

Mechanical testing of thin film nanocellulose composites using buckling mechanics

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ABSTRACT: The Young's modulus of multilayer films containing cellulose nanocrystals (CNCs) and polyethyleneimine (PEI) was measured using a buckling-based method and compared to analogous films containing nanofibrillated cellulose (NFC) and PEI [1]. For films 61 nm to 1.7 μm thick, the Young's modulus was constant but strongly dependent on relative humidity. Films were stiffer at lower relative humidities, with modulus values of 16 ± 5 , 12 ± 1 , and 3.5 ± 0.3 GPa at 30%, 42%, and 64% relative humidities, respectively. CNC/PEI films had larger elastic moduli than NFC/PEI films. Both types of nanocellulose multilayer films showed the same modulus dependence on relative humidity over the range studied. Results suggest that ambient water might have an even more pronounced role in nanocomposites than in traditional natural fiber-reinforced composites. This straightforward buckling-based method has quantified mechanical properties and provided a useful comparison between CNC and NFC films. Furthermore, it qualitatively assesses that the components in the composite film are highly compatible and that the hydrophilicity and hygroscopicity of cellulose and PEI combined do not allow for the full mechanical potential of crystalline cellulose nanoelements to be exploited. This work is one approach toward finding dependable methods to characterize nanocellulose, specifically cellulosic thin films, which is increasingly important as we extract nanocellulose from wood, plants, algae, bacteria, and animals and enter a new age of cellulose materials.

Application: Nanocellulose coatings can be designed with tailored properties based on the Young's modulus values (and relative humidity dependence) reported here for cellulose nanocrystal and nanofibrillated cellulose films. Additionally, the mechanical properties of other thin film materials can be measured using the buckling technique presented.

Recently, nanocellulose has gained attention in the media because of new industrial production in Canada, the United States, and the Nordic countries. Ton per day quantities soon will be manufactured from wood pulp to create novel nanomaterials such as composites, coatings, gels, and foams. Crystalline cellulose has impressive mechanical properties, with a specific Young's modulus comparable to stainless steel and Kevlar [1,2], and thus, nanocellulose has potential as the reinforcing (or load-bearing) component in nanocomposites. However, the mechanical properties of thin film nanocellulose materials are virtually unknown due to the limitations of conventional testing methods.

The term "nanocellulose" commonly refers to both cellulose nanocrystals (CNCs) and nanofibrillated cellulose (NFC), which are two very different colloidal forms of cellulose that can be thought of as cellulosic "rice" (or more specifically, "long-grain rice") and "spaghetti", respectively. Briefly, CNC is what remains when highly crystalline regions in natural cellulose (cellulose I) are isolated from their amorphous cellulose surroundings through an acid hydrolysis process [3]. The nanocrystals are needle-shaped with dimensions of a few nanometers wide by hundreds of nanometers long [4], corresponding to an aspect ratio range of 5–100 for cotton and

wood sources (typically ~20) and 40–100 for algae, tunicate, and bacterial sources [1,5]. CNCs possess charged surface groups, thereby forming a stable colloidal suspension in water with liquid-crystalline properties [6].

Conversely, the spaghetti-like NFC consists of micrometer long, highly entangled, nanoscale fibrils containing amorphous and crystalline cellulose I (and minor quantities of hemicelluloses and cellulose II). NFC is made from mechanical shearing and high-pressure homogenization of wood pulp (often with an enzymatic or chemical pre-treatment) [7–9] resulting in nanofibers that are 5–20 nm in diameter. The aspect-ratio of NFC generally ranges from 25 to 500 (typically ~100) [1,5]. Although CNCs and NFC are chemically similar, the dissimilar physical characteristics imply that the final utility will likely be different; a comparison between the "rice" and "spaghetti" will provide insight into the role of particle size, flexibility, and crystallinity on material properties.

Nanocelluloses possess many favorable properties for use in composite materials aside from high stiffness, including low density, high aspect-ratio, low thermal expansion coefficient, the ability to hold water and retain strength, high surface-area-to-volume ratio, and a chemically reactive surface. Numerous researchers have published information on nanocellulose preparation, structure, physical properties, and surface mod-

ification routes [1,2,5,10-12]. Despite the importance of the mechanical properties of nanocellulose for potential products, the literature provides few measurements of the strength or modulus for individual nanoparticles and submicrometer thin cellulose films. Another property that should be addressed before the reinforcing properties of nanocellulose can be realized is the thermal degradation of cellulose; cellulose degrades before melting and for CNCs this occurs between 250°C and 300°C [13]. This property might be a limiting factor for nanocomposite processing and potential applications. Overall, standardizing the metrology of nanocellulose requires further attention [14].

The elastic modulus of crystalline cellulose has been a topic of debate since the mid-1930s. Theoretical predictions have spanned from 56–220 GPa [1,12] but are typically closer to 100–160 GPa in the axial direction [11] and 10–50 GPa in the transverse direction [1]. X-ray diffraction (XRD), inelastic X-ray scattering (IXS), wave propagation, and Raman spectroscopy on cellulose fibers are the most commonly used experimental methods, generally returning values within the predicted range [12]. For micron-thick or larger films, dynamic mechanical analysis and mini-tensile devices have shown that NFC films have moduli ranging from 6 to 30 GPa [15–17]. Cellulose nanocrystals embedded in epoxy matrices and strained *in situ* during Raman [18] and XRD studies [1] imply modulus values on the order of 105–143 GPa [1]. While the exact value obviously is dependent on the cellulose source and measurement technique, the crystal structure, anisotropy, degree of crystallinity, defects, and environmental conditions also play a major role. Furthermore, structure-property relationships remain ambiguous, perhaps because of variations in natural cellulosic materials and variations in the characterization methods [12].

