



Feature Article

On the use of nanocellulose as reinforcement in polymer matrix composites

Koon-Yang Lee^a, Yvonne Aitomäki^b, Lars A. Berglund^c, Kristiina Oksman^b, Alexander Bismarck^{d,e,*}^a Department of Chemical Engineering, University College London, Torrington Place, WC1E 7JE London, UK^b Composite Centre Sweden, Division of Materials Science, Luleå University of Technology, Luleå, Sweden^c Wallenberg Wood Science Centre, Royal Institute of Technology, Stockholm, Sweden^d Polymer and Composite Engineering (PaCE) Group, Institute of Materials Chemistry and Research, Faculty of Chemistry, University of Vienna, Währinger Straße 42, 1090 Vienna, Austria^e Polymer and Composite Engineering (PaCE) Group, Department of Chemical Engineering, Imperial College London, South Kensington Campus, SW7 2AZ London, UK

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ABSTRACT

Nanocellulose is often being regarded as the next generation renewable reinforcement for the production of high performance biocomposites. This feature article reviews the various nanocellulose reinforced polymer composites reported in literature and discusses the potential of nanocellulose as reinforcement for the production of renewable high performance polymer nanocomposites. The theoretical and experimentally determined tensile properties of nanocellulose are also reviewed. In addition to this, the reinforcing ability of BC and NFC is juxtaposed. In order to analyse the various cellulose-reinforced polymer nanocomposites reported in literature, Cox–Krenchel and rule-of-mixture models have been used to elucidate the potential of nanocellulose in composite applications. There may be potential for improvement since the tensile modulus and strength of most cellulose nanocomposites reported in literature scale linearly with the tensile modulus and strength of the cellulose nanopaper structures. Better dispersion of individual cellulose nanofibres in the polymer matrix may improve composite properties.

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1. Introduction

The development of sustainable or renewable polymeric materials is an active research area that has received much attention [1]. This is mainly driven by the public's growing demand for more

* Corresponding author. Tel.: +43 (1) 4277 71301; fax: +43 (1) 4277 871302.

E-mail addresses: a.bismarck@imperial.ac.uk, alexander.bismarck@univie.ac.at (A. Bismarck).

environmental friendly materials. Unfortunately, the thermo-mechanical performance of renewable polymers is often inferior compared to traditional petroleum based polymers (Fig. 1). For instance, many commercially available polylactides (PLA) are brittle and possess low heat distortion temperatures [2]. The composite materials concept is one solution for creating renewable materials that match or exceed the performance of commonly used petroleum-based engineering polymers. Combining bio-based/renewable polymers with renewable reinforcements could address the property-performance gap between renewable and petroleum-based polymers. In fact, nature utilises composite materials for load-bearing structures. Wood and bone show better mechanical properties than most synthetic bio-based composites and may inspire the development of new materials. Wood as a composite material was further enunciated by Freudenberg [3]; he stated that the cell walls of xylem are analogous to reinforced concrete. In his own words:

“The micelle series of cellulose may be compared with the iron rods, and the lignin together with the hemicellulose with the concrete in reinforced concrete. It is astonishing to see how nature has here made use of two of the best principles of rigidity which the human mind has independently discovered only in our own time.”

In the context of green composites, natural fibres are often regarded as ideal candidate reinforcement because of their low cost, low density, renewable resource origin and biodegradability [4]. Natural fibre-reinforced polymer composites with excellent properties possessing tensile moduli and strengths of up to 40 GPa and 280 MPa, respectively, have been manufactured [5]. Nonetheless, the reinforcing natural fibres themselves do suffer from drawbacks such as limited processing temperature [6], high linear coefficients of thermal expansion [7,8], batch-to-batch variability, moisture sensitivity and low absolute tensile strength compared to synthetic fibres, such as glass, aramid or carbon fibres [4].

Another type of reinforcement for the production of high strength and high toughness renewable composites are paper mats in the form of plant fibre network structures. Paper based laminates, as the name implies, are composites made by laminating sheets of resin-impregnated paper into solid panels. “Papreg”, for example, is a phenolic resin impregnated paper based laminate with high tensile strength developed in 1940 and 1950 [9]. These materials were even used in aircraft structures. Such paper based laminates had a phenolic resin content of 35 wt.% and possessed

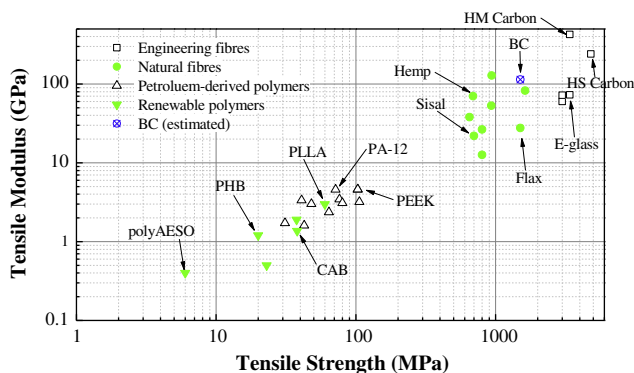


Fig. 1. Comparison between average tensile properties of commonly used synthetic engineering fibres, renewable technical fibres, petroleum-based and renewable polymers, respectively. BC denotes bacterial cellulose. Data obtained from MatWeb (<http://www.matweb.com>) unless stated otherwise. The tensile properties of natural and engineering fibres are obtained from Bismarck et al. [4]. The data for BC and polyAESO were obtained from Hsieh et al. [57] and Lee et al. [154], respectively.

Table 1

A comparison between various pulp-fibre reinforced phenolic resin composites with sisal fibre reinforced and chopped tire cord reinforced phenolic composites [10,11]. E and σ represent the tensile modulus and strength of the fibre-reinforced composites, respectively.

Reinforcement	Resin content (wt.%)	E (GPa)	σ (MPa)
Sisal fibres	40	7.6	72
Chopped tire cords	50	7.6	32
Black spruce kraft pulp	40	13.2	165
Yellow birch neutral sulfite	39	11.7	163
Black spruce Mitscherlich	39	13.1	139
Spruce ground wood	40	9.7	107
Spurce ground wood	12	12.4	97
Straw	30		185
Unbleached Manila hemp			228
Kraft			214

a tensile strength and modulus of 188 MPa and 18.6 GPa, respectively [10]. A summary of the tensile properties of “Papreg” in comparison to sisal fibre or chopped tire cord reinforced phenolic resins is given in Table 1 [10,11]. The concept of “Papreg” was also extended to the hood, fenders, roof, trunk lid and doors of the car Trabant produced since 1957 by VEB Sachsenring Zwickau in the former German Democratic Republic. The material was based on phenolic resin reinforced by waste cotton imported from the former Soviet Union. Whilst research on “Papreg” has disappeared, the material is still produced and sold to date under various trade names, for example as Phenokraft for electrical components. The concept of “Papreg” has been extended recently to sheets of nanocellulose [12–18], more commonly known as nanopapers [19].

