



Optical and mechanical properties of nanofibrillated cellulose: Toward a robust platform for next-generation green technologies



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ABSTRACT

Nanofibrillated cellulose, a polymer that can be obtained from one of the most abundant biopolymers in nature, is being increasingly explored due to its outstanding properties for packaging and device applications. Still, open challenges in engineering its intrinsic properties remain to address. To elucidate the optical and mechanical stability of nanofibrillated cellulose as a standalone platform, herein we report on three main findings: (i) for the first time an experimental determination of the optical bandgap of nanofibrillated cellulose, important for future modeling purposes, based on the onset of the optical bandgap of the nanofibrillated cellulose film at $E_g \approx 275$ nm (4.5 eV), obtained using absorption and cathodoluminescence measurements. In addition, comparing this result with ab-initio calculations of the electronic structure the exciton binding energy is estimated to be $E_{ex} \approx 800$ meV; (ii) hydrostatic pressure experiments revealed that nanofibrillated cellulose is structurally stable at least up to 1.2 GPa; and (iii) surface elastic properties with repeatability better than 5% were observed under moisture cycles with changes of the Young modulus as large as 65%. The results obtained show the precise determination of significant properties as elastic properties and interactions that are compared with similar works and, moreover, demonstrate that nanofibrillated cellulose properties can be reversibly controlled, supporting the extended potential of nanofibrillated cellulose as a robust platform for green-technology applications.

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1. Introduction

Reducing the consumption of oil-based materials and their replacement with renewable and recyclable products is one of the most important challenges in today's society. Nanocellulose, a derivative of cellulose, occurs in two forms, cellulose nanocrystals or whiskers (CNC) (Azizi Samir, Alloin, & Dufresne, 2005), and nanofibrillated cellulose (NFC) (Isogai, Saito, & Fukuzumi, 2011).

Nanocellulose has gained attention as one of the most promising candidates for sustainable replacement of oil-based plastics (Turbak, Snyder, & Sandberg, 1983; Pääkkö et al., 2007) not only because of its abundance in nature, but also due to its low density, biodegradability, well-established industrial use, and its low cost (Klemm et al., 2011), since some types of nanocelluloses are difficult to obtain in large scale and required some purification methods making some of these processes expensive; all crucial characteristics for technological applications. This biopolymer can be extracted from plants using mechanical pulping and it can be easily dispersed in water, providing a cleaner route to production as it is a renewable and recyclable material (Oksman, Mathew, & Sain, 2009; Abdul Khalil et al., 2014). Its properties can vary drastically with the processing method employed (Eichhorn et al., 2009). Nevertheless, the outstanding properties of nanocellulose have captured the attention of a wide range of fields seeking non-hazardous

Abbreviations: NFC, nanofibrillated cellulose; BLS, Brillouin light scattering; QNM AFM, quantitative nanomechanical atomic force microscopy.

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disposable devices with high stability, mainly as a composite material for packaging (Aulin, Salazar-Alvarez, & Lindström, 2012; Lindström, Karabulut, Kulachenko, Sehaqui, & Wågberg, 2012), electronics (Malho, Laaksonen, Walther, Ikkala, & Linder, 2012), energy storage (Nyholm, Nyström, Mihiranyan, & Strømme, 2011), and energy conversion (Liu, Tao, Bai, & Liu, 2012). However, the overall properties of NFC are known to depend strongly on extraction and purification processes (Lee, Buldum, Mantalaris, & Bismarck, 2013). In particular, one of the major drawbacks shown by NFC is the poor stability with respect to moisture, that affects its mechanical integrity (Lindström et al., 2012). As a consequence, the ability to tailor its elastic constants is essential to promote NFC as a promising candidate to replace oil-based materials (Malho et al., 2012; Dufresne, 2013). The application of NFC as a supporting platform for sensing applications has been increasingly reported in recent publications. For example, Nogi, Iwamoto, Nakagaito, and Yano (2009) demonstrated that NFC films are exceptionally good substrates for optical devices due its remarkable optical transparency. Wang et al. (2013) showed the advantages of combining NFC with carbon nanotubes in hybrid aerogels to enhance mechanical and electrical properties, whereas Yan et al. (2014) followed a similar approach by mixing NFC with graphene leading to highly stretchable piezoresistive nanopaper sheets. In spite of the progress observed, the application of cellulose in devices appears restricted to the role of matrix in composite materials and its applicability is usually limited under non-ideal moisture conditions. Here we investigate and determine NFC fundamental optical, mechanical and vibrational properties to extend the application of NFC films as building blocks for nanodevices.

