The structure and mechanics of nanofibrillar cellulose foams

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The Structure and Mechanics of Nanofibrillar Cellulose Foams

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for submission to Soft Matter

Abstract

Crystalline nanofibrillar cellulose has remarkable mechanical properties: a Young’s modulus of about 130 GPa and a tensile strength in the range of 750-1000 MPa. Recently, there has been increasing interest in exploiting these exceptional properties in engineering composites and foams. Here, we compare measurements of the mechanical properties of nanofibrillar cellulose composites and foams with their potential properties based on models for composites and foams. We find that current NFC foams do not yet reach their potential and suggest modifications to their microstructure for improved mechanical performance.
The Structure and Mechanics of Nanofibrillar Cellulose Foams

Introduction

Engineers are increasingly interested in exploiting the remarkable properties of cellulose, the structural fiber of the plant world, at the nanoscale. Its density is low and, in its crystalline form, its Young’s modulus and tensile strength are remarkably high, comparable to advanced engineering alloys and fibers. It is abundantly available and renewable.

The hierarchical structure of plant cell walls is shown in Fig. 1. Cellulose is a long-chain polysaccharide, made up of 7000-15000 monomer units, which are alternately rotated 180° (Niklas, 1992). Cellulose molecules align to form microfibrils (or nanofibrils), about 3-4 nm in diameter, with crystalline regions separated by shorter non-crystalline regions (Dinwoodie, 1981). The cellulose microfibrils themselves are aligned and bound together into macrofibrils, roughly 10-25 nm in diameter, by hemicellulose and either pectin or lignin (Dinwoodie, 1981). In some plant cells, such as parenchyma in potato tubers, the cell wall has only a single, primary layer and the cellulose fibrils are embedded in a matrix of hemicellulose and pectin, while in other plant cells, such as tracheids in softwoods, the cell wall has a primary and several secondary layers, in which the cellulose microfibrils are embedded in a matrix of hemicellulose and lignin.

The Young’s modulus of crystalline cellulose has been measured by x-ray diffraction during tensile deformation while the tensile strength has been measured in tensile tests on plant fibers with high cellulose contents (e.g. flax). Measured values for the Young’s modulus and tensile strength are in the range of 120-140 GPa (Sakurada et al. (1962, 1966); Sakurada and Kaji (1970) and Matsuo and Sawatari (1989)) and 750-1000 MPa (Wainwright et al. (1976) and Vogel (2003)), respectively. The density of cellulose is 1500 kg/m³ (Granta Design, 2011).

Highly crystalline nanofibrillar cellulose (NFC) can be isolated by treating delignified wood pulp with an enzyme, endoglucanase, in a phosphate buffered solution and then mechanically agitating the resulting suspension by passing it...
through a microfluidizer. The resulting NFC fibrils are typically 5-50nm in
diameter and several microns long (Svagan et al., 2007, 2008). Roughly 5%
hemicellulose remains in the fibrils after treatment, which is essential for
maintaining a stable colloidal system, to avoid agglomeration of the nanofibrils.

The main advantage with NFC in the context of foams and aerogels is
that the cell structure can be much finer and more homogeneous than for fiber
based porous structures. Also, with nanoscale fibrils it becomes possible to have
NFC reinforced polymer cell walls.

Freeze-dried NFC foams are prepared from a colloidal suspension of NFC
in water. NFC fibrils are typically 5-50 nm in diameter and have a length of
several micrometers. The fibrils are flexible and have swirled conformations in
the suspension. Due to the high aspect ratio, a very dilute suspension is needed
in order to avoid gelation due to formation of an NFC network; the rheology of
such suspensions has been studied by Paakko et al. (2007). In the present study,
the NFC has no surface charge but the suspension is still stable, possibly because
there is some hemicellulose on the surface of the NFC.