The concept of using nanocellulose as reinforcement originated from the possibility of exploiting the high stiffness and strength of cellulose crystals in composite applications. Nanocellulose can be obtained from various sources including algae [20], a sea animal (tunicate) [21] and plant biomass [22,23]. Nanocellulose can also be produced by biosynthesis by some bacteria, such as bacteria from the *Acetobacter* species [24–27]; in this case it is known as bacterial cellulose. To avoid confusion to the readers, it is worth mentioning at this point that there are numerous terms used to describe nanocellulose, which include: bacterial cellulose, microbial cellulose, cellulose nanofibrils, nanofibrillated cellulose, microfibrillated cellulose, cellulose nanofibres, cellulose nanowhiskers, cellulose whiskers, cellulose nanocrystals and nanocrystalline cellulose. Whilst no agreed terminology exists to describe ‘nanometre scale cellulose’ yet, there have been attempts trying to unify the terminology [16]. In this article, we adopt the generic term ‘nanocellulose’ to describe all of the aforementioned types of non-acid hydrolysed nanometre scale cellulose. This feature article is split into three sections; the first section briefly discusses properties of nanocellulose, followed by a section reviewing the progress to date on the use of nanocellulose obtained from plants and bacteria as reinforcement for various polymers. The last part discusses the reinforcing efficiency of nanocellulose in various polymer matrices. The potential of nanocellulose as reinforcement, in particular the possibilities for high-performance structural applications is assessed in this article.

2. Nanocellulose – A brief introduction

Nanocellulose can be obtained via two approaches: bottom-up by biosynthesis or top-down by disintegration of plant materials. In 1886, Brown [26] observed that cellulose fibres are produced bottom-up by the fermentation of low molecular weight sugars using bacteria from the *Acetobacter* species. The cellulose fibres produced, herein termed bacterial cellulose (BC), are inherently nano-sized ribbon shaped cellulose fibrils, with largest lateral dimension ranging from 25 to 86 nm and lengths of up to several

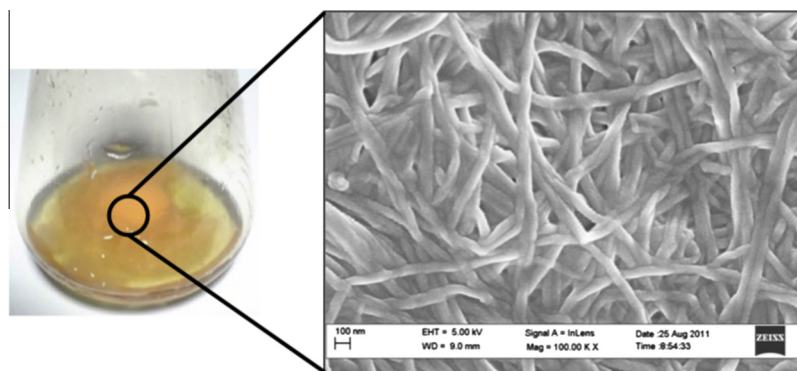


Fig. 2. Image showing a three-day old culture of *Acetobacter xylinum*. The gel-like pellicle can be seen in the culture. Under scanning electron microscope, the pellicle appears to be made of a nanofibrillar network of cellulose. Obtained from Lee et al. [41] with kind permission from ACS publications.

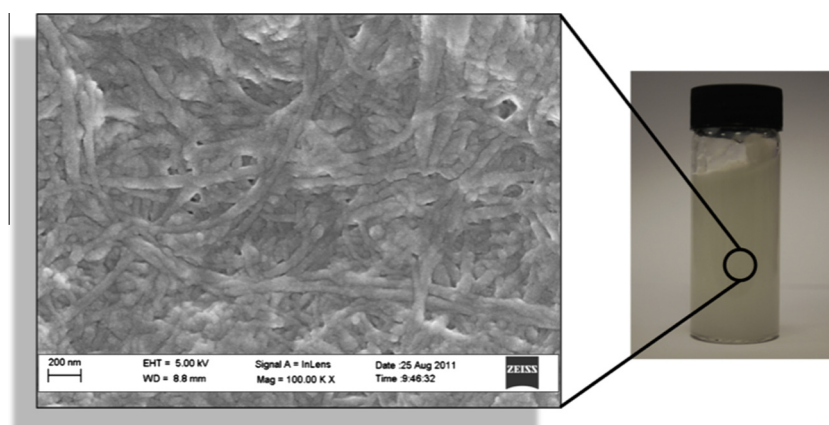


Fig. 3. Image showing the nanometre-scale of a 1 wt.% NFC suspension in water. Obtained from Lee et al. [41] with kind permission from ACS publications.

micrometres (see Fig. 2) [24]. For literature on the biosynthesis of BC and recent advances of BC in various research areas including tissue engineering, biomedical engineering and advanced fibre composites, the readers are referred to recent reviews by Klemm et al. [15,25,28], Blaker et al. [29] and Lee et al. [30]. With regards to nanocellulose produced using the top-down approach, the earliest publication we found describing nanocellulose was published in 1946 by Wuhrmann et al. [31]. The authors treated natural fibres with strong ultrasound to disintegrate larger bundles of natural fibres into smaller elementary fibrils whilst retaining the fibrous texture. Herein, we term this type of nanocellulose, i.e. long and semi-flexible fibrils from wood or any other plant material, nanofibrillated cellulose (NFC). Turbak et al. [22] and Herrick et al. [23] reported the production of NFC from wood using high-pressure homogenisers to reduce the size of wood fibres down to the nanometre scale. More recently, NFC were also produced by grinding of wood pulp [32]. A suspension containing 1 wt.% NFC and the morphology of NFC are shown in Fig. 3. For comprehensive reviews on NFC production and applications, the readers are referred to Siró and Plackett [33], Lavoine et al. [34] and Klemm et al. [16].

Whilst the diameters of NFC and BC are similar (<100 nm), the main difference between the two types of nanocellulose is their purity and crystal structure. BC is essentially pure cellulose. NFC, on the other hand, usually is a composite itself consisting of both cellulose and hemicellulose [35,36]. Lignin is often absent in NFC as bleached pulp is mainly used as starting material. In addition to this, NFC is based on plant cell wall microfibrils where cellulose is organised in extended chain conformation and with a high degree of long-range order. Cellulose is a semicrystalline fibrous polymer

with two different crystal structures in the native state; namely I_α and I_β (see Fig. 4) [37]. Cellulose I_α possesses a one chain triclinic unit cell [38] and cellulose I_β is composed of monoclinic unit cell containing two parallel chains [39]. More importantly, both crystal structures co-exist in the same cellulose sample [40]. However, the relative proportion of I_α and I_β varies in cellulose of different origins; BC is cellulose I_α -rich whereas plant-based cellulose, such as NFC, is I_β -rich. Even though the purity and crystal structures of BC and NFC are different, it is possible that the reinforcing ability of both types of nanocellulose in composites can be similar (Table 2) [41]. When the tensile moduli of BC or NFC reinforced epoxy composites were normalised from 49 vol.% (for BC reinforced epoxy) and 58 vol.% (for NFC reinforced epoxy) to 60 vol.% nanocellulose loading, the stiffness of the nanocomposites was the same. However, even when the BC reinforced epoxy nanocomposites had a lower nanocellulose loading, the tensile strength of the resulting BC reinforced epoxy nanocomposites was slightly higher than that of NFC reinforced epoxy nanocomposites. This was attributed to the high critical surface energy of BC ($\sim 57 \text{ mN m}^{-1}$) compared to NFC (42 mN m^{-1}), which promotes better wetting of BC by the epoxy resin, leading to better adhesion between BC and epoxy resin. It is also possible that BC has higher intrinsic strength (see next section).

3. Tensile properties of nanocellulose

As aforementioned, the major driver for utilising nanocellulose in load-bearing composites is the possibility to exploit the theoretically predicted stiffness and strength of cellulose crystals.

