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 are 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$^{1/2}$.

GRAPHICAL ABSTRACT

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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 nanoscale. 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 nanocellulose 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 nanopapers 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 was produced by laminating BC nanopaper between two thin PLA films [17]. A BC nanopaper 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 nanolaminate-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 nanopaper, followed closely the prediction of the volume-weighted average between the tensile properties of the cellulose nanopaper and the polymer matrix:

\[ E_{\text{nano-composite}} = E_{\text{nanopaper}}V_f + E_{\text{matrix}} \times (1-v_f) \] (1)

\[ \sigma_{\text{nano-composite}} = \sigma_{\text{nanopaper}}V_f + \sigma_{\text{matrix}} \times (1-v_f) \] (2)

where \( E_{\text{nano-composite}} \), \( E_{\text{nanopaper}} \) and \( E_{\text{matrix}} \) denote the tensile moduli of the cellulose nanopaper-reinforced polymer nanocomposites, cellulose nanopaper and matrix, respectively. The terms \( \sigma_{\text{nano-composite}}, \sigma_{\text{nanopaper}} \) and \( \sigma_{\text{matrix}} \) denote the tensile strengths of the nanocomposites, cellulose nanopaper and the matrix, respectively. Finally, \( V_f \) is the volume fraction of cellulose nanopaper in the composites.

Various researchers have reported the tensile properties of cellulose nanomaterials (Table 1). It can be seen from this table that the reported density of cellulose nanopapers varied between 0.72 and 1.61 g cm\(^{-3}\). This variation could be attributed to the differences in the grammage of cellulose nanopapers, as well as the manufacturing process used to produce these cellulose nanopapers. Furthermore, the tensile moduli of cellulose nanopapers reported in the literature vary between 1.4 GPa and 22.5 GPa and the tensile strength of cellulose nanopapers 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 whereas 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 nanopapers. The most appropriate tensile test standards for cellulose nanopapers are 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 nanopapers, presumably due to difficulties in producing larger samples for tensile testing.

Cellulose network in the form of cellulose nanofibres 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 nanopapers is of utmost importance. In this work, tensile tests were conducted on four different test specimen geometries for both BC and CNF nanopapers to elucidate the influence of specimen geometry on the measured tensile properties of cellulose nanopapers (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 nanofibers 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, Xiangsun Ltd., Lugang Township, Changhua County, Taiwan). These nata de coco cubes contain 2.5 wt% BC (dry basis). Sodium hydroxide pellets (Analar NORMAPUR®, purity > 98.8%) 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 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 nata de coco cubes were then rinsed with 5 L of de-ionised water to remove any residual NaOH on the surface of the cubes. After rinsing, the cubes were then blended in another 5 L of de-ionised water to remove any remaining microorganism or soluble polysaccharides. After this purification step, the suspension containing nata de coco cubes was filtered onto a 125 mm diameter filter paper (Grade 413, 5–13 μm particle retention, VWR International Ltd). The wet nanocellulose filter cake was carefully removed from the wet and used filter paper, and sandwiched between two fresh filter papers, followed by two more blotting papers (Grade 3MM CHR, GE Healthcare, Buckinghamshire, UK) and wet pressed between two metal plates (mean particle retention, VWR International Ltd). The wet filter cake was carefully removed from the wet and filter papers, and heat consolidated at 120 °C overnight under a weight of 10 kg. The BC and CNF nanopapers produced were stored in sealed sample bags containing dried silica gel.

2.3. Manufacturing of cellulose nanopapers

To produce BC and CNF nanopapers with grammage of 50 g m⁻², homogeneous nanocellulose suspensions were first produced by blending the nanocellulose for 3 min at consistency of 0.1 wt%, followed by vacuum filtration onto a 125 mm diameter filter paper (Grade 413, 5–13 μm particle retention, VWR International Ltd). The wet nanocellulose filter cake was carefully removed from the wet and used filter paper, and sandwiched between two fresh filter papers, followed by two more blotting papers (Grade 3MM CHR, GE Healthcare, Buckinghamshire, UK) and wet pressed between two metal plates under a weight of 10 kg at room temperature for 10 min. This wet pressing step was repeated once more with fresh filter and blotting papers to further absorb water from the wet nanocellulose filter cake. Cellulose nanopapers were produced by sandwiching the partially dried nanocellulose filter cake from the 2nd wet pressing step between fresh filter and blotting papers, and heat consolidated at 120 °C overnight under a weight of 10 kg. The BC and CNF nanopapers produced were stored in sealed sample bags containing dried silica gel.