During freezing, ice crystals nucleate in the water, and NFC is pushed to
the interstitial regions (Svagan et al., 2010). Fibrils are brought into close contact
during drying as a result of capillary forces pulling the fibrils together as the
water evaporates. Secondary interactions, including hydrogen bonding, then
provide stability to the system. If nucleation takes place fairly homogeneously, a
foam-like structure is formed, which is stable after drying (sublimation of the ice).

In freeze casting, the location of the nucleation sites and the translation of the
freezing front from directional freezing, gives rise to a honeycomb structure
(Deville et al., 2006); this possibly allows for some orientation of the NFC. It has
been shown that NFC may also orient locally in hydrogel structures, and that this
has a favorable effect on mechanical performance of aerogels (Saito et al., 2011). The foam pore size can be controlled by the rate of freezing and the final freezing temperature; pore sizes are typically 10-100 µm. Nanofibrillar cellulose foams can be made by freeze-drying of a suspension of NFC fibrils in water, or in a solution of starch (Svagan et al., 2008, 2010) or xyloglucan biopolymer (Sehaqui et al., 2010a). Typical foam densities range from 7-150 kg/m$^3$, corresponding to volume fractions of solid of 0.005-0.10.

Cellulose foams can also be prepared by dissolving cellulose in an ionic liquid solvent followed by freeze-drying (Deng et al., 2009). Nanostructured cellulose/clay aerogels have also been made by freeze drying, but the high inorganic content leads to substantial brittleness (Gawryla et al., 2009). Bacterial cellulose fibrils have been used to reinforce foams made from an emulsion of acryliclated epoxized soybean oil, polymerized by the addition of cumene hyperoxide (Blaker et al., 2009). The volume fraction of cellulose fibrils in the foam was limited to a few percent by flocculation of the fibrils in the initial emulsion.

The Young's modulus and compressive strength of NFC foams made by lyophilization of NFC fibrils in water (Sehaqui et al., 2010a) are well described by the Gibson and Ashby models for open cell foams (Gibson and Ashby, 1997), with a solid cell Young's modulus of 1.2 GPa and yield strength of 67 MPa. Thin films of NFC of similar composition as the NFC foams have significantly higher moduli (14.7 GPa) and strength (205 MPa) (Henriksson et al., 2008), suggesting that the mechanical properties of the NFC foams could be increased.
Here, our goal is to compare data for the moduli and strengths of NFC foams with models for open-cell foams, to give insight into modifications to the microstructure that could lead to improved mechanical properties. The microstructure and mechanical properties of NFC foams made by lyophilization are characterized by scanning electron microscopy and compression testing. The mechanisms of deformation and failure in NFC foams are identified using a deformation stage in the scanning electron microscope. The properties of a NFC thin film, with a composition similar to that of the foams, are measured by nanoindentation.

Materials and Methods

NFC foams and NFC thin films were obtained from Professor Lars Berglund at the School of Chemical Science and Engineering, KTH, Stockholm, Sweden. The process described here uses never dried, bleached, sulfite pulp from spruce, supplied by Nordic Paper Seffle AB (Saffle, Sweden), with fibers that are about 30 µm in diameter and 2-3 mm long. The pulp fibers are about 90% cellulose, with the remainder mainly hemicellulose; the pulp fibers are delignified and have almost no extractives. The NFC foams were made by lyophilization (freeze-drying) of a suspension of NFC, using a previously reported method (Henriksson et al., 2007; Sehaqui et al., 2010a).

The pulp was first subjected to a pretreatment involving enzymatic degradation and mechanical beating. The pretreated pulp was then passed through a microfluidizer (Microfluidics Ind., USA) eight times to produce cellulose nanofibrils. A suspension of 2 wt% NFC in water was successfully obtained. To prepare NFC foams with 3 different densities, the 2 wt% NFC suspension was then either diluted, by adding more water to the suspension, or concentrated, by high speed centrifugation (20,000 rpm for 15 minutes), to obtain suspensions with different NFC concentrations. All the NFC suspensions were degassed in vacuum before being placed in aluminum cups for freeze-drying. To
avoid macroscopic cracking during freeze-drying, the samples were pre-cooled at 4°C before they were frozen in liquid nitrogen (-196°C). Some samples were submerged directly in the liquid nitrogen in order to generate a crack surface for direct observation of the microstructure in the scanning electron microscope (SEM). All samples were sublimated in a benchtop freeze dry system (6 liter FreeZone, Labconco, Kansas City, MO) as previously described by Sehaqui et al. (2010a). The resulting samples, in the shape of circular disks roughly 40 mm in diameter and 14 mm thick, had a thin skin on the surface. NFC foams with densities between 7 and 63 kg/m³ were successfully prepared.

