

All-cellulose nanocomposites by surface selective dissolution of bacterial cellulose

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Abstract All-cellulose nanocomposites using bacterial cellulose (BC) as a single raw material were prepared by a surface selective dissolution method. The effect of the immersion time of BC in the solvent (lithium chloride/*N,N*-dimethylacetamide) during preparation on the nanocomposite properties was investigated. The structure, morphology and mechanical properties of the nanocomposites were characterized by X-ray diffraction, scanning electron microscopy, and tensile testing. The optimum immersion time of 10 min allowed the preparation of nanocomposites with an average tensile strength of 411 MPa and Young's modulus of 18 GPa. With the longest immersion time of 60 min, the prepared composite sheet turns to express a very high toughness characteristic possessing a work-to-fracture as high as 16 MJ/m³. These biobased nanocomposites show high performances thanks to their unique structure and properties.

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Introduction

In the last decade, a growing environmental awareness has inspired a deliberate attempt to develop biobased composite materials (Heijenrath and Peijs 1996; Peijs et al. 1998; Peijs 2000; Singleton et al. 2003). The combination of natural cellulosic fibres and petro- or biobased polymeric matrices has been driven by their potential positive ecological benefits with respect to ultimate disposability and the use of renewable resources. The issue of surface interactions between natural fibres and polymer matrices are usually minimised by fibre surface or matrix modifications or addition of compatibilisers or coupling agents to achieve the effective composites (Garkhail et al. 2000; Stamboulis et al. 2000). Nowadays, natural fibre reinforced composites are increasingly replacing glass fibre reinforced composites as a viable alternative in various applications particularly in automotive industry (Averous and Boquillon 2004; Bledzki and Gassan 1999; Lu et al. 2006; Mohanty et al. 2000; Nishino et al. 2003; Oksman et al. 2006; Samir et al. 2005; Soykeabkaew et al. 2004).

The use of nano-scale fillers as reinforcement in biobased composites is another technology that has

been extensively investigated. With their nanometric size effect and extremely high specific-surface area, nano-fillers have the potential for significant reinforcement in composite materials at very small filler loadings and providing some unique outstanding properties as compare to their conventional micro-composite counterparts (e.g. natural fibre reinforced composites; Grunert and Winter 2002; Samir et al. 2005). Studies incorporated clay, chitin or cellulose whisker as reinforcement into polyvinyl alcohol (PVA), polylactic acid (PLA), polycaprolactone (PCL), polyvinyl acetate (PVAc), polyhydroxy butyrate (PHB), cellulose acetate butyrate (CAB), starch and aliphatic polyesters to create bio-nanocomposites have been reported (Garcia de Rodriguez et al. 2006; Jung et al. 2007; Lu et al. 2006; Oksman et al. 2006; Orts et al. 2005; Samir et al. 2005; Wibowo et al. 2006; Wu et al. 2007; Yu et al. 2003). Lately, bacterial cellulose (BC), which presents a unique network structure of a random assembly of ribbon shaped nano-fibres, has also drawn scientific attention as reinforcement for polymers. BC has recently been incorporated in hydroxyapatite (HAp), polylactic acid (PLA), polyvinyl alcohol (PVA), cellulose acetate butyrate (CAB) and also as a hybrid material in apple and radish pulp (Gea et al. 2007; Gindl and Keckes 2004; Millon and Wan 2006; Wan et al. 2006, 2007). An example of the high-strength composites of BC sheets reinforced phenolic resin attaining an impressive Young's modulus of 28 GPa has as well been reported (Nakagaito et al. 2005).

BC is synthesised by various bacteria belonging to the genera *Acetobacter*, *Rhizobium*, *Agrobacterium*, and *Sarcina* (Jonas and Farah 1998). However, the most efficient producers are Gram-negative, acetic acid bacteria *Acetobacter xylinum* (Bielecki et al. 2004). In a culture medium containing carbon and nitrogen sources, cultivated bacteria produce extracellular cellulose, an ultrafine ribbons network structure in the form of a highly hydrated pellicle (Barud et al. 2007; Nakagaito et al. 2005). Dimensions of the ribbons are roughly 3–4 nm (thickness) and 70–130 nm (width). They are made from cellulose chains aggregated to form sub-fibrils, which have a width of approximately 1.5 nm and then the sub-fibrils are crystallized into microfibrils, which subsequently form bundles, while the latter form ribbons (Bielecki et al. 2004; Jonas and Farah 1998; Yamanaka et al. 2000). The unique properties of BC;

i.e. high purity, high crystallinity, high mechanical strength, high water-holding capacity, high porosity and good biocompatibility have made it find a multitude of applications in paper, textile, and food industries, and as a biomaterial in cosmetics and medicine (Bielecki et al. 2004; Jonas and Farah 1998; Zhou et al. 2007). An acoustic diaphragm of high fidelity loudspeakers and headphones marketed by Sony Corp. is another successful application that has reached the level of practical use (Iguchi et al. 2000). For this application, a high dynamic Young's modulus, close to 30 GPa, for sheets obtained from BC pellicles has been reported (Nishi et al. 1990; Yamanaka et al. 1989). This indicated that the ultrastructure of BC produced superior physical properties (Yamanaka et al. 2000). Recently, measurements using atomic force microscopy by Guhados and co-workers (2005) revealed a Young's modulus of 78 ± 17 GPa for BC ribbons with widths ranging from 35 to 90 nm. By using Raman spectroscopic technique, an estimation of the higher value of 114 GPa Young's modulus of a single filament BC is obtained (Hsieh et al. 2008). In fact, the crystal modulus of cellulose I (the type of cellulose polymorphs for native cellulose including BC) in the direction parallel to the chain axis measured by X-ray diffraction was calculated to be 138 GPa (Nishino et al. 1995). Clearly, this information indicates to a high modulus which renders a promising candidate as reinforcement for bionanocomposites.