2. Experimental

2.1. Materials

The nanofibrillated cellulose (NFC) film was prepared from an aqueous native birch pulp by first grinding and then passing through a homogenizer as already reported elsewhere (Isogai et al., 2011), as depicted in Fig. 1a. Preparation of NFC films was carried out using a tip sonicator (Vibra-Cell VCX 750, Sonics & Materials Inc.) to enhance the dispersy of the NFC fibrils. 2.5 kJ of energy was applied to the fibril dispersions using 40% of the full output, because a light sonication is known to open up the fine structure of the NFC aggregates and increase the homogeneity of the dispersion. The fibril dispersions were pipetted in an ultrasound sonicator to remove the bubbles before film formation. Free-standing films were then created by vacuum filtration from aqueous fibril dispersions, wherein NFC concentration was 2.0 g/l. The dispersions were filtrated using a Durapore membrane (GVWP, 0.22 μm , Millipore, USA) and an O-ring to determine the diameter of the film. A gentle press was applied to the films after filtration using a 300 g load for 10 min to prevent wrinkling. At the end the films were dried overnight in an oven at +65 °C.

2.2. Methods

2.2.1. Structural characterization

For a top view image, the NFC sample was mounted with carbon tape on a sample holder and measured with a FEI Quanta 650 FEG environmental scanning electron microscope using an electron energy of 2 keV. In order to measure the cross section of the NFC film, the sample was torn apart in liquid nitrogen. The cross section was measured using a FEI Magellan 400L extreme resolution scanning electron microscope using 1 keV electron energy. X-ray diffraction patterns of the NFC film were obtained by a PANalytical X'Pert PRO diffractometer using a Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) with a

current of 40 mA and an anode voltage of 45 kV. Data were recorded from detector angle $2\theta = 12\text{--}26^\circ$ with a step size of 0.05° . Surface analysis of the sample was performed by X-ray photoelectron spectroscopy (XPS) experiments using a PHI 5500 Multitechnique System (from Physical electronics) with a monochromatic X-ray source (Al K α line of 1486.6 eV energy and 350 W), placed perpendicular to the analyzer axis and calibrated using the 3d5/2 line of Ag with a full width at half maximum (FWHM) of 0.8 eV. The analyzed area was a circle of 0.8 mm diameter, and the selected resolution for the spectra was 187.5 eV of pass energy and 0.8 eV/step for the general spectra and 23.5 eV of pass energy and 0.1 eV/step for the spectra of the different elements. All measurements were made in an ultra-high vacuum chamber pressure between 5×10^{-9} and 2×10^{-8} Torr. Raman scattering spectra were collected using a confocal LabRam HR800 spectrometer (Horiba JobinYvon) with spectral resolution better than 0.5 cm^{-1} . Measurements under pressure were carried out using the diamond anvil cell (DAC) technique. A 4:1 mixture of methanol and ethanol was employed as the pressure-transmitting medium. Pressure was monitored in situ by the shift in the ruby R1 line. Fourier transform infrared spectroscopy (FTIR) was performed with a Bruker spectrometer using an attenuated total reflection setup, with a DTGS detector from 4000 cm^{-1} to 400 cm^{-1} with a spectral resolution of 4 cm^{-1} and 32 scans per spectrum.

2.2.2. Optical characterization

The absorbance and circular dichroism spectra of the nanocellulose film were measured on a UV–vis spectrophotometer Jasco 715 with a polarimeter power supply PS-150J at 20 °C. Cathodoluminescence spectra were recorded using a Gatan MonoCL2 grating spectrometer attached to a Philips XL30 scanning electron microscope (SEM). The spectra were acquired with 5 kV at $1000\times$ magnification with a sample current of 100 nA.

2.2.3. Thermal characterization

Dynamic thermogravimetric measurements were performed by using a Mettler TGA/SDTA851e instrument. Temperature programs for dynamic tests were run from 30 °C to 300 °C at a heating rate of 10 °C/min. These tests were carried out under anhydrous nitrogen atmosphere (50 ml/min) in order to prevent any thermoxidative degradation inside the aluminum capsule (70 μL). Differential scanning calorimetry were carried out in a DSC822e de Mettler Toledo from room temperature to 300 °C at a heating rate of 10 °C/min under anhydrous nitrogen atmosphere (50 ml/min) in an aluminum capsule (40 μL).

2.2.4. Mechanical characterization

Nanoindentation experiments were carried out using a commercial a UMIS indenter from Fischer–Cripps Laboratory, operated in the load-control mode and using a Berkovich-type, pyramid-shaped, diamond indenter. Peak force quantitative nanomechanics mode (QNM) atomic force microscopy (AFM) was performed using a Multimode 8 Nanoscope V electronics. Commercially available AFM probe TAP 525 (nominal spring constant: 40 nN/nm) from Bruker. Spring constant (measured by thermal noise method) 17: 43.8 nN/nm. Sensitivity: 57 nm/V. Set point: 250 nN. Peak force amplitude: 50 nm. Force limit in DMT mode: 2 μN . DMT modulus limit: 20 GPa. The experiments were performed inside an inert gas chamber with controllable moisture. The humidity was controlled by a flow of inert nitrogen stream for anhydrous environment or a stream of nitrogen bubbled through a sparger containing millipore water for a moist atmosphere. The moisture of the chamber was monitored by an Oregon Scientific humidity sensor. Brillouin spectroscopy measurements were performed on a six-pass tandem type interferometer (JRS Scientific Instruments) using 180° (backscattering) and 90° geometries. The 514.5 nm laser line of an argon-ion

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