Conventional testing devices do not have the ability to hold, or the sensitivity to strain, nanoscale cellulose particles or free-standing thin films. Direct measurements on nanosized cellulose particles or films are limited to atomic force microscopy (AFM) three-point bending tests [19], AFM indentation tests [14,20,21] and the buckling method presented here [15]. Briefly, the axial Young's modulus of tunicate-derived CNCs measured by AFM three-point bending tests was 151 GPa [19] and the transverse modulus of wood-derived CNCs measured by AFM indentation was 18–50 GPa [20]. Exploiting these mechanical properties in composite materials will require careful design to maximize crystallinity, cellulose-cellulose interactions, and interfacial compatibility between cellulose and the matrix. All in all, this means that a better fundamental understanding of the mechanical properties of both cellulose and cellulose composite thin films is essential to fully understand the potential of cellulose nanofibers, nanocrystals, and their networks.

This work presents new mechanical measurements of layered composite films containing CNC “rice” and polyethyleneimine (PEI), a branched water soluble cationic polymer. This system was chosen to directly compare to recently pub-

lished work on films of NFC “spaghetti” and PEI [15]. Specifically, we examined the effect of relative humidity (RH) and compressive strain on the Young's modulus of CNC materials compared with NFC. Moreover, we demonstrate for the first time, the applicability of the strain-induced elastic buckling instability for mechanical measurement (SIEBIMM) technique [22] to CNC films spanning a thickness range of two orders of magnitude (nanometers to micrometers).

BUCKLING-BASED METHODOLOGY

The SIEBIMM technique was invented by Stafford et al. in 2004 at the National Institute of Standards and Technology as a way to determine the Young's modulus of supported polymer films [22,23]. It has since been extended to include a wide range of nanomaterials, including polyelectrolyte multilayer films [24–27], such as those tested here. The method measures how a rigid material buckles when compressed on a soft substrate, by attaching a thin film to an elastic, thick substrate, usually polydimethylsiloxane (PDMS). Buckling, or surface wrinkling, of constrained materials is an instability phenomenon such as those first described mathematically by Euler in the 18th century. Buckling is a common occurrence; for example, human skin wrinkles perpendicular to the compressive strain direction when pinched between two fingers. Compressive stress can be generated by mechanical compression, as shown in our work; however, thermal compressive stress, the result of differences between the film and the substrate's thermal expansion coefficient, often is used as well to create surface patterns [26,28–30], study diffusion kinetics and polymer dynamics [29], and to determine thermal transitions [31] in thin films.

When compressing or straining a rigid thin film on a soft substrate, the two-layered structure will buckle uniformly. From the measured buckling wavelength (λ) and film thickness (d_f), combined with the known Young's modulus of the substrate (E_s) and the Poisson's ratios of both materials (ν_s and ν_f), the Young's modulus can be calculated for the supported thin film (E_f) according to Eq. (1).

$$E_f = 3E_s \frac{(1 - \nu_f^2)}{(1 - \nu_s^2)} \left(\frac{\lambda}{2\pi d_f} \right)^3 \quad (1)$$

Buckling occurs above a critical stress (σ_c), whereby the total elastic strain energy is minimized, balancing the energy required to bend the film and the energy required to deform the substrate. The solutions to Eq. (1) are valid only for elastic deformations and if 1) applied strain is low ($\epsilon \ll 10\%$), 2) the film's elastic modulus is much larger than that of the substrate, 3) the substrate is much thicker than the thin film, 4) the amplitude of the wave pattern is much smaller than the wavelength, and 5) the film's width is large compared to its thickness [22,23].

The SIEBIMM technique is precise, fast, and simple, because there is no need for expensive equipment to carry out

the measurements and the wavelength can be measured by various microscopies or light scattering. Furthermore, the extent of compression theoretically affects the amplitude of the wave pattern but not the wavelength, so that the exact strain does not need to be known for data processing.

To date, this buckling method has been used to study a variety of wet and dry polymers, hydrogels, thin metal films, carbon nanotubes, metal nanowires, and polymer composites, ranging in thickness from 5–500 nm over a modulus range of MPa to TPa [22,23,27,32]. These works are well summarized in a recent review of buckling as a high throughput characterization technique and as a force sensing system [33]. Other buckling studies have shown that the incorporation of nanoparticles into polymer films can be used to alleviate strain and avoid buckling that can cause unwanted surface patterns during the heat treatment of coatings [26]. If nanoparticles in a composite are not strongly bound to the matrix, buckling does not occur. In our case, the adhesion between nanocellulose and PEI is sufficient for the entire composite film to wrinkle uniformly. We have demonstrated the applicability of SIEBIMM to anisotropic nanoparticles of cellulose, both CNCs and NFC [15], where interfacial compatibility with the surrounding matrix is high. We also have extended the methodology to thicker films than previously measured: polyelectrolyte multilayer films containing CNCs with thicknesses up to 1.7 μm .