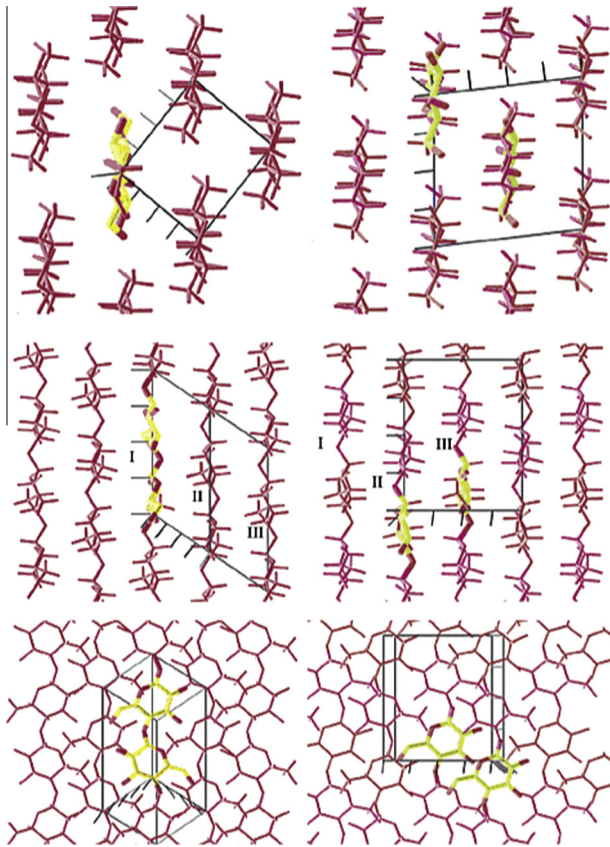


Fig. 4. Projections of cellulose I_{α} (left) and I_{β} (right), respectively. Top row: down the chain axes. Middle row: perpendicular to the chain axis and in the plane of hydrogen bonded sheets. Bottom row: perpendicular to the hydrogen bonded sheets. Obtained from Nishiyama et al. [38] with kind permission from ACS.

Table 2

A comparison between the tensile performance of BC and NFC reinforced epoxy nanocomposites. v_f , E , E_{norm} and σ denote the nanocellulose loading, Young's modulus, normalised Young's modulus to 60 vol.%, and tensile strength of the nanocomposites, respectively. Adapted from Lee et al. [41].

Nanocellulose	v_f (vol.%)	E (GPa)	$E_{\text{norm}} = E/v_f \times 60$ (GPa)	σ (MPa)
BC	49 ± 2	7.1 ± 0.1	8.7 ± 0.2	102 ± 1
NFC	58 ± 1	8.5 ± 0.2	8.8 ± 0.2	96 ± 1

Although it is challenging to determine the true modulus and strength of cellulose crystals [12], theoretical calculations and numerical simulations were used to estimate the axial modulus of a cellulose crystal to be approximately 58–180 GPa [42–49]. Gilis [50] obtained a theoretical cellulose crystal stiffness of nearly 300 GPa when he considered inter-chain hydrogen bonds and straightening of the cellulose chains in his calculations. The mechanisms for cellulose deformation are discussed in-depth in a recent

Table 3

Theoretical tensile strength of cellulose crystals.

Calculation assumptions	$\sigma_{\text{theoretical}}$ (MPa)	References
Stress to cause cohesive fracture based on intra-chain link energy	7340	[52]
Stress to cause chain scission based on potential energy function	22600 ¹ and 17150 ²	1. [54] 2. [52]
Stress to cause separation of chains if ends are all in one transverse plane	280	[52]
Stress to cause sliding fracture	1260 ¹ and 1190 ²	1. [54] 2. [52]
Stress normal to chain axis to rupture hydrogen bonds	300	[9]
Ultimate shear strength	323	[53]

molecular dynamics study [51]. It is also worth pointing out that at the current state of knowledge, quantitative predictions of the tensile properties of cellulose are not so reliable due to uncertainties with respect to force fields at atomistic scale.

As for the tensile strength of cellulose, theoretical predictions indicate that cellulose crystals have a tensile strength in the range of 0.3–22 GPa [9,52–54]. The predicted high tensile strength of cellulose is due to the extended chain conformation of crystalline cellulose [55], the high density of covalent bonds per cross-sectional area and the large number of inter- and intra-molecular hydrogen bonding sites. Table 3 summarises the theoretical tensile strength of cellulose crystals when assuming different failure mechanisms. An important consideration is that experimental strength data for strong, brittle fibres or nanofibre films depend on the specimen size; smaller specimens tend to have a higher strength. The reason is that strength is controlled by the largest defect in brittle specimens [56].

Raman spectroscopy and X-ray diffraction have been used to verify the theoretical values for the tensile modulus of nanocellulose fibres experimentally. The values for a single cellulose nanofibres obtained from these measurements were found to be between 100 and 160 GPa [57–61]. These values are in good agreement with the theoretical axial modulus of cellulose crystals. In their original study, Sakurada et al. [60] used ramie fibres with a small microfibrillar angle which were uniaxially loaded while measuring the axial crystal displacement using in-situ X-ray diffraction. The measured tensile modulus was 134 GPa. The only uncertainty for this measured tensile modulus is the true cross-sectional area of a plant fibre cell. The experimental evaluation of the tensile strength of single cellulose nanofibre, on the other hand, is more challenging. A method to determine the strength of a single nanocellulose fibre was suggested by Sehaqui et al. [62]. They prepared wood-based NFC nanopapers, which were drawn into thin strips with a Herman's orientation factor lower than 0.56. The measured tensile strength of these strips was 430 MPa. This value cannot be taken as the single fibre strength but it can be viewed as a lower bound of the tensile strength of single NFC fibre. It should be possible to improve the degree of NFC orientation and nanofibre straightness within the strips or NFC fibres and use their tensile strength as an indirect measure for the tensile strength of nanocellulose. Saito et al. [63] used a more direct approach; sonication-induced fragmentation of single 2, 2, 6, 6, tetramethyl-piperidinyloxy-1-oxyl (TEMPO) oxidised wood NFC was used to determine the critical length. Based on modelling of the local stresses, the arithmetic mean of the tensile strengths varied between 1.6 and 3.0 GPa. These values are much lower than the theoretical value predicted by Mark [53] but are in approximate agreement with the tensile strength of cellulose crystals predicted when the failure mechanism involves sliding fracture (see Table 3) [52,54]. Sonication-induced fragmentation has been also used to fragment single bacterial cellulose nanofibre. However, the same authors found that bacterial cellulose nanofibres could not be fragmented with their existing experimental setup at the time of this publication [64]. Although BC has larger diameters than NFC, BC could also possess

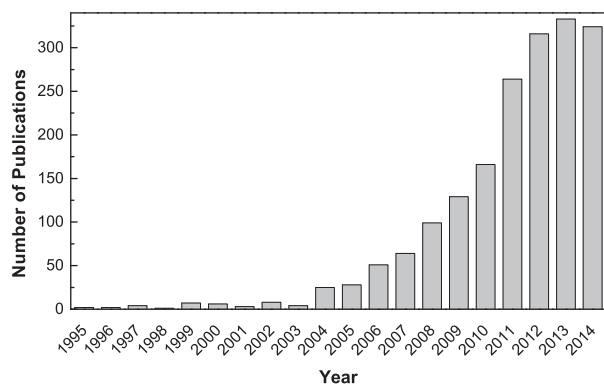


Fig. 5. Number of publications in the area of cellulose nanocomposites. The title-abstract-keywords search was performed on Scopus using the terms ‘cellulose AND nanocomposite’.

higher strength than TEMPO-oxidised NFC, presumably due to higher degree of polymerisation (BC: ~2000–6000 [65], NFC: ~200–1000 [66]). In fact, the mean strengths of tunicate whiskers are in the range of 3–6 GPa [63]. When we attempt to estimate the modulus and strength of cellulose nanofibres, possible reference materials are elementary single plant fibres, such as flax or ramie. Based on direct experimental data [55], the elementary plant fibres have a modulus of 100 GPa and a tensile strength of 1 GPa. Although a ‘virgin’ cellulose nanofibre is expected to exceed these values, the disintegration process, however, may damage the structure, which will affect its properties.