In the present study, BC was chosen as a raw material to prepare all-cellulose nanocomposites using a surface selective dissolution processing method. A similar preparation technique used to prepare all-cellulose composites of micro-size natural ligno-cellulosic fibres and regenerated cellulose fibres have been previously reported by Nishino et al. (2004), Nishino and Arimoto (2007), Qin et al. (2008) and Soykeabkaew et al. (2008a, b). This preparation technique is inspired by mono-material based concepts such as single polymer composites or self-reinforced polymer composites. These composites are basically monomaterials and therefore fully recyclable and environmentally friendly. In addition, since both fibre and matrix are composed of the same material they show excellent interfacial compatibility. Next to more traditional ways of creating all-polymer composites through the impregnation of polymer fibres with a polymer matrix of a slightly

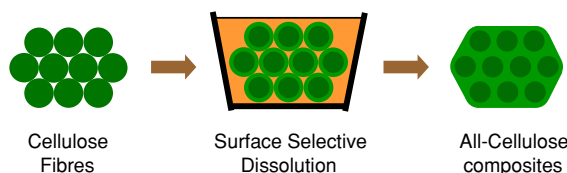


Fig. 1 Surface selective dissolution process to prepare all-cellulose composites

lower melting temperature, the selective melting of the fibre or tape surface and subsequently ‘welding’ fibres or tapes together has been proposed for the manufacture of all-polypropylene composites by Ward and Hine (1997, 2004) and Peijs and co-workers (Alcock et al. 2006, 2007; Cabrera et al. 2004; Peijs 2003). These all-polypropylene composites have exceptionally high fibre volume fraction of around 90% which makes them highly competitive with conventional glass fibre-reinforced composites of much lower fibre loadings in various potential applications, notably the automotive and sports industry.

However, in the case of cellulose where melting is not an option, unlike in the previously mentioned thermoplastic fibres, the matrix phase needs to be created through a surface selective dissolution process rather than melting as illustrated in Fig. 1. The effect of the immersion time of BC in the solvent during preparation, which determines how much of the outer layer of the fibres is dissolved to form a matrix phase, on nanocomposites’ properties was investigated. The structure and morphology of the prepared nanocomposites were examined by using X-ray diffraction and scanning electron microscopy. Tensile testing was used to characterize the mechanical properties of the nanocomposites.

Experimental

Preparation of bacterial cellulose (BC) sheets

BC pellicles were produced by the bacterial strain *Acetobacter xylinum* in a static culture medium of 50 g glucose, 5 g yeast-extract, 5 g $(\text{NH}_4)_2\text{SO}_4$, 4 g KH_2PO_4 , and 0.1 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in a litre of water for 14 days at 28 °C (Gea et al. 2007; Iguchi et al. 2000). Thereafter, the gel-like BC pellicles were purified to remove bacteria cells by firstly washing in

running water, then in 5% w/v NaOH and finally in 2.5% v/v NaOCl. The pellicles were roughly 8 mm thick and cut into square pieces of $9 \times 9 \text{ cm}^2$. BC sheets were produced by compressing a pellicle between metal meshes (approximately 30 μm diameter pores) using a Rondol Hydraulic Press under a relatively low pressure of 0.25 MPa at 115 °C for 5 min (Gea et al. 2007; Nakgaito et al. 2005; Yamanaka et al. 1989). The obtained sheets were roughly 30–40 μm thick.

Preparation of all-cellulose nanocomposites using BC sheet

The previously prepared BC sheet was cut into square pieces of $4 \times 4 \text{ cm}^2$ and was then pre-treated by immersion in distilled water, acetone and *N,N*-dimethylacetamide (DMAc) respectively, each for 1 h at room temperature (Dupont 2003; Nishino and Arimoto 2007). After that, the activated BC sheet was immersed in 8% wt/v lithium chloride (LiCl)/DMAc solvent at the specified immersion times of 5, 10, 15, 20, 40 and 60 min for the surface selective dissolution. Then, the BC sheet was taken out of the solvent and immersed in methanol for 24 h to extract DMAc and LiCl from the system. The specimen was then dried in a compression moulding machine (Rondol Hydraulic Press) under a relatively low pressure of 1.25 MPa at 50 °C for 1 h.

Characterizations

The morphology and microstructure of BC and all-cellulose nanocomposite sheets prepared from BC were examined with a field emission scanning electron microscope (FESEM), JEOL JSM 6300F at an accelerating voltage of 10 kV. Prior to examination, the surface of the specimen was coated with a thin layer of gold, $\sim 20 \text{ nm}$.

X-ray diffraction profiles were detected using Cu $K\alpha$ radiation, generated with RINT-2000 (Rigaku Co.) at 40 kV, 20 mA which was irradiated perpendicular to the surface of BC and BC nanocomposite sheets.

Mechanical properties of BC and BC nanocomposite sheets were investigated by a tensile tester, Instron 5584, at room temperature. The gauge length of the specimen of 5 mm width was 15 mm and a cross-head speed of 15 mm/min was used for the

tests. Ultimate tensile strength, Young's modulus and elongation at break of the specimen were evaluated. The results were reported as the average value from measurements of at least five specimens.

Prior to all measurements, the specimens were conditioned at the controlled relative humidity of $55.9 \pm 0.3\%$ at 20°C (according to ASTM E104).

Results and discussion

Figure 2 shows a comparison of the X-ray diffraction profiles of bacterial cellulose (BC) and all-cellulose nanocomposites prepared from bacterial cellulose (BC nanocomposites). It reveals that after an immersion time of up to 20 min of BC in the solvent during preparation, the X-ray diffraction patterns of the resulting BC nanocomposites remain similar to that of the original BC. However, after 40 min immersion time, the crystallinity of the prepared BC nanocomposites is found to be noticeably reduced as indicated by their broader diffraction peaks. This suggests that at such long immersion times, a significant fraction of the ribbons is dissolved to form the matrix phase (non-crystalline domain), which results in a reduction of the overall crystallinity of the BC nanocomposite (Nishino et al. 2004; Shibasaki et al. 1997; Soykeabkaew et al. 2008a, b). Processing X-ray diffraction data by means of Scherrer's equation (Eq. 1) also reveals that the crystallite size in the BC nanocomposites is reduced with immersion time (see Fig. 2). This is undoubtedly due to the longer immersion times where more cellulose is dissolved and hence smaller cellulose crystallites remain (Nishino et al. 2004; Soykeabkaew et al. 2008a).

$$D = \lambda / \beta \cos \theta \quad (1)$$

where $\lambda = 1.5418 \text{ \AA}$, β : corrected integral width, θ : Bragg angle for the crystallographic plane ($1\bar{1}0$) reflections (Kim et al. 2002; Watanabe et al. 1998).

