Ultrathin film coatings of aligned cellulose nanocrystals from a convective-shear assembly system and their surface mechanical properties

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Ultrathin films of aligned cellulose nanocrystals (CNCs) were deposited on solid supports by using convective and shear forces. Compared to previous systems involving high electric or magnetic fields to control the orientation of these rod-like natural nanoparticles, the proposed process of alignment was very simple, inexpensive and with potential for scale up. The effect of concentration of CNC in aqueous suspensions, type of solid support, relative humidity and rates of withdrawal of the deposition plate were determined by using atomic force microscopy (AFM) and ellipsometry. The degree of orientation was quantified from the number density of CNCs in leading angles by using image analyses. Also, the contribution of shear and capillary forces on alignment parallel and normal to the withdrawal direction was elucidated. The best alignment of CNCs in the withdrawal direction, favored by shear effects, was achieved with gold and silica supports with a pre-adsorbed cationic polyelectrolyte layer and at a CNC suspension concentration above 2.5% (w/w), below the critical concentration for chiral nematic phase separation. Compared to the bare solid support, nanoindentation of the obtained coatings of ultrathin films of oriented CNCs provided enhanced surface mechanical strength and wear resistance. A transverse Young’s modulus, hardness and coefficient of friction of 8.3 ± 0.9 GPa, 0.38 ± 0.03 GPa and 0.51 ± 0.23 GPa, respectively, were measured. Notably, the transverse Young’s modulus was found to be in agreement with reported values predicted by molecular modeling and measured for single CNCs by using atomic force microscopy.

1 Introduction

Cellulose nanocrystals (CNCs) have been used as a reinforcing material in composites to improve their mechanical properties. This is in part due to their relatively high intrinsic strength, high aspect ratio and low density. The use of CNCs in high performance coatings is attractive not only because of their properties but also because they may provide a platform for fundamental studies related to their assembly. Thin films of CNCs have been produced by film casting, spin coating, and by the Langmuir–Blodgett techniques. Recently, Rojas and coworkers also used the Langmuir–Schaeffer surface lifting method to produce dense layers of CNC on hydrophobic supports. When used in composites, CNCs have been shown to affect markedly the properties of the resultant materials, depending on the processing conditions and their supramolecular organization.

In general, the possibility to control the architecture of two- and three-dimensional arrays of proteins, nanoparticles and nanomaterials is critical in applications related to biotechnology (vaccines, diagnostics, etc.), biosensing, electronics, optics, microengineering and electrocatalysts. The same can be stated about the emerging possibility of CNCs as building blocks for a broad range of structures. In such cases the additional benefit of improved mechanical characteristics with aligned CNCs might be realized.

Above a certain concentration of CNC in aqueous suspensions they self-assemble into chiral nematic structures. The orientation of the CNCs is slightly different at each of the nematic planes due to rotation of the magnetic director about the perpendicular cholesteric axis. Taking advantage of such phenomena, several techniques have been used in attempts to control the alignment of CNCs. These techniques include the rotational shearing of gels and the application of intense magnetic and electric fields. Recently, radially oriented submonolayers of CNC were produced by spin-coating and the response of myoblasts to the surfaces was assessed. The techniques used for parallel alignment of CNCs are time consuming and expensive, especially because of the requirement of high (electric or magnetic) fields. Additionally, control over the thickness of the final films has not been easily accomplished.

This work focuses on a new application of capillary and shear forces to align CNCs in ultrathin films taking advantage of...
systems to assemble particles onto solid supports. Among them, a convective assembly system used to deposit arrays and coatings of spherical colloids was found most useful. In this case the organization of spherical particles occurs when the thickness of a film is reduced due to solvent evaporation, and the particles in the meniscus are pulled together by attractive capillary forces; concurrently a flux of liquid toward the interface compensates for the mass of liquid evaporated. In other systems a suspension of particles has been dropped onto an angled stationary substrate, while in others, the substrate has been placed vertically into a vessel filled with a suspension of particles and withdrawn at a constant speed. More recently, a droplet of suspension has been trapped between two plates. The top plate was set at a given angle and was moved with a linear motor. In this latter study, several factors influenced the convective assembly. The coating thickness and the organization of the spherical particles in the film were found to depend on the nanoparticle concentration, type of solid support, deposition speed, humidity and temperature.

Due to potential benefits in coating applications, the mechanical strength properties of nanocoatings with CNCs are of interest. X-Ray diffraction, Raman spectroscopy and AFM have been applied to investigate the mechanical moduli of cellulosic structures, especially cellulose I in the cell wall and cellulose nanocrystals. Most studies have been conducted on fiber bundles, cast films and single CNCs. Attention has mainly focused on the elastic properties along the axial direction of the cellulose chain . However, only a few reports are available on the transversal elastic modulus , which include the use of molecular modeling and AFM measurements with single nanocrystals.