4. Nanocellulose as reinforcement for polymer nanocomposites

The first use of nanocellulose as reinforcement for various polymer including polypropylene, polystyrene and high density polyethylene was reported by Boldizar et al. [67] although the full implications of using nanocellulose as reinforcement were not apparent. Later the strong reinforcing effects of small amounts of nanocellulose were demonstrated and clarified by Favier et al. [68,69]. They used nanocellulose whiskers¹ derived from tunicate to reinforce styrene and butyl acrylate copolymer latex with nanocellulose whisker loading fractions of up to 6 vol.%. Even at such low nanocellulose loading, the nanocomposites had significantly higher mechanical properties than the neat polymer in its elastomeric state. The authors ascribed this improvement to the formation of a rigid cellulose whisker network within the nanocomposites due to percolation of the nanocellulose whiskers. The nanocellulose percolation threshold was estimated to be between 1 and 6 vol.% depending on the cellulose source [13]. Dufresne and Vignon [70] later demonstrated that potato pulp-derived nanofibrillated cellulose obtained using a homogeniser showed similar improvements of starch matrix in its elastomeric state. Since then, significant research effort has been poured into the manufacturing and production of high performance and/or multifunctional nanocellulose reinforced polymer composites. The number of publications on cellulose nanocomposites has increased exponentially over the past decade (see Fig. 5).

4.1. Reinforcing ability of BC in polymer nanocomposites

The use of BC as reinforcement in nanocomposites was first demonstrated by Gindl and Keckes [71]. The authors reinforced cellulose acetate butyrate (CAB) with various BC loading fractions.

¹ These whiskers were obtained by acid hydrolysis of tunicin. This hydrolysed form of nanocellulose from tunicin is commonly known as tunicate whiskers.

Table 4

Tensile properties of BC reinforced CAB nanocomposites. v_f , E and σ denote the BC loading fractions, tensile modulus and tensile strength, respectively. Adapted from Gindl and Keckes [71].

Nanocomposites	v_f (vol.%)	E (GPa)	σ (MPa)
CAB	0	1.2	25.9
BC reinforced CAB	10	3.2	52.6
	32	5.8	128.9

At a BC loading of 32 vol.%, the tensile properties of the resulting nanocomposites improved by as much as 5 times compared to neat CAB (Table 4). This implies that BC serves as excellent nano-reinforcement for polymers. Fig. 6 summarises the tensile properties of BC reinforced polymer nanocomposites reported by various authors in literature since then [41,71–94]. It can be seen from Fig. 6 that BC reinforced polymer nanocomposites with tensile moduli and strengths as high as 21 GPa and 320 MPa, respectively, at 60 vol.% BC loading ($v_{f, BC}$) have been manufactured. Tensile strengths of up to 420 MPa were reported but at $v_{f, BC} = 84$ vol.% [93]. In order to ascertain whether BC as reinforcement does produce high performance structural materials, a comparison is made against a typical commercially available bulk polymer made from renewable resources. Here, we chose poly(L-lactic acid) (PLLA) as benchmark for comparison due to its availability at a reasonable price and its already widespread use. Whilst PLLA may possess poor impact properties and low thermal stability, it is still one of the high performance non-petroleum derived polymers [2]. PLLA has a tensile modulus and strength of 4.0 ± 0.1 GPa and 63 ± 2 MPa, respectively [74]. These values are indicated as dashed lines in Fig. 6. By comparing the data collected for all BC reinforced polymer nanocomposites against our benchmark PLLA, we can see that both the tensile moduli and strengths of most BC reinforced polymer nanocomposites performed equally well or worse than PLLA when the composites had a BC loading fraction $v_{f, BC} < 30$ vol.%. However, it should be noted that not all data tabulated in Fig. 6 used engineering polymers as the matrix and therefore, are not meant to produce high performance structural materials.

Numerous studies have been dedicated to hydrophobise the surface of BC in order to improve the compatibility between BC and hydrophobic polymer matrices. When BC was hydrophobised using dodecanoic acid in an esterification reaction, measured contact angles of PLLA droplets on the modified BC showed that the wettability of PLLA on BC significantly increased (see Fig. 7) [82]. This indicates that hydrophobisation of BC does indeed improve the interaction between BC and PLLA. Model PLLA nanocomposites containing 5 wt.% modified BC also showed improvements in tensile modulus and strength of 50% and 12%, respectively, over neat PLLA. However, when compared to PLLA nanocomposites containing 5 wt.% neat BC, the improvements of modified BC-PLLA composite over neat BC-PLLA composite were only marginal (5% in tensile modulus, but no improvement in tensile strength was observed). Moreover, chemical modification of BC (or nanocellulose in general) is very laborious. Solvent exchange should be used as it was found that when freeze-dried BC was modified, severe bulk modification occurred but surface-only modification was observed when the BC was solvent exchanged from water through methanol into pyridine (the reaction medium) [95]. Therefore, the simplest solution to realise truly high performance BC reinforced polymer nanocomposites is to increase the BC loading of unmodified beyond 30 vol.%. Whilst we also recognise that conventional extrusion methods might not be able to disperse $v_{f, BC} > 15$ vol.% because of the tendency of nanocellulose to aggregate [96], other composite manufacturing techniques could be explored. These include wet impregnation of BC pellicles [91] and vacuum assisted resin infusion [41].