In line with the X-ray diffraction results, scanning electron micrographs of the prepared BC nanocomposites illustrate that with increasing immersion time, larger amounts of matrix phase are created in each planar layer of the structure (see Fig. 3) and noticeably, on the sheet surface (see Fig. 4). From the series of SEM pictures, it was also found that the size of the ribbons in the BC nanocomposites structure is gradually decreased with immersion time. Obviously, after

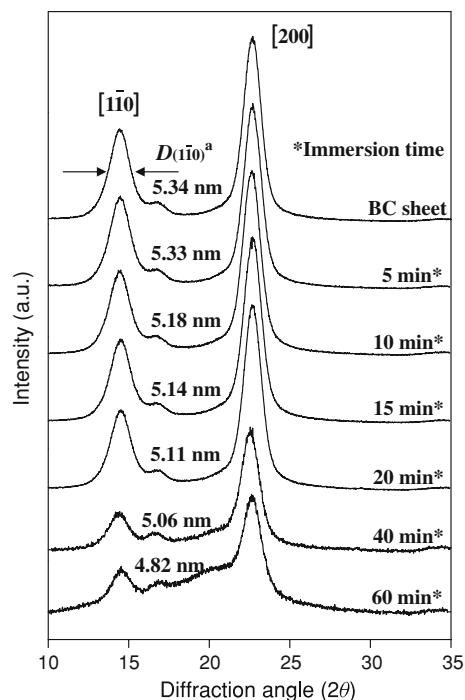


Fig. 2 X-ray diffraction profiles of bacterial cellulose (BC sheet) and all-cellulose nanocomposites prepared with bacterial cellulose at various immersion times. ^aEstimated crystallite size (D) of a crystallographic plane ($1\bar{1}0$)

40 and 60 min immersion time, much smaller ribbons as compared to the original BC ribbons are observed.

Table 1 gives information for the mechanical properties of BC sheets, treated BC sheets and BC nanocomposites. It shows that the treatment of the BC sheets with oxidant and alkali solutions significantly improves their properties since traces of contaminants which were suspected to affect the formation of hydrogen-bonding were removed by the treatment (Iguchi et al. 2000). For BC nanocomposites, the tensile test results show that the composite prepared with 10 min immersion time exhibits the best mechanical properties; i.e. an average tensile strength of 411 MPa and Young's modulus of 18 GPa. Presumably, at this optimum preparation condition, the amount of BC ribbon surfaces that is selectively dissolved to form the matrix phase is adequate to provide an efficient additional-bonding to the already strong-hydrogen bonded network of BC ribbons in the nanocomposite structure (see Fig. 4, 10 min). Meanwhile, the remaining ribbon cores were still largely unaffected and hence maintain most of their initial structure and strength. This leads to an

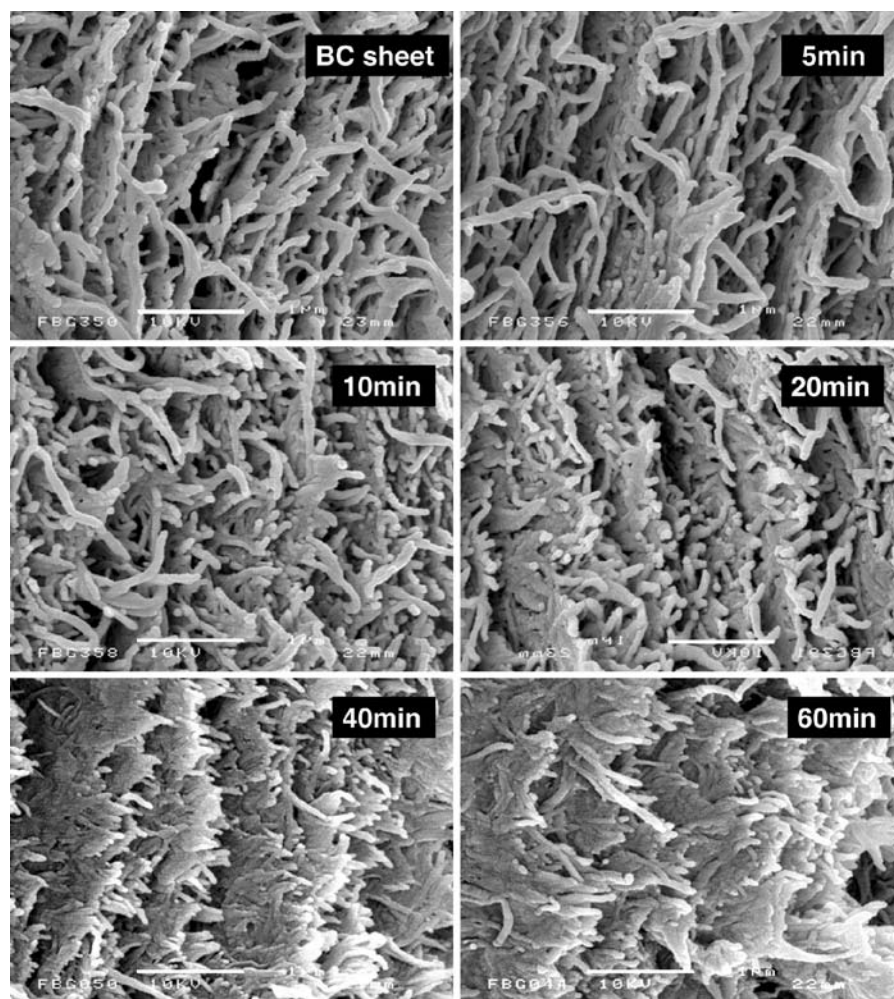


Fig. 3 Scanning electron micrographs of the fracture surface of bacterial cellulose (BC sheet) and all-cellulose nanocomposites prepared with bacterial cellulose at various immersion times. The length of the scale bar is 1 μ m

optimum in properties of this BC nanocomposite. In addition, a slight enhancement in tensile strength over the original BC sheet is also observed (see Table 1). For the BC nanocomposite of 5 min immersion time, a smaller fraction of the ribbon surfaces is dissolved to form the matrix phase which may possibly not be enough to provide an efficient additional-bonding for the ribbon network structure. As illustrated in the SEM picture (Fig. 4, 5 min), very thin layers of newly formed matrix are covering the ribbon network. This results in similar or even worse mechanical properties of BC nanocomposites as compared to neat BC sheet. On the other hand, for BC nanocomposites prepared with 15–60 min immersion time, (Fig. 5) larger amounts of matrix phase are formed since larger

fractions of the ribbons are dissolved with increasing immersion time. Nevertheless, the more the ribbons are dissolved, the less of the original BC structure and strength remains. Therefore, with increasing immersion time, a gradual reduction in the BC nanocomposites' modulus and strength is obtained (see Table 1).

