

# (ULTRA-)LOW GRAMMAGE BACTERIAL CELLULOSE NANOPAPER-REINFORCED POLYLACTIDE COMPOSITE LAMINATES

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## Abstract

One of the rate-limiting steps in the large-scale production of cellulose nanopaper-reinforced polymer composites is the time-consuming dewatering step to produce the reinforcing cellulose nanopapers. In this work, we present a method to reduce the dewatering time of bacterial cellulose (BC)-in-water suspension by reducing the grammage of BC nanopaper to be produced. The influence of BC nanopaper grammage on the tensile properties of BC nanopaper-reinforced polylactide (PLLA) composites is also investigated in this work. BC nanopaper with grammages of 5, 10, 25 and 50 g m<sup>-2</sup> were produced and it was found that reducing the grammage of BC nanopaper from 50 g m<sup>-2</sup> to 5 g m<sup>-2</sup> led to a three-fold reduction in the dewatering time of BC-in-water suspension. The porosity of the BC nanopapers, however, increased with decreasing BC nanopaper grammage. While the tensile properties of BC nanopapers were found to decrease with decreasing BC nanopaper grammage, no significant difference in the reinforcing ability of BC nanopaper with different grammages for PLLA was observed. PLLA composite laminates reinforced with BC nanopaper at different grammages possessed a tensile modulus of 10.5-11.8 GPa and tensile strength of 95-111 MPa, respectively, at a  $v_{f, \text{fibres}} = 39\text{-}53$  vol.-%, independent of the grammage and tensile properties of the reinforcing BC nanopaper(s).

## 1. Introduction

Cellulosic fibres in the nanometre scale, more commonly known as nanocellulose, is a family of high performance bio-based nanofibres with tensile moduli and strengths estimated to be 100-160 GPa and 0.3-22 GPa, respectively [1,2]. Nanocellulose possesses the combined properties of cellulose, e.g. broad chemical modification capacity [3] and high crystallinity (up to 80% for cellulose nanocrystals) [4], with the features of a nano-material [5], e.g. high surface energy (~65 mJ m<sup>-2</sup>) [6] and high specific surface area (up to 605 m<sup>2</sup> g<sup>-1</sup>) [7]. Nanocellulose is also a lightweight material (~1.5 g cm<sup>-3</sup>) with low toxicity and abundant in nature. Thus, nanocellulose is often explored for nano-reinforcement of polymers.

Nanocellulose can be obtained via two approaches: top-down or bottom-up. In the top-down approach, woody biomass such as wood pulp is passed through high-pressure homogenisers [8,9], microfluidisers [10] or stone grinders [11] to liberate the elementary microfibrils from the micrometre-sized pulp fibres [12]. Wood-derived nanocellulose is more commonly known as nanofibrillated cellulose (NFC). The bottom-up approach, on the other hand, utilises cellulose-producing bacteria,

such as from the *Komagataeibacter* species, to convert low molecular weight sugars to nanocellulose [13]. These microbially-synthesised nanocellulose, also known as bacterial cellulose (BC), is an ultrapure form of nanocellulose without impurities such as hemicellulose or traces of lignin that are often present in NFC [14].

A method to efficiently utilise nanocellulose as reinforcement for advanced composite applications is to exploit the reinforcing ability of a dried and well-consolidated nanocellulose network, e.g. cellulose nanopaper. Henriksson et al. [15] fabricated NFC nanopaper-reinforced melamine formaldehyde (MF) composites by immersing a single sheet of reinforcing NFC nanopaper in a water/MF solution, followed by drying and crosslinking. The authors obtained a tensile modulus and strength of 15.7 GPa and 108 MPa, respectively for a NFC nanopaper loading of 87 wt.-%. NFC nanopaper has also been incorporated into epoxy resin [16]. Vacuum assisted resin infusion was used to impregnate the NFC nanopaper with epoxy and produce a composite with a NFC nanopaper loading of 40 vol.-%. The resulting NFC nanopaper-reinforced epoxy composites possessed a tensile modulus and strength of 7.1 GPa and 103 MPa, respectively.

