Sample geometry dependency on the measured tensile properties of cellulose nanopapers

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HIGHLIGHTS

• Influence of test specimen geometries on the tensile properties of CNF and BC nanopapers is investigated.
• Tensile moduli of both CNF and BC nanopapers were not significantly influenced by test specimen geometries used.
• It is essential to use an independent strain measurement system to determine the tensile moduli of cellulose nanopapers.
• Tensile strength of both CNF and BC nanopapers were found to be significantly influenced by test specimen geometries.
• Fracture toughness test showed that $K_{IC}$, CNF nanopaper = 7.3 MPa m$^{1/2}$ and $K_{IC}$, BC nanopaper = 6.6 MPa m$^{1/2}$.

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ABSTRACT

Miniaturised test specimens are often used for the tensile testing of cellulose nanopapers as there are currently no standardised test geometries to evaluate their tensile properties. In this work, we report the influence of test specimen geometries on the measured tensile properties of plant-derived cellulose nanofibres (CNF) and microbially synthesised bacterial cellulose (BC) nanopapers. Four test specimen geometries were studied: (i) miniaturised dog bone specimen with 2 mm width, (ii) miniaturised rectangular specimen with 5 mm width, (iii) standard dog bone specimen with 5 mm width and (iv) standard rectangular specimen with 15 mm width. It was found that the tensile moduli of both CNF and BC nanopapers were not significantly influenced by the test specimen geometries if an independent strain measurement system (video extensometer) was employed. The average tensile strength of the cellulose nanopapers is also influenced by test specimen geometries. It was observed that the smaller the test specimen width, the higher the average tensile strength of the cellulose nanopapers. This can be described by the weakest link theory, whereby the probability of defects present in the cellulose nanopapers increases with increasing test specimen width. The Poisson's ratio and fracture resistance of CNF and BC nanopapers are also discussed.

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1. Introduction

Nanometre scale cellulose fibres, or nanocellulose, are emerging nano-reinforcement for polymers. The major driver for utilising nanocellulose as reinforcement is the possibility of exploiting the high tensile stiffness and strength of cellulose crystals [1]. Raman spectroscopy and X-ray diffraction have estimated the tensile moduli of a single nanocellulose fibre to be between 100 and 160 GPa [2–5]. The tensile strength of a single nanocellulose fibre was estimated to be 900 MPa based on experiments conducted on single elementary flax and hemp fibres [6]. More recently, Saito et al. [7] used ultrasound-induced fragmentation of nanocellulose fibres to estimate the tensile strength of a single 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO) oxidised nanocellulose fibre. The authors estimated the tensile strength of single wood- and tunicate-derived nanocellulose fibre to be 1.6 GPa and 3.2 GPa, respectively based on this method.

Nanocellulose can be produced via two approaches: top-down or bottom-up. In the top-down approach, lignocellulosic biomass such as wood pulp can be exposed to high intensity ultrasound [8] to isolate the cellulose nanofibres from fibre bundles or passed through stone grinders [9,10], high pressure homogenisers or microfluidisers [11,12] to fibrillate these fibres to the nanometre scale. This lignocellulosic biomass-derived nanocellulose is more commonly known as cellulose nanofibres1 (CNF). In the bottom-up approach, nanocellulose is produced by the fermentation of low molecular weight sugars using cellulose-producing bacteria, such as from the Acetobacter species [13]. Microbially synthesised cellulose, more commonly known as bacterial cellulose (BC), is secreted by the bacteria in the form of wet pellets (thick biofilm). BC is synthesised directly as nanofibres of approximately ~50 nm in diameter and several micrometres in length [13]. Nanocellulose can also be extracted from certain algae and tunicates [14].

A pre-requisite to producing high performance nanocellulose (CNF or BC) reinforced polymer composites is to incorporate high loadings of nanocellulose (typically ~30 vol%) into the polymer matrix [15]. In this context, high performance cellulose nanocarbons can be used directly as reinforcement for polymers. We have previously showed that BC- and CNF-reinforced epoxy composites with 49 vol% and 58 vol% nanocellulose loadings, respectively, can be manufactured by stacking sheets of cellulose nanocarbons together, followed by vacuum assisted resin infusion and cross-linking of the epoxy resin [16]. The resulting BC- and CNF-reinforced epoxy possessed tensile moduli and strengths of ~8 GPa and ~100 MPa, respectively. More recently, high performance BC-reinforced polylactide (PLA) nanocomposites with a laminated composite architecture were produced by laminating BC nanocarbons between two thin PLA films [17]. A BC nanocarbon loading of 65 vol% was achieved and the resulting composites possessed a tensile modulus and strength of 6.9 GPa and 125 MPa, respectively. The tensile properties of these cellulose nanocarbon-reinforced polymer composites, as well as cellulose nanocomposites fabricated by various researchers [15] were found to be governed predominantly by the tensile properties of the cellulose nanocarbon used, following closely the prediction of the volume-weighted average between the tensile properties of the cellulose nanocarbon and the polymer matrix:

\[
\sigma_{\text{nanocomposite}} = \sigma_{\text{nano-carbon}}v_I + \sigma_{\text{matrix}} \times (1-v_I)
\]

where \(\sigma_{\text{nano-carbon}}\) denote the tensile moduli of the cellulose nanocarbon-reinforced polymer nanocomposites, and \(\sigma_{\text{matrix}}\) denote the tensile strengths of the nanocomposites, cellulose nanocarbons and the matrix, respectively. Finally, \(v_I\) is the volume fraction of cellulose nanocarbons in the composites.