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)

Table 1

<table>
<thead>
<tr>
<th>Nanopaper</th>
<th>Origin</th>
<th>ρ (g cm⁻³)</th>
<th>l × w (min × mm)</th>
<th>t (µm)</th>
<th>Testing speed (min⁻¹)</th>
<th>E (GPa)</th>
<th>σ (MPa)</th>
<th>ε (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC</td>
<td>A. aceti</td>
<td>1.1</td>
<td>35 × 5</td>
<td>50</td>
<td>1</td>
<td>18</td>
<td>231</td>
<td>2.1</td>
<td>[18]</td>
</tr>
<tr>
<td>A. xylinus</td>
<td>1.64</td>
<td>30 × 1</td>
<td>7</td>
<td>0.5</td>
<td>1</td>
<td>9.7 ± 2.1</td>
<td>240 ± 87</td>
<td>2.6 ± 0.5</td>
<td>[2]</td>
</tr>
<tr>
<td>G. xylinus</td>
<td>0.72</td>
<td>30 × 2³</td>
<td>79</td>
<td>1</td>
<td>1</td>
<td>12 ± 1.1</td>
<td>123 ± 7</td>
<td>7.5 ± 0.6</td>
<td>[16]</td>
</tr>
<tr>
<td></td>
<td>1.3</td>
<td>20 × 4</td>
<td>1</td>
<td>1</td>
<td>1.3 ± 1.2</td>
<td>185 ± 18</td>
<td>6.5 ± 1</td>
<td></td>
<td>[21]</td>
</tr>
<tr>
<td>A. aceti</td>
<td>1.61</td>
<td>20 × 5</td>
<td>40–60</td>
<td>2</td>
<td>9.3 ± 0.7</td>
<td>449 ± 22</td>
<td>10.3 ± 0.6</td>
<td></td>
<td>[23]</td>
</tr>
<tr>
<td>G. xylinus</td>
<td>0.95</td>
<td>35 × 2³</td>
<td>1</td>
<td>1</td>
<td>9.5 ± 0.8d</td>
<td>270 ± 10</td>
<td>6.2 ± 0.2</td>
<td></td>
<td>[17]</td>
</tr>
<tr>
<td>CNF</td>
<td>Kraft, Lodge pole pine</td>
<td>0.9</td>
<td>35 × 5</td>
<td>20</td>
<td>0.6</td>
<td>9.4 ± 0.3</td>
<td>192 ± 14</td>
<td>3.1 ± 0.4</td>
<td>[26]</td>
</tr>
<tr>
<td>Kraft, Silver birch</td>
<td>0.93</td>
<td>35 × 2³</td>
<td>1</td>
<td></td>
<td>10²</td>
<td>140²</td>
<td></td>
<td></td>
<td>[19]</td>
</tr>
<tr>
<td>Soda, Canola straw</td>
<td>1.3</td>
<td>20 × 4</td>
<td>1</td>
<td></td>
<td>12.8 ± 1.4d</td>
<td>103 ± 13</td>
<td>4.2 ± 0.4</td>
<td></td>
<td>[20]</td>
</tr>
<tr>
<td>Soda, Spruce</td>
<td>1.07</td>
<td>50 × 15</td>
<td>33</td>
<td>1</td>
<td>13.6 ± 1.0</td>
<td>114 ± 8</td>
<td>5.7 ± 1</td>
<td></td>
<td>[21]</td>
</tr>
<tr>
<td>Kraft, Douglas fir</td>
<td>1.53</td>
<td>20 × 3</td>
<td>60</td>
<td>1</td>
<td>13</td>
<td>223</td>
<td></td>
<td></td>
<td>[28]</td>
</tr>
<tr>
<td>Sulfitte, Softwood</td>
<td>1.14</td>
<td>60 × 5</td>
<td>200</td>
<td></td>
<td>13</td>
<td>180</td>
<td>2.1</td>
<td></td>
<td>[29]</td>
</tr>
<tr>
<td>Sulfitte, Softwood</td>
<td>1.34</td>
<td>60 × 6</td>
<td>70</td>
<td></td>
<td>14</td>
<td>104</td>
<td>2.6</td>
<td></td>
<td>[30]</td>
</tr>
<tr>
<td>Sulfitte, Softwood</td>
<td>0.36</td>
<td>40 × 5</td>
<td>60–80</td>
<td>5</td>
<td>13.2 ± 0.6c</td>
<td>214 ± 7</td>
<td>10.1 ± 1.4</td>
<td></td>
<td>[31]</td>
</tr>
<tr>
<td>Sulfitte, Softwood</td>
<td>1.34</td>
<td>50 × 15</td>
<td>40</td>
<td>5</td>
<td>13.4 ± 0.3c</td>
<td>232 ± 19</td>
<td>5 ± 1.1</td>