BC nanopaper has also been exploited as 2-D reinforcement for polymers. BC nanopaper-reinforced phenol formaldehyde (PF) composites have been fabricated by immersing dried and well-consolidated sheet of BC nanopapers into a PF resin diluted with methanol [17]. The PF-impregnated BC nanopapers were then air-dried, stacked and heat consolidated to produce the BC nanopaper-reinforced PF composites containing 25 sheets of BC nanopapers. Bending modulus and strength as high as ~20 GPa and ~350 MPa, respectively, have been obtained for composites containing BC nanopaper loading of 88 wt.-%. A simpler approach to produce BC nanopaper-reinforced polymer composites have been described by Montri Kittiphant et al. [18], whereby the authors sandwiched a sheet of BC nanopaper between two thin polylactide films and heat consolidated the layout to produce the BC nanopaper-reinforced polylactide. At a BC nanopaper loading of 65 vol.-%, a tensile modulus and strength of 6.9 GPa and 125 MPa, respectively, were obtained for the fabricated BC nanopaper-reinforced polylactide composite; approximately two-fold increase compared to neat polylactide.

While it is evident that both BC and NFC nanopapers serve as excellent 2-D reinforcement for polymers, the rate-limiting step towards the large-scale production of these high-performance cellulose nanopaper-reinforced polymer composites is the time-consuming dewatering step to produce cellulose nanopaper. Cellulose nanopaper is typically produced by first creating a suspension of nanocellulose-in-water at ~0.1-0.5 wt.-% consistency. The nanocellulose-in-water suspension is then dewatered using vacuum-assisted or gravity-driven filtration, followed by heat consolidation. We have previously observed that the dewatering time of BC- and NFC-in-water suspensions to produce 60 g m<sup>-2</sup> nanopaper was 5 min and 40 min, respectively [19]. Dewatering times of NFC-in-water suspension as low as 10 min and as high as 3-4 h have also been previously reported [20,21], depending on the type of nanocellulose and the filter medium used. The dewatering time of NFC-in-water suspensions is often longer than BC-in-water suspensions as NFC forms a homogeneous suspension in water while aggregates or bundles of BC is often observed, due to difficulties in disrupting the three-dimensional nanofibrous network of BC pellicles using a low energy blender [22]. The bundles of BC have higher hydrodynamic diameter, which led to higher settling velocity compared to NFC, which is more homogeneously dispersed. Furthermore, NFC also contains significant amount of hemicellulose, which has high water holding capacity, leading to longer dewatering time.

The dewatering time of a wood pulp suspension to produce conventional papers, on the other hand, is typically less than 2 min [23]. A new strategy is therefore needed to reduce the dewatering time of nanocellulose suspension for the large-scale manufacturing of high performance cellulose nanopaper-reinforced polymers. In this work, we report the production of (ultra-)low grammage BC nanopaper as a mean to reduce the dewatering time of nanocellulose suspension. Model BC nanopaper with grammages of 5, 10, 25 and 50 g m<sup>-2</sup> were produced and the influences of BC nanopaper grammage on the dewatering time, as well as mechanical properties of BC nanopaper are investigated. The

reinforcing ability of (ultra-)low grammage BC nanopaper for polylactide is also elucidated in this work.

## 2. Experimental

### 2.1 Materials

Poly(L-lactic acid) (PLLA) (L9000, molecular weight  $\geq 150$  kDa, D-content  $\approx 1.5\%$ ) was purchased from Biomer GmbH and used as the matrix for the production of BC-reinforced PLLA composites. Sodium hydroxide (pellets, purity  $> 98.5\%$ ) was purchased from VWR International (Lutterworth, UK). 1,4-Dioxane (ACS Reagent, purity  $\geq 99\%$ ) was purchased from Sigma-Aldrich (Gillingham, UK). These materials were used as received without further purification. BC in the form of commercially available nata de coco (coconut gel in syrup) was purchased from a retailer (Xiangsun Ltd, Lugang Township, Changhua County, Taiwan).