Various researchers have reported the tensile properties of cellulose nanocarbons (Table 1). It can be seen from this table that the reported density of cellulose nanocarbons varied between 0.72 and 1.61 g cm\(^{-3}\). This variation could be attributed to the differences in the grammage of cellulose nanocarbons, as well as the manufacturing process used to produce these cellulose nanocarbons. Furthermore, the tensile moduli cellulose nanocarbons reported in the literature vary between 1.4 GPa and 22.5 GPa and the tensile strength of cellulose nanocarbons vary between 23 MPa and 515 MPa, with various test specimen dimensions and geometries used. In addition to this, some studies employed an independent (video) strain measurement to monitor the strain experienced by the test specimens whilst others used a compliance correction method to back calculate the strain experienced by the test specimens. To the best of the authors’ knowledge, there are currently no standardised test methods for evaluating the tensile properties of cellulose nanocarbons. The most appropriate tensile test standards for cellulose nanocarbons is the test standards for papers and paperboards (such as BS EN ISO 1924 and TAPPI T494), which recommend rectangular tensile test specimens with dimensions of 180 mm between clamping lines and 15 mm width. Nevertheless, miniaturised tensile test specimens are still often used to quantify the tensile properties of cellulose nanocarbons, presumably due to difficulties in producing larger samples for tensile testing.

Cellulose network in the form of cellulose nanocarbons represents a conceptually important material structure [31] for various applications, including filtration membranes [52], packaging [53], electronics [54] and as nano-reinforcement for polymers [15]. Therefore, an accurate method for determining the mechanical properties of cellulose nanocarbons is of utmost importance. In this work, tensile tests were conducted on four different test specimen geometries for both BC and CNF nanocarbons to elucidate the influence of specimen geometry on the measured tensile properties of cellulose nanocarbons (at constant crosshead speed). The importance of an independent strain measurement of the test specimens is also discussed. An understanding of the influence of test specimen geometry on the measured tensile properties of cellulose nanocarbons is not only in the interpretation of the mechanical response but also in the design and optimisation of the mechanical properties of nanocellulose-reinforced polymer composites.

2. Experimental

2.1. Materials

CNF in the form of an aqueous gel with a consistency of 1.5 wt% was used in this work. To produce CNF, once-dried birch kraft pulp containing approximately 23% amorphous xylan was soaked at 2.2% consistency overnight and dispersed using a high-shear mixer (Dispermix, Ystral GmbH) for 10 min at 2000 rpm. This pulp suspension was then fed into a Masuko supermasscolloider (Masuko Sangyo Co., Kawaguchi, Japan) and passed through the grinder five times. BC was extracted from commercially available nata de coco cubes (Coconut gel in syrup, Xingsun Ltd., Lugang Township, Changhua County, Taiwan). These nata de coco cubes contain 2.5% BC (dry basis). Sodium hydroxide pellets (AnalaR NORMAPUR®, purity > 98.5%) were purchased from VWR International Ltd. (Lutterworth, UK).

2.2. Extraction and purification of BC

For each batch of 150 g of nata de coco, the cubes were first soaked and dispersed in 3.5 L of de-ionised water using a magnetic stirrer and heated to 80 °C. Once the desired temperature was achieved, 14 g of NaOH pellets were added into this dispersion to produce a 0.1 N
2.3. Manufacturing of cellulose nanopapers

The suspension was then centrifuged at 7000 rpm for 2 min to produce a homogeneous BC suspension. The BC suspension was then blended in another 5 L of de-ionised water using a kitchen blender (Breville VBL065) operating at maximum power output of 800 W for 2 min to produce a homogeneous BC suspension. The BC suspension was then left to stir for 2 h at 80 °C to remove any remaining microorganism or soluble polysaccharides. After this purification step, the suspension containing nata de coco cubes was poured onto a metal sieve (mesh size = 300 μm) to drain away the NaOH solution. The cubes were then rinsed with 5 L of de-ionised water using a kitchen blender (Breville VBL065) operating at maximum power output of 800 W for 2 min to produce a homogeneous BC suspension. The BC suspension was then centrifuged at 7000 rpm for 2 min to produce a homogeneous BC suspension. The concentration of the BC suspension was then adjusted to 0.5 wt% using 50% NaOH solution.

2.4. Characterisation of cellulose nanopapers

2.4.1. Porosity of the cellulose nanopapers

The true density (ρ) of BC and CNF was obtained using He pycnometry (Accupyc II 1340, Micromeritics Ltd., Hexton, UK) and wet pressed between two metal plates (Buckinghamshire, UK) and wet pressed between two metal plates (Buckinghamshire, UK) and wet pressed between two metal plates. The density of the BC and CNF nanopapers was produced by sandwiching the partially dried cellulose nanopapers between filter paper, and then heat consolidated at 120 °C over-night under a weight of 10 kg. The BC and CNF nanopapers produced were stored in sealed sample bags containing dried silica gel.