EXPERIMENTAL

Materials

PEI, $M_w = 750000$ g/mol, 50% (w/v) in water, was purchased from Sigma-Aldrich (Oakville, ON, Canada) and poly(allylamine hydrochloride) (PAH), $M_w = 120000$ g/mol to ~ 200000 g/mol, was purchased from Polysciences (Warrington, PA, USA); both polycations were used as received. All water used was ultrapurified (Type I) water with a resistivity of 18.2 M Ω cm (Barnstead NANOpure DIamond system, Thermo Scientific; Asheville, NC, USA).

Preparation of cellulose nanocrystals (CNCs)

Suspensions of CNCs were prepared from ashless cotton filter aid by sulfuric acid hydrolysis, as described previously [34]. To purify, the suspension was centrifuged, dialyzed, sonicated, placed over Dowex Marathon C hydrogen form resin (Sigma-Aldrich; Milwaukee, WI, USA), and filtered through glass microfiber filters. The resulting suspension was approximately 1% cellulose by weight (experimental yield of 56%). The surface charge density of CNCs was calculated to be 0.41 ± 0.03 e/nm² from conductometric titration, with average crystal dimensions of 118 nm $\times$ 8 nm from AFM images.

PDMS substrate preparation

The substrate purchased for buckling measurements was PDMS Dow SYLGAND 184 silicone elastomer (base and catalyst). Substrates were prepared by mixing the elastomer base and cross-linking curing agent in a 10:1 w/w ratio. After thor-

ough mixing of the elastomer with the curing agent to achieve homogeneity, the mixture was degassed under vacuum for an hour, poured into a customized aluminum mold (60 mm $\times$ 60 mm $\times$ 4 mm) with a polished silicon wafer as the base, and then degassed for another half hour. After degassing, the mixture in the mold was cured at 100°C for 1 h. After cooling, the 4 mm thick PDMS was cut into 5 cm $\times$ 1 cm strips, rinsed with purified water and ethanol, and air dried before film assembly.

PDMS modulus measurements

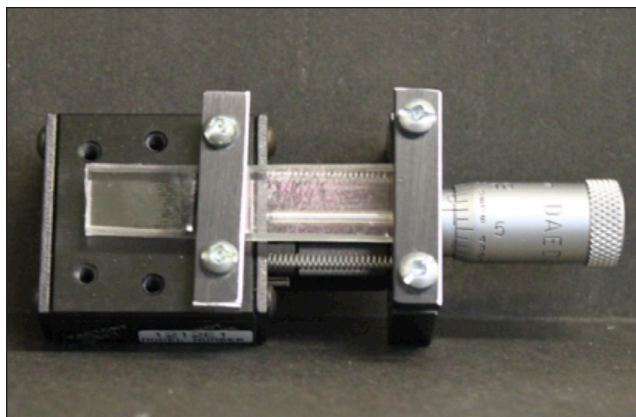
The Young's modulus of the PDMS substrates (E_y) was determined as specified in the ASTM D575-91(2012), "Standard Test Methods for Rubber Properties in Compression." Samples were pre-conditioned minimally for 24 h at 23°C and 50% RH; modulus measurements also were carried out at 23°C and 50% RH. Specifically, cylindrical PDMS pucks were prepared in a customized aluminum mold, 20 mm in diameter by 12.5 mm in height. The pucks were measured in compression mode using an Instron Universal tester (Model 4411, Instron; High Wycombe, UK) with a 500 N load cell at a compression rate of 12 mm/min. The Young's modulus of PDMS was determined to be 3.06 ± 0.06 MPa from the slope of the initial linear region of the stress-strain curves. Modulus values are an average of 28 samples from seven batches; this large number of samples was tested to confirm the reproducibility of this value, which is larger than normally reported for PDMS. We expect that the degassing step, mold design, and mixing time all affect the modulus and that these values are acceptable and in accordance with the ASTM standard.

Multilayer film preparation

PAH and PEI solutions of concentration 1 g/L and a 1 wt. % CNC suspension were prepared without any ionic strength or pH adjustments. The measured pH values for PAH, PEI, and CNC were 4.1, 10, and 3.5, respectively. Polyelectrolyte multilayer films were prepared using layer-by-layer assembly as described by Decher [35], whereby the PDMS substrates were dipped into polyelectrolyte solutions as follows: 20 min in a precursor PAH solution, then 20 min in a CNC suspension, followed by 10 min in a PEI solution. Each adsorption step was followed by three 2-min rinsing steps in purified water. After the initial PAH precursor layer, the adsorption steps alternated between CNCs and PEI, which is denoted as PAH(CNC/PEI)_{*x*}, where *x* is the number of bilayers. Substrates with an outer layer of PEI have integer *x* values, whereas outer layers of CNCs have half integer *x* values. Multilayer films up to PAH(CNC/PEI)_{44.5} were prepared.

Film thickness and buckling measurements

The thicknesses of the multilayer films on PDMS substrates (d_p) were determined using a variable angle spectroscopic ellipsometer from J. A. Woollam (Lincoln, NE, USA) using an angle range of 45° to 65°. The spectroscopic ellipsometry data were fitted using a Cauchy model with the parameters of A: 1.394, B: 0.0006, and C: 0.0002.