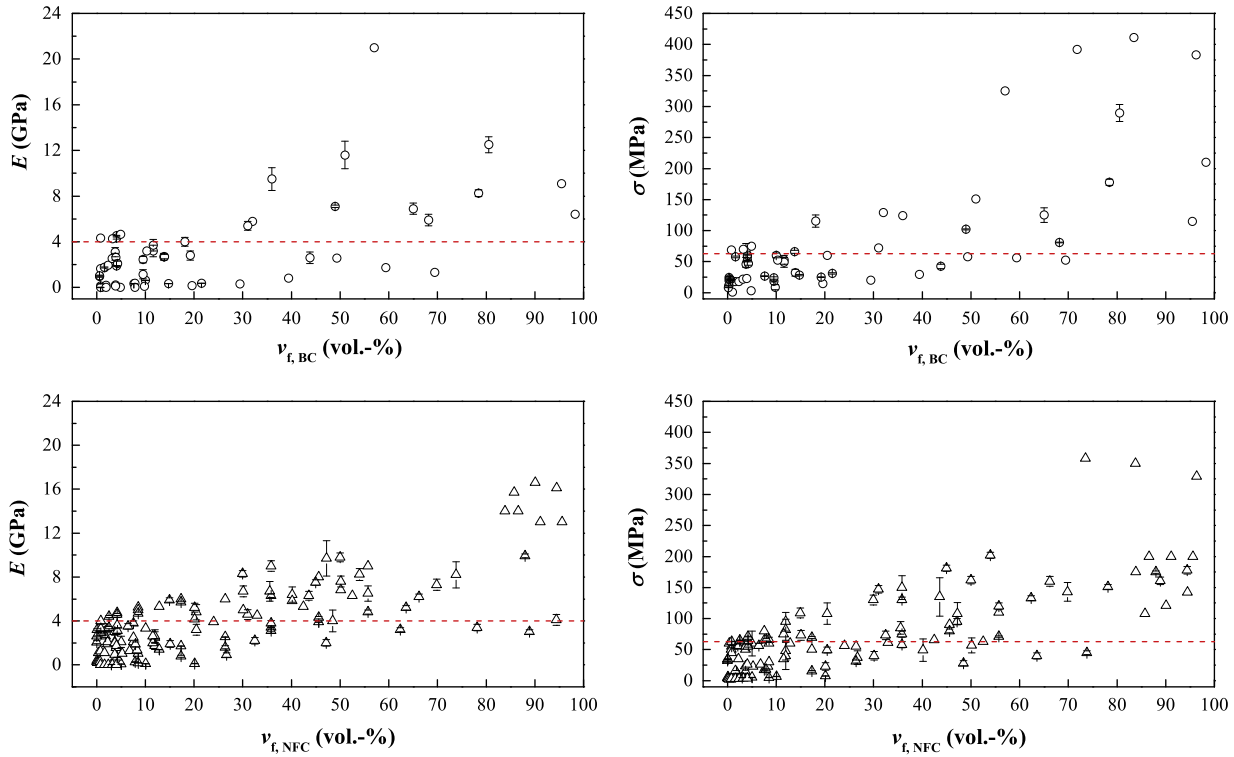


Fig. 6. Tensile properties of BC reinforced polymer composites [41,71–94] and NFC reinforced polymer composites in literature [84,93,97,100–130]. E , σ , $v_{f, BC}$ and $v_{f, NFC}$ denote the tensile modulus, tensile strength, BC and NFC loadings, respectively. The dashed lines indicate the tensile properties of poly(L-lactic acid), taken as $E = 4.0 \pm 0.1$ GPa and $\sigma = 63 \pm 2$ MPa, respectively.

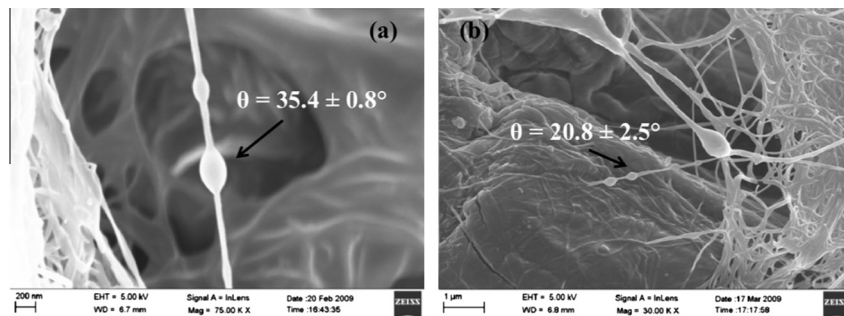


Fig. 7. PLLA melt droplets of (a) neat BC nanofibre and (b) dodecanoic acid esterified BC nanofibre. The contact angle between the nanofibre and PLLA (θ) was evaluated using the generalised drop length-height method. Images obtained from Lee et al. [82] with kind permission from Elsevier.

4.2. Reinforcing ability of NFC in polymer nanocomposites

NFC was first demonstrated to improve the mechanical performance of a polymer (potato-starch) by Dufresne et al. [97]. Later on, Nakagaito and Yano [98] showed that NFC also improved the tensile performance of a phenol–formaldehyde resin. Zimmermann et al. [99] showed that NFC improved the properties of hydroxypropylated cellulose (HPC) and Henriksson et al. [100] used melamine formaldehyde (MF) to impregnate nanopaper. The tensile performance of NFC reinforced polymer nanocomposites as a function of NFC loading ($v_{f, NFC}$) reported by various authors is summarised in Fig. 6 [84,93,97,100–130]. It is apparent that much more data are available for NFC reinforced polymer nanocomposites than for BC reinforced polymer nanocomposites. This is not surprising as numerous methods can be used to produce large quantities of NFC in laboratories. The readers are referred to a review by Siró and Plackett [33] for the various methods of producing NFC. The production of BC, on the other hand, relies on the biosynthesis of cellulose by bacteria. It could take weeks under laboratory

conditions to produce enough BC for composite manufacturing. However, it should be noted that the large-scale production of BC has been achieved by *fzmb*, some of it using a novel aerosol bioreactor [30,131–133]. BC can also be produced in static cultures in large quantities as a dessert known as *nata de coco* [134].

The properties of some NFC reinforced polymer nanocomposites exceed our benchmark PLLA even when $v_{f, NFC} < 10$ vol.%. The matrices for these high performance NFC model nanocomposites were PLLA [128], regenerated cellulose [106], enzymatically modified rye arabinosylan [102] and polyvinyl alcohol [114], respectively. In the case of arabinosylan as matrix for NFC composites [102], the authors used a biomimetic approach, whereby they enzymatically modified the arabinosylan to mimic the chemical structure of arabinosylan in cereal and softwood. As for polyvinyl alcohol (PVA) as matrix [114], the use of water-soluble polymers is postulated to aid the dispersion of NFC within the matrix. These studies aside, NFC reinforced polymer nanocomposites outperform PLLA only when $v_{f, NFC} > 30$ vol.%. When $v_{f, NFC}$ was increased towards 90 vol.%, tensile moduli and strengths of ~ 14 GPa and

~350 MPa were obtained for the resulting nanocomposites [93], exceeding even the tensile properties of randomly oriented glass fibre-reinforced polypropylene composites with a glass fibre loading fraction of 60 wt.% [135,136]. One may note that NFC/HEC composites can reach 200 MPa strength at $v_{f, \text{NFC}} = 54 \text{ vol.}\%$ [125].

4.3. Discussion: BC versus NFC as reinforcement for polymers

It is apparent that high performance nanocellulose reinforced structural polymer composites can be manufactured. However, this is only the case at high nanocellulose content, for instance if $v_f > 30 \text{ wt.}\%$ (see Section 4.1 And 4.2). In simpler terms, there is no homeopathic effect in nanocellulose reinforced polymer composites as often observed for carbon nanotube reinforced polymers [137,138]. The exception is nanocellulose-reinforced elastomers; in such matrices nanocellulose does provide very strong reinforcement effects at low loading fractions [139,140]. This enhancement has been hypothesised to be due to the formation of a percolating network of cellulose nanowhiskers [141] or nanofibres [142] within elastomers, held together by hydrogen bonds [143]. Furthermore, the reinforcing efficiency of nanocellulose in elastomers is higher than in engineering polymers [144,145]. This was thought to be due the fact that elastomers resulted in the strain of the nanocomposites to be closer to that of the nanofibres. Even though the mechanical performance of elastomers reinforced by nanocellulose increased significantly over neat elastomers (especially at elevated temperatures), it does not offer a route to produce structural materials. Furthermore, if the manufacturing of nanocomposites with low loading fractions of nanocellulose failed to achieve good nanocellulose dispersion, the formation of a percolating network will be unlikely. In this case, the nanocellulose will behave just like a micrometre-sized filler rather than nano-reinforcement. This is the main challenge when low loading fractions of nanocellulose are to be utilised in elastomers as nano-reinforcement.