Nanoindentation, on the other hand, has been widely used in the determination of the elastic modulus of thin films created from different engineered materials as well as from the cell wall of cellulosic fibers. In nanoindentation tip displacement, the load and time are continuously recorded and the Young's modulus and hardness can be calculated by using models such as Oliver and Pharr’s.

The goal of this study was to deposit ultrathin coatings consisting of rod-like CNCs on solid supports and with controlled orientation or alignment with the longer term objective to modulate nanoscale architectures. These coatings are expected to offer important advantages over conventional approaches because of the expected mechanical strength, unique surface performance and possible applications beyond coatings such as those related to cell attachment and proliferation, tissue development, etc. The process and conditions of CNC deposition were first optimized for the formation of aligned nanoparticles. The convective-shear assembly was found to be simple and fast and it did not demand expensive equipment. Also, because of the possibility of continuous operation it is expected to be suitable for scaling up. The concentration of CNCs, withdrawal rate, humidity and the type of solid support were varied to study their effect on the properties of the resulting ultrathin films. Also, multilayer films consisting of CNCs combined with adhesive interlayers of poly(ethyleneimine) were manufactured using the same approach. Key mechanical properties of the resulting ultrathin films were determined, including the transverse Young’s modulus, the hardness as well as the coefficient of friction and wear resistance. The possible surface strength benefits that can be gained through the formation of aligned CNC films are expected to broaden the possible applications of such sustainable, biologically derived material.

2 Materials and methods

2.1 Materials

Ramie fibers from Stucken Melchers GmbH & Co., Germany, were used in the production of cellulose nanocrystals. Microcrystalline cellulose (Avicel PH-101) from Fluka Chemical Corporation was used in the preparation of regenerated cellulose. Poly(ethyleneimine), PEI, from BASF Corporation was employed to create a cationic surface layer on the mineral substrate used as a solid support for the CNC films. 50% 4-methylmorpholine N-oxide and dimethyl sulfoxide were purchased from Sigma-Aldrich. Silicon wafers, 350–600 μm thickness and with no orientation, were purchased from Wafer World, Inc. (West Palm Beach, FL). Gold slides (1” x 3” x 0.040” with a coating of 50 Å Ti and 1000 Å Au), mica sheets (grade V5, 10 x 40 mm; thickness 0.23 mm) and glass microscope slides (3” x 1” x 1.0 mm) were acquired from EMF-Corp (Ithaca, NY), Ted Pella, Inc. (Redding, CA) and Fisher (Pittsburgh, PA), respectively.

2.2 Cellulose nanocrystals

Ramie fibers were purified via soxhlet extraction, then hydrolyzed with 65% sulfuric acid at 55 °C for 30 min under continuous stirring; the resulting suspension was filtered through a sintered Buchner funnel, washed with deionized water and recovered by subsequent centrifugations at 10 000 rpm (10 °C) for 10 min each. Finally the resulting suspension was dialyzed against deionized water and then against Milli-Q water for a few weeks; the resulting master stock suspension was stored at 4 °C until use. The dimensions of the CNCs were 185 ± 25 and 6.5 ± 0.7 nm in length and width, respectively, as determined from TEM images, the crystallinity index was 88% as measured by X-ray diffraction and the surface charge was 0.30 e nm⁻² as determined by the concentration of sulfate groups on the surface (0.76%) from sulfur elemental analyses.

2.3 Films of regenerated cellulose

Regenerated films of cellulose were prepared following a technique reported earlier. Briefly, microcrystalline cellulose was dissolved in 4-methylmorpholine N-oxide and dimethyl sulfoxide to a final concentration of 5 mg ml⁻¹. This solution was spin coated (Laurell Technologies model WS-400A-6NPP) at 5000 rpm for 40 s onto a silicon wafer with pre-adsorbed PEI. The films were dried in an oven at 80 °C for 2 h and then hydrated for 4 h in Milli-Q water. This procedure was repeated at least 5 times, in order to obtain films of given thicknesses for further studies with nanoindentation.