Table 1

| Nanopaper | Origin | $\rho$ (g cm$^{-3}$) | $l \times w$ (mm × mm) | $t$ (μm) | Testing speed (min$^{-1}$) | $E$ (GPa) | $\sigma$ (MPa) | $\varepsilon$ (%) |
|-----------|--------|----------------------|------------------------|--------|--------------------------|---------|-------------|-------------|
| BC        | A. aceti | 1.1 | 35 × 5 | 50 | 1 | 18 | 22.5$^a$ | 515$^a$ | 2.1 |
|           | A. xylinus | 1.1 | 35 × 5 | 50 | 1 | 18 | 22.5$^a$ | 515$^a$ | 2.1 |
|           | G. xylinus | 0.93 | 35 × 2$^b$ | 1 | 12 | 11 ± 1$^c$ | 320 ± 100 | 7.8 ± 0.6 |
|           | G. xylinus | 1.3 | 20 × 4 | 1 | 17 | 12 ± 1$^c$ | 215 ± 60 | 6.5 ± 1.0 |
|           | G. xylinus | 50 | 50 | 12 | 17 | 12 ± 1$^c$ | 320 ± 100 | 7.8 ± 0.6 |
|           | A. aceti | 0.93 | 35 × 2$^b$ | 1 | 12 | 11 ± 1$^c$ | 320 ± 100 | 7.8 ± 0.6 |
|           | G. xylinus | 1.61 | 35 × 2$^b$ | 1 | 9.5 ± 0.8$^d$ | 270 ± 10 | 6.2 ± 0.2 |
| CNF       | Kraft, Lodge pole pine | 0.9 | 35 × 5 | 1 | 17 | 12 ± 1$^c$ | 320 ± 100 | 7.8 ± 0.6 |
|           | Kraft, Silver birch | 0.93 | 35 × 2$^b$ | 1 | 12 | 11 ± 1$^c$ | 320 ± 100 | 7.8 ± 0.6 |
|           | Soda, Canola straw | 1.3 | 20 × 4 | 1 | 17 | 12 ± 1$^c$ | 320 ± 100 | 7.8 ± 0.6 |
|           | Soda, Spruce | 1.07 | 50 × 15 | 33 | 12 | 11 ± 1$^c$ | 320 ± 100 | 7.8 ± 0.6 |
|           | Kraft, Douglas fir | 1.53 | 20 × 3 | 60 | 1 | 17 | 12 ± 1$^c$ | 320 ± 100 | 7.8 ± 0.6 |
|           | Sulfite, Softwood | 1.14 | 60 × 5 | 200 | 1 | 17 | 12 ± 1$^c$ | 320 ± 100 | 7.8 ± 0.6 |
|           | Sulfite, Softwood | 1.34 | 60 × 6 | 70 | 1 | 17 | 12 ± 1$^c$ | 320 ± 100 | 7.8 ± 0.6 |
|           | Sulfite, Softwood | 40 × 5 | 60–80 | 1 | 17 | 12 ± 1$^c$ | 320 ± 100 | 7.8 ± 0.6 |
|           | Sulfite, Softwood | 50 × 15 | 40 | 5 | 17 | 12 ± 1$^c$ | 320 ± 100 | 7.8 ± 0.6 |
|           | Sulfite, Softwood | 1.28 | 60 × 5 | 60–80 | 1 | 17 | 12 ± 1$^c$ | 320 ± 100 | 7.8 ± 0.6 |
|           | Soda, Palm fruit | 0.97 | 100 × 10 | 100 | 10 | 17 | 12 ± 1$^c$ | 320 ± 100 | 7.8 ± 0.6 |
|           | Kraft, Bagasse | 0.93 | 35 × 2$^b$ | 1 | 12 | 11 ± 1$^c$ | 320 ± 100 | 7.8 ± 0.6 |
|           | Kraft, Hardwood | 320 × 5 | 65 | 1 | 17 | 12 ± 1$^c$ | 320 ± 100 | 7.8 ± 0.6 |
|           | Kraft, Softwood | 50 × 4$^a$ | 1 | 17 | 12 ± 1$^c$ | 320 ± 100 | 7.8 ± 0.6 |
|           | Kraft, Softwood | 1.47 | 30 × 4$^a$ | 1 | 17 | 12 ± 1$^c$ | 320 ± 100 | 7.8 ± 0.6 |
|           | Kraft, Silver birch | 0.93 | 35 × 2$^b$ | 1 | 12 | 11 ± 1$^c$ | 320 ± 100 | 7.8 ± 0.6 |
|           | Kraft, Almond shell | 38 × 5 | 70–90 | 3 | 17 | 12 ± 1$^c$ | 320 ± 100 | 7.8 ± 0.6 |
|           | Kraft, Spinifex | 25 × 6 | 1 | 17 | 12 ± 1$^c$ | 320 ± 100 | 7.8 ± 0.6 |
|           | Kraft, Spinifex | 30 × 5 | 1 | 17 | 12 ± 1$^c$ | 320 ± 100 | 7.8 ± 0.6 |
|           | Kraft, Spinifex | 50 × 15 | 5 | 17 | 12 ± 1$^c$ | 320 ± 100 | 7.8 ± 0.6 |
|           | Kraft, Peanut shell | 1.39 | 40 × 5 | 60–90 | 1 | 17 | 12 ± 1$^c$ | 320 ± 100 | 7.8 ± 0.6 |
|           | Kraft, Carrot | 20 × 5 | 80–100 | 2 | 17 | 12 ± 1$^c$ | 320 ± 100 | 7.8 ± 0.6 |
|           | Kraft, Jack pinecone | 10 × 3$^b$ | 1 | 17 | 12 ± 1$^c$ | 320 ± 100 | 7.8 ± 0.6 |
|           | Kraft, Poplar tree | 35 × 5 | 60 | 1 | 17 | 12 ± 1$^c$ | 320 ± 100 | 7.8 ± 0.6 |
|           | Kraft, Maple stalks | 20 × w | 8.8 ± 0.8 | 96 ± 3 | 17 | 12 ± 1$^c$ | 320 ± 100 | 7.8 ± 0.6 |

$^a$ Values estimated from figures.