NFC thin films were made by vacuum filtration of a suspension of NFC in water. The 2 wt% NFC suspension was diluted with water, and mixed at 8000 rpm for 10 minutes using an Ultra Turrax mixer (D125 Basic, IKA, Wilmington NC), to give an NFC suspension with a concentration of 0.2 wt%. The suspension was degassed for 10 minutes with a water vacuum pump and then vacuum filtrated on a glass filter funnel using a 0.65 µm filter membrane (DVPP, Millipore, Billerica, MA), according to a previously reported method for nanopaper (Henriksson et al., 2008). The wet cake, formed at the end of the filtration, was stacked between a metallic wire net and filter papers and then dried using a laboratory sheet dryer (Rapid Köthen) at 93°C under vacuum of ca. 70 mbar for 10 minutes (Sehaqui et al., 2010b). The average density of the NFC thin film was 1070 kg/m³. The average thickness of the NFC thin film was 75 µm.

**Microstructural characterization**

Specimens for microstructural characterization were all freeze fractured before sublimation of the ice phase in the processing of the foam, to avoid any artifacts associated with cutting the surface of the foam. The specimens were fixed onto a metal stub with conductive carbon tape and coated with gold. Images of the samples were obtained in a scanning electron microscope (SEM) (Leo VP438 or JEOL JSM 6610LV).

*Compression testing*
Roughly cubic specimens (15mm x 15mm x 14mm) of NFC foam were tested in compression using a table-top Instron testing machine (Model 4201, Intron Corp., Canton, MA) with the loading direction aligned with the thickness direction (14mm) of the as-received disks. Six specimens of the 16 and 27 kg/m$^3$ densities and five of the 63 kg/m$^3$ density foam were tested. Each specimen was compressed 1.4 mm per minute; specimen displacement was obtained from the crosshead displacement. Data was acquired at a rate of 1000 Hz. The Young’s moduli of the foams were calculated from the initial linear part of the stress-strain curves and the compressive strengths were calculated from the intersection of the slopes of the linear-elastic regime and the stress plateau regime on the stress-strain curves. Three specimens of each density were unloaded and reloaded to determine if the stress plateau was elastic or plastic. Strain recovery was measured by loading specimens to 20\% strain, completely unloaded them and then measuring the height of the specimen, using calipers, at several time points over 3 hours after unloading.

**Observations of deformation and failure in the scanning electron microscope**

Cubic specimens of NFC foams, 10mm on each side, of each nominal density, were tested in compression in the through-thickness direction in a deformation stage in the SEM. The deformation stage was instrumented with a load cell and a stepper motor allowing the load-deformation curve for each sample to be obtained. Images of the undeformed and deformed specimens were obtained at different points along the stress-strain curve and at various magnifications at each strain.

**Nanoindentation**

Samples of the NFC thin film (20mm x 20mm x 75 μm) were bonded to metal substrates and tested in a Hysitron (Model TI 900, Minneapolis, MN) nanoindenter, recording load and indentation depth. Three sets of tests were conducted using a Berkovich diamond tip and controlling the maximum depth of each indentation (at 100, 200 and 400 μm); roughly 30 indents were performed at each depth. A second set of tests was conducted using a conospherical tip and
controlling the maximum load (at 5mN) for each indentation; roughly 100
indentations were made with this setup. Both tips were made of diamond (E =
1140 GPa, ν = 0.07). The Young’s modulus and hardness for each indentation on
the sample was obtained using the Oliver-Pharr method (Oliver and Pharr, 2004).
The Young’s modulus was obtained by analyzing the elastic recovery during the
initial unloading, assuming that Poisson’s ratio for the film is 0.33:

\[
\frac{1}{E_r} = \frac{1-\nu^2}{E_s} + \frac{1-\nu_i^2}{E_i}
\]

and the hardness was obtained from

\[
H = \frac{P_{\text{max}}}{A}
\]

where \(P_{\text{max}}\) is the maximum load of the indentation and \(A\) is the contact area
under load.