2.4 CNC films from convective-shear assembly

A schematic illustration of the convective-shear assembly setup used for the production of coating films of CNCs is shown in
Fig. 1a. It included a solid support and a moving or withdrawal plate. The gold and silica substrates were cleaned with a solution consisting of sulfuric acid (70%) and hydrogen peroxide (30%) for 20 min followed by a thorough rinse with deionized and Milli-Q water. In the production of cationic silica, silicon wafers were treated with a 500 ppm PEI solution for 20 min, followed by rinsing with Milli-Q water. The respective substrate was placed in the horizontal stage of the assembly device (Fig. 1a) and CNC suspension was added between the inclined plate and the substrate. Two parameters were kept constant, namely, the volume of suspension used, 10 μl, and the angle of inclination of the withdrawal plate, 12° with respect to the substrate. The three-phase line was formed at the interphase where the front of the suspension, the solid substrate and the air phase meet, as indicated in Fig. 1a. The solid support was fixed on the stage and the glass slide moved at a constant speed. The withdraw velocity was precisely controlled by attaching the inclined plate to the syringe pump motor assembly (NE 500 New Era pump system Inc., Wantaugh, NY). After the deposition was completed, the films were allowed to air-dry in a laminar flow cabinet. For multilayer films, silicon wafers were first treated with the PEI solution by immersion in a solution of 500 ppm for 20 min, then rinsed with Milli-Q water and dried with nitrogen nozzle. CNCs were then deposited with the setup shown in Fig. 1a and the procedure was repeated as many times as required to obtain targeted number of layers. In the case of nanindentation studies 10 deposition cycles were carried out.

2.5 Atomic Force Microscope (AFM)

An AFM XE 100 from Park Systems (Santa Clara, CA) was used in a non-contact mode to obtain topographic images of the supports before and after CNC deposition. A pyramidal silicon tip with a radius less than 10 nm and with an aluminium coating on the backside (Park Systems, Santa Clara, CA) was used with an applied constant force of 42 N m⁻¹ and 330 KHz frequency. The XE-100 scanner configuration allowed simultaneous recording of X–Y and Z signals. The X–Y scanner moved the sample in the horizontal direction and the Z scanner traced the topography of the sample moving the cantilever in the vertical direction. The coordinate information allowed interpretation of the orientation direction of the CNCs in the images. At least three different films, at three different positions, were imaged for each deposition condition used. The images were analyzed using the XEI software, and only a flatten process of one regression order was used to correct the slope of the tip/sample interaction. Scans of different sizes were obtained but only the 2.5 × 2.5 μm² sizes are reported here, unless stated otherwise.

2.6 Ellipsometry

A variable angle spectroscopic ellipsometer (VASE, J. A. Woollam Co., Inc.) with a wide spectral range capability of 190–1100 nm was used to measure the film thickness. Data were collected at different angles of incidence (55, 60, 65, 70 and 75°), between 300 and 800 nm. The ellipsometric amplitude ratio, \( \Psi \), and the phase difference, \( \Delta \), data were fit using a Cauchy model, assuming a refractive index of 1.56 for cellulose. In order to increase the fitting accuracy the Bruggeman model of the effective medium approximation (EMA) layer was employed. This approximation allowed proper film thickness analysis by incorporating air as an integral part of the ultrathin film and to consider the effect of roughness.

2.7 Degree of CNC alignment

As explained before, the convective-shear assembly setup used to align the CNCs within thin films deposited from aqueous
suspensions is shown in Fig. 1. After obtaining AFM images of the resultant films a Matlab code was used to determine the degree of CNC alignment. This code used AFM topography images by performing a grain partition and filtering the sizes of the grains. The angles of leading edge or the long axis of the CNCs were determined in a polar plot between 0 and 90° with respect to the withdrawal direction and the degree of CNC alignment was defined as the number % of CNCs in the angle range between 0 and 20° in the withdrawal direction. Considering symmetry conditions for the angles between 0 and 90, and 90 and 180° the respective number % of CNCs counted at the given angle were added to the number collected for the 0 to 90° angle range. The histograms (number % of CNCs) for a given angle range were obtained. Typically, more than 300 CNCs were counted in each image analysis and at least 3 different locations, from 3 different films, were analyzed for each condition.

2.8 Nanoindentation

A TI 900 TribolIndenter from Hysitron Inc. (Minneapolis, MN) equipped with a Berkovich three-sided pyramidal diamond tip of 50 nm radius of curvature was used to measure the mechanical properties of multilayers of CNC assemblies. The apparatus used a load of 3 μN and a displacement resolution of 4 nm. The lateral positioning accuracy is reported to be ±20 nm, according to the manufacturer.

For the indentations the peak load force was controlled between 5 and 35 μN with a total 15 seconds testing time per load (5 s loading, 5 s hold and 5 s unloading). The unloading load–depth curve was used to analyze the nanoindentants and fitting of the data using the Oliver–Pharr approach to obtain the hardness and Young’s modulus. The friction coefficient was measured at four different load forces (10, 15, 20 and 25 μN) with a 1 μm scratch length. In the wear tests four different load forces (10, 15, 20 and 25 μN) were applied for four passes in a 5 × 5 μm scan area. Indentation in wear tests was followed by imaging a larger size area (10 × 10 μm) that contained the scratched region. The peak load forces were selected so that the indentation depth remained less than 20% of the film thickness, to prevent the influence of the substrate in the measurement of the mechanical properties. Three different points for at least three different samples were tested to determine the average values reported.