$^b$ Dog bone shaped tensile test specimens.

$^c$ Tensile modulus determined from engineering strain of the test specimen.

$^d$ Tensile modulus determined from compliance correction.

$^e$ Tensile modulus determined from strain monitored using a non-contact (optical) extensometer.
measured on freeze-dried samples. Freeze-dried BC and CNF were produced by dispersing the previously prepared BC and CNF suspensions in Falcon tubes at a consistency of 0.05 wt% and flash frozen in liquid nitrogen prior to freeze-drying (Christ Alpha 1-2 LDplus, Newtown, UK). The envelope density ($\rho_e$) of BC and CNF nanopapers was determined using mercury intrusion porosimetry (Autopore IV 9500, Micromeritics Ltd., Hexton, UK) as it was found to be a suitable method to determine $\rho_e$ of cellulose nanopapers [55]. Prior to the measurement, BC and CNF nanopapers were dried at 80 °C overnight. With $\rho$ and $\rho_e$ known, the porosity ($P$) of the cellulose nanopapers can be calculated using the following equation:

$$P(\%) = \left(1 - \frac{\rho_e}{\rho}\right) \times 100$$  \hspace{1cm} (3)

2.4.2. Air resistance of the cellulose nanopapers

The air resistance of BC and CNF nanopapers was determined using a Gurley densometer equipped with an automated digital timer (Model 4150N & Model 4320, Gurley Precision Instruments, Troy, NY, USA). Circular test specimens of 1.5 in. (~3.8 cm) in diameter were cut and clamped between two rubber gasket O-rings located in the measuring chamber with a cross-sectional area of 1 in.$^2$ (~6.5 cm$^2$). The air resistance of the cellulose nanopapers was determined by measuring the time taken for 2.5 cm$^3$ of air to pass through the nanopapers at a pressure differential of 12.2 inH$_2$O (~3.0 kPa).

2.4.3. Tensile testing of cellulose nanopapers

4 different tensile test specimens were studied in this work (Fig. 1): (a) miniaturised dog bone shape, (b) miniaturised rectangular shape, (c) standard dog bone shape and (d) standard rectangular shape. The green dashed lines are the gauge length of the sample.

![Fig. 1. A schematic showing the 4 different tensile test specimen geometries used in this study. (a) miniaturised dog bone shape, (b) miniaturised rectangular shape, (c) standard dog bone shape and (d) standard rectangular shape. The green dashed lines are the gauge length of the sample.](image1)

| Nanopapers | $\rho$ (g cm$^{-3}$) | $\rho_e$ (g cm$^{-3}$) | $P$ (%) | Air resistance (s) |
|------------|----------------------|-----------------------|--------|---------------------|
| CNF        | 1.51 ± 0.01          | 1.37                  | 9.2    | >172800             |
| BC         | 1.51 ± 0.02          | 1.08                  | 28.6   | 12368 ± 4955        |

![Fig. 2. High resolution field emission scanning electron micrographs showing the morphology of (a) BC and (b) CNF nanofibres. Obtained from [16] with kind permission from ACS Publications.](image2)
specimens, potentially leading to earlier onset failure within the gripping zone of the test specimens. After securing the test specimens onto the testing cards, the exposed length of the miniaturised rectangular test specimens and standard rectangular test specimens were 25 mm and 50 mm, respectively.

Miniaturised tensile tests were carried out using a micro-tensile tester (Model MT-200, Deben UK Ltd., Woolpit, UK) equipped with a 200 N load cell. Tensile tests of the standard test specimens were performed using an Instron universal tester (Model 5969, Instron, High Wycombe, UK) equipped with a 1 kN load cell. Prior to the test, two points were marked in the axial and transverse directions on the surface of the test specimens, respectively. The strain of the test specimens was then monitored and recorded based on the movements of these marked points using a non-contacting video extensometer (iMetrum Ltd., Bristol, UK). The tensile tests were conducted at a crosshead displacement speed of 0.5 mm min$^{-1}$. Average results of 5 test specimens were reported for each type of sample geometry.

2.4.4. Fracture toughness of the nanopapers

The fracture toughness ($K_{IC}$) of BC and CNF nanopapers was obtained from single edge-notched specimens with dimensions of 25 mm in overall length ($L$) and 15 mm in width ($W$). An initial crack with length ($a$) was introduced at the centreline of the test specimen from the specimen’s edge using a sharp scalpel. The single edge-notched cellulose nanopapers were then loaded in tension using a micro-tensile tester equipped with a 200 N load cell. Prior to the test, two points were marked in the axial and transverse directions on the surface of the test specimens, respectively. The strain of the test specimens was then monitored and recorded based on the movements of these marked points using a non-contacting video extensometer (iMetrum Ltd., Bristol, UK). The tensile tests were conducted at a crosshead displacement speed of 0.5 mm min$^{-1}$. Average results of 5 test specimens were reported for each type of sample geometry.

