BETTER THROUGH SYNERGY: HYBRIDISED CELLULOSE FOR NANOPAPER COMPOSITES

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Abstract

This study is about the manufacture of hybridised cellulose nanopapers made from bacterial cellulose (BC) processed in various ways. BC was extracted from Nata de Coco, a food product popular in southeast Asia, and either used as it was, refined by grinding in a disc mill (r-BC) or after TEMPO-mediated oxidation (T-BC). These three grades of BC were then combined in binary or ternary blends and processed similar to traditional paper making to manufacture nanopapers. A paper comprised of nanocellulose produced by TEMPO-mediated oxidation of birch Kraft-pulp (TEMPO-CNF) was used as reference. The network structure of the papers was investigated by scanning electron microscopy and tensile tests were performed to analyse the mechanical properties. Hybridised T-BC and BC nanopapers were found to yield higher tensile properties than nanopapers made from the individual constituents. However, the effect of hybridisation was lower compared to blends of BC and TEMPO-CNF. The results suggest that in order to achieve optimal nanopapers properties it is advantageous to combine nanocelluloses from different sources as this enables achieving a wider variety of nanofibril diameters which is favourable for hybridisation.

1. Introduction

A material often referred to in the ongoing quest for regrowing and environmentally friendly composite materials is nanocellulose or cellulose nanofibres (CNF) [1]. Cellulose fibres are ideal candidates for the manufacture of environmentally friendly materials and composites. Cellulose fibres are composed of the most abundant biopolymer on the planet [2] with an annual production capacity of 10^8 metric tons of pulp for papermaking [3] and over 3×10^9 t round wood [4]. Furthermore, this material offers exceptional mechanical properties and good chemical resistance. Individual elementary cellulose fibrils have been estimated to possess tensile strengths of up to 1 GPa [5]. Raman spectroscopy and X-Ray diffraction showed they have Young's moduli of up to 160 GPa [6–9] which is comparable to steel. As a composite material cellulose fibres have been used for ages by nature and humans in the form of wood [10], a material that offers unrivalled strength to weight ratios, albeit, the mechanical properties of wood cannot match those of pure cellulose fibrils. The reason for this is the inhomogeneity and impurity of wood [11], as it not only consists of cellulose but also hemicelluloses and a wide variety of extractives such as lignin. Thus, in order to utilise its full potential, higher degrees of purity and uniformity of cellulose have to be achieved. This goal can be either reached by purifying, bleaching and mechanically or chemically treating wood pulp [12] or by utilizing cellulose sequestering bacteria [13]. The use of bacteria enables the production of cellulose nanofibrils without by-compounds that are usually present in other cellulose sources [14, 15]. Thus, bacterial cellulose (BC) shows higher crystallinity but usually larger fibril diameters than CNF extracted from plant matter.

Networks of nanocelluloses, i.e. cellulose nanopapers, have gained importance in applications like water filtration [16, 17], electronics [18] and packaging materials [19]. Also, layered nanopaper-composites [20] have received significant attention in recent years and a wide variety of publications dealt with their manufacture, formulation and improvement [21, 22]. It was found that the properties of laminated nanopaper-composites are directly influenced by the properties of the nanopapers used in their manufacture [23]. For example, one approach was to optimise the porosity of nanopapers [23] for better interaction between matrix and reinforcement in the final composite by using different dispersion media. This enabled the control of the porosities in a range from 20 % when using water up to 74 % when using tert-butanol as dispersion medium. Similarly, Gustafsson *et al.* [24] investigated the influence of drying conditions on nanopaper porosity and found that slower water removal led to smaller pore sizes. This was attributed to capillary forces acting on the fibres during drying.

Another concept is hybridisation, whereby cellulosic materials on different size scales are combined to achieve the desired improvement of properties such as density, porosity and in particular tensile strength. For example Xu *et al.* [25] combined CNF and cellulose nanocrystals (CNC) and found that the addition of CNC increased the optical transparency of their (hybridised) nanopapers. They attributed this to an increase in smoothness and a decrease of porosity. CNC acted as void-fillers within the CNF network. Gonzalez *et al.* [26] found similar effects when studying the interaction of TEMPO-oxidised CNF and macroscopic cellulose pulp fibres. The authors showed that an increase of TEMPO-oxidised CNF fraction also led to decreased porosity and an increase of surface smoothness and transparency of their hybridised multi-scale papers. This also led to an increase of the tensile properties of the papers with an increase of the TEMPO-oxidised CNF content.