### 2.2 Purification of BC from nata de coco

The purification of BC from nata de coco has been described in our previous work [22]. Briefly, 150 g of nata de coco cubes were added to 3.5 L of de-ionised water and heated to 80 °C under stirring. 14 g of NaOH pellets were then added into this dispersion to form a 0.1 N NaOH aqueous solution and the solution was left to stir at 80 °C for 2 h. After this purification step, the dispersion was poured onto a metal sieve (mesh size = 300  $\mu\text{m}$ ) to recover the purified nata de coco cubes. The cubes were then rinsed with 5 L of de-ionised water prior to blending (Breville VBL065) in another 5 L of de-ionised water for 2 min to create a homogeneous suspension of BC-in-water. The suspension was centrifuged (SIGMA 4-16S, SciQuip Ltd., Newton, UK) at  $6800\times g$  to remove the excess water. This blending-centrifugation step was repeated until neutral pH was attained for the BC-in-water suspension. The final consistency of the BC-in-water suspension was adjusted to 2 wt.-% by centrifugation prior to subsequent use.

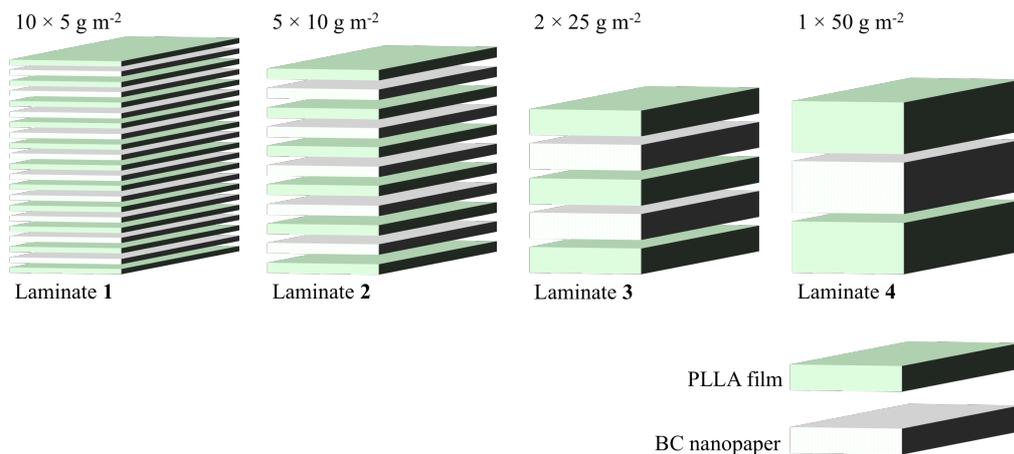
### 2.3 Manufacturing of BC nanopapers with different grammages

In this work, 5 g m<sup>-2</sup>, 10 g m<sup>-2</sup>, 25 g m<sup>-2</sup> and 50 g m<sup>-2</sup> BC nanopapers were produced. To produce the desired BC nanopaper grammage, an equivalent amount of the previously purified BC-in-water suspension was first dispersed in 500 mL of de-ionised water for 5 min using a blender (Breville VBL065). This BC-in-water suspension was then vacuum filtered at a reduced pressure of 0.1 bar onto a 12 cm diameter woven polyester peel ply (AeroFilm<sup>®</sup> PP180, 85 g m<sup>-2</sup>, Easy Composites Ltd., Staffordshire, UK) placed on top of a cellulose filter paper (Grade 413, 5-13  $\mu\text{m}$  particle retention, VWR International Ltd., Lutterworth, UK) in a Büchner funnel. A polyester peel ply was placed on top of the cellulose filter paper to aid the subsequent processing of the wet BC filter cakes as a robust filter medium was required. Without the polyester peel ply, the wet BC filter cakes used to produce (ultra-)low grammage BC nanopapers (5 g m<sup>-2</sup> and 10 g m<sup>-2</sup>) were too fragile to be removed from the used cellulose filter paper.

After the filtration step, the polyester peel ply (with the wet BC filter cake still on top) was carefully separated from the used cellulose filter paper. It was then sandwiched between fresh filter and blotting papers (Grade 3MM CHR, VWR international Ltd, Lutterworth, UK), followed by wet pressing under a weight of 10 kg for 10 min to absorb the excess water. This step was repeated twice, with fresh filter and blotting papers used at every step. A final heat consolidation step was then performed in a hydraulic hot press (4122 CE, Carver Inc., Wabash, IN, USA) using a compaction force of 1 t at 120 °C for 30 min to further dry and consolidate the BC filter cake into a BC nanopaper. Once the nanopaper had cooled to room temperature, it was then carefully separated from the polyester peel ply. All BC nanopapers manufactured were stored in a sealed environment containing silica gel pouches to keep the BC nanopapers dry.