2.4.5. Scanning electron microscopy (SEM)

The fracture surfaces of the test specimens from the fracture toughness test were characterised using a large chamber scanning electron microscope (S-3700N, Hitachi, Tokyo, Japan). An accelerating voltage of 15 kV was used. The samples were glued onto aluminium stubs and Au coated (Agar auto sputter coater, Agar Scientific, Stansted, UK) using a coating current of 40 mA for 1 min.

3. Results and discussion

The morphology (see Fig. 2) of BC and CNF nanopapers used in this work have been reported in a previous study of ours [16]. Both types of nanocellulose possess uniform fibre diameters of approximately 50 nm. The uniformity of BC nanofibres is not surprising as these nanofibres are synthesised in a well-controlled manner by the cellulose-producing bacteria. As for CNF, passing the starting kraft pulp through a high shear stone grinder (Masuko supermasscolloider) multiple times ensured that the resulting CNF possessed a uniform fibre diameter.

Table 2 summarises the density, porosity and air resistance of cellulose nanopapers manufactured in this work. The true density of CNF and BC was measured to be 1.51 g m$^{-3}$. BC nanopapers were also found to possess higher porosity compared to CNF nanopapers (Table 2). The higher porosity of BC nanopapers is postulated to be due to the inhomogeneous dispersion of BC in water prior to nanopaper production. Aggregates or bundles of BC can be observed in the BC suspension (Fig. 3a). This is a result of difficulties in disrupting the three-dimensional nanofibrous network of BC pellicles using a low energy blender. The CNF suspension, on the other hand, is more homogeneous. This leads to a more uniform formation of nanocellulose network within the CNF nanopaper compared to BC nanopaper (see Fig. 3b), forming a more
densely packed nanocellulose network in CNF nanopaper compared to BC nanopaper. Even though both the nanopapers were found to be porous, CNF nanopaper was found to be impermeable to air whilst 2.5 cm$^3$ of air passes through 1 in.$^2$ of BC nanopaper in ~12,000 s at a pressure differential of 12.2 in H$^2$O.

3.1. Influence of the sample geometry on the tensile modulus of nanopapers

Fig. 4 shows the representative stress–strain curves of CNF and BC nanopapers for each test specimen geometry studied in this work. The stress-strain behaviour of CNF and BC nanopapers are similar. When a cellulose nanopaper is loaded under tension, it exhibits an initial elastic behaviour followed by inelastic deformation with a clear brittle and catastrophic failure.

The measured tensile properties of the cellulose nanopapers are tabulated in Table 3. Overall, CNF nanopapers possessed slightly higher tensile moduli and strengths compared to BC nanopapers. Tensile moduli and strengths as high as 16.1 GPa and 182 MPa, respectively, were obtained for miniaturised dog bone test specimens of CNF nanopapers. For the same type of test specimen, the tensile modulus and strength of BC nanopapers was measured to be 15.2 GPa and 149 MPa, respectively. This slight difference in the measured tensile modulus and strength of CNF and BC nanopapers of the same test specimen geometry could be attributed to the higher porosity of BC nanopapers compared to CNF nanopapers.

From Table 3, it can also be seen that the tensile moduli of both CNF and BC nanopapers do not differ much between different tensile test specimen geometries. The tensile moduli of CNF and BC nanopapers varied (within errors) between 14.5 and 16.1 GPa and 13.4–15.2 GPa, respectively, between different test specimen geometries. The elastic modulus of conventional paper is a function of pulp fibre modulus, degree of fibre-fibre bonding and fibre length [57]. Similar concepts can also be applied to cellulose nanopapers. Within the same type of nanocellulose (either BC nanopapers or CNF nanopapers), the aforementioned attributes of the nanocellulose fibres and nanocellulose network are expected to be the same. As a result, the measured tensile moduli of cellulose nanopapers are not significantly affected by the different specimen geometries. It is worth mentioning at this point that the specific tensile moduli of BC nanopapers were found to be higher than CNF nanopapers. One possibility for this is the intrinsic modulus of BC nanofibres could be higher than CNF [15].

In our study, the strain of the test specimens was determined from a non-contact video extensometer. Herein, we also compare the calculated tensile moduli of the cellulose nanopapers if an independent strain measurement was not used (Table 3). In this context, the strain of the test specimens was obtained from the crosshead displacement recorded by the test machine divided by the initial defined gauge length of the test specimens. A significant discrepancy can be observed between the tensile moduli determined from an independent strain measurement and strain calculated from the crosshead displacement of the test machine. The tensile moduli calculated from the crosshead displacement of the test machine are consistently lower than that of the tensile moduli determined from an independent strain measurement. These values are also highly inconsistent, with tensile moduli values ranging between 6 and 13 GPa. Any mechanical system will deform, however slightly, when subjected to an applied force. These could include the frame of the test equipment, the load cell, the grips used etc. These deformations are known as the system compliance and could potentially lead to significant error in calculating the deformation of the test specimen. The crosshead displacement output recorded by the system is the sum of the test equipment compliance and test specimen deformation:

$$\frac{1}{\Delta L} = \frac{1}{C_f} + \frac{1}{E} \times \frac{l_c}{A}$$

Table 3. Tensile properties of CNF and BC nanopapers for different specimen geometries. $E$, $\sigma$, $\varepsilon$, and $\nu$ denote the tensile modulus, tensile strength, tensile index, strain-to-failure and Poisson’s ratio of the cellulose nanopapers, respectively.