<td></td>
<td>[32]</td>
</tr>
<tr>
<td>Sulfitte, Softwood</td>
<td>1.28</td>
<td>60 × 5</td>
<td>60–80</td>
<td>5</td>
<td>9.9 ± 0.2</td>
<td>175 ± 2</td>
<td>8.5 ± 0.5</td>
<td></td>
<td>[33]</td>
</tr>
<tr>
<td>Soda, Palm fruit</td>
<td>0.97</td>
<td>75 × 5</td>
<td>60</td>
<td>5</td>
<td>17.9 ± 1.2</td>
<td>137 ± 7</td>
<td>0.4 ± 0.1</td>
<td></td>
<td>[34]</td>
</tr>
<tr>
<td>Kraft, Bagasse</td>
<td>62.5</td>
<td></td>
<td>100 × 10</td>
<td>100</td>
<td>10⁴</td>
<td>135⁴</td>
<td></td>
<td></td>
<td>[35]</td>
</tr>
<tr>
<td>Kraft, Hardwood</td>
<td>112 ± 2.3</td>
<td>230 × 23</td>
<td>72 ± 2.1</td>
<td></td>
<td>10³</td>
<td>131 ± 17</td>
<td></td>
<td></td>
<td>[36]</td>
</tr>
<tr>
<td>Kraft, Softwood</td>
<td>8.5⁴</td>
<td>95</td>
<td>4³</td>
<td></td>
<td>10³</td>
<td>131 ± 17</td>
<td></td>
<td></td>
<td>[37]</td>
</tr>
<tr>
<td>Kraft, Softwood</td>
<td>1.15</td>
<td>30 × 4⁴</td>
<td>1</td>
<td></td>
<td>11.5 ± 0.7</td>
<td>158 ± 16</td>
<td>2.1 ± 0.5</td>
<td></td>
<td>[38]</td>
</tr>
<tr>
<td>Kraft, Softwood</td>
<td>1.47</td>
<td>50 × 5</td>
<td>200</td>
<td>2</td>
<td>1.4 ± 0.2³</td>
<td>23 ± 13</td>
<td>2.6 ± 0.3</td>
<td></td>
<td>[40]</td>
</tr>
<tr>
<td>Kraft, Almond shell</td>
<td>38 ± 5</td>
<td>70–90</td>
<td>3</td>
<td></td>
<td>5.3 ± 0.3</td>
<td>65 ± 3</td>
<td>4.2 ± 0.2</td>
<td></td>
<td>[42]</td>
</tr>
<tr>
<td>Kraft, Spinifex</td>
<td>25 ± 6</td>
<td></td>
<td>84 ± 5</td>
<td>1</td>
<td>3.2 ± 0.2</td>
<td>84 ± 5</td>
<td>18 ± 0.2</td>
<td></td>
<td>[43]</td>
</tr>
<tr>
<td>Kraft, 38 × 5</td>
<td>149 ± 0.7</td>
<td>243 ± 16</td>
<td>6 ± 0.2</td>
<td></td>
<td>14.5 ± 0.8d</td>
<td>243 ± 16</td>
<td>6 ± 0.2</td>
<td></td>
<td>[44]</td>
</tr>
<tr>
<td>Kraft, Canola straw</td>
<td>0.97</td>
<td>145</td>
<td>100</td>
<td>1</td>
<td>14.5³</td>
<td>132³</td>
<td>5.5³</td>
<td></td>
<td>[45]</td>
</tr>
<tr>
<td>Kraft, Silver birch</td>
<td>1.39</td>
<td>40 × 5</td>
<td>60–90</td>
<td>1</td>
<td>18.5 ± 1.5</td>
<td>130 ± 12</td>
<td>4.5 ± 1</td>
<td></td>
<td>[46]</td>
</tr>
<tr>
<td>Kraft, Peanut shell</td>
<td>1.39</td>
<td>40 × 5</td>
<td>60–90</td>
<td>1</td>
<td>23 ± 1.3</td>
<td>243 ± 28</td>
<td>8.7 ± 0.7</td>
<td></td>
<td>[47]</td>
</tr>
<tr>
<td>Kraft, Carrot</td>
<td>10 × 3³</td>
<td>17³</td>
<td>273³</td>
<td></td>
<td>9.3 ± 0.8</td>
<td>273³</td>
<td></td>
<td></td>
<td>[48]</td>
</tr>
<tr>
<td>Kraft, Poplar tree</td>
<td>35 × 5</td>
<td>60</td>
<td>1</td>
<td></td>
<td>18.3</td>
<td>147</td>
<td>0.9</td>
<td></td>
<td>[49]</td>
</tr>
<tr>
<td>Kraft, Maize stalks</td>
<td>20 × w</td>
<td>8.8 ± 0.8</td>
<td>96 ± 3</td>
<td></td>
<td>2.3 ± 0.3</td>
<td></td>
<td></td>
<td></td>
<td>[50]</td>
</tr>
</tbody>
</table>