In a recent study [27], our group created blends of nanocelluloses derived from different sources and prepared with different chemical and mechanical treatments. These nanocelluloses had different fibril diameters and lengths and blends were prepared in order to combine their individual advantages such as ductility and high tensile strength, while simultaneously counterbalancing their flaws. The concept of combining different classes of cellulose nanofibrils had not been explored before and our study showed that the desired goal was achieved by combining bacterial cellulose (BC) with cellulose nanofibres prepared by TEMPO-mediated oxidation [28] of birch Kraft-pulp (TEMPO-CNF). This inspired us to investigate the possibility of utilizing solely differently processed BC having different fibre diameter and surface charge to create hybridised BC nanopapers. Hybridizing BC with different properties was anticipated to result in even stronger papers due to better compatibility and the higher crystallinity and purity of BC.

2. Experimental

2.1. Materials

Sodium hypochlorite and sodium hydroxide were purchased from W. Neuber’s Enkel (Vienna, Austria). Sodium bromide, (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) and hydrochloric acid were purchased from Sigma Aldrich. All chemicals were used as received without further purification. Bacterial cellulose in the form of “Nata de Coco” was purchased from a local Asian foods store. Distilled water was used unless specified otherwise.

2.2. Extraction of Bacterial Cellulose.

2 kg of Nata de Coco were submerged in 10 L of water for 12 h to remove the sugar syrup. The extract was submerged in water and squeezed by hand 5 times to further reduce the residual sugar content. Then it was soaked in sodium hydroxide solution (0.1 mol/L) at 80 °C for one hour and left to cool and soak for additional 12 h. The BC was subsequently washed until neutral and blended in a kitchen blender at a consistency of 1.5 wt.-% for 3 min.

2.3. Preparation of mechanically refined BC (r-BC)

The previously prepared BC suspension was diluted to a consistency of 0.3 wt.-% and blended to ensure homogeneity. The suspension was passed 20 times through a disc mill (MKCA6-23 Fuchs disc mill Granomat JP 150, Switzerland) to mechanically refine the BC fibres. The resulting suspension was filtered through a filter cloth to concentrate it to a consistency of 2 wt.-%. The material and papers produced thereof were termed r-BC while unrefined BC was referred to as BC.

2.4. TEMPO-mediated oxidation of BC (T-BC)

TEMPO-oxidised BC (T-BC) was produced from BC following the route established by Saito *et al.* [28, 29]. The suspension (20.2 g dry cellulose content) was diluted to a consistency of 1 wt.-%, blended (Braun Multiquick 5 MX 2050) for 5 min and then transferred to a beaker placed on a magnetic stirrer. To this dispersion, NaBr (3.6 g, 35 mmol) and TEMPO (0.38 g, 2.4 mmol) were added and stirred for 20 min until the TEMPO had fully dissolved. Afterwards 23 g (37 mmol) NaClO solution (12 wt.-%) were added to start the cellulose oxidation reaction. During the reaction, the pH of the cellulose dispersion was kept between 10 and 10.5 by the addition of 0.1 M NaOH solution, as needed. After the pH of the cellulose dispersion remained constant, the reaction mixture was stirred for another 20 min before being neutralised with 0.1 M HCl. Afterwards, the TEMPO-oxidised pulp was transferred into a Büchner-Funnel and washed with approximately 4 L of water. To disintegrate the TEMPO-oxidised BC into nanofibrils, the cellulose dispersion was diluted with water to a consistency of around 1.5% and blended (Braun Multiquick 5 MX 2050) for 40 min. The cellulose was left to cool down to room temperature and then stored at 6 °C until further use.

2.5. Nanopaper preparation

Nanopapers were prepared from BC, r-BC and T-BC as well as blends of the three materials. Binary mixtures (1:1 by weight) were prepared from BC/r-BC, BC/T-BC and r-BC/T-BC. A ternary mixture was prepared by blending all three types of nanocellulose in the ratio of 1:1:1 by weight. For the preparation of neat or hybridised papers, the suspensions were blended for 2 min in deionised water at a consistency of 0.2 wt.-%.