Interestingly, compared to the all-cellulose nanocomposites prepared by partial dissolution of microcrystalline cellulose powder of Gindl and Keckes (2005) and the recently reported nanopaper prepared from cellulose nanofibrils by Henriksson et al. (2008), the optimum BC nanocomposite in this work (BCC 10 min) has nearly twice the tensile strength. Furthermore, a similar high value of work-to-fracture

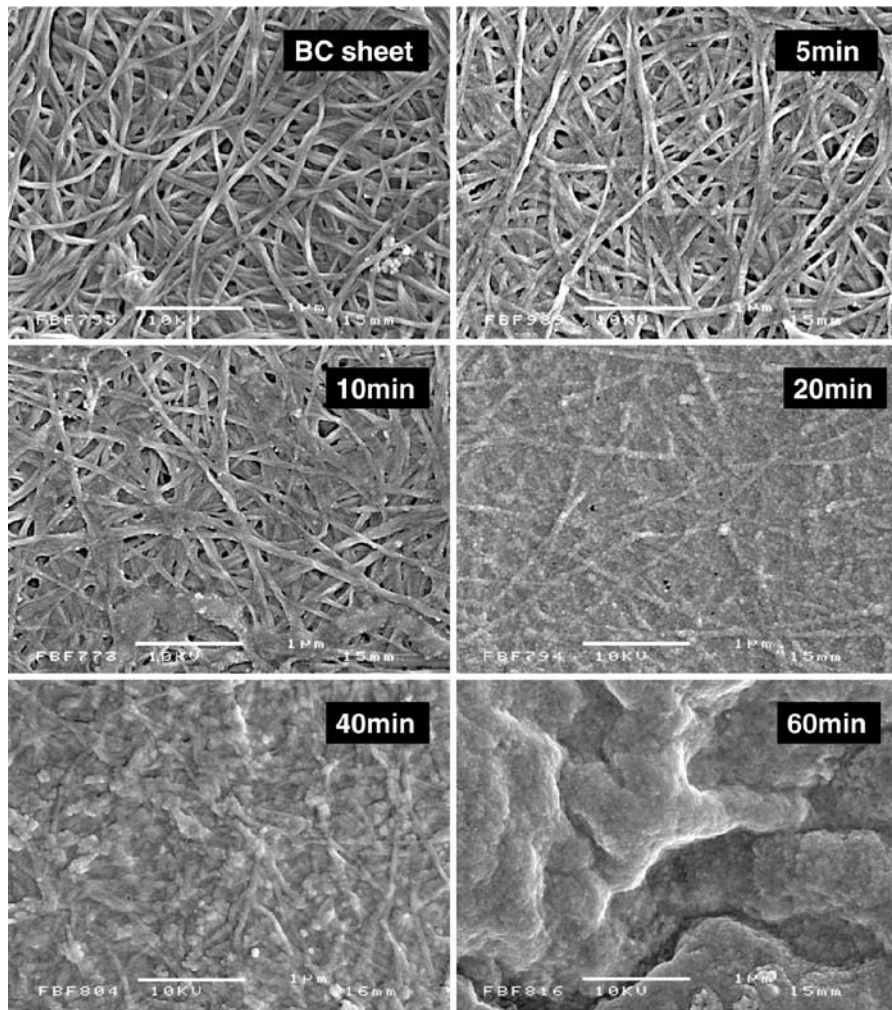


Fig. 4 Scanning electron micrographs of the sheet surface of bacterial cellulose (BC sheet) and all-cellulose nanocomposites prepared with bacterial cellulose at various immersion times. The length of the *scale bar* is 1 μm

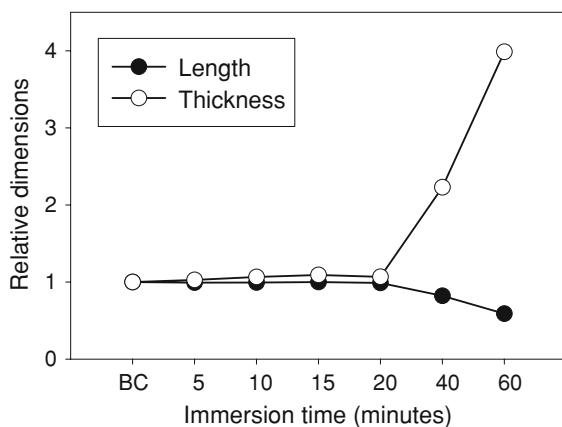
as observed in this all-cellulose nanocomposites and nanopaper is obtained for the BC nanocomposite prepared with the longest immersion time (BCC 60 min), expressing a very high toughness characteristic (Table 1). Noticeably, the elongation at break of this BC nanocomposite increases approximately nine times with regard to the original BC sheet. This is supposedly related to the fact that the resulting composite sheet has swollen in the thickness direction, leading to a significant reduction in the amount of inter-planar hydrogen bonds formed, which allows for slippage between BC planar layers and consequently considerably extension of the BC nanocomposite structure.