Notes:

- **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, Newtontown, 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:

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

### Table 2

<table>
<thead>
<tr>
<th>Nanopapers</th>
<th>$\rho$ (g cm$^{-3}$)</th>
<th>$\rho_e$ (g cm$^{-3}$)</th>
<th>$P$ (%)</th>
<th>Air resistance (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNF</td>
<td>1.51 ± 0.01</td>
<td>1.37</td>
<td>9.2</td>
<td>&gt;172800</td>
</tr>
<tr>
<td>BC</td>
<td>1.51 ± 0.02</td>
<td>1.08</td>
<td>28.6</td>
<td>12368 ± 4955</td>
</tr>
</tbody>
</table>

#### 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.](image)

Our preliminary results (data not presented here) showed that preparing the test specimens using a razor or scalpel blade could induce defects on the edges of the test specimens, leading to lower measured tensile properties of the samples. Therefore, all the test specimens were cut using a manual cutting press (ZCP020, Zwick Testing Machines Ltd., Herefordshire, UK) equipped with the appropriate geometry of cutting die. Prior to the test, all the test specimens were secured onto paper testing cards (140 g m$^{-2}$) using a two-part cold curing epoxy resin (Araldite 2011, Huntsman Advanced Materials, UK). This was to avoid the clamps of the tensile tester from damaging the ends of the test specimens.

![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.](image)
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 of $a$ 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 at a crosshead displacement speed of 0.5 mm min$^{-1}$. The initial crack length ($a$) was maintained between 3.1 and 4.3 mm to ensure that the ratio between initial crack length and test specimen width ($a/w$) remained between 0.2 and 0.29. This was to maximise the efficiency of the function $Y$ (Eq. (5)) [56].

$$Y = 1.99 - 0.41 \frac{a}{w} + 18.7 \left(\frac{a}{w}\right)^2 - 38.48 \left(\frac{a}{w}\right)^3 + 53.85 \left(\frac{a}{w}\right)^4$$

The fracture toughness, $K_{ic}$, of the cellulose nanopapers was calculated from the maximum stress ($\sigma_{max}$) when crack propagation occurred using the following Eq. (4):

$$K_{ic} = Y \sigma_{max} a^{3/2}$$

where $Y$ is [56]:

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

Fig. 3. (a) 0.1 wt% CNF and BC dispersed in water and (b) the homogeneity of produced BC and CNF nanopapers.

Fig. 4. Representative stress-strain curves of CNF and BC nanopapers for 4 different test specimen geometries.

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.

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The fracture toughness, $K_{ic}$, of the cellulose nanopapers was calculated from the maximum stress ($\sigma_{max}$) when crack propagation occurred using the following Eq. (4):

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where $Y$ is [56]:

$$Y = 1.99 - 0.41 \frac{a}{w} + 18.7 \left(\frac{a}{w}\right)^2 - 38.48 \left(\frac{a}{w}\right)^3 + 53.85 \left(\frac{a}{w}\right)^4$$

The initial crack length ($a$) was maintained between 3.1 and 4.3 mm to ensure that the ratio between initial crack length and test specimen width ($a/w$) remained between 0.2 and 0.29. This was to maximise the efficiency of the function $Y$ (Eq. (5)) [56].