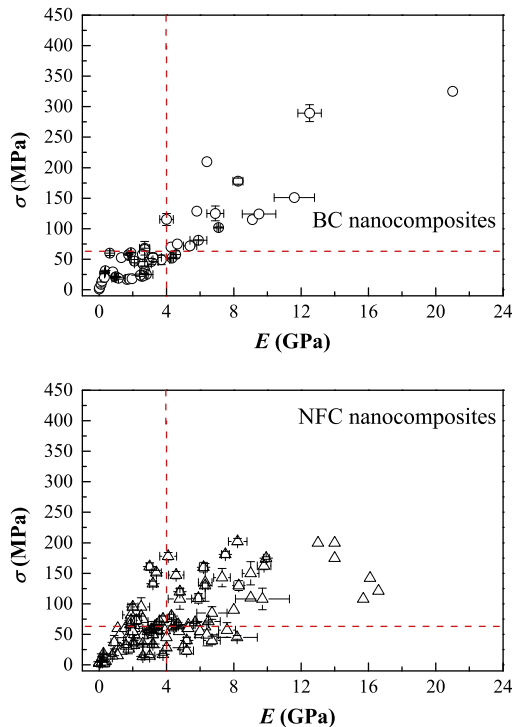


Fig. 8. Tensile strength (σ) versus modulus (E) curves for BC reinforced (top) and NFC reinforced (bottom) polymer nanocomposites. Note that not all data points in Fig. 6 can be shown in this figure as not all authors report both the tensile modulus and strength of their manufactured cellulose nanocomposites.

In order to assess whether BC and NFC could be used as reinforcement to produce structural materials, we have plotted the tensile moduli against tensile strengths of BC and NFC reinforced polymer nanocomposites (Fig. 8). Approximately 20% of the data for both BC and NFC composites reported in literature exceed the overall tensile performance of PLLA, i.e. data points on the first quadrant of Fig. 8. More importantly, it can be seen from Fig. 8 that a linear relationship is observed for the modulus against strength of BC reinforced polymer nanocomposites whilst the data scatter is significantly higher for the NFC reinforced nanocomposites. The reason is unclear but includes contributions from factors such as variations in NFC geometry, composition, intrinsic properties, degree of dispersion, orientation distribution and porosity of the composites. It is also interesting to note that the highest tensile modulus and strength of 21 GPa and 320 MPa at $v_{f, \text{BC}} = 60 \text{ vol.}\%$, respectively, was obtained for BC reinforced polymer nanocomposites. The maximum tensile modulus and tensile strength for NFC reinforced polymer nanocomposites, on the other hand, were “only” 14 GPa and 350 MPa at $v_{f, \text{NFC}} = 90 \text{ vol.}\%$, respectively. Whilst theoretical and experimental studies indicate that NFC and BC may possess similar modulus and strength, the observed difference suggests that the intrinsic properties of BC may be superior to NFC.

5. Micromechanical modelling to investigate the reinforcing potential of BC- and NFC-reinforced model polymer nanocomposites

Numerous micromechanical models have been developed to predict the tensile strength and modulus of short fibre-reinforced polymer composites. Micromechanical models have been reviewed by Robinson and Robinson [146], Chow [147] and Asloun et al. [148]. Cellulose nanocomposites have complex structures; the nanofibres (i) tend to be curved due to a combination of high aspect ratio, small diameter and the preparation methods used for making the nanocomposites and (ii) because they possess alternating disordered (amorphous) and crystalline domains along the main axis. Furthermore, although the fibre orientation is often assumed to be random-in-the-plane, there is usually significant out-of-plane orientation [62]. However, when assuming BC and NFC fibres behave as random short fibres, these micromechanical models might still be useful to predict and verify experimental data. In this section, we use micromechanical models to investigate the various BC and NFC reinforced nanocomposites reported in literature.

5.1. Tensile modulus of cellulose reinforced nanocomposites

One of the most commonly used micromechanical model for the prediction of tensile moduli of randomly oriented short fibre composites is the Cox-Krenchel model [149,150]. This model was developed based on the classical shear-lag theory. The assumptions used in the development of this model are (i) fibre and matrix response elastically, (ii) no axial loads on the fibre ends and (iii) perfect fibre-matrix interface. The Cox-Krenchel model is written as:

$$E_{\text{composite}} = \eta_0 \eta_L v_f E_f + (1 - v_f) E_m \quad (1)$$

where $E_{\text{composite}}$, η_0 , η_L , v_f , E_f and E_m represent the predicted tensile modulus of the composite, fibre orientation factor, fibre volume fraction, tensile modulus of the fibre and matrix, respectively. The limited stress transfer efficiency caused by the fact that the fibres have a finite length, η_L , can be obtained from ‘shear-lag’ model:

$$\eta_L = 1 - \frac{\tan h\left(\frac{\beta L}{2}\right)}{\frac{\beta L}{2}} \quad (2)$$

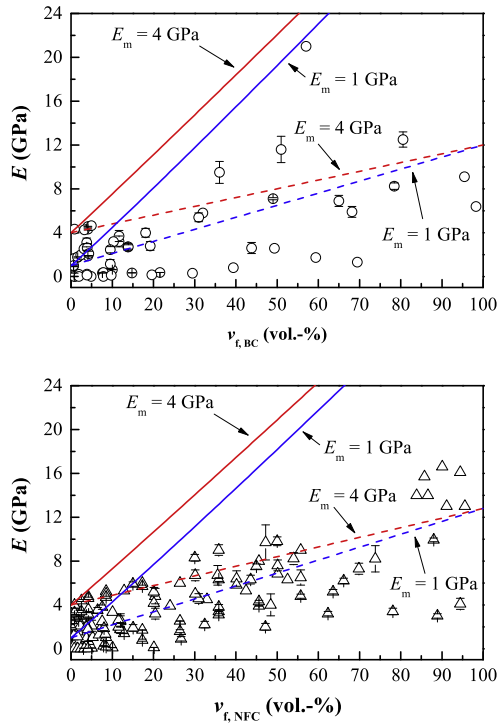


Fig. 9. A comparison between theoretical and experimental tensile modulus of BC and NFC reinforced model composites. The hollow icons represent the experimental data obtained by various authors. The solid line denotes theoretical values obtained using Cox–Krenchel model. The dashed line denotes theoretical values obtained using rule-of-mixture.

$$\beta = \frac{2}{d} \left[\frac{2 \times G_m}{E_f \ln \left(\sqrt{\frac{\pi}{X_i \times v_f}} \right)} \right]^{0.5} \quad (3)$$

$$G_m = \frac{E_m}{2 \times (1 + \nu)} \quad (4)$$

where L , d , G_m , X_i and ν denote the fibre length, fibre diameter, shear modulus of the matrix, packing of fibres in the composites and Poisson ratio of the matrix, respectively. However, there appears to be some confusion regarding the value used for X_i in the literature. This confusion stems from the definition of mean centre-to-centre spacing between fibres and was first raised by Thomason and Vlugg [135]. The values for X_i obtained could be 1 or $\sqrt{3}/2$ for square or hexagonal packing of fibres, respectively when the mean centre-to-centre spacing between fibres is assumed to be R . On the other hand, if one assumes the mean centre-to-centre spacing between fibres to be $2R$, we will obtain $X_i = 4$ and $2\sqrt{3}$ for square packing and hexagonal packing of fibres, respectively. In the original publication by Cox [149], $X_i = \sqrt{3}/2$ was used. Therefore, our analysis will use value for X_i of $\sqrt{3}/2$ for hexagonal packing of fibres, with a mean centre-to-centre fibre spacing of R .