## 2.4 Fabrication of BC nanopaper-reinforced PLLA composite laminates

BC nanopaper-reinforced PLLA composite laminates were produced using film-stacking method. The stacking sequences of BC nanopaper with different grammages and PLLA are shown in Fig. 1. These stacking sequences were chosen such that the overall grammage of the BC nanopaper(s) within the composite laminates was kept constant at  $50 \text{ g m}^{-2}$ . Prior to producing the composite laminates, thin PLLA films were produced by solution casting. Briefly, PLLA pellets were dissolved in 1,4-dioxane at a mass ratio of 1:12 at  $65 \text{ }^\circ\text{C}$  overnight under magnetic stirring. Once the polymer solution was cooled to room temperature, it was then casted onto a toughened glass plate using an automated film applicator (Elcometer 4340, Elcometer Ltd., Manchester, UK) and the solvent was evaporated to produce thin PLLA film. The speed of the casting knife was set to be  $5 \text{ mm s}^{-1}$ . The fabricated BC nanopapers and PLLA films were then stacked in accordance to the stacking sequence shown in Fig. 1 and sandwiched between two heat-resistant and non-stick polyimide films (UPILEX®, Goodfellow Cambridge Ltd., Huntingdon, UK). The lay-up was pre-heated in a hydraulic hot press (4122 CE, Carver Inc., Wabash, IN, USA) to  $180 \text{ }^\circ\text{C}$  for 3 min, followed by a consolidation step at the same temperature for 2 min using a compaction force of 1 t. Model BC nanopaper-reinforced PLLA composite laminates reinforced with  $10 \times 5 \text{ g m}^{-2}$ ,  $5 \times 10 \text{ g m}^{-2}$ ,  $2 \times 25 \text{ g m}^{-2}$  and  $1 \times 50 \text{ g m}^{-2}$  BC nanopaper(s) are herein termed Laminate 1, Laminate 2, Laminate 3 and Laminate 4, respectively. All composite laminates were stored in a sealed environment containing silica gel pouches to keep the composite laminates dry prior to subsequent use. As a control, neat PLLA film was also produced by hot pressing PLLA pellets directly at a temperature of  $180 \text{ }^\circ\text{C}$  using a compaction force of 1 t for 2 min.



**Figure 1: The stacking sequence of the BC nanopaper-reinforced PLLA composite laminates fabricated in this work. Laminate 1 possessed 10 sheets of reinforcing  $5 \text{ g m}^{-2}$  BC nanopapers; Laminate 2 possessed 5 sheets of reinforcing  $10 \text{ g m}^{-2}$  BC nanopapers; Laminate 3 possessed 2 sheets of reinforcing  $25 \text{ g m}^{-2}$  BC nanopapers; Laminate 4 possessed 1 sheet of reinforcing  $50 \text{ g m}^{-2}$  BC nanopaper, respectively.**

## 2.5 Characterisation of BC nanopapers and their respective model PLLA composites

The internal morphology of the BC nanopapers was investigated using a large chamber SEM (S-3700N, Hitachi, Tokyo, Japan) operated at an accelerating voltage of 10 kV. Prior to SEM, the tensile fractured samples were attached onto aluminium stubs using carbon tabs and Au coated (Agar auto sputter coater, Agar Scientific, Stansted, UK) at 40 mA for 20 s. The tensile properties of BC nanopapers and the model BC nanopaper-reinforced PLLA composite laminates were characterised in accordance to BS EN ISO 527: 2012. Prior to the test, dog bone shape test specimens were cut using a manual cutting press (ZCP020, Zwick Testing Machines Ltd., Leominster, UK). The test specimens possessed an overall length of 35 mm, a gauge length of 10 mm and the narrowest part of the dog bone shape specimen has a width of 2 mm, respectively. To avoid damaging the gripping zone of the test specimens, which could potentially lead to earlier onset failure of the specimens, all test specimens were secured onto  $140 \text{ g m}^{-2}$  paper testing cards using a two-part cold curing epoxy resin (Araldite