As shown by the stress-strain curves of these BC nanocomposites (Fig. 6a), with increasing immersion time, an obvious reduction trend in the composites' tensile properties is apparent. In light of these results it is interesting to compare our data based on nano-size cellulose fibres with the isotropic all-cellulose composites based on micro-size cellulose fibres as recently introduced by Nishino and Arimoto (2007). In their work, Nishino and Arimoto developed a random all-cellulose composite, using filter paper as a cellulose source in combination with the similar selective dissolution process, where part of the fibre skin was dissolved to form the matrix. Unlike our BC composites, these all-cellulose composites showed a strong

Table 1 Mechanical properties of bacterial cellulose sheets^a, treated bacterial cellulose sheets^b, all-cellulose nanocomposites prepared with bacterial cellulose (this work) and microcrystalline cellulose powder^c and the recently reported high toughness cellulose nanopaper^d

Materials	Modulus (GPa)	Tensile strength (MPa)	Strain (%)	Work-to-fracture (MJ/m ³)
BC sheets ^a	15–35	200–300	1.5–2.0	–
Treated BC sheet ^b	23	510	4.4	12.6
Treated BC sheet (this work)	20 (1.7)	395 (36)	3.5 (0.6)	7.3 (1.8)
BCC 5 min	16 (1.0)	392 (23)	4.1 (0.3)	8.2 (1.1)
BCC 10 min	18 (0.8)	411 (22)	4.3 (0.3)	9.0 (1.1)
BCC 15 min	16 (0.6)	309 (25)	3.4 (0.4)	5.5 (1.2)
BCC 20 min	11 (0.6)	188 (19)	3.5 (0.4)	3.5 (0.6)
BCC 40 min	4.4 (0.3)	97 (15)	10.6 (1.6)	6.0 (1.4)
BCC 60 min	2.6 (0.4)	75 (15)	29.7 (4.0)	15.8 (4.1)
All-cellulose nanocomposites ^c with ratio of cellulose I/III				
= 24/76	12.6	218.6	10.7	18.2
= 43/57	13.1	242.8	8.6	16.3
= 59/41	14.9	215.1	3.6	5.6
Nanopaper from cellulose nanofibrils ^d	13 (0.6)	214 (7)	10.1 (1.4)	15.1 (1.9)

^a Klemm et al. 2005; ^b Nakagaito et al. 2005; ^c Gindl and Keckes 2005; ^d Henriksson et al. 2008

**Fig. 5** Effect of the immersion time on the final dimension of all-cellulose nanocomposites prepared with bacterial cellulose as compared to the original dimension of the starting sheet

improvement in tensile strength with immersion time (up to almost five folds the initial strength of the filter paper from 50 MPa to 211 MPa for the composite, Fig. 6b). In comparison to BC, filter paper consists of a loosely formed, much weaker, micro-size cellulose fibre network with the appearance of larger voids and less hydrogen bonded fibre–fibre interactions (Fig. 7b). After the surface selective dissolution process these voids are filled with cellulose matrix leading to a strong interface and good stress transfer capability

of the resulting composites and as a result a marked increase in strength of the all-cellulose composite sheet. The improvement in the composite's interface with increasing immersion time was also evident through the observed improvement in optical transparency with immersion time of these all-cellulose composites (Nishino and Arimoto 2007).

On the other hand, BC sheets have already a very strong network structure as a result of the nano-size cellulose ribbons, which allows them to form more extensive hydrogen bonding (Fig. 7a; Yamanaka et al. 2000). Another reason for the high initial strength of the BC sheets is possibly due to another interesting feature of BC, the continuity of the fibrils that are not necessarily linear but possess “three-way branching points” as observed by Yamanaka et al. (1989). As shown in this previous work and Gea et al. (2007), when BC pellicles were mechanically fragmented and sheets prepared, the modulus and strength decreased to about a half to a third of the values of sheets from non-disintegrated BC pellicles, and they presumed that it was due to the loss of continuity of the original network structure. A similar phenomenon was also reported by Nakagaito et al. (2005) who illustrated the stress-strain curves of the treated BC sheet (with continuous nano-fibril network) compared to the sheet prepared from microfibrillated cellulose (MFC) obtained through

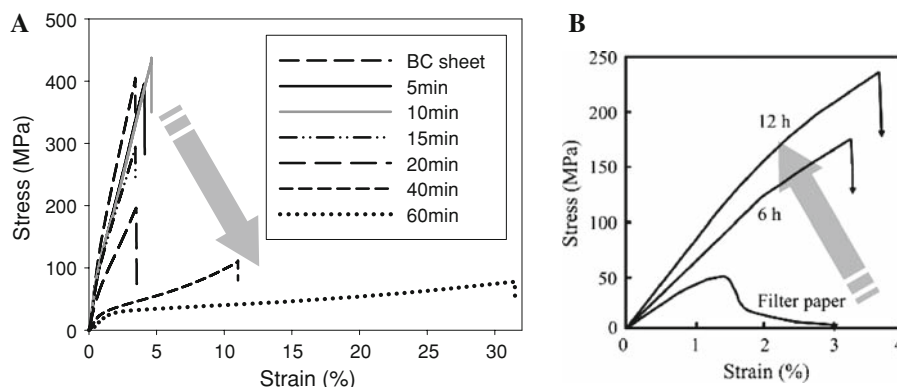
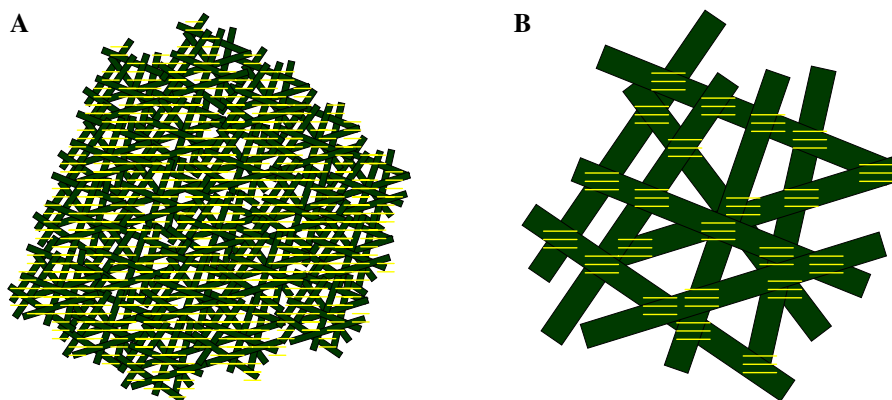


Fig. 6 Stress-strain curves of **a** bacterial cellulose (BC) sheet and all-cellulose composites prepared with nano-size bacterial cellulose at various immersion times and **b** all-cellulose

composites prepared with micro-size cellulose fibres of filter paper (Nishino and Arimoto 2007)

Fig. 7 Schematic illustrating extensive hydrogen bonding in **a** bacterial cellulose (nano-size network) compared to **b** cellulose paper (micro-size network)



fibrillation of Kraft pulp (with definite-length microfibril network). For the BC nanocomposite in this current work, at the optimum preparation condition of 10 min immersion time, only a slight enhancement in the network structure caused by the additional-bonding from the newly created matrix is obtained. Since the BC sheets have already a high initial level of inter-fibre bonding through extensive hydrogen bonding of the continuous nano-ribbons no further improvements are observed with further dissolution times.