To fabricate (hybridised) bacterial cellulose nanopapers, the nanocellulose-in-water suspensions were vacuum-filtered onto a cellulose filter paper (VWR 413, 5-13 µm pore size, Lutterworth, UK). The filter cake was wet-pressed under a weight of 10 kg between blotting papers (3MM Chr VWR, Lutterworth, UK) for 5 min to remove excess water. The compressed wet filter cakes (with a moisture content of approximately 85%) were then further consolidated by sandwiching the filter cakes between fresh blotting papers and metal plates, followed by hot pressing (type 25-12-2H, Carver Inc., Wabash, USA) under a weight 1 t for 1 h at 120°C.

2.6. Nanopaper characterisation

2.6.1. Tensile properties of hybridised bacterial cellulose nanopapers

Tensile testing was done on a minimum of 5 specimens per sample at 26 °C and 44 % RH using an Instron universal test frame (Model 5969 Dual Column Universal Testing System, Instron, Darmstadt, Germany) equipped with a 1 kN load cell and a non-contact video extensometer (Gig ProE, iMETRIUM, Bristol, UK). For this purpose, tensile test specimens were punched from the nanopapers (Zwick ZCP 020 Manual Cutting Press, Zwick, Ulm, Germany) with specimen shapes in accordance to EN ISO 527-2, Type 5B. Prior to testing, these samples were weighed and their thickness was measured at 5 different spots using a digital micrometre (705-1229, RS components, Corby, UK). These values were also used to determine the density and porosity of the samples. The gauge length for the tests was set to 15 mm and a testing speed of 1 mm min^{-1} was set. The Young's modulus was analysed in the linear elastic region as a secant between strength values separated by 0.2 % strain.

2.6.2. Morphology of hybridised bacterial cellulose nanopapers

The surface morphology of the nanopapers was investigated by scanning electron microscopy (SEM, Zeiss Supra 55VP, Austria) operated at an acceleration voltage of 2 kV and a working distance of 7.3 mm. Prior to SEM, the nanopapers were mounted on aluminium sample holders using carbon tape and coated with a 5 nm layer of gold.

3. Results and discussion

3.1. Nanopaper preparation, density and porosity

Bacterial cellulose nanopapers of BC, r-BC and T-BC as well as various mixtures thereof were prepared and their densities were determined. From the densities and the skeletal density of cellulose (1500 kg m^{-3} [23]) the porosity of the nanopapers was calculated. The results are collected in Table 1.

Table 1. Density ρ [kg m^{-3}] and porosity P [%] of the prepared bacterial cellulose nanopapers and blends thereof.

	BC	r-BC	T-BC	BC/r-BC	BC/T-BC	r-BC/T-BC	BC/r-BC/ T-BC
ρ [kg m^{-3}]	1000 ± 20	1090 ± 60	1070 ± 30	1020 ± 20	1060 ± 10	1060 ± 20	1040 ± 10
P [%]	33 ± 1	27 ± 4	29 ± 2	32 ± 1	30 ± 1	29 ± 1	30 ± 1

The results of density and porosity showed tighter packing for r-BC and T-BC compared to BC nanopapers. Contrary to expectations, T-BC nanopapers had a higher porosity than r-BC nanopapers suggesting that it consisted of bigger fibres. While the blends had lower porosity than neat BC nanopapers, they had porosities similar to neat r-BC and T-BC meaning that the increase in packing efficiency that was found in our previous work [27] did not occur in hybridised bacterial cellulose nanopapers. This indicated that T-BC were not as finely defibrillated as TEMPO-CNF in our previous study.

3.2. Tensile properties of (hybridised) bacterial cellulose nanopapers

The mechanical properties of the BC nanopapers were determined by tensile tests and representative strain stress curves are depicted in Figure 1. The values of tensile strength, Young's modulus and strain to break are collected in Table 2. It also contains the results of papers prepared from a blend of TEMPO-oxidised birch Kraft pulp (TEMPO-CNF) and a blend of TEMPO-CNF and BC (termed TEMPO-CNF/BC) from literature [27] as reference.

