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Electroacoustic characterization of conventional and electrosterically stabilized nanocrystalline celluloses

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ABSTRACT

Nanoparticles are widely used as drug carriers, texturizing agents, fat replacers, and reinforcing inclusions. Because of a growing interest in non-renewable materials, much research has focused on nanocellulose derivatives, which are biodegradable, biocompatible, and easily synthesized. Among nanocellulose derivatives, nanocrystalline cellulose (NCC) has been known for half a century, but its utility is limited because its colloidal stability is challenged by added salt. On the other hand, electrosterically stabilized nanocrystalline cellulose (ENCC) has recently been observed to have superior colloidal stability. Here, we use electrokinetic-sonic-amplitude (ESA) and acoustic attenuation spectroscopy to assess NCC and ENCC ζ-potentials and sizes over wide ranges of pH and ionic strength. The results attest to a soft, porous layer of dicarboxylic cellulose (DCC) polymers that expands and collapses with ionic strength, electrosterically stabilizing ENCC dispersions at ionic strengths up to at least 200 mmol L^{-1}.

1. Introduction

Cellulose is a natural polymer comprising repeated anhydroglucose units linked by β-1,4-glycosidic bonds (C–O–C) [1]. Because of its high abundance and biodegradability, it is a key source of industrial scale recyclable materials. Cellulose exists in trees and plants, is produced by photosynthesis, and is synthesized by some bacteria and organisms (tunicates) [1]. Green and renewable replacements for fossil-derived materials have turned attention to cellulose products [2]. These ‘green’ nanoparticles are from renewable sources, have large surface to volume ratios, and have other unique properties.

Two distinct cellulosic nanoparticulates are nanocrystalline cellulose (NCC) and nanofibrillar cellulose (NFC). The former was produced for the first time by a harsh hydrolysis of plant materials, and an ultrasonication post-treatment [3]; and the latter was prepared by subjecting a wood-pulp slurry to a high pressure homogenizer [4]. NCC and NFC particles have widths in the range 3–10 nm [5,6]; however, because of hydrolysis and dissolution of amorphous regions, lengths of NCC are in the range 100–200 nm [5], whereas NFC can be up to several microns long [7].

High crystallinity imparts NCC with a high tensile strength (7.5–7.7 GPa) [8], high elastic modulus (up to 220 GPa) [9,10], and very low thermal expansion coefficient (0.1 ppm K^{-1}) [11]. In addition to these mechanical properties, optical properties [12–15], such as birefringence [12], have paved the way for NCC applications in decorative materials, security papers, foods, emulsions/dispersions (as a texturizing agent and fat replacer), hygiene/absorbent materials, packaging materials, and nanocomposites (as reinforcing inclusions) [16,17]. Recent studies suggest NCC applications in the pharmaceutical industry as a tablet binder [18] or a bioimaging agent [19], expedited by a high surface charge density [20,21].

In the conventional chemical hydrolysis approach, the cellulose microfibrils are broken into individual glucose units using a strong acid, and the dissolution of amorphous domains produces short nanocelluloses. Mechanical fibrillation of wood fibers produces longer microfibrils, but consumes considerable energy and leaves most NFC bundled. Some groups have proposed a combination of enzymatic and mechanical treatments to reduce the energy demand [22,23]. In contrast to acid-pretreatment, enzyme-pretreatment decreases the degree of polymerization less, producing high-aspect-ratio nanofibers [24].

In an alternative approach, the C_6 hydroxyl group was selectively converted to carboxyl via NaClO and $NaClO_2$ oxidation in the presence of 2, 2, 6, 6-tetramethylpiperidinyl-1-oxyl (TEMPO) as a catalyst [7]. Following oxidation, a mild mechanical post-treatment

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was introduced to cleave NFC bundles [7]. Yang [25] used pre-iodate oxidation [26] and chlorite oxidations [27] to selectively convert alcohol groups on C_2 and C_3 to carboxyl groups. The resulting ionic charge breaks fibers at amorphous domains into NCC with protruding dicarboxylated cellulose (DCC) chains. This so-called electrosterically stabilized NCC (ENCC) [25] has a higher charge density than conventional NCC, improving colloidal stability.

To understand the NCC and ENCC colloidal properties, we explored electrokinetic-sonic-amplitude and acoustic-attenuation spectroscopy to ascertain the apparent ζ-potential and particle size. Electroacoustic phenomena have been used to measure the dynamic mobility and infer the corresponding ζ-potential [28] to characterize coated [29] and/or concentrated [30,31] nanoparticles and emulsions [32], to monitor polymer adsorption [33], and to assess pigment stability in the printing industry [34].

Electrokinetic-sonic-amplitude and acoustic-attenuation spectroscopy are typically used for concentrated and turbid colloids at MHz frequencies, while other techniques, such as electrophoretic light scattering (ELS), can sometimes fail because of weak emerging signals [35]. An ability to acquire the particle mobility under conditions when particles flocculate is a compelling advantage of electroacoustic spectroscopy. Electroacoustic spectroscopy as a characterization method has been developed for decades, as reviewed by Hunter [36].

As shown by Yang [37], ENCC suspensions are stable in a high ionic strength medium (up to ≈2 M), whereas NCC suspensions are prone to aggregation at much lower ionic strength (<30 mmol L^{-1}) [38]. In this study, we explore the capabilities of the Acoustosizer II instrument (Colloidal Dynamics, LLC, FL, U.S.A.) to assess the charge and size of NCC and ENCC nanoparticulates.