3 Results and discussion

CNC films obtained by cast evaporation and studied under an optical microscopy with cross-polarized light show nanocrystal patterns due to their assembly in aqueous suspensions at given concentrations. The so-called fingerprint patterns of the cholesteric texture can be distinguished by their characteristic alternating light and dark bands which represent the rotation of the nematic director. Several parameters affect the chiral nematic phase of CNC, such as ionic strength, temperature, concentration and external forces. It has been observed that the behavior of CNCs in aqueous suspensions under shear depends on the ratio of two Leslie viscosities, either flow-aligning, where the director adopts a stable position during flow, or tumbling, where the director has no stable position. Overall, it is expected that by controlling shear forces, or electric and magnetic fields, it is possible to change the rotation of the nematic director to achieve ordered structures in 2-D assemblies. As such, the effects of shear and capillary forces on CNC alignment are discussed further.

3.1 Alignment of CNCs by shear forces

The convective-shear assembly setup was used to organize CNCs with different degrees of alignment with respect to the withdrawal direction (Fig. 1a) and the degree of alignment of CNCs is discussed in terms of the number % of CNCs aligned in the 0–20° of the withdrawal direction. Two extreme, illustrative results are provided in Fig. 1b–d. The upper panels of Fig. 1b and c show an ultrathin film of cellulose nanocrystals deposited on a gold substrate that were preferentially oriented parallel to the withdrawal direction. The respective histograms indicated that ca. 70 number % of CNCs were parallel to the withdrawal direction (see polar histogram in Fig. 1d, top). The bottom panels of Fig. 1b and c show that the cellulose nanocrystals coated onto a mica surface were oriented mainly normal to the withdrawal direction (only 5% of CNCs parallel to the withdrawal direction, see polar histogram in Fig. 1d, bottom).

The effects of the substrate type and the concentration of cellulose nanocrystals in aqueous suspension as well as the withdrawal speed in the convective-shear assembly setup were investigated. Also considered were the influence of the relative humidity of the surrounding air, and the resulting changes in the drying rate. The primary film parameters that were evaluated included the thickness of the CNC layers, surface roughness and degree of CNC alignment.

3.1.1 Effect of solid support. To evaluate the effect of the solid support on the degree of CNC alignment, five different substrates were tested, namely, mica sheets with a high negative charge density; less negatively charged silica wafers; positively charged silicon wafers with pre-adsorbed polyethyleneimine (PEI), and high and low surface energy gold-based slides. The low surface energy substrates were prepared by reacting alkylthiol with freshly cleaned gold. It is worth noting that the CNCs used in this study were produced by sulfuric acid hydrolysis; consequently they were negatively charged due to the presence of residual sulfate ester groups.

Different degrees of alignment were obtained in the different regions of the film, as determined by AFM and image processing. At the edge of the film, i.e., at the beginning of the deposition process, the CNCs were more randomly distributed compared to areas where the film was well developed (after reaching stable conditions for nanoparticle deposition). This behavior was more pronounced on the mica substrate. Therefore, the areas of the films that were used in the determination of the degree of alignment (see for example Table 1) corresponded to average values measured in the middle section, at three-fourths the total film length and close to the end edge of the film.

The CNC films shown in Fig. 2 on mica (a) and silica (c), i.e., substrates with same charge type than that of the CNCs were less aligned than those deposited on gold (b) or on silica with pre-adsorbed PEI (d). One would expect that the CNCs alignment would have been more pronounced on the negatively charged substrates, compared to the positively charged one (PEI). In fact, it has been reported that ordered arrays of colloidal spheres on
solid supports are achieved when a higher mobility of the particles is favored, for example, when electrostatic repulsion forces for systems of equal electrostatic charges are present in the film before the solvent evaporates.

23 In the case of gold surfaces (Fig. 2b) the shear forces appeared to be determinant in CNC alignment. On the other hand, layers of CNCs were difficult to form on the hydrophobic substrates, using same operation conditions, likely due to the reduced wetting by the aqueous phase. The fact that different substrates produced different degrees of CNC alignment highlights the influence of their charge and surface energy.

Overall, the induced orientation of CNCs is determined by a complex balance of forces, mainly, hydrodynamic (shear and drag), Brownian, surface tension (capillary forces) and electrostatic interactions (between the negatively charged CNCs and between the CNCs and the substrate). Thus, it appears that the poor alignment of CNC observed in the case of the negatively charged solid support can be explained by the dominant and counterbalancing effects of shear and capillary forces acting normal and parallel to the three phase contact line, respectively.