Results

Scanning electron micrographs of three densities of NFC foams are shown
in Fig. 2. Instead of the polyhedral cells typical of many foams, the present NFC
foams are made up of irregular sheets, tens of microns in length, that are
occasionally connected to other sheets. The sheets themselves are curved and
porous, with pores varying in size from hundreds of nanometers to several
microns (Fig. 2g). In addition to the sheets, there are occasional fibrils, roughly
50 nm in diameter at the thinnest dimension, and increasing in diameter towards
the sheets (Fig. 2h).

Scanning electron micrographs of the NFC film, of the same composition
as the NFC foams, are shown in Fig. 3. The orthogonal grid of small sheets
perpendicular to the surface of the film (Fig. 3a,b) reflects the pattern of the
membrane on which the films are made. The higher magnification images , of
the surface of the film itself, show a uniform surface with no porosity.

Compressive stress strain curves for three nominal densities of NFC foam
are shown in Fig. 4. The curves for the two densest foams are typical of cellular
materials, with an initial linear elastic regime up to a strain of about 12%
followed by a stress plateau and, at high strains (~70%), a regime of densification.
On unloading after the beginning of the stress plateau, the linear elastic
deformation is recovered, but there is substantial plastic deformation. The curve for the lowest density foam increased without any noticeable stress plateau. The values of the Young’s modulus and plateau stress of the samples are listed in Table 1.

Strain recovery after loading to 20% strain, within the stress plateau regime, and then unloading completely was measured using calipers over a period of 3 hours after unloading, at which point the strain asymptotically approached a value of 4.5 and 11.7% in the 27 kg/m³ and 63 kg/m³ specimens, respectively. We were unable to obtain reliable data in tests on the lowest density specimens (16 kg/m³), as it was difficult to ascertain when the calipers contacted the specimen without deforming it.

The Young’s moduli and compressive strengths of the NFC foams are plotted against relative density in Fig. 5, which also includes data from the literature. The data from this study is similar to that from other studies, although slightly lower. In particular, we note that for the combined data, the Young’s modulus varies roughly with density squared and the compressive strength varies with density raised to the 3/2 power.

Micrographs illustrating the compressive deformation of the 27 kg/m³ density NFC foam within the scanning electron microscope are shown in Fig. 6, along with the corresponding stress-strain curve; the specimen was compressed in the horizontal direction. The initially unloaded specimens (top row of images) were loaded to 20% strain (second row), at which point they were completely unloaded (third row), and then reloaded to 47% strain (bottom row). At 20% strain, bending of the smaller cell edges in the foam is evident (2, 4 in Fig. 6) while the larger, plate-like structures (1, 3 in Fig. 6) appear to move monolithically as the material around them deforms. At 20% strain, cracking of one cell edge (near 2) is evident in the medium and high magnification images. On unloading, there is substantial plastic deformation visible in the micrographs, consistent with the stress-strain curve (Fig. 6e). At 47% strain, the cell walls are closer together, and in some places, are touching: foam is starting to densify locally; correspondingly, the stress-strain curve is just starting to rise more steeply.
The Young’s modulus and hardness of the NFC thin film, from nanoindentation tests, are given in Table 2. The average modulus and hardness for the depth control measurements are 8.03 GPa and 0.575 GPa, respectively; there is no significant difference between the moduli measured at different depths of indentation, but there is a significant difference between the hardness tests at different depths of indentation (F-test, with a level of significance of 0.05). The modulus and hardness for the load control experiments were measured to be slightly higher, 10.5 GPa and 1.0 GPa, respectively; both the modulus and hardness are statistically significantly different from those of the depth control tests (F-test, with a level of significance of 0.05).