It should also be noticed that as compared to micro-size cellulose fibres in the study of Nishino and Arimoto (2007) and Soykeabkaew et al. (2008a, b), nano-size BC ribbons require much shorter time-scales for the dissolution process. This is clearly due to the nano-size of the BC fibres implying a very high total fibre surface area per unit mass of BC available to interact with the solvent and therefore shortening the dissolution times.

Conclusions

All-cellulose nanocomposites of bacterial cellulose (BC nanocomposites) were prepared by a surface selective dissolution method. During preparation, as the immersion time of BC in the solvent was increased, larger fractions of BC ribbon surfaces were dissolved to form the matrix phase resulting in smaller BC ribbons as well as cellulose crystallites retained in the BC nanocomposite structure. Tensile tests showed that an immersion time of 10 min was the optimum processing condition to produce BC nanocomposites with the best overall mechanical properties. At this preparation condition, the amount of newly formed matrix phase could provide some additional-bonding to the BC fibre network, while the remaining BC ribbon cores still maintained most of their initial structure and strength. Larger immersion times, however, resulted in a decrease in properties

due to a loss of the original BC fibre structure and are a further indication of the very strong initial hydrogen bonded network of continuous nano-size cellulose ribbons in BC. In addition, for the longest 60 min immersion time, the prepared BC nanocomposite sheet turns to show a very high toughness performance with a strain-to-failure as high as 30%.

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References

- Alcock B, Cabrera NO, Barkoula N-M, Peijs T (2006) The mechanical properties of unidirectional all-polypropylene composites. *Compos Part A-Appl S* 37(5):716–726. doi:[10.1016/j.compositesa.2005.07.002](https://doi.org/10.1016/j.compositesa.2005.07.002)
- Alcock B, Cabrera NO, Barkoula N-M, Spoelstra AB, Loos J, Peijs T (2007) The mechanical properties of woven tape all-polypropylene composites. *Compos Part A-Appl S* 38(1):147–161. doi:[10.1016/j.compositesa.2006.01.003](https://doi.org/10.1016/j.compositesa.2006.01.003)
- Averous L, Boquillon N (2004) Biocomposites based on plasticized starch: thermal and mechanical behaviours. *Carbohydr Polym* 56:111–122. doi:[10.1016/j.carbpol.2003.11.015](https://doi.org/10.1016/j.carbpol.2003.11.015)
- Barud HS, Ribeiro CA, Crespi MS, Martines MAU, Dexpert-Ghys J, Marques RFC, Messaddeq Y, Ribeiro SJL (2007) Thermal characterization of bacterial cellulose–phosphate composite membranes. *J Therm Anal Calorim* 87:815–818. doi:[10.1007/s10973-006-8170-5](https://doi.org/10.1007/s10973-006-8170-5)
- Bielecki S, Krystynowicz A, Turkiewicz M, Kalinowska H (2004) Bacterial cellulose. In: *Polysaccharides I: polysaccharides from prokaryotes*. Biopolymers, vol 5. WILEY-VCH, Weinheim, pp 37–45
- Bledzki AK, Gassan J (1999) Composites reinforced with cellulose based fibres. *Prog Polym Sci* 24:221–274. doi:[10.1016/S0079-6700\(98\)00018-5](https://doi.org/10.1016/S0079-6700(98)00018-5)
- Cabrera N, Alcock B, Loos J, Peijs T (2004) Processing of all-polypropylene composites for ultimate recyclability. *Proc Inst Mech Eng J Mater Des Appl* 218:145–155
- Dupont A-L (2003) Cellulose in lithium chloride/N, N-dimethylacetamide, optimisation of a dissolution method using paper substrates and stability of the solutions. *Polymer (Guildf)* 44:4117–4126. doi:[10.1016/S0032-3861\(03\)00398-7](https://doi.org/10.1016/S0032-3861(03)00398-7)
- Garcia de Rodriguez NL, Thielemans W, Dufresne A (2006) Sisal cellulose whiskers reinforced polyvinyl acetate nanocomposites. *Cellulose* 13:261–270. doi:[10.1007/s10570-005-9039-7](https://doi.org/10.1007/s10570-005-9039-7)
- Garkhail SK, Heijenrath RWH, Peijs T (2000) Mechanical properties of natural-fibre-mat-reinforced thermoplastics based on flax fibres and polypropylene. *Appl Compos Mater* 7(5–6):351–372. doi:[10.1023/A:1026590124038](https://doi.org/10.1023/A:1026590124038)
- Gea S, Torres FG, Troncoso OP, Reynolds CT, Vilaseca F, Iguchi M, Peijs T (2007) Biocomposites based on bacterial cellulose and apple and radish pulp. *J Biobased Mater Bio* 22:497–501
- Gindl W, Keckes J (2004) Tensile properties of cellulose acetate butyrate composites reinforced with bacterial cellulose. *Compos Sci Technol* 64:2407–2413. doi:[10.1016/j.compscitech.2004.05.001](https://doi.org/10.1016/j.compscitech.2004.05.001)
- Gindl W, Keckes J (2005) All-cellulose nanocomposite. *Polymer (Guildf)* 46:10221–10225. doi:[10.1016/j.polymer.2005.08.040](https://doi.org/10.1016/j.polymer.2005.08.040)
- Grunert M, Winter WT (2002) Nanocomposites of cellulose acetate butyrate reinforced with cellulose nanocrystals. *J Polym Environ* 10:27–30. doi:[10.1023/A:1021065905986](https://doi.org/10.1023/A:1021065905986)
- Guhados G, Wan W, Hutter JL (2005) Measurement of the elastic modulus of single bacterial cellulose fibers using atomic force microscopy. *Langmuir* 21:6642–6646. doi:[10.1021/la0504311](https://doi.org/10.1021/la0504311)
- Heijenrath R, Peijs T (1996) Natural-fibre-mat-reinforced thermoplastic composites based on flax fibres and polypropylene. *Adv Compos Lett* 5(3):81–85
- Henriksson M, Berglund LA, Isaksson P, Lindstrom T, Nishino T (2008) Cellulose nanopaper structures of high toughness. *Biomacromolecules* 9:1579–1585. doi:[10.1021/bm800038n](https://doi.org/10.1021/bm800038n)
- Hsieh YC, Yano H, Nogi M, Eichhorn SJ (2008) An estimation of the Young's modulus of bacterial cellulose filaments. *Cellulose* 15:507–513. doi:[10.1007/s10570-008-9206-8](https://doi.org/10.1007/s10570-008-9206-8)
- Iguchi M, Yamanaka S, Budhiono A (2000) Review: bacterial cellulose—a masterpiece of nature's arts. *J Mater Sci* 35:261–270. doi:[10.1023/A:1004775229149](https://doi.org/10.1023/A:1004775229149)
- Jonas R, Farah LF (1998) Production and application of microbial cellulose. *Polym Degrad Stabil* 59:101–106. doi:[10.1016/S0141-3910\(97\)00197-3](https://doi.org/10.1016/S0141-3910(97)00197-3)
- Jung HM, Lee EM, Ji BC, Deng Y, Yun JD, Yeum JH (2007) Poly(vinyl acetate)/poly(vinyl alcohol)/montmorillonite nanocomposite microspheres prepared by suspension polymerization and saponification. *Colloid Polym Sci* 285:705–710. doi:[10.1007/s00396-006-1623-3](https://doi.org/10.1007/s00396-006-1623-3)
- Kim D-Y, Nishiyama Y, Kuga S (2002) Surface acetylation of bacterial cellulose. *Cellulose* 9:361–367. doi:[10.1023/A:1021140726936](https://doi.org/10.1023/A:1021140726936)
- Klemm D, Heublein B, Fink HP, Bohn A (2005) Cellulose: fascinating biopolymer and sustainable raw material. *Angew Chem Int Ed* 44:3358–3393. doi:[10.1002/anie.200460587](https://doi.org/10.1002/anie.200460587)
- Lu Y, Weng L, Cao X (2006) Morphological, thermal and mechanical properties of ramie crystallites-reinforced plasticized starch biocomposites. *Carbohydr Polym* 63:198–204. doi:[10.1016/j.carbpol.2005.08.027](https://doi.org/10.1016/j.carbpol.2005.08.027)
- Millon LE, Wan WK (2006) The polyvinyl alcohol-bacterial cellulose system as a new nanocomposite for biomedical applications. *J Biomed Mater Res-B* 79B:245–253. doi:[10.1002/jbm.b.30535](https://doi.org/10.1002/jbm.b.30535)
- Mohanty AK, Khan MA, Hinrichsen G (2000) Surface modification of jute and its influence on performance of biodegradable jute-fabric/Biopol composites. *Compos Sci Technol* 60:1115–1124. doi:[10.1016/S0266-3538\(00\)00012-9](https://doi.org/10.1016/S0266-3538(00)00012-9)