1. Photograph of the homebuilt strain device used for buckling. The polydimethylsiloxane (PDMS) slab coated with poly(allylamine hydrochloride) (PAH)/[cellulose nanocrystals (CNC)/polyethyleneimine (PEI)]_{14.5} is attached with screw clamps and a micrometer dial is used to adjust the spacing of the clamps. The iridescent appearance of the PDMS is the result of uniform buckling of the supported nanocellulose multilayer film.

Buckling measurements were performed under three different relative humidity conditions: 30%, 42%, and 64% RH. The moisture content in the films was not measured. For each relative humidity condition, the CNC/PEI multilayer films were pre-conditioned for 24 h and then tested at the same relative humidity. To compress the films by a controlled amount, the multilayer films on PDMS were fixed with screw clamps onto a homebuilt strain stage (**Fig. 1**). The wavelengths of the periodic buckles were measured by optical microscopy in reflectance mode. At 30% and 64% RH, an Olympus BX51 microscope equipped with a QImaging Retiga-EXi camera was used and at 42% RH, a Leica DMR microscope equipped with Nikon Coolpix 950 camera was used. More than 100 buckled regions were digitally analyzed from five (or more) microscope images for each film tested and the average value was used to determine the modulus. E_f values were calculated from Eq. (1) using $\nu_s = 0.50$ and $\nu_f = 0.33$ [15] and λ values obtained from digitally analyzing the microscopy images for PAH(CNC/PEI)_x, where $x = 2.5, 7.5, 14.5, 29.5$, and 44.5. To test the effect of strain, the samples were compressed up to 5%, but, unless otherwise stated, the values presented are at 1% compressive strain.

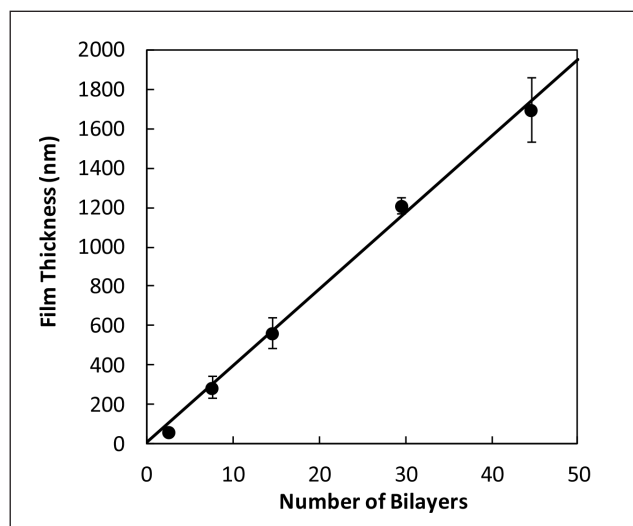
A noncontact, scanning, white-light microscope-based interferometer (Zygo New View 5032; Middlefield, CT, USA) was used to measure buckling amplitude and wavelength at 64% RH. Data was analyzed using MetroPro 8.1.5 software from Zygo.

All error intervals and error bars shown (Δx) are confidence intervals calculated from the standard deviation (S_x) of repeat measurements (N), i.e., $\Delta x = S_x \times t\text{-value}/(N)^{1/2}$, where the t -value is the Student's t -distribution at a confidence level of 95% for $N-1$ degrees of freedom, for individual measurements.

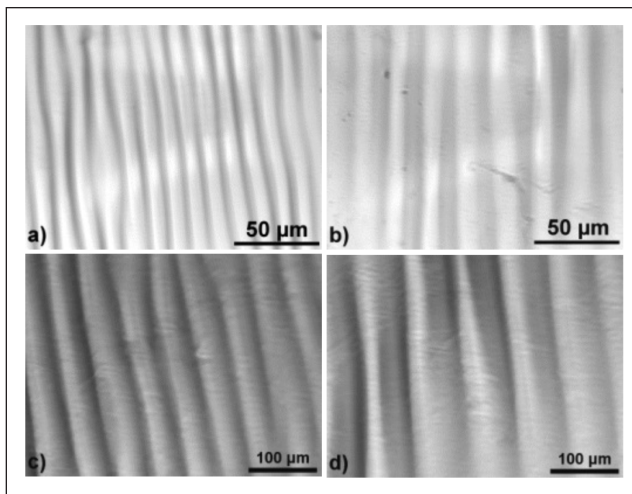
RESULTS AND DISCUSSION

Some of the first applications that come to mind for nanocellulose are films and coatings, including barrier films, bioactive films, transparent films, flexible displays, separation membranes, thin-film sensors, etc. Using the layer-by-layer technique to adsorb alternating layers of charged polymers with nanocellulose has been demonstrated to give reproducible films that uniformly cover large substrate areas with the ability to tailor composition, surface roughness, film thickness, and optical properties [34,36–42]. Here, the multilayer system of CNC/PEI assembled on a PDMS substrate with a PAH adhesive layer was prepared to compare with equivalent NFC/PEI films [15]. Film build-up was found to be linear from 2.5 to 44.5 bilayers (**Fig. 2**).