**Discussion**

The microstructure of the present NFC foams differs significantly from that of most synthetic polymer foams in that it is made up of irregular sheets, occasionally connected to other sheets by smaller struts, rather than the usual polyhedral cells. Even smaller fibrils, roughly 50 nm in diameter at the thinnest, are visible, which correspond to several cellulose macrofibrils. The compressive stress strain curves for the higher density NFC foams are similar to those of other cellular materials, with linear elastic, stress plateau and densification regimes. In the lowest density NFC foam, there is no clear distinction between the linear elastic and stress plateau regime. The data are consistent with those of a previous study that varied the density of similar NFC foams and found that the Young’s modulus and the stress plateau depend on relative density to the powers 2 and 3/2, respectively (Fig. 5, Sehaqui et al., 2010a). Observations of compressive deformation of the foams in the SEM show bending deformation in the smaller struts, while the larger plates appear to move monolithically. The unloading stress-strain curves, as well as observations of the deformation on loading and unloading in the scanning electron microscope indicate that the stress plateau is associated with plastic deformation of the cell walls during bending as well as some cracking.

The Young’s modulus of an open cell foam that deforms by bending of the cell edges is given by (Gibson and Ashby, 1997):
\[ E^* = C_1 E_s \left( \frac{\rho^*}{\rho_s} \right)^2 \]  

(3)

where \( E^* \) and \( \rho^* \) are the Young's modulus and density of the foam, \( E_s \) and \( \rho_s \) are those of the solid from which the foam is made and \( C_1 \) is a constant related to the cell geometry; for many open-cell foams with polyhedral cells \( C_1 \sim 1 \).

Models for the plastic stress plateau of open cell foams (Gibson and Ashby, 1997) give:

\[ \sigma_{pl}^* = C_2 \sigma_{ys} \left( \frac{\rho^*}{\rho_s} \right)^{3/2} \]  

(4)

where \( \sigma_{pl}^* \) and \( \sigma_{ys} \) are the plateau stress of the foam and the yield strength of the solid cell wall material, respectively, and \( C_2 \) is a dimensionless constant related to the cell geometry of the foam; it is obtained by fitting eqn (4) to data; for many polymer and metal foams that fail plastically \( C_2 \sim 0.3 \).

The data from the literature illustrate the effect of changing the composition and relative density of NFC foams. Svagan et al. (2008, 2011) studied NFC/amylopectin starch foams and varied the fractions of NFC and amylopectin while maintaining the relative density roughly constant (at about 0.08). The moduli and plateau stress of the foams vary by factor of roughly 5, reflecting the different values of \( E_s \) for the different compositions. Sehaqui et al. (2010a) studied NFC foams made by a similar process to those of this study, varying the relative density, and found that the modulus and plateau stress depended on relative density as described by eqn (3) and (4).

The pooled data, from this study and the literature, for the Young’s modulus of NFC foams are well described by eqn (3) (Fig. 5a). The moduli vary as density squared, reflecting the bending of the cell walls in the NFC foams. The NFC foams in the Sehaqui et al. (2010a) study had a polyhedral cell structure, for which we would expect \( C_1 \sim 1 \). The value of \( E_s \) for the data of the Sehaqui et al. (2010a) study is then estimated to be 1.2 GPa, based on extrapolation of the foam data to a fully dense material, with \( \rho^*/\rho_s = 1 \).