| Test specimen geometry | $E$ (GPa) | $\sigma$ (MPa) | $\varepsilon$ (%) | $\nu$ | $C_s$ (M/m g$^2$) | $C_f$ (M/m g$^2$) | $\rho$ (g/m$^3$) |
|-----------------------|----------|---------------|------------------|------|----------------|----------------|-------------|
| CNF nanopapers        |          |               |                  |      |                |                |             |
| 10 mm dogbone         | 16.1 ± 0.7 | 11.8 ± 1.2 | 7.1 ± 0.7 | 182 ± 13 | 133 ± 13 | 131 ± 7 | 4.4 ± 1.7 |
|                       | 15.3 ± 0.5 | 10.6 ± 0.5 | 5.8 ± 0.8 | 168 ± 10 | 129 ± 10 | 127 ± 4 | 4.5 ± 0.3 |
| 20 mm dogbone         | 14.5 ± 0.5 | 10.5 ± 0.5 | 5.8 ± 0.8 | 168 ± 10 | 129 ± 10 | 127 ± 4 | 4.5 ± 0.3 |
| 30 mm dogbone         | 13.4 ± 0.5 | 10.5 ± 0.5 | 5.8 ± 0.8 | 168 ± 10 | 129 ± 10 | 127 ± 4 | 4.5 ± 0.3 |
| BC nanopapers         |          |               |                  |      |                |                |             |
| 10 mm dogbone         | 15.2 ± 0.7 | 14.1 ± 1.2 | 7.2 ± 0.7 | 149 ± 13 | 138 ± 13 | 110 ± 4 | 2.7 ± 0.6 |
|                       | 14.3 ± 1.1 | 13.2 ± 1.1 | 10.9 ± 1.1 | 147 ± 16 | 136 ± 16 | 116 ± 5 | 3.6 ± 0.9 |
| 20 mm dogbone         | 13.4 ± 1.5 | 12.4 ± 1.1 | 6.2 ± 0.6 | 138 ± 15 | 128 ± 15 | 111 ± 2 | 2.7 ± 0.4 |
| 30 mm dogbone         | 14.3 ± 1.4 | 13.2 ± 1.1 | 11.1 ± 3.4 | 143 ± 14 | 130 ± 14 | 111 ± 7 | 2.4 ± 0.4 |

a Tensile modulus determined using a non-contact video extensometer.

b Tensile modulus determined from the cross-head displacement of the testing machine.
where \( \frac{dF}{dl} \) is the slope of the recorded load–displacement curve, \( C_f \) is the compliance of the test equipment, \( L_i \) is the initial gauge length and \( A \) is the cross-sectional area of the test specimen, respectively. The derivation of this equation can be found in the supplementary information. From this equation, it can be inferred that unless the test equipment is infinitely stiff (\( C_f \rightarrow \infty \)), the tensile modulus of a test specimen calculated from the crosshead displacement of the test equipment is prone to errors.

3.2. Influence of the sample geometry on the tensile strength of nanopapers

The tensile strength (\( \tau_{\text{max}} \)) as well as the tensile index (\( \tau_{\text{index}} \)), which represent the maximum force per unit width and grammage of the manufactured CNF and BC nanopapers, are also summarised in Table 3. A tensile strength of 182 MPa was measured for CNF nanopaper on miniaturised dog bone test specimen. When miniaturised rectangular test specimens or standard dog bone test specimens were used, the measured tensile strength decreased to \( \sim 165 \) MPa. It should be noted that for both of these geometries, the width of the test specimens was the same (5 mm). When standard rectangular test specimens with a width of 15 mm were used, the measured tensile strength decreases to 157 MPa. When the width of BC nanopaper test specimen was increased from 2 mm to 15 mm, the measured tensile strength decreased by 20% from 149 MPa to 120 MPa. The tensile indices of the CNF and BC nanopapers also followed the same trend as the tensile strengths of CNF and BC nanopapers. The observed decrease in average tensile strength (and tensile index) of cellulose nanopaper when test specimen width was increased can be explained by the weakest link theory proposed (and tensile index) of cellulose nanopaper when test specimen width was increased can be explained by the weakest link theory proposed by Freudenthal [58]. The tensile failure of cellulose nanopapers is a result of local deformation in a weak spot or an area with lower density within the cellulose nanopapers. An increase in test specimen width increases the probability of the presence of a defect, such as the presence of agglomerates of nanofibres or pores, responsible for lowering the tensile strength of cellulose nanopapers. This is consistent with the lower strain at failure of both CNF and BC nanopapers when the width of the test specimen was 15 mm. It should also be noted that decrease in the tensile strength of CNF nanopaper is within the standard deviation of the measurements but this is not the case for BC nanopaper. This is postulated to be due to CNF nanopapers possessing lower porosity and to the better formation of the nanocellulose network compared to BC nanopapers, which implies that the specimens are less prone to defects.

![Graph](image)

**Fig. 5.** Representative load (\( F \)) – displacement (\( d \)) curves of the single edge notched BC and CNF nanopaper samples loaded under tension.

