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Sample geometry dependency on the measured tensile properties of cellulose nanopapers

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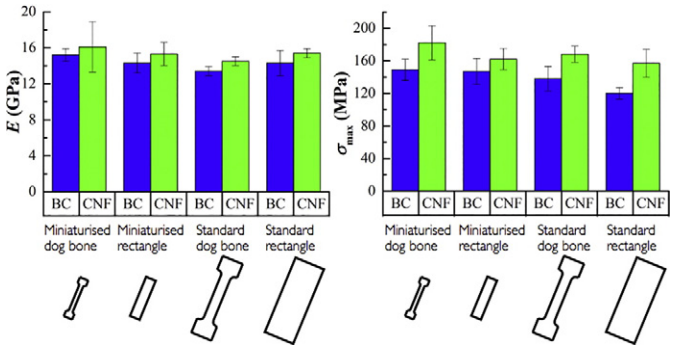
HIGHLIGHTS

- 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 $K_{1c,\,\mathrm{CNF\ nanopaper}} = 7.3$ MPa $m^{1/2}$ and $K_{1c,\,\mathrm{BC\ nanopaper}} = 6.6$ 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 nanometre scale. This lignocellulosic biomass-derived nanocellulose is more commonly known as cellulose nanofibres[1] (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 pellicles (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 nanopapers 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 nanopaper-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 used, following closely the prediction of the volume-weighted average between the tensile properties of the cellulose nanopaper and the polymer matrix:

$$E_{\text{nanocomposite}} = E_{\text{nanopaper}} v_{\text{f}} + E_{\text{matrix}} \times (1 - v_{\text{f}}) \quad (1)$$

$$\sigma_{\text{nanocomposite}} = \sigma_{\text{nanopaper}} v_{\text{f}} + \sigma_{\text{matrix}} \times (1 - v_{\text{f}}) \quad (2)$$

where $E_{nanocomposite}$, $E_{nanopaper}$ and E_{matrix} denote the tensile moduli of the cellulose nanopaper-reinforced polymer nanocomposites, cellulose nanopaper and matrix, respectively. The terms $\sigma_{nanocomposite}$, $\sigma_{nanopaper}$ and σ_{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 nanopapers (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 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 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 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 nanopapers 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 upmost 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 nanopapers 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 > 98.5%) 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

[1] The term microfibrillated cellulose and nanofibrillated cellulose are also often used in literature.