Two dimensionless numbers are useful to quantify the relative effect of capillary and shear forces. These are the capillary number, \( Ca = \frac{\mu W_0}{\sigma} \), where \( \sigma \) is the surface tension, \( \mu \) the viscosity and \( W_0 \) withdrawal velocity (shear) and a fluid property number, \( m \) which is defined by \( m = \left( \frac{g \rho^3 \mu^4}{\sigma^3} \right)^{1/2} \) which also includes the density and gravitational force, \( g \). No attempt was made here to fully characterize the system by using \( Ca \) and \( m \) since the density \( \rho \) and viscosity of the films are expected to vary during deposition. Since CNC suspensions are shear-thinning \( Ca \) depends on the withdrawal rates in a complex way. However, average capillary numbers were determined to be relatively small, between ca. 0.3 \( \times \) 10^{-4} and 1 \( \times \) 10^{-4} for the highest and lowest withdrawal rates, respectively. Finally, related effects of concentration gradients are relevant because the evaporation at the back end of the film leads to a higher CNC concentration. This could translate into a better alignment in the withdrawal direction, from the middle towards the end section of the film.

### 3.1.2 Multilayer films

Multilayer films of different thicknesses can be obtained by adjusting the CNC concentration and withdrawal rate. As explained in the “Materials” section, TEM

<table>
<thead>
<tr>
<th>Substrate</th>
<th>% CNC alignment between 0 and 20°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>31 ± 20</td>
</tr>
<tr>
<td>Mica</td>
<td>27 ± 19</td>
</tr>
<tr>
<td>Gold</td>
<td>55 ± 16</td>
</tr>
<tr>
<td>Silica with pre-adsorbed PEI</td>
<td>44 ± 12</td>
</tr>
</tbody>
</table>

**Table 1** Percentage of CNCs aligned in the 0–20° angle range with the withdrawal direction as reference after utilizing solid supports in a convective-shear assembly setup (Fig. 1a). The % CNC number distribution was obtained from image analysis and respective polar histograms (see Fig. 1d).

*Fig. 2* AFM 2.5 \( \times \) 2.5 \( \mu \)m height images for four different substrates: mica (a), gold (b), silica (c), and silica with pre-adsorbed PEI (d). The films were deposited from 2.5% CNC aqueous suspension at a withdrawal speed of 8.4 cm h^{-1}.
imaging indicated a width of 6.5 ± 0.7 nm for individual CNC particles which would also correspond to the thickness of a CNC monolayer film. Typically, film thicknesses after convective-shear deposition under the conditions used in films reported in Fig. 3b and d, using cationic substrates, were equivalent to ca. three CNC layers. CNC films obtained by the Langmuir–Schaeffer technique, as reported in our earlier publication, were subjected to AFM imaging and found not to exhibit any particular alignment (Fig. 3a and c). Relative to the vertical direction (vertical axis taken as zero degrees) the CNC number distribution of the respective leading angles was determined to be 12% (0–20°), 14% (20–40°), 23% (40–60°) and 51% (60–90°). On the other hand, films obtained by using the convective-shear assembly setup showed a distinctive alignment of CNCs, with 70% of the particles aligned in the 0–20° angle range. The better alignment obtained in the latter case can be explained by attractive electrostatic forces that helped to pin the first CNC layer onto the solid support while repulsion forces between the contiguous CNC facilitated better mobility and therefore better alignment under the dominant shear. Also, it is possible that pinning down the first layer could create higher shear forces that improved organization or alignment of CNCs above it. These hypotheses are supported by the observed effect of initial CNC concentration (see Fig. 4): monolayer films made at low concentrations exhibited poor alignment while multilayer films displayed better alignment. Other considerations are discussed further in this discussion.

3.1.3 Effect of suspension concentration on CNC assembly. Generally, the thickness of films obtained by convective assembly of spherical particles can be controlled by varying the solids concentration in the casting suspension and the withdrawal.
In fact, CNC film thicknesses were observed to increase with CNC concentration, for a given withdrawal rate (see Fig. 4 and Table 2). Roughly, a CNC monolayer was formed at concentrations below 1% while multilayer films were produced at concentrations above 1% (see ellipsometric thicknesses in Table 2).