The thickness increment is 39 nm/bilayer, implying that the high molecular weight and branched nature of PEI allows for thick films to be formed where each bilayer is many CNCs thick, perhaps as many as four. PEI is highly charged (>6 meq/g) [43] compared to CNCs (0.211 meq/g), and along with the geometric constraints from the CNC particle size, charge compensation within a single adsorption step is unlikely, even if multiple layers of CNCs adsorb. The branched nature of PEI allows for cationic charge to extend away from the surface and the “bilayers” probably are not discrete stratified layers but tend toward the more disordered, interpenetrated structure normally predicted for layer-by-layer films [35]. When similar multilayer systems of CNCs and linear polycations PAH and poly(diallyldimethylammonium chloride) were assembled on silicon wafers, the thickness increment was 12–20 nm/bilayer [34,37,41], also corresponding to multiple layers of CNCs per adsorption step. In comparison, the thickness increment is only 4 nm/bilayer in NFC/PEI films [15]. NFC has a charge of 0.515 meq/g [44], making it more than two times more charged than CNCs, and thus thinner films are expected



2. Thickness of PAH(CNC/PEI)_x multilayer films on PDMS as a function of the number of bilayers. (The solid line is the linear regression analysis with $y = 39.033x$, $R^2 = 0.9965$.)

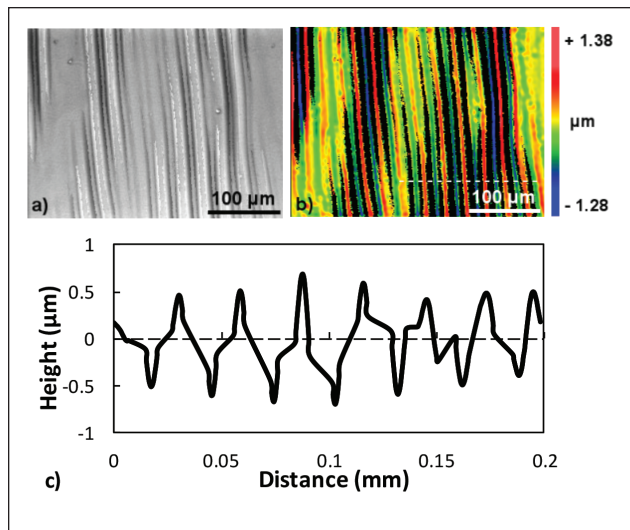


3. Optical microscopy images of buckled PAH(CNC/PEI)_x multilayer films undergoing a compressive strain of 1% for (a) 7.5 bilayers, (b) 14.5 bilayers, (c) 29.5 bilayers, and (d) 44.5 bilayers at 23°C and 64% relative humidity (RH).

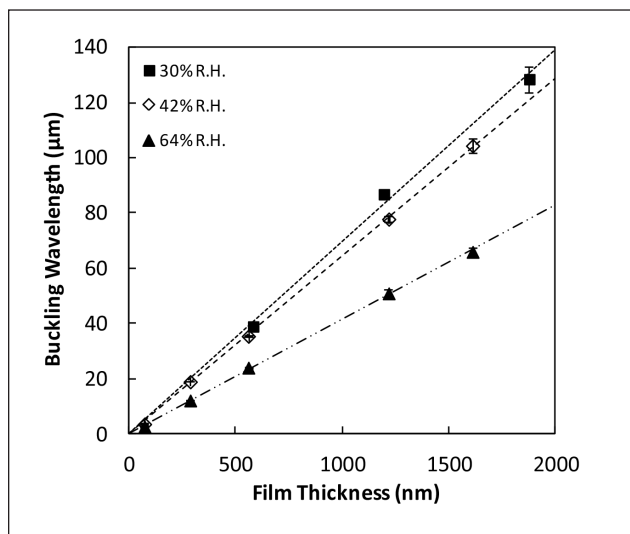
because less material is needed for charge compensation (also aided by the thinner average particle diameter of NFC compared to CNCs). The molecular weight of PEI used in the NFC/PEI films was 60 kDa compared with the 750 kDa PEI used here. These physical properties have allowed us to prepare multilayer films with CNCs that span in thickness from 61 nm to 1.7 μm with only a small number of deposition steps.

The multilayer films were compressed using a home-built strain device (Fig. 1), and long-range surface wrinkling patterns were observed by optical microscopy (**Fig. 3**). The buckling wavelength increased with film thickness and minimal defects or cracking were detected in the wave pattern. This implies good compatibility between the film components and good adhesion of the film to the PDMS substrate. For thicker films, the buckling was not as uniform as for thin films, which likely is caused by a slight unevenness in the distribution of components, which becomes increasingly apparent as more layers are built up.