A comparison between the predicted tensile moduli for BC and NFC reinforced polymer nanocomposites and experimental data obtained by various authors is shown in Fig. 9. For calculating the tensile moduli of cellulose nanocomposites we chose imaginary matrix moduli (E_m) of 4 GPa and 1 GPa as these values represent the upper and lower bounds of bulk technical and engineering polymers, such as polypropylene, polyamide and high performance epoxy resins. An average fibril modulus of $E_f = 114$ GPa was used for BC reinforced model polymer nanocomposites [57]. This value was back-calculated from the molecular deformation of nanocellulose

in cellulose nanocomposites studied using Raman spectroscopy. For the case of NFC reinforcements, an average fibril modulus of $E_f = 107$ GPa was used. This value was measured experimentally in 3-point bending mode using AFM [151]. The other input parameters for the prediction of BC and NFC reinforced polymer nanocomposites are $\eta_0 = 3/8$, assuming an in-plane isotropic orientation of fibres in the nanocomposites, $L = 0.005$ mm (from Fig. 2 and Fig. 3), $\nu = 0.34$ [152] and $d = 0.00005$ mm (from Fig. 2 and Fig. 3), respectively.

It can be seen from Fig. 9 that at low BC and NFC loading, the experimental values lie in the region of moduli predicted by the Cox–Krenchel model. However, a negative deviation from the predictions can be observed when $v_{f, BC}$ and $v_{f, NFC}$ exceed 10 vol.%. This implies that at this $v_{f, BC}$ and $v_{f, NFC}$, the single fibre tensile modulus is not anymore fully utilised. Nonetheless, it should also be noted the tensile modulus of BC reinforced model polymer nanocomposite prepared by Yano et al. [91] clearly stood out, matching again the prediction obtained using the Cox–Krenchel model. This agreement would suggest that in this particular nanocomposite the single fibre tensile modulus of BC was fully utilised. Yano et al. [91] used a wet impregnation technique, whereby the dried BC pellicle was impregnated with an epoxy resin under vacuum for 12 h followed by curing of the resin using ultraviolet light. It is hypothesised that starting with wet BC pellicles is important for the result, although the specific reasons are unclear. However, it is not clear why the same improvement in the tensile modulus of NFC reinforced polymer nanocomposites could not be achieved when using the same drying and wet impregnation method to impregnate NFC mats [127]. This question remains to be elucidated by future research. One possibility is that the intrinsic modulus of BC ribbons is higher.

It is also worth mentioning that the ‘grafting from’ approach and culturing of BC in presence of water-(in)soluble polymers did also not yield nanocomposites that fully utilise the tensile modulus of single nanocellulose fibre [72,88]. Instead, the tensile modulus of these nanocomposites can be best describes by the rule-of-mixture when using the properties of very high cellulose network density, i.e. ‘nanopaper’, at a given fibre volume fraction. In order to verify this, we have also plotted the predicted tensile modulus of the nanocomposites (Fig. 9) obtained using the conventional rule-of-mixture:

$$E_{composite} = v_f E_f + (1 - v_f) E_m \quad (5)$$

where E_f corresponds to the typical tensile modulus of nanopapers. However, there are variations in the tensile moduli reported for cellulose nanopaper structures. Values ranging from between 9.4 GPa [86] and 14 GPa [19] have been presented in the literature. In this article, tensile moduli of nanopapers were assumed to be 12 GPa and 12.8 GPa for BC and NFC nanopaper, respectively, based on a study by Lee et al. [41]. It can be seen from Fig. 9 that the prediction from Eq. (5) matches more closely most experimental values compared to Eqs. (1)–(4). This analysis suggests that instead of utilising the stiffness of individual cellulose nanofibres, the stiffness of cellulose nanopaper was controlling the moduli of high fibril volume fraction cellulose nanocomposites. Not surprisingly, it appears rather difficult to impregnate a high volume fraction nanocellulose network with monomers or polymers at a single fibre level. This is postulated to be due to the tendency of nanocellulose to form strong bonds between adjacent fibrils. This causes the formation of a dense network layer of nanocellulose, which is difficult to impregnate.

5.2. Predicting the tensile strength of cellulose reinforced nanocomposites

To predict the tensile strength of randomly-oriented short fibre composites, the model developed by Kelly and Tyson [153] and

modified for short and non-aligned fibre-reinforced composites is often used [74,135,154]. This model can be written as:

$$\sigma_{\text{composite}} = \eta_{0,v} \left[\sum_i \frac{L_i v_i}{2L_c} + v_j \sum_j \left(1 - \frac{L_c}{2L_j} \right) \right] \sigma_f + (1 - v_f) \sigma_m \quad (6)$$

where $\sigma_{\text{composite}}$, σ_f , σ_m and v_f denote the predicted strength of the composite, fibre strength, matrix strength and fibre volume fraction, respectively. In this equation, L_c represents the critical fibre length. v_i is the fibre volume fraction of fibres of length L_i , which is shorter than the critical fibre length and v_j the fibre volume fraction of fibres of length L_j , which is longer than the critical fibre length. $\eta_{0,v}$ is a ‘virtual orientation factor’ that accounts for the random orientation of fibres in the composites. Thomason and Vlugh [135] found a value of 0.2 for $\eta_{0,v}$ by fitting the experimentally measured tensile strength for randomly oriented discontinuous glass fibre reinforced polypropylene composites. We have also recently observed that $\eta_{0,v} = 0.2$ fitted our experimental data of BC reinforced modified PLLA nanocomposites [74,154]. Fukuda and Chou [155] have also derived values² for $\eta_{0,v}$ based on the ‘critical zone’ concept. The authors defined the ‘critical zone’ as a pair of planes separated by a distance, which cuts across the section normal to the applied tensile stress and fibre alignment direction. A limiting value for $\eta_{0,v}$ of 0.27 was obtained by the authors, which corresponds to all fibres bridges (i.e. the fibres cutting across this zone) in the defined ‘critical zone’. Our approximation value of $\eta_{0,v} = 0.2$ corresponds to fibre bridging and ending in the ‘critical zone’.

However, it should be noted that this micromechanical analysis remains empirical as $\eta_{0,v}$ has to be obtained first (usually via experiments). Moreover, tensile strength is a complex property that depends on the process of failure, which has not been clarified for cellulose nanocomposites. Furthermore, another important parameter in Eq. (6) is the length and critical length of the nanocellulose fibres in the composites. Whilst the critical fibre lengths of TEMPO-oxidised wood nanofibres and tunicate whiskers have recently been obtained using ultrasonic fragmentation techniques [63], these critical lengths do correspond to the lengths at which these fibres did fragment in water, not in a representative polymer matrix.

We established in Section 5.1 that the tensile modulus of the nanocomposites can be best described by the rule-of-mixture when using the properties of very high cellulose network density (i.e. ‘nanopaper’). Here we take a similar approach to describing the tensile strength of cellulose nanocomposites using an empirical rule-of-mixtures approach with the ‘nanopaper’ tensile strength as input parameter:

$$\sigma_{\text{composite}} = v_f \sigma_f + (1 - v_f) \sigma_m \quad (7)$$

where σ_f corresponds to the tensile strength of cellulose nanopaper. The prediction from Eq. (7) could be taken as the lower bound tensile strength of cellulose nanocomposites as the tensile strength of a single cellulose nanofibre is assumed to be under-utilised in most composites. Similar to the case for tensile modulus of cellulose nanopaper, there are large variations in reported tensile strengths for cellulose nanopaper. Values ranging from between 103 MPa [41] and 449 MPa [156] have been published in literature. The vast difference in the tensile strength of nanopapers could be attributed to the difference in intrinsic cellulose nanofibre strength and in the quality of the nanopaper [19]. In this article, we used the highest reported tensile strengths of BC and NFC nanopapers of 449 MPa [156] and 232 MPa [157] respectively. For the polymer matrix tensile strength we assumed an average value of 60 MPa, representing a typical tensile strength for engineering polymers. With these input parameters, Eq. (7) describes the maximum of the lower