The foams in this study had moduli somewhat lower than those of Sehaqui et al. (2010a). The cell structure of the foams in this study was made up of a combination of smaller, thinner cell edges and larger plates and did not have the usual polyhedral cell structure of most foams, so that we expect the value of
C to be less than one. The NFC thin film has a value of $E_{\text{thin film}}$ of roughly 9 GPa, much higher than the estimated value of $E_s$ in the Sehaqui et al. (2010a) study. As we were unable to perform nanoindentation tests on cell wall material obtained directly from our NFC foam specimens, this is our best estimate for $E_s$, although it is possible that the NFC thin films are not completely representative of the solid in the NFC foam. The foam deforms primarily by bending of smaller struts, with little deformation of the larger, more rigid, plates. The plates contribute to the relative density of the NFC foam, but do not contribute to the resistance to the bending deformation; they instead move more or less monolithically along with the bending of the smaller struts. The Young’s modulus of the foam is then controlled by the bending of only the smaller, thinner struts, which make up only a fraction of the measured relative density of the foam. If the "foam" region and "plate" region have similar volume fractions in the NFC foams of different relative density, then the foam modulus still varies with relative density squared, but the constant is lower than expected.

The pooled data for the plateau stress for NFC foams from this study and from the literature are well described by eqn (4) (Fig. 5b). The plateau stress varies as the relative density to the $3/2$ power, reflecting the formation of plastic hinges in the bent cell walls. Assuming that $C_2 = 0.3$, and extrapolating to the fully dense material, Sehaqui et al. (2010a) estimated that the solid cell wall yield strength for their foams was $\sigma_{ys} = 67$ MPa.

In the foams in this study, the plateau stress of the NFC arises from plastic deformation of the smaller, thinner struts, along with some cracking at larger deformations. We expect the value of $C_2$ for the NFC foams in this study to be less than 0.3, as the cell geometry differs from the more common polyhedra and the cell structure is less well connected than in most foams. The average hardness of the NFC thin film (from all the tests) is 681 MPa, suggesting that the yield strength of the NFC thin film is 227 MPa. As with the modulus, the plateau stress may be controlled by the bending of the smaller, thinner struts, which make up only a fraction of the relative density of the NFC foam, so that the plateau stress is less than would be predicted based on a more uniform structure made of NFC with a yield strength of 227 MPa.
Based on the model for open-cell foams (eqn 3 and 4), and using the average properties of the solid NFC thin film of $E_s = 8.65$ GPa and $\sigma_{ys} = 227$ MPa, the modulus and plateau stress for a NFC foam with a uniform polyhedral cell structure and with the solid cell wall properties of the NFC thin film are expected to be roughly 7 and 3 times greater, respectively, than those reported here. Such models give a good description of solid foams with polyhedral cells with the solid material more uniformly distributed throughout the foam than is observed in NFC foams (Gibson and Ashby, 1997). With better control of the cell structure, eliminating the thin thread-like struts and developing a more polyhedral cell structure with the solid material distributed more uniformly in the cell edges and faces, NFC foams have the potential for greatly improved mechanical properties.

**Conclusions**

The microstructure of the NFC foams in this study have a structure of irregular sheets that are occasionally connected to other sheets by smaller, thinner struts. Compressive deformation of the NFC foams is by bending of the smaller, thinner struts. The stress plateau is controlled by plastic deformation; following initial plasticity, cracking is observed in some members. The modulus and plateau stress of the NFC foams depend on the relative density of the foam raised to the powers 2 and 3/2, respectively, consistent with models for open-cell foams. The modulus and plateau strength of the NFC foams is controlled by the smaller, thinner cell edges, while the larger sheets move monolithically, contributing little to the foam properties. There is potential to greatly improve the mechanical properties of NFC foams with better control of the cell structure.