Standard optical microscopy does not measure the buckling amplitude; however, better contrast in the microscopy images implies a larger amplitude, which was seen for thicker films or films compressed at higher strains. Although AFM can be used to quantitatively measure buckling amplitude [33], we used a white-light microscope-based interferometer (**Fig. 4**). The ability of light in the microscope to properly interfere from the top and bottom of the buckles is strongly dependent on the angle of incidence and how evenly the film is clamped in the strain device. “Shadows” result from off-normal light interactions and hence, information is lost. Although the buckling pattern height analysis in Fig. 4c is not perfect, we can ascertain that the buckling amplitude is about 1 μm for a film that is 570 nm thick with a buckling wavelength of 25 μm. We do not believe that Fig. 4 implies that more than one mode of buckling is



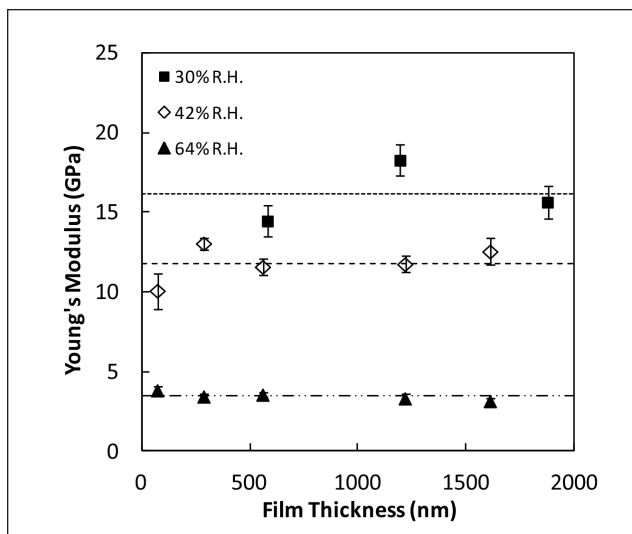
4. Buckling pattern of PAH(CNC/PEI)_{14.5} measured by Zygo microscopy at a compressive strain of 1% at 23°C and 64% RH: (a) optical intensity map, (b) Zygo surface image, (c) height analysis of the buckles along the dotted white line shown in (b).



5. Buckling wavelength for PAH(CNC/PEI)_x films ranging in thickness from 61 nm to 1.7 μm at (■) 30% RH, (◇) 42% RH, and (▲) 64% RH. (Dotted lines are linear regression analyses for the three RH conditions.)

occurring; we suspect that the deviation from a smooth wave pattern is merely a defect of the interferometric imaging technique.

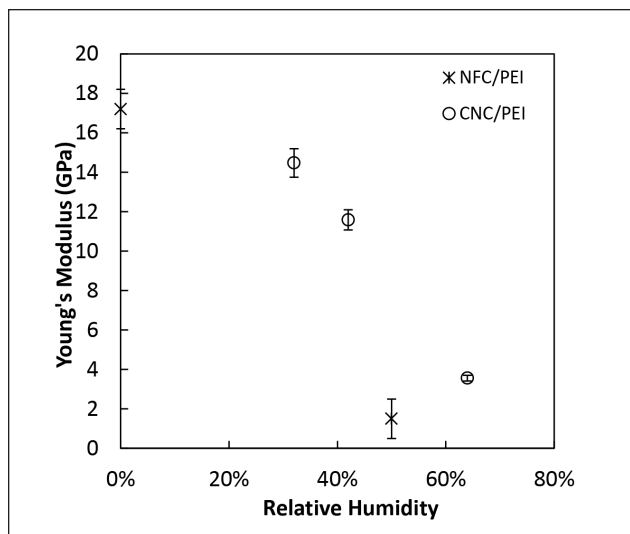
To understand the effect of relative humidity on the Young’s modulus of CNC/PEI multilayer films, buckling measurements were performed at 30%, 42%, and 64% RH. Films were allowed to precondition for 24 h at each relative humidity condition before the buckling measurements. Unfortunately, the moisture content inside the films was not determined. Under all conditions, the buckling wavelengths increase linearly with film thickness, as predicted by Eq. (1) and shown in **Fig. 5**. Larger error bars on data points for



6. Young's modulus, as calculated by strain-induced elastic buckling instability for mechanical measurement (SIEBIMM), for PAH(CNC/PEI)_x films ranging in thickness from 61 nm to 1.7 μm at (■) 30% RH, (◇) 42% RH, and (▲) 64% RH. (Dotted lines show the average modulus value for the three relative humidity conditions.)

thicker films attest to the buckling patterns being less uniform, likely from a less uniform composite film structure. The larger wavelengths at lower relative humidities indicate a stiffer film when there is less ambient water available for plasticization of the film, similar to the NFC/PEI films [15]. **Figure 6** displays the Young's moduli calculated from the buckling wavelengths using Eq. (1); the values are 16 ± 5 , 12 ± 1 , and 3.5 ± 0.3 GPa for 30%, 42%, and 64% RH, respectively. We can conclude that the SIEBIMM technique has successfully quantified the elastic modulus of nanocellulose thin films and that the stiffness is essentially constant over the thickness range of 61 nm to 1.7 μm. This is the largest reported thickness range over which the Young's modulus of a supported thin film has been measured to be constant [33].

The calculated moduli error intervals (± 5 , ± 1 , and ± 0.3 GPa for 30%, 42%, and 64% RH, respectively) come from the standard deviation of the E_f values from the five films that were measured at each relative humidity condition. Errors bars in Fig. 6 (± 0.2 –1.5 GPa) stem from the standard deviation of the measured buckling wavelengths only. Conversely, if the error is propagated from the experimentally determined uncertainty in E_s , λ , and d_f and we assume a 1% uncertainty for v_s and v_f we find much larger moduli error intervals of ± 25 , ± 23 , and ± 6 GPa from lowest to highest relative humidity. This large propagated error highlights the importance of well-chosen constants and repeated measurements of experimentally determined values. The cubed dependence of the film thickness and buckling wavelength (Eq. [1]) make precise measurements of these values critical. Nolte et al. [24] have previously described large uncertainty in using SIEBIMM for films thinner than 70 nm, which largely stems from the difficulty in measuring film thicknesses precisely.