2011). Tensile tests were carried out using a micro-tensile tester (Model MT-200, Deben UK Ltd., Woolpit, UK) equipped with a 200 N load cell. A pair of dots was marked on the surface of each test specimen in the direction of load. The strain of the test specimen was then evaluated by monitoring the movement of these two dots using a non-contact optical extensometer (iMetrum Ltd., Bristol, UK). All tensile tests were conducted using a crosshead displacement speed of  $0.2 \text{ mm min}^{-1}$ , which corresponded to a test specimen strain rate of  $2 \times 10^{-4} \text{ s}^{-1}$ . The reported tensile properties were averaged over 5 test specimens.

### 3.0 Results and Discussion

#### 3.1 Dewatering time of the BC-in-water suspensions

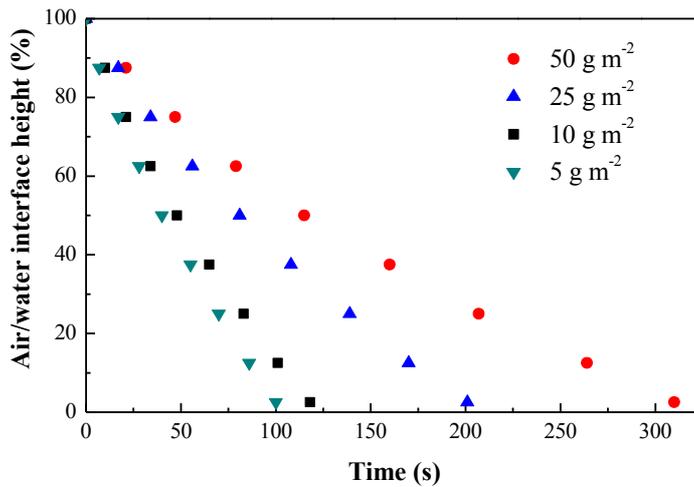


Figure 2: Dewatering time of the BC-in-water suspensions to produce BC nanopaper with different grammages.