**Acknowledgements**

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Table 1 Young's modulus and plateau stress of NFC foams

<table>
<thead>
<tr>
<th>Density, ( \rho^* ) (kg/m(^3))</th>
<th>Relative density(^1) (-)</th>
<th>Young's modulus, ( E^* ) (MPa)</th>
<th>Plateau stress, ( \sigma_{pl}^* ) (kPa)</th>
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<tr>
<td>15.8 [0.5]</td>
<td>0.011</td>
<td>0.062 [0.017]</td>
<td>-</td>
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<tr>
<td>26.5 [1.0]</td>
<td>0.018</td>
<td>0.249 [0.058]</td>
<td>35.0 [9.8]</td>
</tr>
<tr>
<td>63.0 [2.0]</td>
<td>0.042</td>
<td>1.76 [0.163]</td>
<td>198 [32]</td>
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\(^1\) Relative density calculated assuming the density of the solid cell wall is 1500 kg/m\(^3\), the value for cellulose. [values in brackets are standard deviations]

Table 2 Modulus and hardness of NFC thin film from nanoindentation

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<tr>
<th>Method</th>
<th>Reduced Modulus, ( E_r ) (GPa)</th>
<th>Specimen Modulus, ( E ) (GPa)</th>
<th>Hardness, ( H ) (GPa)</th>
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<tr>
<td>Depth control (100 mm) Berkovich tip</td>
<td>9.49 [2.30]</td>
<td>8.51 [2.08]</td>
<td>0.682 [0.198]</td>
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<tr>
<td>Depth control (200 mm) Berkovich tip</td>
<td>8.62 [2.47]</td>
<td>7.73 [2.23]</td>
<td>0.505 [0.133]</td>
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<tr>
<td>Depth control (400 mm) Berkovich tip</td>
<td>8.77 [1.48]</td>
<td>7.86 [1.33]</td>
<td>0.538 [0.141]</td>
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<tr>
<td>Load control (5mN) Conospherical tip</td>
<td>11.7 [1.57]</td>
<td>10.5 [1.41]</td>
<td>1.0 [0.112]</td>
</tr>
</tbody>
</table>

[values in brackets are standard deviations]
References


Granta Design (2011) CES Selector (Material database software)


Svagan AJ Azizi Samir MAS and Berglund LA (2007) Biomimetic polysaccharide nanocomposites of high cellulose content and high toughness. Biomacromolecules 8, 2556-2563.


Figure Captions

Fig. 1 Hierarchical structure of plant cell walls, showing (a) cellulose crystal structure (b) cellulose macrofibril, made up of several microfibrils (c) cellulose macrofibril, with hemicellulose and pectin matrix in the primary cell wall and (d) primary and secondary layers in wood cell wall. (a, b and d from Gibson LJ, Ashby MF and Harley BA (2010) with permission of Cambridge University Press; (c) from Niklas (1992), with permission of University of Chicago Press.)

Fig. 2 Scanning electron micrographs of three nominal densities of NFC foams (a,b) 7 kg/m$^3$ (c,d) 26 kg/m$^3$ and (e,f) 63 kg/m$^3$. (g) Micrograph showing pores within the sheets of the foam (h) Higher magnification micrograph showing fibrils of 50-200 nm diameter.

Fig. 3 Scanning electron micrographs of the NFC thin film showing (a) the orthogonal grid reflecting the filter paper used in making the films (b) the small sheets perpendicular to the surface of the film.

Fig. 4 Compressive stress strain curves for individual specimens of NFC foams (a) 15 kg/m$^3$ (b) 28 kg/m$^3$ and (c) 62 kg/m$^3$.

Fig. 5 (a) The Young's moduli and (b) the plateau stress of NFC foams, plotted against relative density.

Fig. 6 Scanning electron microscope images of 27 kg/m$^3$ NFC foam under compressive deformation (from left to right in the images) (a) unloaded (b) loaded to 20% strain (c) unloaded and (d) reloaded to 47% strain. (e) The compressive stress-strain curve during the deformation in the SEM.
Figure 1
Figure 2
Figure 3
Figure 4
Figure 5

(a) Young’s modulus, $E$ (MPa)

(b) Plateau stress (kPa)

- **This study NFC foams**
- **Svagan et al. (2008, 2011)**
- **NFC/amylopectin foams**
- **Sehaqui et al. (2010a)**

Relative density, $\rho/\rho_s$ (kg/m$^3$)
Figure 6

pre-loading at 20% strain at zero load after unloading at 47% strain
Figure 6

(e)