The representative stress strain curves in Figure 1 have the typical shape for nanopapers, enduring steep inelastic deformation and yielding at around 1 % strain. T-BC and BC/T-BC showed a steeper slope in the yielding region and consecutively had a lower strain to break than BC and r-BC in the same region. The fact that all samples started to yield in approximately the same region indicates that their network structures were very similar, as yielding is the reorientation of the network structures. The different slopes of T-BC and BC/T-BC can be explained by differences in hornification, which is the introduction of permanent hydrogen bonds between fibres. This is promoted by carboxylic groups [30, 31] and means that those bonds had to be broken during the reorientation of the network while yielding. As anticipated, mechanical refining led to a decrease in tensile strength due to a shortening of the fibrils [27]. Counterintuitively, TEMPO-mediated oxidation of BC led to a decrease of its mechanical properties, and the resulting nanopapers were not as strong as those prepared from TEMPO-CNF. However, T-BC nanopapers had a 40 % higher strain to break than TEMPO-CNF nanopapers. Although the combination of T-BC and BC had a positive effect on the overall strength of the nanopapers and the BC/T-BC nanopapers showed higher tensile strengths than either of its constituents, the positive effect of hybridisation was significantly less pronounced than for nanopapers comprised of TEMPO-CNF and BC (compare Table 2). This indicates, that the higher crystallinity of the BC fibrils led to a different behaviour during TEMPO-mediated oxidation. One reason might be, that the BC fibrils were shortened due to stronger oxidation in the amorphous regions of the fibrils, while crystalline regions of the bacterial cellulose fibre bundles were only oxidised on their surface, as the oxidant was not able to penetrate into the highly crystalline structures. This yielded shorter but not thinner fibres. To investigate this hypothesis, SEM studies of the fibre networks were done.

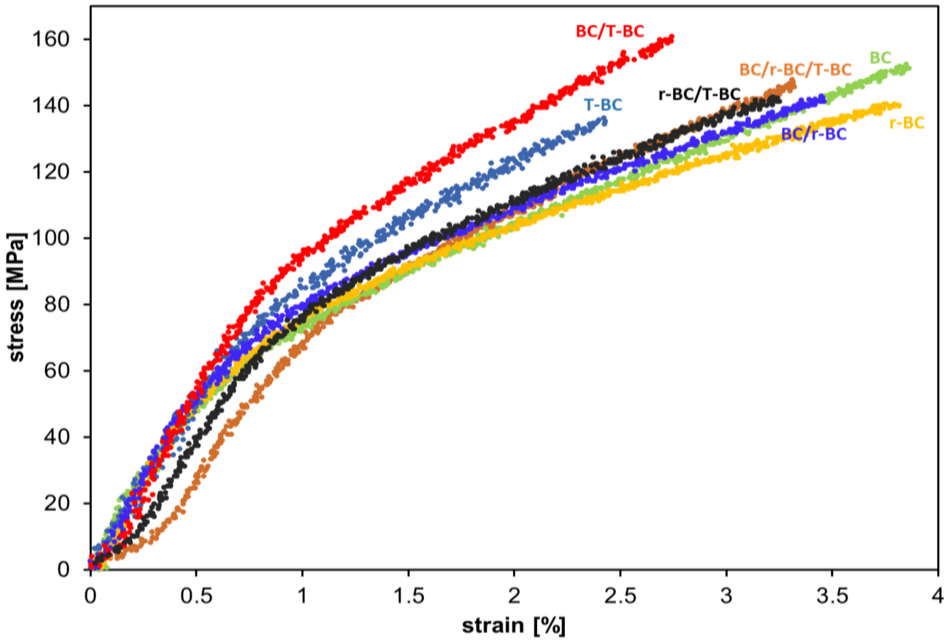

Figure 1. Representative stress-strain curves of bacterial cellulose nanopapers and (hybridised) blends thereof.

Table 2. Ultimate tensile strength σ, strain to break ε and Young's modulus E of all pure and blend nanopapers as well as TEMPO-CNF and BC/TEMPO-CNF from literature [27].

	σ (MPa)	ε (%)	E (GPa)
BC	153 ± 7	3.6 ± 0.2	15.9 ± 3.0
r-BC	141 ± 6	3.7 ± 0.1	14.4 ± 2.8
T-BC	135 ± 9	2.2 ± 0.2	15.0 ± 2.2
BC/r-BC	145 ± 2	3.5 ± 0.3	15.0 ± 1.5
BC/T-BC	161 ± 6	3.0 ± 0.3	13.3 ± 1.4
r-BC/T-BC	140 ± 4	3.2 ± 0.2	12.1 ± 2.8
BC/r-BC/T-BC	152 ± 5	3.3 ± 0.2	14.6 ± 4.2
TEMPO-CNF [27]	160 ± 14	1.3 ± 0.1	16.7 ± 0.5
BC/TEMPO-CNF [27]	197 ± 6	2.0 ± 0.7	14.9 ± 0.8

3.1. Surface morphology and network structure of bacterial cellulose nanopapers

To investigate the surface morphology and the network structure, SEM images were taken of all nanopapers produced. Additionally, SEM images of a paper prepared from TEMPO-oxidised birch Kraft pulp were taken to draw conclusions about the nature of the TEMPO-mediated oxidation of BC. The SEM images are collected in Figure 2.