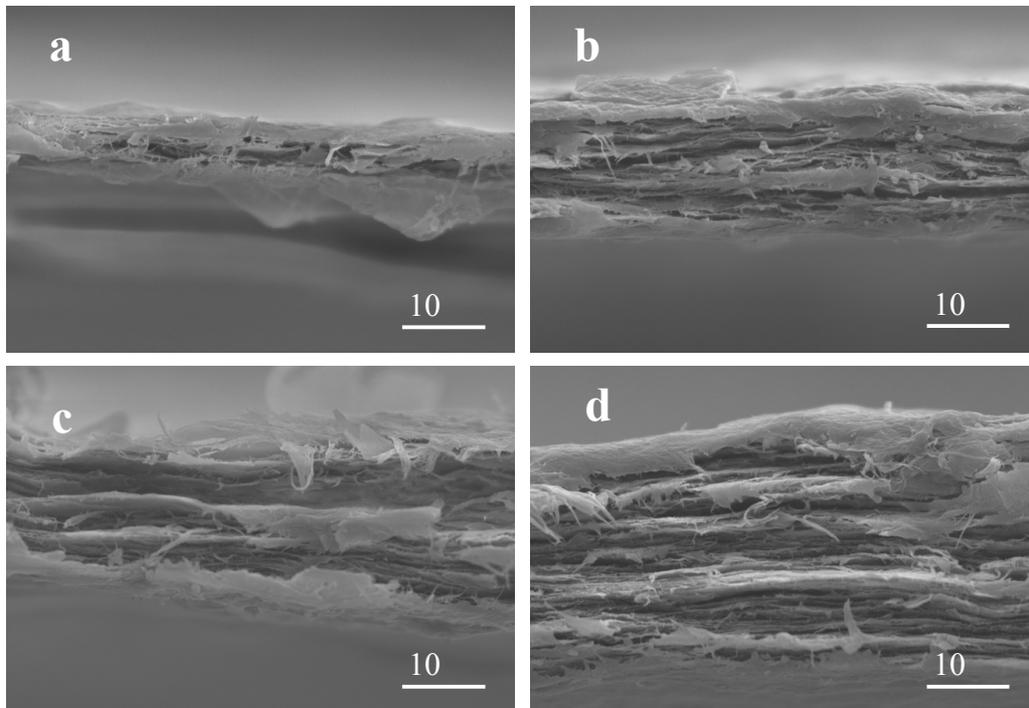


Figure 3: Tensile fractured surfaces of (a)  $5 \text{ g m}^{-2}$ , (b)  $10 \text{ g m}^{-2}$ , (c)  $25 \text{ g m}^{-2}$  and (d)  $50 \text{ g m}^{-2}$  BC nanopaper, respectively, revealing the layered structure of BC nanopapers.

The dewatering time of BC-in-water suspensions to produce BC nanopapers with grammages of 5, 10, 25 and 50 g m<sup>-2</sup> is shown in Fig 2. It can be seen from this figure that the lower the grammage of BC nanopaper to be produced, the faster the dewatering time of BC-in-water suspension. At the start of the dewatering process, BC is deposited on the filter medium (in this study, the filter medium used was a polyester peel ply on top of cellulose filter paper) as a thin layer of BC nanofibre network. As the dewatering progresses, BC further deposit on over the other on top of this thin layer of BC nanofibre network, forming a layered structure (see Fig. 3 for the SEM images showing the internal morphology of fabricated BC nanopapers). Similar layered structure has also been observed by numerous researchers [24–26]. The build-up of the BC filter cake led to an increase in the flow resistance (e.g. a reduction in the permeability) of water through the filter cake. As a result, the dewatering time of producing a 5 g m<sup>-2</sup> nanopaper, which has the thinnest filter cake, was significantly lower than the dewatering time to produce a 50 g m<sup>-2</sup> BC nanopaper, which has the thickest filter cake.

### 3.2 Tensile properties of BC nanopapers at different grammage

The representative stress-strain curves of the fabricated BC nanopapers at different grammages tested in uniaxial tension exhibited an initial elastic deformation, followed by inelastic deformation prior to catastrophic failure (results not shown). The tensile modulus and strength of 5 g m<sup>-2</sup> BC nanopaper were measured to be 2.4 GPa and 31 MPa, respectively (see Table 1). Increasing the grammage of BC nanopaper led to a progressive increase in tensile modulus and strength of up to 12.2 GPa and 134 MPa, respectively, for 50 g m<sup>-2</sup> BC nanopaper. Similar trends have been observed for conventional paper made from micrometre-sized pulp fibres, whereby the tensile properties of paper increase with increasing paper grammage [28,29]. It can also be seen from Table 1 that both the specific tensile modulus and strength of BC nanopapers increased with increasing nanopaper grammage, suggesting that difference in the porosity of the BC nanopapers is not the sole reason for the observed tensile properties variation.

**Table 1: Tensile modulus ( $E$ ), tensile strength ( $\sigma^*$ ), strain-at-break ( $\epsilon^*$ ), specific tensile modulus ( $E/\rho_e$ ), specific tensile strength ( $\sigma^*/\rho_e$ ) and work of fracture ( $U_T$ ) of the fabricated BC nanopapers.**

Sample	$E$ [GPa]	$\sigma^*$ [MPa]	$\epsilon^*$ [%]	$E/\rho_e$ [GPa cm <sup>3</sup> g <sup>-1</sup> ]	$\sigma^*/\rho_e$ [MPa cm <sup>3</sup> g <sup>-1</sup> ]	$U_T$ [J m <sup>-3</sup> ]
5 g m <sup>-2</sup>	2.4 ± 0.2	31 ± 3	1.9 ± 0.1	7.3 ± 1.2	91 ± 18	0.3 ± 0.1
10 g m <sup>-2</sup>	5.0 ± 0.2	59 ± 2	2.3 ± 0.2	10.9 ± 1.8	128 ± 26	0.7 ± 0.1
25 g m <sup>-2</sup>	8.9 ± 0.6	104 ± 3	3.2 ± 0.2	13.1 ± 2.2	153 ± 31	2.1 ± 0.1
50 g m <sup>-2</sup>	12.2 ± 0.5	134 ± 3	3.0 ± 0.1	15.6 ± 2.6	172 ± 35	2.5 ± 0.1