Geometrical hindrance can account for the low orientation of CNCs at the concentrations below 1% reported in Table 2, in agreement with observations made in CNC suspensions. Geometrical hindrance can account for the low orientation of CNCs at the concentrations below 1% reported in Table 2, in agreement with observations made in CNC suspensions. The shear rate during deposition from 0.1% CNC suspension was calculated to be ca. 2.5 s⁻¹; similar low shear fields favored more random orientation of CNCs in diluted aqueous media. For concentrations above 1% (w/w) the alignment of CNCs in the withdrawal direction was clearly increased with concentration, as can be observed in Fig. 4 and Table 2.

### Table 2
Effect of aqueous suspension CNC concentration on the ellipsometric thickness and CNC alignment of ultrathin films. CNC films were deposited on silica with pre-adsorbed PEI. As a reference it is noted that the TEM thickness of a single CNC was measured to be 6.5 ± 1 nm.

<table>
<thead>
<tr>
<th>Concentration/% w/w</th>
<th>Ellipsometric thickness/nm</th>
<th>% CNC aligned between 0 and 20°</th>
</tr>
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<tbody>
<tr>
<td>0.1</td>
<td>7.4 ± 0.5</td>
<td>33 ± 7</td>
</tr>
<tr>
<td>0.5</td>
<td>9.4 ± 0.8</td>
<td>20 ± 7</td>
</tr>
<tr>
<td>1.0</td>
<td>20.8 ± 0.4</td>
<td>33 ± 8</td>
</tr>
<tr>
<td>2.5</td>
<td>37.8 ± 0.8</td>
<td>44 ± 12</td>
</tr>
<tr>
<td>4.5</td>
<td>63.5 ± 7.4</td>
<td>68 ± 9</td>
</tr>
</tbody>
</table>

### Table 3
Thickness and degree of alignment of CNCs in ultrathin films deposited at different withdrawal rates on silica substrates with pre-adsorbed PEI (CNC concentration in aqueous suspension was 2.5%).

<table>
<thead>
<tr>
<th>Withdrawal rate/cm h⁻¹</th>
<th>Ellipsometric thickness/nm</th>
<th>CNC aligned between 0 and ±20° (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2</td>
<td>85.4 ± 2</td>
<td>41 ± 19</td>
</tr>
<tr>
<td>6.3</td>
<td>40.6 ± 1.7</td>
<td>57 ± 7</td>
</tr>
<tr>
<td>8.4</td>
<td>37.8 ± 1</td>
<td>44 ± 12</td>
</tr>
<tr>
<td>16.8</td>
<td>19.0 ± 2</td>
<td>44 ± 20</td>
</tr>
<tr>
<td>21.0</td>
<td>19.2 ± 2</td>
<td>37 ± 16</td>
</tr>
<tr>
<td>25.2</td>
<td>16.7 ± 6.7</td>
<td>38 ± 10</td>
</tr>
</tbody>
</table>

Fig. 4  AFM 2.5 μm × 2.5 μm height images of ultrathin films of CNC obtained from aqueous suspensions of different concentrations deposited on silica substrates with pre-adsorbed PEI by using a convective-shear assembly setup operated at a withdrawal speed of 8.4 cm h⁻¹. CNC concentrations used were 0.1 (a), 0.5 (b), 1 (c), 2.5 (d) and 4.5% (e).

3.1.4 Effect of withdrawal rate and relative humidity on CNC assembly. Under the conditions of CNC assembly used, the alignment occurred mainly in the direction normal to the three phase contact line, as shown in Fig. 1, i.e., in the direction parallel to the withdrawal axis. This fact supports the hypothesis that shear forces were leading factors for CNC alignment, as demonstrated in the case of rod-like Tobacco Mosaic virus studied by Velev et al. In order to investigate this issue further the withdrawal speed of the upper plate was varied. It was observed that at low withdrawal rates the CNC alignment was first improved with the withdrawal rate (see Table 3). However, maximum order was achieved at intermediate shear rates while at the highest withdrawal rates tested (21–25.2 cm h⁻¹) the CNCs became less ordered.

It is proposed that as the liquid front was pulled in the withdrawal direction by surface tension forces and as the withdrawal
rate increased the thickness of the resulting film decreased, thereby shifting the architecture of the film from a multiple layer towards a monolayer. At the highest shear rates only one or two layers were deposited. As these layers were bound irreversibly to the cationic substrate, they were randomly oriented (low degree of alignment) while in thicker films the overlying layers were generally better oriented. These observations are in agreement with the previous discussion for the effect of CNC concentration on particle alignment.

Film depositions were performed at different air relative humidity while keeping constant the withdrawal rate at 8.4 cm h⁻¹ and CNC concentration at 2.5%. It was observed that the thickness of the assembled CNC layers on silica with a pre-adsorbed layer of PEI increased with the reduction of the air relative humidity. This effect can be explained by an increased evaporation at a lower relative humidity which led to a faster assembly and the formation of thicker films. However, no significant difference in CNC alignment was observed (see Fig. 5).