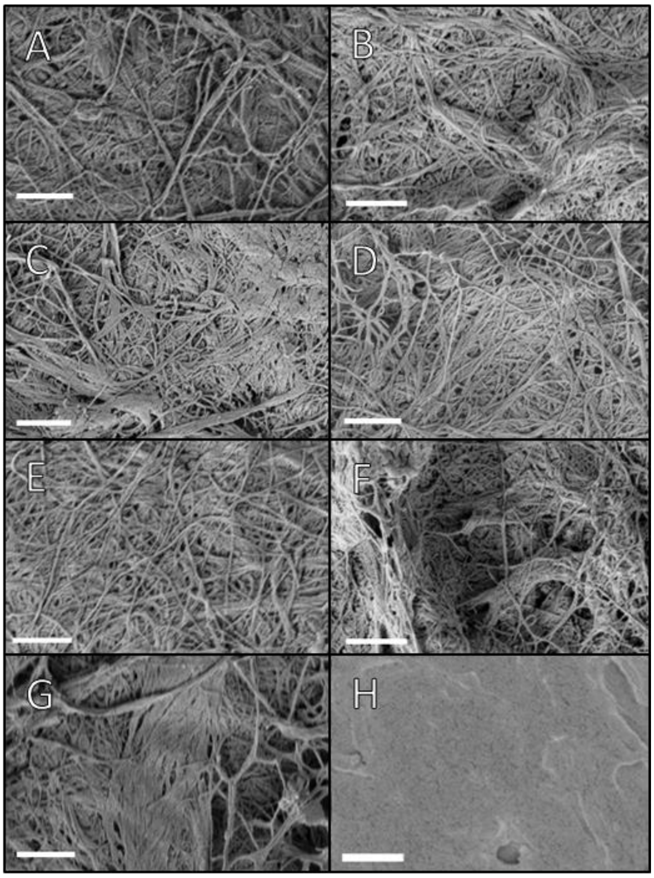

Figure 2. SEM images of bacterial cellulose nanopapers. BC (A), r-BC (B), T-BC (C), BC/r-BC (D), BC/T-BC (E), r-BC/T-BC (F) and BC/r-BC/T-BC (G). Furthermore the surface of TEMPO-CNF (H) [27] is shown as reference. All scale bars are 1 µm.

Contrary to the expectation that TEMPO-BC would consist of uniform fibrils with small diameters, all samples exhibited a similar network structure (Figure 2). The prevalent fibril diameter of all samples was around 30 nm. The network structure of BC was composed of uniform fibres with some agglomerates. The same was true for r-BC in which also damaged and fringed fibres could be observed. Figure 2 (C) shows that fibrils were mostly intact and in the same size range as neat BC (A). T-BC (C) hardly had regions of too small features to be observable in SEM, which is characteristic for TEMPO-oxidised cellulose (H). These results confirm the results of tensile tests that showed that T-BC was more ductile than TEMPO-CNF, which is often caused by larger fibrils. Hybridised blends also showed similar network structures, with small fibrils interpenetrating the network formed of larger fibrils. No significant differences could be observed for the various blends.

4. Conclusions

The results substantiate the hypothesis that for good hybridisation, nanocelluloses of significantly different diameters are needed. While the combination of BC and T-BC yielded some positive effects, they were significantly less pronounced than anticipated. T-BC fibrils were not defibrillated enough to enable for better fibril stacking. The amount of defibrillation achieved was not sufficient to counteract the detrimental effect of the oxidation procedure, as this procedure proposedly shortened the fibrils. The same was true for mechanical refinement of BC. Although BC fibres were defibrillated, the supposed damages done to the fibre structure outweighed any positive effects that possibly could have been achieved by fibres with smaller diameters. The insights gained from this study suggest, that for further optimisation of BC nanopapers it is necessary to combine it with other high performance classes of cellulose such as TEMPO-CNF with different charge contents, fibril dimensions or cellulose nanocrystals.

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