2. Materials and methods

2.1. Materials

For pH titration, NaOH and HCl were purchased from Fisher Scientific (ON, Canada), and for salt titration, KCl was purchased from Sigma Aldrich (ON, Canada). Silica nanoparticles ($d \approx 450$ nm, 5% w/v) were purchased from Colloidal Dynamics, LLC, FL, U.S.A., and used as received. LUDOX AS-30 colloidal silica nanoparticles ($d \approx 30$ nm, 30% w/v) were supplied by Sigma Aldrich (ON, Canada). Polar KiSW (potassium tungstosilicate salt) solution was provided by Colloidal Dynamics (LLC, FL, U.S.A.) and used to calibrate the ESA instrument as received. Aqueous NCC (4% w/v) suspension was provided by Louis Godbout, produced following Revol [14], and fractionated ENCC (1% w/v) suspension was provided by Han Yang, produced according to Yang [25]. These NCC and ENCC suspensions were received dialyzed and at neutral pH. The sample conductivity and pH were verified to be consistent before all ESA measurements.

2.2. Methods

Conductometric titration was performed to obtain NCC and ENCC surface charge densities using a Metrohm 836 Titrando titrator (ON, Canada). A sample with 0.02 g of solids and 2 mL of 20 mmol L^{-1} NaCl were added to 140 mL of Milli-Q water [25]. Starting from $pH = 2.7$, 10 mmol L^{-1} NaOH solution was added at 0.1 mL min^{-1} to the suspension up to $pH = 11$. This furnished the start and end points of surface active group neutralization equivalent base volume by which the charge density was calculated.

Electroacoustic spectra were obtained using an Acoustosizer II (Colloidal Dynamics, LLC, FL, U.S.A.) integrated electrokinetic-sonic-amplitude (ESA) and acoustic attenuation instrument. The cell and sample temperatures were allowed to equilibrate (23 °C) before each run. Colloidal dispersions were continuously pumped through the cell using a peristaltic pump to promote suspension homogeneity at constant flow rate. The instrument was calibrated each day to ascertain the data acquisition and analysis accuracy. At all pH values and added KCl concentrations, background tests were conducted using electrolytes having the same ionic strength as the suspensions containing NCC and ENCC. These furnish the background ion signal that is subtracted by the Acoustosizer II software from the NCC or ENCC dispersion signals at the same pH/salt concentration. A detailed description of the instrument is available in the Acoustosizer II Operators Guide [39]. Briefly, attenuation coefficients α at various frequencies f are measured by the instrument, from which an equivalent spherical particle diameter $d = 2a$ is estimated by fitting theoretical models. based on the model proposed by Allegra [40] and Bhosale [41]:

$$\alpha = \frac{1}{9}\phi\omega^2 a^2 \frac{\rho}{c\mu}\left(\frac{\rho_p}{\rho} - 1\right)^2 \tag{1}$$

Here, ϕ is the particle volume fraction, ρ and ρ_p are the solvent and particle densities, respectively, μ denotes solvent viscosity, and c is the speed of sound in the solvent. An example of attenuation-based particle size characterization is presented in Fig. 1, from which it can be seen that Eq. 1 is valid for particles $\lesssim 100$ nm.

The ESA is proportional to the particle-averaged dynamic electrophoretic mobility M [42], which in general depends on the particle size, surface charge, and ionic strength of the electrolyte:

$$\mathrm{ESA} = A(\omega)\phi\frac{\Delta\rho}{\rho}M \tag{2}$$

Here, A is a complex-valued instrumental factor that is ascertained by the instrument calibration, ϕ is the particle volume fraction, and $\Delta\rho = \rho_p - \rho$ the particle density minus the electrolyte density. According to the manufacturer, the reported ζ-potential is obtained from the dynamic mobility according to an extended version of O'Brien theory [43]:

$$M = \frac{\epsilon\zeta}{\eta(2+\phi)}\,\frac{(2-2\phi) - 3\phi(F-1) - [2\lambda^2/(3+3\lambda+\lambda^2)]}{1 + (\Delta\rho/\rho)\{\phi F + [2\lambda^2/3(3+3\lambda+\lambda^2)]\}} \tag{3}$$

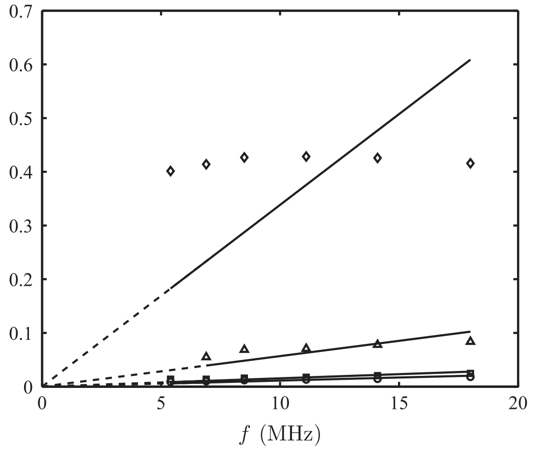

Fig. 1. Dimensionless attenuation coefficient $\chi = \alpha c/(\phi f)$, measured using the Acoustosizer II instrument, versus frequency f for NCC (circles), 30 nm silica (squares), ENCC (triangles), and 450 nm silica (diamonds) nanoparticles at pH and salt concentrations reported in Fig. 6 (NCC and ENCC) and supporting information (silica nanoparticles). Solid lines show the best linear fit corresponding to particle diameter 64, 31, 144, and 146 nm for NCC, 30 nm silica, ENCC, and 450 nm silica, respectively, with $R^2 \approx 0.98$, 0.99, 0.88, and 0.16. The reported particle size by the instrument agrees well with the attenuation theory for small nanoparticles (*i.e.*, NCC: 60 nm and 30 nm silica: 30 nm), while it uses a patented method to report large particle sizes accurately (*i.e.*, ENCC: 220 nm and 450 nm silica: 480 nm).