3.3. Influence of test specimen geometry on the Poisson’s ratio of nanopapers

In Table 3, we also report the Poisson’s ratios of cellulose nanopapers tested in tension. The Poisson’s ratios of CNF and BC nanopapers were found to be \(-0.30\) and \(-0.10\), respectively. Poisson’s ratio is a function of the packing of the structural elements and is closely related to the ratio between bulk and shear moduli of the nanofibre network [59]. The higher the ratio between the bulk and shear moduli, the higher the Poisson’s ratio of the resulting nanofibre network. As a result, the less porous CNF nanopapers possessed higher Poisson’s ratio compared to the more porous BC nanopapers. In addition to this, the bulk and shear moduli of the nanofibre network are expected to be the same within the same type of nanocellulose fibres and nanofibre network. Therefore, the Poisson’s ratio of the cellulose nanopapers is independent of test specimen geometry used.

3.4. Fracture resistance of cellulose nanopapers

Although defects within a cellulose nanopaper could be minimised, for example, by improving the processing parameters for nanopaper manufacturing, it is highly unlikely that they could be completely eliminated. It is therefore desirable to quantify the fracture resistance of BC and CNF nanopapers. Single edged-notched BC and CNF nanopapers were tested in tension and the representative load–displacement curves are shown in Fig. 5. The initial linear part of the load–displacement curves correspond to the strain potential energy stored in the cellulose nanopaper when a load was applied. When the applied load was high enough to create a new surface area, the introduced crack started to propagate until the test specimen failed catastrophically.

The critical stress intensity factors (\( K_{\text{IC}} \)) of CNF and BC nanopapers are tabulated in Table 4. The higher \( K_{\text{IC}} \) values of CNF nanopapers (7.3 MPa m\(^{1/2}\)) compared to BC nanopapers (6.6 MPa m\(^{1/2}\)) can be attributed to the lower intrinsic porosity of CNF nanopapers (\(-10\%) compared to BC nanopapers (\(-30\%). It is worth mentioning that the measured \( K_{\text{IC}} \) values of both BC and CNF nanopapers are comparable to that of the fracture toughness of single edge notched aramid fibres [60]. The fracture surfaces of the single edge notched cellulose nanopapers are shown in Fig. 6. Two very different fracture morphologies can be observed. Crack propagates along the path of the least resistance. In the case of CNF nanopaper, the crack is hypothesised to propagate along the brittle hemicellulose [61]. Our CNF contains approximately 23% hemicellulose content. As BC nanopaper is pure nanocellulose without the presence of hemicellulose, crack can only propagate by the defibrillation of the nanocellulose network. As a result, the fracture surface of the single edged-notched BC nanopapers showed significant defibrillation, which suggests fibre-fibre debonding during crack propagation. This was not observed in the fracture surface of single edged-notched CNF nanopaper.

In addition to this, single edge-notched CNF nanopapers failed catastrophically when maximum load was reached whilst the single edge-notched BC nanopapers showed a delayed catastrophic failure (see Fig. 5). In fact, single edge-notched BC nanopapers took \(-20\) s for the complete fracture of the specimens when peak force was reached (Table 4). CNF nanopapers, on the other hand, fractured immediately when peak force was reached. This can be attributed to the differences in homogeneity of CNF and BC nanopapers. When the crack front encounters inhomogeneity in the areal density of nanocellulose across the through thickness of BC nanopapers locally, it propagates faster in the region of lower areal density as there are less fibre-fibre bonds in this region. As a result, the test specimen could still sustain load (albeit

| Sample      | \( K_{\text{IC}} \) (MPa m\(^{1/2}\)) | \( t \) (s) |
|-------------|-----------------------------------|------------|
| CNF nanopaper | 7.3 ± 0.3                         | 0.7 ± 0.2  |
| BC nanopaper  | 6.6 ± 0.2                         | 19.8 ± 5   |
lower) as the displacement of the single edge-notched test specimen increased, delaying the catastrophic failure of the BC nanopaper. It is also postulated that BC possessed longer nanofibre length compared to CNF, leading to the observed difference in fracture behaviour of the cellulose nanopapers.

4. Conclusions

The influence of test specimen geometries on the measured tensile properties of CNF and BC nanopapers was studied in this work. Overall, the tensile moduli ($E$) and strengths ($\sigma$) of CNF nanopapers were found to be higher than that of BC nanopapers (CNF nanopaper: $E = 16.1$–$14.5$ GPa, $\sigma = 182$–$157$ MPa and BC nanopaper: $E = 15.2$–$13.4$ GPa, $\sigma = 149$–$120$ MPa). This is attributed to the lower porosity of CNF nanopaper (~10%) compared to BC nanopapers (~30%) manufactured in this work. The tensile moduli (calculated from the strain of the test specimens determined from a non-contact video extensometer) of both CNF and BC nanopapers were not strongly dependent on the geometry of the tensile test specimen used. However, if test specimen strain was calculated from the crosshead displacement of the test machine divided by the initial defined gauge length of the test specimen, the tensile moduli was found to be consistently lower than that determined from the non-contact video extensometer. This difference is a result of the compliance of the test equipment and emphasises the importance of using an independent strain measurement when performing tensile testing of cellulose nanopapers.

The average tensile strength of cellulose nanopapers was the highest when the test was conducted on miniaturised dog bone test specimens with 2 mm (CNF nanopaper: $\sigma = 182$ MPa, BC nanopaper: $\sigma = 129$ MPa). The average tensile strength of CNF and BC nanopapers decreased when the tensile test specimen width increased to 15 mm. This is due to the fact that wider test specimens are more prone to defects or flaws. CNF nanopapers was also found to possess higher Poisson’s ratio compared to BC nanopapers (~0.3 for CNF nanopapers and ~0.1 for BC nanopapers). This is a result of the lower porosity of CNF nanopaper (~10%) compared to BC nanopapers (~30%).