### 3.3 Tensile properties of model BC nanopaper-reinforced PLLA composite

Table 2 summarises the tensile properties of model BC nanopaper-reinforced PLLA composite laminates reinforced with 10 sheets of 5 g m<sup>-2</sup> (Laminate 1), 5 sheets of 10 g m<sup>-2</sup> (Laminate 2), 2 sheets of 25 g m<sup>-2</sup> (Laminate 3) and 1 sheet of 50 g m<sup>-2</sup> (Laminate 4) BC nanopaper(s), respectively. It can be seen from Table 3 that all BC nanopapers possessed excellent reinforcing ability for PLLA to produce high performance model BC nanopaper-reinforced PLLA composite laminates. Tensile moduli of between 10.5 and 11.8 GPa were obtained for the model BC nanopaper-reinforced PLLA composite laminates at  $v_{f,BC} = 39 - 53$  vol.-%. The tensile strengths of the model BC nanopaper-reinforced PLLA composite laminates were measured to be between 95 and 111 MPa. The slight variation of tensile properties between the model composite laminates can be attributed to the variation in  $v_{f,BC}$  and porosity of the composites. By contrast, the tensile modulus and strength of neat PLLA were measured to be only 3.6 GPa and 57.5 MPa, respectively.

**Table 2: Tensile properties of BC nanopaper-reinforced composite laminates. Fibre volume fraction ( $v_{f, \text{fibres}}$ ), tensile modulus ( $E$ ), tensile strength ( $\sigma^*$ ) and strain-at-break ( $\epsilon^*$ ), envelop density ( $\rho_e$ ), theoretical density ( $\rho_{c, \text{void free}}$ ) and porosity ( $P_{\text{composites}}$ ) the composites and neat PLLA.**

Sample	$v_{f, \text{fibres}}$ [%]	$E$ [GPa]	$\sigma^*$ [MPa]	$\epsilon^*$ [%]	$\rho_e$ [g cm <sup>-3</sup> ]	$\rho_{c, \text{void free}}$ [g cm <sup>-3</sup> ]	$P_{\text{composites}}$ [%]
PLLA	0	3.6 ± 0.1	57.5 ± 1.0	3.5 ± 0.4	1.26 ± 0.01	1.26 ± 0.01	0 ± 0
Laminate 1	39 ± 3	10.7 ± 0.4	95.0 ± 0.9	2.2 ± 0.1	1.25 ± 0.07	1.36 ± 0.01	8 ± 1
Laminate 2	48 ± 2	11.2 ± 0.4	102.4 ± 1.8	2.5 ± 0.1	1.23 ± 0.02	1.38 ± 0.01	11 ± 1
Laminate 3	50 ± 3	10.5 ± 0.2	100.7 ± 1.9	3.0 ± 0.1	1.16 ± 0.01	1.39 ± 0.01	16 ± 1
Laminate 4	53 ± 2	11.8 ± 0.2	111.4 ± 2.2	2.4 ± 0.1	1.28 ± 0.07	1.39 ± 0.01	8 ± 1

#### 4.0 Conclusions

Four bacterial cellulose (BC) nanopaper reinforced polylactide laminated composites containing 50 g m<sup>-2</sup> of BC nanopapers were produced using 10, 5, 2 and 1 layer(s) of 5 g m<sup>-2</sup>, 10 g m<sup>-2</sup>, 25 g m<sup>-2</sup> and 50 g m<sup>-2</sup> BC nanopapers, respectively. The low grammage paper were proven quicker to produce because of a filtration time cut by a third and possessed the highest porosity (78%). Tensile properties of the nanopapers were found to drop with lower grammages resulting in the 5 g m<sup>-2</sup> BC nanopapers possessing the lowest tensile modulus and strength, at 2.4 GPa and 30 MPa respectively. The composite containing 10 layers of 5 g m<sup>-2</sup> BC nanopapers, with a tensile strength and modulus around 100 MPa and 11 GPa respectively, possessed tensile properties equivalent to that of composites made with higher grammage BC nanopapers.

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