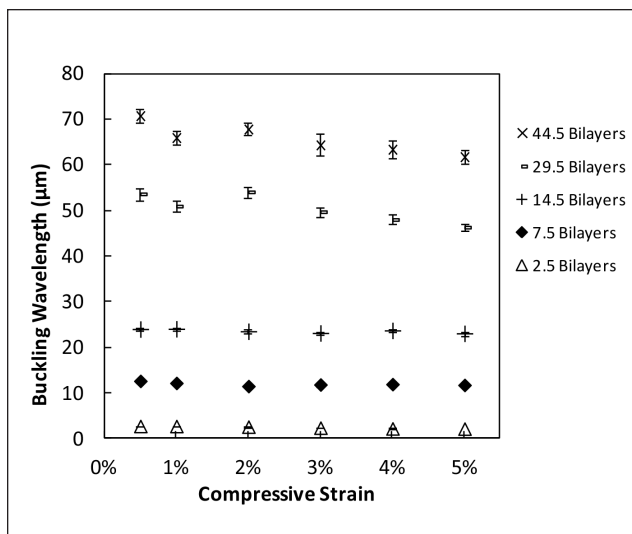


7. Dependence of Young's modulus on RH for nanocellulose multilayer films with 14.5 bilayers: (X) NFC/PEI from previously published data [1] and (O) CNC/PEI.

Figure 7 shows a direct comparison of a multilayer film with 14.5 bilayers containing either CNCs or NFC with PEI. Overall, these results show that the multilayer films containing CNCs have a larger Young's modulus than NFC films. From this data, we deduce that both nanocellulose-PEI multilayer composites are strongly relative humidity-dependent, which is attributed to the hydrophilic nature of cellulose and the hygroscopic behavior of PEI. Water and PEI interfere with the cellulose-cellulose van der Waals interactions and hydrogen bonds that are needed between cellulose nanoparticles to attain moduli near the predicted value. As in paper, the cellulose network is only as strong as its weakest link; here the cellulose-cellulose joints are inhibited by PEI to begin with, and especially at high relative humidity where cellulose-cellulose H-bonds are replaced with cellulose-water H-bonds.

Natural fiber composites have always been limited by their relative humidity dependence [45,46]. Here we see that nanocellulose composites also appear to be strongly affected by ambient water. Over the small relative humidity range tested, the Young's modulus decreases by about 0.3 GPa for every percent change in relative humidity for both nanocellulose films, which is substantial. (Note, however, that there are only two data points for NFC/PEI films.) While we recognize that the mechanical properties of this multilayer composite limits its potential applications, relative humidity has a strong effect and must be carefully controlled during mechanical testing of CNC and NFC nanocomposites.

To understand why the CNC/PEI films consistently had a larger Young's modulus than the NFC/PEI films, we turn to the most noteworthy differences between these nanocelluloses, including the degree of crystallinity, the particle dimensions, and the surface charge density. These three properties are directly related to parameters that determine nanocomposite modulus, namely, 1) the reinforcing agent's mechanical



8. Effect of compressive strain on buckling wavelength for PAH(CNC/PEI)_x films with (Δ) 2.5 bilayers, (◆) 7.5 bilayers, (+) 14.5 bilayers, (-) 29.5 bilayers, and (x) 44.5 bilayers.

properties, 2) the aspect-ratio, and 3) the volume fraction of composite components. Interfacial compatibility between the reinforcing agent and the matrix also plays a key role; however, we expect the compatibility of CNC and NFC with PEI to be comparable. The dependence of the Young's modulus on these parameters can be predicted using a range of mean-field theories in 1D, 2D, and 3D. Specifically, the Halpin-Tsai and Halpin-Kardos models have been applied successfully to describe CNC composites where a larger aspect-ratio, larger volume fraction, and better interfacial stiffness all lead to a higher modulus material [1]; these predictions are now discussed within the context of the current experiments:

1. The high modulus predicted for cellulose stems from its crystalline structure and inter- and intra-molecular hydrogen bonding; therefore, because CNCs are more crystalline than NFC (87% vs. 70%, respectively) [17], they are a stiffer reinforcing agent. Despite the high modulus of crystalline cellulose, the ability of CNCs to bend also has been reported [20], which lends itself well to flexible thin film applications and this buckling-based method. No differences in buckling uniformity or cracking tendencies were observed between CNC and NFC films, despite the difference in their crystallinity. Higher crystallinity in CNC films might be one reason that modulus values calculated in this work are higher for CNC/PEI films than NFC/PEI films.

2. On the other hand, the smaller aspect-ratio of CNCs would forecast weaker composites than NFC, assuming all other things being equal, which is the opposite of what we observed. The nanocellulose aspect-ratio also might have led to a difference in the dependence of the Young's modulus on compressive strain. There was no significant change in the Young's modulus with compressive strain for the thinnest CNC/PEI films, which is predicted from the buckling theory for strains under 5% [47] or 10% [33]. However, a slight de-

pendence was observed for films above 1.2 μm in thickness (**Fig. 8**). In contrast, the Young's modulus for NFC/PEI films was found to decrease by about 20% over the strain range of 3%-10% [15]. This might be because the length of NFC particles is on the same order of magnitude as the buckling wavelength. As such, users of the buckling method with high aspect-ratio nanoparticles are cautioned to report modulus values at a set (and preferably low) strain value to ensure valid comparisons.