Overall, it can be concluded that aligned CNCs can be obtained under a set of conditions of concentration, withdrawal speed and substrate. The degrees of alignment in the films presented here are comparable to those obtained after application of high electric fields [13]. However, in this latter case a special setup and large electric field strengths and frequencies, on the order of 2500–5000 V cm⁻¹ and 5 × 10⁶ Hz, respectively, were needed. Similar observations can be made for experiments that used magnetic fields of 7 Tesla over a period of hours or days in a solid state NMR spectrometer.

Finally, for CNC films to be considered in coating and other applications their mechanical properties have to be evaluated. Thus, the next section discusses the surface mechanical properties of the obtained ultrathin films of CNCs.

3.2 Mechanical properties of ordered CNC films

Multiple depositions by using the convective-shear assembly setup were performed in order to obtain relatively thicker, ca. 200 nm, CNC films. PEI interlayers were used to improve CNC layer cohesion. The elastic transversal modulus, hardness, friction coefficient and wear resistance were measured for the silica surface coated with such CNC films. Even though humidity was not controlled during the measurements, water absorption by cellulose nanocrystals was expected to be limited. Therefore, small variations in humidity may only produce minor changes in the reported mechanical properties. Fig. 6a shows the penetration depth of the tip of a nanoindenter as a function of the loads applied. In order to determine related mechanical properties it was ensured that the penetration of a nanoindenter as a function of the loads applied. In order to determine related mechanical properties it was ensured that the penetration of a nanoindenter was never above 20% of the film thickness. This allowed minimizing contributions from the substrate on the measured elastic modulus of the coating film. It was observed that a tip
penetration equivalent to 20% in a typical CNC film was reached at a normal force of about 25 mN.

3.2.1 Transverse elastic modulus of CNC films. It was found that the elastic transversal modulus of CNC films (8.3 ± 0.9 GPa, Fig. 6b) was of the same order of magnitude than values predicted by molecular modeling and also recently reported for the single CNC measured using AFM, i.e., 11–57 GPa, and 18–50 GPa (Tunicate CNCs), respectively. The reason for the comparatively lower modulus in the present study might be related to the fact that multilayer structures intercalated with PEI layers were the ones probed as opposed to the pure CNC in van der Waals contact which is assumed in molecular modeling or in AFM measurement with a single CNC. The hardness of CNC films was found to be in the range of 0.38 ± 0.03 GPa (see Fig. 6c). To our knowledge no values for the hardness of CNC films are available in the literature. Published values for the hardness of wood (0.358 and 0.387 GPa) and microcrystalline cellulose (0.01–1 GPa) have been reported.

The mechanical properties for films of regenerated cellulose obtained by spin coating having an elastic transversal modulus and a hardness of 13.1 ± 2.3 GPa and 0.50 ± 0.1 GPa, respectively, did not differ substantially from those measured in oriented CNC films. The comparatively high values for the elastic transverse modulus for films of regenerated cellulose can be explained by the possibility that the axes of cellulose chains lie both parallel and normal to the silica surface while in the case of films with CNCs chain axes lie parallel to surface. A more pronounced difference in the mechanical properties would be found if these films were tested in the axial direction since the axial elastic modulus of CNCs is distinctively high, 110–200 GPa, compared to values expected for regenerated cellulose.

While in the case of cellulose films the transverse elastic modulus and the hardness reached somewhat constant values with the penetration of the probe, this was not the case for the reference bare silica surface: the elastic modulus was observed to increase with penetration depth in the range tested. For silica, a minimum penetration depth of 20 nm was calculated to be needed in order for the respective mechanical properties to become independent of the depth of probing, a situation that was not ensured with the normal loads that were applied. In fact, the loads applied produced only a tip penetration in silica of only 5 nm. As a reference, 172 and 12.75 GPa for the elastic modulus and a hardness, respectively, have been reported for silica.

3.2.2 Friction and wear resistance of CNC films. Coatings are usually applied to improve the material performance, including tribological, electrical, optical, electronic, chemical or magnetic functions. Composite tribological coatings have been designed primarily to have a specific friction behavior and a high wear resistance. Controlling the friction of a coating may be beneficial in a number of applications; for example, in the automobile and aeronautic industries the reduction of friction often means a reduction in energy consumption. On the other hand, wear determines the lifetime of materials and it is critical in many processes. Materials commonly used for related coatings include nitrides, carbides, oxides and their combinations, as well as molybdenum disulfide, diamond-like carbon and diamond. Recently mineral nanocrystalline multilayer coatings with superior mechanical and tribological properties were developed.
In the present investigation the friction coefficient of CNC films was measured at four different load forces (10, 15, 20 and 25 \( \mu \text{N} \)) using a 1 \( \mu \text{m} \) scratch length. The friction coefficients for silica (0.22 \( \pm \) 0.18), regenerated cellulose (0.73 \( \pm \) 0.26) and CNCs (0.51 \( \pm \) 0.23) were obtained (see Fig. 7). Low friction coatings often display a friction coefficient from 0.05 to 0.25 in dry sliding.\(^{48}\) Other applications demand higher friction coefficients such as in brakes, bolted joints and safety connectors.\(^{48}\) It can be concluded that the friction coefficient for CNC films was relatively high for an application requiring low values.