- Nakagaito AN, Iwamoto S, Yano H (2005) Bacterial cellulose: the ultimate nano-scalar cellulose morphology for the production of high-strength composites. *Appl Phys A-Mater* 80:93–97. doi:[10.1007/s00339-004-2932-3](https://doi.org/10.1007/s00339-004-2932-3)
- Nishi Y, Uryu M, Yamanaka S, Watanabe K, Kitamura N, Iguchi M, Mitsuhashi S (1990) Structure and mechanical properties of sheets prepared from bacterial cellulose. Part 2 Improvement of the mechanical properties of sheets and their applicability to diaphragms of electroacoustic transducers. *J Mater Sci* 25:2997–3001. doi:[10.1007/BF00584917](https://doi.org/10.1007/BF00584917)
- Nishino T, Arimoto N (2007) All-cellulose composite prepared by selective dissolving of fiber surface. *Biomacromolecules* 8:2712–2716. doi:[10.1021/bm0703416](https://doi.org/10.1021/bm0703416)
- Nishino T, Takano K, Nakamae K (1995) Elastic modulus of the crystalline regions of cellulose polymorphs. *J Polym Sci Pol Phys* 33:1647–1651. doi:[10.1002/polb.1995.090331110](https://doi.org/10.1002/polb.1995.090331110)
- Nishino T, Hirao K, Kotera M, Nakamae K, Inagaki H (2003) Kenaf reinforced biodegradable composite. *Compos Sci Technol* 63:1281–1286. doi:[10.1016/S0266-3538\(03\)00099-X](https://doi.org/10.1016/S0266-3538(03)00099-X)
- Nishino T, Matsuda I, Hirao K (2004) All-cellulose composite. *Macromolecules* 37:7683–7687. doi:[10.1021/ma049300h](https://doi.org/10.1021/ma049300h)
- Oksman K, Mathew AP, Bondeson D, Kvien I (2006) Manufacturing process of cellulose whiskers/poly(lactic acid) nanocomposites. *Compos Sci Technol* 66:2776–2784. doi:[10.1016/j.compscitech.2006.03.002](https://doi.org/10.1016/j.compscitech.2006.03.002)
- Orts WJ, Shey J, Imam HS, Glenn GM, Guttman ME, Revol J-F (2005) Application of cellulose microfibrils in polymer nanocomposites. *J Polym Environ* 13:301–306. doi:[10.1007/s10924-005-5514-3](https://doi.org/10.1007/s10924-005-5514-3)
- Peijs T (2000) Natural fiber based composites. *Mater Technol* 15(4):281–285
- Peijs T (2003) Composites for recyclability. *Mater Today* 6(4):30–35. doi:[10.1016/S1369-7021\(03\)00428-0](https://doi.org/10.1016/S1369-7021(03)00428-0)
- Peijs T, Garkhail S, Heijenrath R, van den Oever M, Bos H (1998) Thermoplastic composites based on flax fibres and polypropylene: influence of fibre length and fibre volume fraction on mechanical properties. *Macromol Symp* 127:193–203
- Qin C, Soykeabkaew N, Xiuyuan N, Peijs T (2008) The effect of fibre volume fraction and mercerization on the properties of all-cellulose composites. *Carbohydr Polym* 71(3):458–467. doi:[10.1016/j.carbpol.2007.06.019](https://doi.org/10.1016/j.carbpol.2007.06.019)
- Samir MASA, Alloin F, Dufresne A (2005) Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field. *Biomacromolecules* 6:612–626. doi:[10.1021/bm0493685](https://doi.org/10.1021/bm0493685)
- Shibazaki H, Kuga S, Okano T (1997) Mercerization and acid hydrolysis of bacterial cellulose. *Cellulose* 4:75–87. doi:[10.1023/A:1024273218783](https://doi.org/10.1023/A:1024273218783)
- Singleton ACN, Baillie CA, Beaumont PWR, Peijs T (2003) On the mechanical properties, deformation and fracture of a natural fibre/recycled polymer composite. *Compos Part B-Eng* 34(6):519–526. doi:[10.1016/S1359-8368\(03\)00042-8](https://doi.org/10.1016/S1359-8368(03)00042-8)
- Soykeabkaew N, Supaphol P, Rujiravanit R (2004) Preparation and characterization of jute- and flax-reinforced starch-based composite foams. *Carbohydr Polym* 58:53–63. doi:[10.1016/j.carbpol.2004.06.037](https://doi.org/10.1016/j.carbpol.2004.06.037)