3. Finally, a higher volume fraction of the reinforcing agent would lead to stiffer nanocomposites, but it was outside the scope of this work to quantify the relative volume fractions of nanocellulose and PEI in our multilayer films. In both cases, we suspect the nanocellulose content to exceed 85% [15]. The PEI molecular weight (10-fold higher in CNC/PEI films) and nanoparticle surface charge density (two-fold lower for CNC than NFC) are major factors in determining volume fraction for electrostatically adsorbed multilayer films. We thus suspect a higher volume fraction of nanocellulose in the CNC films over the NFC films because of the drive toward charge compensation, but we cannot easily predict the effect of PEI molecular weight and polymer architecture on volume fraction.

Overall, parameters 1 and 3 and the higher molecular weight PEI all support CNC/PEI films having better mechanical properties than the NFC/PEI films.

CONCLUSIONS

Nanomechanical property measurements have been identified as one of the "grand challenges" in standardizing metrology for nanocellulose [1]. Here, we present a robust and facile way to measure the Young's modulus of thin film composites containing CNCs and compare it to recent work on similar NFC films. The method involves measuring how supported thin films buckle when compressed on PDMS substrates. We encourage other researchers to use this technique on their nanocellulose thin films or composite materials; however, we suggest that care be taken to control (and report) environmental conditions of temperature and relative humidity, and to use small and consistent compressive strains.

As films and coatings represent one of the most promising applications for nanocellulose, the SIEBIMM method is a helpful technique to gain quantitative mechanical property data and may prove useful in the future to create patterned cellulose surfaces or as a way to assess dispersibility of components in nanocomposites. The main conclusions from this work are as follows:

1. Long-range, uniform buckling patterns were observed for compressed CNC/PEI multilayer films on PDMS over a thickness range of 61 nm to 1.7 μm.
2. The Young's modulus of CNC/PEI multilayer films was constant over this thickness range, with values of 16 ± 5 , 12 ± 1 , and 3.5 ± 0.3 GPa at 30%, 42%, and 64% RH, respectively.
3. The Young's modulus was larger at all relative humidity values for CNC films compared to NFC films; crystallinity,

aspect-ratio, PEI molecular weight, interfacial compatibility, and volume fraction are all important factors to consider when predicting nanocomposite moduli.

4. The relative humidity dependence of the Young's modulus for nanocellulose and PEI composites is exceptionally prominent; this trend is likely generalizable to other nanocellulose composite films. **TJ**

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Our research aims to design high-performance materials from nanocellulose by elucidating structure-property relationships. Quantifying mechanical properties is one part of these efforts, despite the challenges often associated with measuring nanomaterials. We believe that nanocomposite thin films and coatings containing cellulose nanocrystals (CNCs) and/or nanofibrillated cellulose (NFC) are some of the most promising potential applications for nanocellulose, and thus understanding how film composition, thickness, environmental conditions, and mechanical stress affect the elastic modulus is of utmost importance.

This work builds on our past research, which demonstrates that measuring mechanical properties using the buckling-based method is straightforward and works well for nanocellulose thin films. Very little work has been done that directly measures mechanical properties of pure nanocellulose or nanocellulose thin film composites.

One challenge in using this buckling method is ensuring that the thin film is well adhered to the compressible substrate; depositing a hydrophilic cellulose film on a hydrophobic rubber surface was difficult and required an extra polymer adhesive layer.

We found that the elastic modulus of nanocellulose composites containing hygroscopic polymers is far below what is predicted for crystalline cellulose.

The most interesting discovery was that CNC and NFC films had the same (extreme!) dependence on humidity, but that the CNC films overall were stiffer compared to NFC.

We can now compare the difference in composite properties for CNC versus NFC films, contributing to the standardization of metrology for nanocellulose, which is increasingly important as industrial production of nanocellulose has recently begun. We hope that these results and measurement methods can contribute to the R&D efforts of various partners.

The next step is to use the buckling method to test "all-nanocellulose" coatings and nanocomposites containing less moisture-sensitive polymers and to compare nanomechanical testing to more conventional macro-scale testing.



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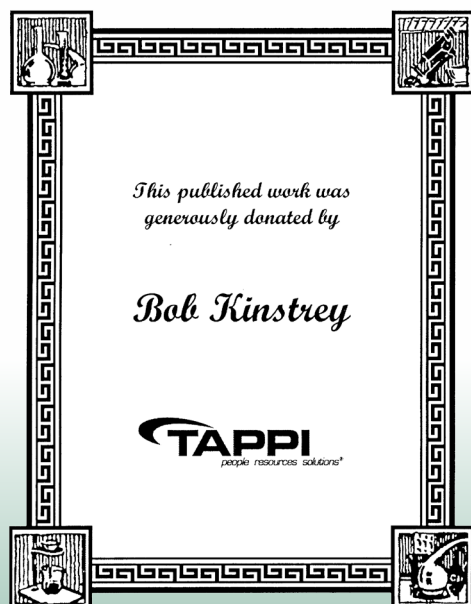


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