The wear resistance of the cellulose films was measured by scratching repeatedly a 5 \( \times \) 5 \( \mu \text{m} \) area under constant load force, followed by scanning a larger area, enclosing the scratched region, under a low load. The wear height or volume, a measure of the wear resistance (larger height is produced with materials with lower wear resistance), was determined by analyzing the height profile of the scratched area. For CNC films, two types of nanocrystal coating film structures were investigated: one corresponded to CNC multilayers deposited in the same withdrawal direction (Fig. 8c and Table 4, parallel directions) and another consisting of CNC films deposited with alternate support rotation, by 90° between layers. In this latter case contiguous nanocrystal layers were aligned in normal directions (Fig. 8d and Table 4, cross directions).

In Fig. 8, images of the coatings after the wear test are presented. As expected, the bare silica supports had the highest wear resistance (lowest wear volume as reported in Table 4). The regenerated cellulose film was disrupted to a large extent, as observed in the scratched area, presenting the highest wear volume (see Table 4 and Fig. 8b). In the case of CNC multilayers it appeared that CNCs were dragged during scratching, as can be observed in Fig. 8c and d in which lines with lighter color intensity (higher Z height) on the scratch edges were observed. The force applied by the tip seemed to disrupt the electrostatic interactions that held together the CNC layers with the PEI adhesive interlayers. As to the two arrangements of CNC films, the wear resistance appeared to be the same within the experimental error. Finally, the applied load (10–25 \( \mu \text{N} \)) did not seem to have a significant effect on the wear resistance of the films (Table 4).

### Table 4 Wear resistance as measured by the wear volume at different applied forces

<table>
<thead>
<tr>
<th>Force/( \mu \text{N} )</th>
<th>Wear volume/( \mu \text{m}^3 )</th>
<th>Regenerated cellulose</th>
<th>CNC, parallel direction</th>
<th>CNC, cross directions</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.02 ( \pm ) 0.003</td>
<td>0.57 ( \pm ) 0.2</td>
<td>0.56 ( \pm ) 0.2</td>
<td>0.4 ( \pm ) 0.2</td>
</tr>
<tr>
<td>15</td>
<td>0.02 ( \pm ) 0.01</td>
<td>0.68 ( \pm ) 0.4</td>
<td>0.60 ( \pm ) 0.3</td>
<td>0.56 ( \pm ) 0.1</td>
</tr>
<tr>
<td>20</td>
<td>0.02 ( \pm ) 0.008</td>
<td>0.53 ( \pm ) 0.2</td>
<td>0.53 ( \pm ) 0.2</td>
<td>0.52 ( \pm ) 0.1</td>
</tr>
<tr>
<td>25</td>
<td>0.03 ( \pm ) 0.007</td>
<td>0.64 ( \pm ) 0.4</td>
<td>0.53 ( \pm ) 0.2</td>
<td>0.53 ( \pm ) 0.2</td>
</tr>
</tbody>
</table>

4 Conclusions

Ultrathin films of aligned CNCs were successfully obtained in a convective-shear assembly setup that was employed under conditions that favored alignment to a different extent depending on the suspension concentration, withdrawal speed, and substrate type. The degree of orientation of CNCs in these films was comparable with those obtained after application of high electric fields, 40–60 number % of CNCs in angles between 0 and 20° with respect to the withdrawal direction. CNC alignment was explained to depend on a balance of forces that included hydrodynamic (shear and drag), surface tension (capillary forces), and electrostatic interactions. Best alignment was obtained in cases where the shear force was dominant.

Nanoindentation was used to determine key mechanical properties of coating films of aligned CNCs. An elastic transversal modulus and hardness of 8.3 \( \pm \) 1 and 0.38 \( \pm \) 0.03 GPa, respectively, were obtained. The friction coefficient of CNC films was found to be higher than desired for applications with high tribological demands. Finally, measurement of wear resistance was found to be challenging due to the mobility of the CNCs and CNC layers during nanoindentation tests since PEI interlayer adhesion was lower than typical forces applied with the nanoindenter tip.
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References