- Soykeabkaew N, Arimoto N, Nishino T, Peijs T (2008a) All-cellulose composites by surface selective dissolution of aligned ligno-cellulosic fibres. *Compos Sci Technol* 68:2201–2207. doi:[10.1016/j.compscitech.2008.03.023](https://doi.org/10.1016/j.compscitech.2008.03.023)
- Soykeabkaew N, Nishino T, Peijs T (2008) All-cellulose composites of regenerated cellulose fibres by surface selective dissolution. *Compos Part A-Appl S*. doi:[10.1016/j.compositesa.2008.10.021](https://doi.org/10.1016/j.compositesa.2008.10.021)
- Stamboulis A, Baillie CA, Garkhail SK, Van Melick HGH, Peijs T (2000) Environmental durability of flax fibres and their composites based on polypropylene matrix. *Appl Compos Mater* 7(5–6):273–294. doi:[10.1023/A:1026581922221](https://doi.org/10.1023/A:1026581922221)
- Wan YZ, Hong L, Jia SR, Huang Y, Zhu Y, Wang YL, Jiang HJ (2006) Synthesis and characterization of hydroxyapatite-bacterial cellulose nanocomposites. *Compos Sci Technol* 66:1825–1832. doi:[10.1016/j.compscitech.2005.11.027](https://doi.org/10.1016/j.compscitech.2005.11.027)
- Wan YZ, Huang Y, Yuan CD, Raman S, Zhuh Y, Jiang HJ, He F, Gao C (2007) Biomimetic synthesis of hydroxyapatite/bacterial cellulose nanocomposites for biomedical applications. *Mater Sci Eng C-Biomim* 27:855–864. doi:[10.1016/j.msec.2006.10.002](https://doi.org/10.1016/j.msec.2006.10.002)
- Ward IM, Hine PJ (1997) Novel composites by hot compaction of fibers. *Polym Eng Sci* 37(11):1809–1814. doi:[10.1002/pen.11830](https://doi.org/10.1002/pen.11830)
- Ward IM, Hine PJ (2004) The science and technology of hot compaction. *Polymer (Guildf)* 45:1413–1427. doi:[10.1016/j.polymer.2003.11.050](https://doi.org/10.1016/j.polymer.2003.11.050)
- Watanabe K, Tabuchi M, Morinaga Y, Yoshinaga F (1998) Structural features and properties of bacterial cellulose produced in agitated culture. *Cellulose* 5:187–200. doi:[10.1023/A:1009272904582](https://doi.org/10.1023/A:1009272904582)
- Wibowo AC, Misra M, Park H-M, Drzal LT, Schalek R, Mohanty AK (2006) Biodegradable nanocomposites from cellulose acetate: mechanical, morphological, and thermal properties. *Compos Part A-Appl S* 37:1428–1433. doi:[10.1016/j.compositesa.2005.06.019](https://doi.org/10.1016/j.compositesa.2005.06.019)
- Wu X, Torres FG, Vilaseca F, Peijs T (2007) Influence of the processing conditions on the mechanical properties of chitin whisker reinforced poly(caprolactone) nanocomposites. *J Biobased Mater Bio* 1(3):341–350. doi:[10.1166/jbmb.2007.008](https://doi.org/10.1166/jbmb.2007.008)
- Yamanaka S, Watanabe K, Kitamura N, Iguchi M, Mitsuhashi S, Nishi Y, Uryu M (1989) Structure and mechanical properties of sheets prepared from bacterial cellulose. *J Mater Sci* 24:3141–3145. doi:[10.1007/BF01139032](https://doi.org/10.1007/BF01139032)
- Yamanaka S, Ishihara M, Sugiyama J (2000) Structural modification of bacterial cellulose. *Cellulose* 7:213–225. doi:[10.1023/A:1009208022957](https://doi.org/10.1023/A:1009208022957)
- Yu Y-H, Lin C-Y, Yeh J-M, Lin W-H (2003) Preparation and properties of poly(vinyl alcohol)-clay nanocomposite materials. *Polymer (Guildf)* 44:3553–3560. doi:[10.1016/S0032-3861\(03\)00062-4](https://doi.org/10.1016/S0032-3861(03)00062-4)
- Zhou LL, Sun DP, Hu LY, Li YW, Yang JZ (2007) Effect of addition of sodium alginate on bacterial cellulose production by *Acetobacter xylinum*. *J Ind Microbiol Biotechnol* 34:483–489. doi:[10.1007/s10295-007-0218-4](https://doi.org/10.1007/s10295-007-0218-4)