Index (CI), Crystallite Size (D\textsubscript{hkl}), and Silice Content (SI, %) for Ball Milling Samples at Different Times.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>CI (%)</th>
<th>D\textsubscript{hkl} (nm ± 10^{-2})</th>
<th>SI (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>88.01 ± 0.11</td>
<td>4.99 ± 0.61</td>
<td>- (i)</td>
</tr>
<tr>
<td>60</td>
<td>36.97± 0.22</td>
<td>1.30± 0.09</td>
<td>0.52 ± 0.22 (ii)</td>
</tr>
<tr>
<td>120</td>
<td>34.29± 0.23</td>
<td>1.36± 0.02</td>
<td>39.47 ± 1.89 (iii)</td>
</tr>
<tr>
<td>180</td>
<td>42.79± 0.31</td>
<td>1.41± 0.07</td>
<td>41.22 ± 2.55 (iv)</td>
</tr>
<tr>
<td>240</td>
<td>45.46± 0.33</td>
<td>1.41± 0.09</td>
<td>71.19 ± 3.47 (v)</td>
</tr>
</tbody>
</table>

* Values in the columns have significant differences (p < 0.05) in comparison with time 0 min.
Indeed, $D_{hkl}$ values for C decreasing their size unprogressively (Table 1), suggesting that cotton fibers are better fitted to a heterogeneous milling model. Studies reveal that the microstructure of C cellulose is fibrous and low-strength, and the crystallites could be perturbed in a discontinuous way [31], [34] While a stretch relationship between CI and $D_{hkl}$ was found, a detailed comparison using the calculated values of percent crystalline index reduction (%CIR) and crystallite size was made (Fig. 4). As was explained, fluctuations are found at different times of milling but at 120 min occurs two important events in these results. A clear decrease in the values is found for both variables but for %CIR at 120 min (61.04%), the small value for CI (34.29%) is associated with a more amorphous material in which small particles are found [35]. In the %CIR after this time, a decrease in the values is observed, due to the re-agglomeration of the samples, that produced a more amorphous material [5]. Also, $D_{hkl}$ values at 60 min show the lowest crystallite size (1.30 nm) followed by 120 min (1.36 nm) but after that time, the re-agglomeration provoke an increase of the crystal lattices (1.41 nm), may be due to the intra e inter molecular interaction of hydrogen bonds [11], [29]. Since statistical analysis show that values for crystallite do not have significant differences ($p < 0.05$), the milling time 120 min as choose to be a better time to obtain the small crystallite size.

IV. CONCLUSIONS

Changes in the composition, crystallinity index and, crystallite size of ball milling samples of cotton cellulose were found in this investigation. Results prove that ball milling produces powders with nanosized material with some cross-contamination due to the ball milling process. Milling time of 120 min was achieved as a better time to obtain the small crystallite size, highest amorphous contribution, and lowest cross-contamination of SiO$_2$. These results prove the importance of the physicochemical study of cellulose samples using a physical method (ball-milling) to achieve nanoparticles but more studies in the evaluation of size with high-resolution microscopes are needed. Further studies could include a detailed study of STEM and TEM images to evaluate the nanomaterial. Finally, these kinds of materials can be used in the reinforcement of bioplastics, biopolymers, filters, etc., to reduce the uses of polluting plastics and create a more biodegradable material.

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