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.

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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 inH$^2$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 CNF 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 non-contact video extensometer. 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:

$$\frac{1}{C_s} + \frac{1}{E} \times \frac{L_c}{A}$$

Table 3: Tensile properties of CNF and BC nanopapers for different specimen geometries. $E$, $\sigma_{max}$, $\epsilon$, and $\nu$ denote the tensile modulus, tensile strength, tensile index, strain-to-failure and Poisson's ratio of the cellulose nanopapers, respectively.

<table>
<thead>
<tr>
<th>Test specimen geometry</th>
<th>$E$ (GPa)</th>
<th>$\sigma_{max}$ (MPa)</th>
<th>$\epsilon$ (%)</th>
<th>$\nu$</th>
<th>$\rho$ (g cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNF nanopapers</td>
<td>16±1</td>
<td>11.8±0.7</td>
<td>5.8±0.8</td>
<td>4.5±0.3</td>
<td>0.3±0.08</td>
</tr>
<tr>
<td></td>
<td>15.3±0.5</td>
<td>10.9±0.5</td>
<td>4.5±0.5</td>
<td>3.5±0.2</td>
<td>0.11±0.05</td>
</tr>
<tr>
<td></td>
<td>14.5±0.5</td>
<td>10.6±0.5</td>
<td>4.5±0.5</td>
<td>3.5±0.2</td>
<td>0.11±0.05</td>
</tr>
<tr>
<td></td>
<td>13.4±0.5</td>
<td>12.4±0.5</td>
<td>6.2±0.6</td>
<td>6.2±0.6</td>
<td>0.14±0.08</td>
</tr>
<tr>
<td>BC nanopapers</td>
<td>15.2±2.8</td>
<td>11.2±2.8</td>
<td>5.8±0.8</td>
<td>4.5±0.3</td>
<td>0.36±0.05</td>
</tr>
<tr>
<td></td>
<td>14.3±1.4</td>
<td>10.9±1.1</td>
<td>4.5±0.5</td>
<td>3.5±0.2</td>
<td>0.11±0.05</td>
</tr>
<tr>
<td></td>
<td>13.4±1.5</td>
<td>12.2±1.5</td>
<td>4.5±0.5</td>
<td>3.5±0.2</td>
<td>0.11±0.05</td>
</tr>
</tbody>
</table>
where $\sigma_{\max}$ is the slope of the recorded load–displacement curve, $C_\varepsilon$ 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 ($C_\varepsilon \to \infty$), 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 ($\sigma_{\text{max}}$), as well as the tensile index ($\sigma_{\text{max}}/A$), 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 ~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 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.

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 $K_{\text{IC}}$ value 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 debonding of the nanocellulose network. As a result, the fracture surface of the single edged-notch BC nanopapers showed significant debonding, which suggests fibre-fibre debonding during crack propagation. This was not observed in the fracture surface of single edged-notch 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

<table>
<thead>
<tr>
<th>Sample</th>
<th>$K_{\text{IC}}$ (MPa m$^{1/2}$)</th>
<th>$t$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNF nanopaper</td>
<td>7.3 ± 0.3</td>
<td>0.7 ± 0.2</td>
</tr>
<tr>
<td>BC nanopaper</td>
<td>6.6 ± 0.2</td>
<td>19.8 ± 5</td>
</tr>
</tbody>
</table>
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 divided by the initial 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 emphasizes 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: $\sigma$ = 149 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 vs ~0.1 for BC nanopapers). This is a result of the lower porosity of CNF nanopapers compared to BC nanopapers. Furthermore, we observed that the Poisson's ratio of CNF and BC nanopapers was independent of test specimen geometries used. Fracture resistance of single edge notched cellulose nanopapers were conducted. CNF nanopaper possessed higher critical stress intensity factor ($K_{IC}$) compared to BC nanopapers (CNF nanopaper: $K_{IC}$ = 7.3 MPa m$^{1/2}$, BC nanopaper: $K_{IC}$ = 6.6 MPa m$^{1/2}$). CNF nanopapers fractured catastrophically when peak force was achieved. The crack on single edge notched BC nanopapers, on the other hand, propagated for ~20 s before catastrophic fracture. This is due to inhomogeneity in the areal density of BC across the through thickness of the BC nanopapers.

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Appendix A. Supplementary data

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References