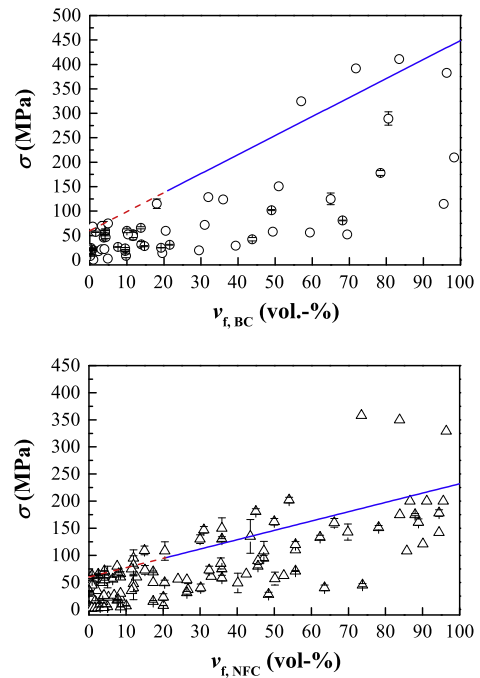


Fig. 10. A comparison between theoretical and experimental tensile strength of BC and NFC reinforced model composites. The hollow icons represent data obtained by various authors. The solid blue lines represent theoretical values obtained from conventional rule-of-mixture. The dashed red lines represent an imaginary state whereby cellulose nanopapers can be used to reinforce polymer matrices at such low loading.

bound tensile strength of cellulose nanocomposites. It should also be noted that Eq. (7) describes the maximum of the lower bound tensile strength for cellulose nanocomposites. The term ‘maximum’ refers to the highest reported tensile strength of cellulose nanopapers. Fig. 10 shows the indicated strength obtained using conventional rule-of-mixture. The nature of the transition from a percolated but sparse nanocellulose network within the polymer matrix to a dense cellulose nanopaper reinforcement is not known. We expect the percolating cellulose network in the nanocomposites to be rather loose and therefore it should perhaps not be regarded as a very dense cellulose network (i.e. ‘nanopaper’) between 6 vol.% and 18 vol.%. Nonetheless, a recent study showed that the cellulose network could be considered as a nanopaper within the cellulose nanocomposites with loading fractions of 18 vol.% [76]. Therefore, the predicted tensile strength values for less than 18 vol.% (red dashed lines) should be regarded as purely theoretical as the nanocellulose might not exist as a dense nanopaper network but instead be a 3D percolated network of cellulose nanofibres.

Our analysis shows that there is still potential for strength improvement in random-in-the-plane BC-reinforced polymer nanocomposites, since most data points lie below the lower bound tensile strength predicted using the rule-of-mixture. Higher tensile strength of the cellulose nanofiber network is probably a key to improved nanocomposite strength. The BC-reinforced polymer nanocomposites produced by Yano et al. [91] and Zhou et al. [90] stand out in the present comparison, exceeding the maximum achievable lower bound tensile strength values. Both of these studies actually used BC pellicles, where the polymer matrix was adsorbed or impregnated. It is likely that these authors managed to utilise the tensile strength of individual BC nanofibres.

For the case of NFC-reinforced polymer nanocomposites, several data points stood out, exceeding our maximum lower bound predictions using Eq. (7). These nanocomposites were manufactured by simple co-filtering a water suspension of NFC containing

² In their original paper, the term ‘coefficient of alignment’ was used.

water-soluble polymer, followed by consolidation and cross-linking. This is indeed a convenient way of manufacturing high performance NFC-reinforced nanocomposites. The use of water-soluble polymers however limits the number of potential applications of nanocellulose composites. Comparing NFC to BC, our analysis did clearly show that high performance BC-reinforced polymer nanocomposites are more difficult to prepare due to challenges with composite fabrication methods.

6. Summary and outlook

Nanocellulose is a promising reinforcement for renewable nanocomposites and has recently gained significant research interest due to the possibility of exploiting the stiffness and strength of cellulose crystals. In this feature article, we critically discussed the use of NFC and BC as nanoreinforcement for polymers. The tensile properties of NFC and BC reinforced polymer nanocomposites produced by various authors in the literature have been compiled in this article. PLLA was chosen as our benchmark comparison as it is bio-derived and possesses a good mechanical performance profile compared to other green polymers. When comparing the tensile properties of the nanocomposites to PLLA, it was found only 20% of the nanocomposites reported in the literature exceed the tensile properties of PLLA. In addition to this, most of these composites do not even exceed the mechanical performance of pulp paper reinforced phenolic resins, known as ‘papreg’, which was invented in the 1940s [9–11]. Moreover, a nanocellulose loading of greater than 30 vol.% is required to produce cellulose reinforced polymer nanocomposites with tensile properties exceeding those of our benchmark polymer, indicating that low nanofibre content does not lead to dramatic property improvements in nanocellulose reinforced polymer composites. Indeed, many reports of strong reinforcement effects for nanocomposites in general at low nanoparticle content rely on modification effects of the polymer structure. Examples include crystallization or molecular orientation effects [158,159].

Whilst both NFC and BC serve as excellent nano-reinforcement for the production of high performance nanocomposites, it was observed that BC does outperform NFC as reinforcement. A tensile modulus and strength of 21 GPa and 320 MPa, respectively, were obtained for random-in-the-plane BC reinforced epoxy composites at $v_{f, BC} = 60$ vol.% [91]. These values are the highest reported so far for cellulose-reinforced nanocomposites. The maximum tensile modulus and strength of NFC reinforced polymer nanocomposites, on the other hand, was “only” 14 GPa and 350 MPa, respectively. It should also be noted that this was only achieved at $v_{f, NFC} = 90$ vol.%. This indicates a difference in intrinsic mechanical properties of NFC and BC fibrils. Another possibility is the presence of hemi-cellulose (up to 30 wt.%). Defects in the form of fibril agglomerates may also be detrimental to NFC nanocomposite strength.

The Cox–Krenchel model has also been used to study the tensile modulus of various cellulose-reinforced polymer nanocomposites. A negative deviation from the predicted tensile modulus was observed at high v_f , indicating that the tensile stiffness of individual cellulose nanofibres has not been fully exploited or has yet to be fully exploited. Instead, most studies utilised only the tensile modulus of cellulose ‘nanopapers’ (nanofibre networks), which is much lower compared to the modulus and strength of single nanofibres. This has been verified by comparing the tensile modulus and strength of various cellulose-reinforced polymer nanocomposites with values predicted using the rule-of-mixture, with the tensile modulus and strength of nanopapers (BC: 12.0 GPa and 449 MPa, respectively; NFC: 12.8 GPa and 232 MPa, respectively) instead of nanofibres.

We have shown so far that high performance cellulose-reinforced polymer nanocomposites that exceed the mechanical

properties of PLLA can be produced if and only if v_f was increased beyond 30 vol.%. However, a few challenges have yet to be addressed; One of the key challenges is to produce nanocomposites that do not only utilise the tensile modulus of cellulose ‘nanopapers’ but the tensile stiffness (and strength) of individual nanocellulose fibrils. The wetting of nanocellulose by the polymer matrix and the uniform distribution of nanocellulose within the nanocomposites should also be addressed. It was also shown by Yano et al. [91] that impregnating a uniform three-dimensional BC pellicle with a suitable epoxy resin produces truly high performance cellulose reinforced polymer nanocomposites. This method, however, is very laborious and not commercially viable. Therefore, novel manufacturing routes should be exploited to control the cellulose nanofibre dispersion and orientation distribution. To further reduce the cost of nanocellulose, the composite manufacturing method explored should also be technically feasible and commercially viable. This may motivate industry to further exploit nanocellulose in commercial applications.

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