This is due to the fact that wider test specimens are more prone to defects or flaws. CNF nanopapers was also found to possess higher Poisson’s ratio compared to BC nanopapers (~0.3 for CNF nanopapers and ~0.1 for BC nanopapers). This is a result of the lower porosity of CNF nanopaper (~10%) compared to BC nanopapers (~30%).

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Appendix A. Supplementary data

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References

[1] S.J. Eichhorn, C. Baillie, N. Zafeiropoulos, L.Y. Mwaikambo, M.P. Ansell, A. Dufresne, K.M. Entwistle, P.J. Herrera-Franco, G.C. Escamilla, L. Groom, M. Hughes, C. Hill, T.G. Rials, P. Wild, Review: current international research into cellulosic fibres and composites, J. Mater. Sci. 36 (2001) 2107–2131, http://dx.doi.org/10.1023/A:1017512052969.
[2] Y.C. Hsieh, H. Yano, M. Nogi, S.J. Eichhorn, An estimation of the Young’s modulus of bacterial cellulose filaments, Cellulose 15 (2008) 507–513, http://dx.doi.org/10.1007/s10570-008-9206-6.
[3] I. Sakurada, Y. Nukushima, T. Ito, Experimental determination of elastic modulus of crystalline regions in oriented polymers, J. Polym. Sci. 57 (1962) 651–660, http://dx.doi.org/10.1002/pol.1962.1205716551.
[4] M. Matsson, C. Sawatari, Y. Iwai, F. Ozaki, Effect of orientation distribution and crystallinity on the measurement by X-ray-diffraction of the crystal-lattice moduli of cellulose-I and cellulose-II, Macromolecules 23 (1990) 3266–3275, http://dx.doi.org/10.1021/ma00215a012.
[5] A. Rusli, S.J. Eichhorn, Determination of the stiffness of cellulose nanowhiskers and the fiber-matrix interface in a nanocomposite using Raman spectroscopy, Appl. Phys. Lett. 93 (2008) 033111, http://dx.doi.org/10.1063/1.2963491.
[6] S.A. Wainwright, W.D. Biggs, J.D. Curry, J.M. Gosline, Mechanical Design in Organisms, Princeton University Press, 1982.
[7] T. Saito, R. Kuramae, J. Wohlert, L.A. Berglund, A. Isogai, An ultrastrong nanofibrillar biomaterial: the strength of single cellulose nanofibrils revealed via sonication-induced fragmentation, Biomacromolecules 14 (2013) 248–253, http://dx.doi.org/10.1021/bm301674x.
[8] K. Wuhrmann, A. Heuberger, K. Mühlethaler, Elektronenmikroskopische Untersuchungen an Zellulosefasern nach Behandlung mit Ultraschall, Experientia 2 (1946) 105–107.
[9] T. Taniguchi, K. Okamura, New films produced from microfibrillated natural fibres, Polym. Int. 47 (1998) 291–294, http://dx.doi.org/10.1002/(SICI)1097-0266(199811)47:3<291::AID-POLI116>3.0.CO;2-1.
[10] P. Lahtinen, S. Liukkonen, J. Pere, A. Sneck, H. Kangas, A comparative study of fibrillated fibers from different mechanical and chemical pulps, BioResources 9 (2014) 2115–2127, http://dx.doi.org/10.15376/biores.9.2.2115-2127.
[11] F.W. Herrick, R.L. Casebier, J.K. Hamilton, K.R. Sandberg, In: A. Sarko (Ed.), Microfibrillated Cellulose: Morphology and Accessibility, Wiley 1983, pp. 797–813.
[12] A.F. Turbak, F.W. Snyder, K.R. Sandberg, Microfibrillated cellulose, a new cellulose product: properties, uses, and commercial potential, J. Appl. Polym. Sci.: Appl. Polym. Symp. 37 (1983) 815–827.
[13] K.Y. Lee, G. Baldum, A. Mantalaris, A. Bismarck, More than meets the eye in bacterial cellulose: biosynthesis, bioprocessing, and applications in advanced fiber composites, Macromol. Biosci. 14 (2014) 10–22, http://dx.doi.org/10.1002/mabi.201300288.
[14] D. Klein, F. Kramer, S. Moritz, T. Lindstrom, M. Akerfors, D. Gray, A. Dorris, Nanocelluloses: a new family of nature-based materials, Angew. Chem. Int. Ed. 50 (2011) 5438–5466, http://dx.doi.org/10.1002/anie.201001273.
[15] K.-Y. Lee, Y. Aitomäki, L.A. Berglund, K. Oksman, A. Bismarck, On the use of nanocelluloses as reinforcement in polymer matrix composites, Compos. Sci. Technol. 105 (2014) 15–27, http://dx.doi.org/10.1016/j.compscitech.2014.08.032.
[16] K.-Y. Lee, T. Tamminen, K. Schuller, H. Klikskinen, J. Samela, A. Bismarck, High performance cellulose nanocomposites: comparing the reinforcing ability of bacterial cellulose and nanofibrillated cellulose, ACS Appl. Mater. Interfaces 4 (2012) 4078–4086, http://dx.doi.org/10.1021/am300852a.
[17] T. Montrikittiphan, M. Tang, K.Y. Lee, C.K. Williams, A. Bismarck, Bacterial cellulose nanopaper as reinforcement for polylactide composites: renewable thermoplastic
