Carbohydrate Polymers 314 (2023) 120915

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Impact of bacterial cellulose on the physical properties and printing quality of fine papers

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ARTICLE INFO

Keywords:
Bacterial nanocellulose
Cellulose nanofibrils
Mineral filler
Papermaking
Paper coating

ABSTRACT

Bacterial nanocellulose (BNC), due to its inherent nanometric scale and strength properties, can be considered as a good candidate to be used in papermaking. This work explored the possibility of using it in the production of fine paper as a wet-end component and for the paper coating. Filler-containing handsheet production was performed with and without the presence of common additives typically used in the furnish of office papers. It was found that, under optimized conditions, BNC mechanically treated by high-pressure homogenization could improve all the evaluated paper properties (mechanical, optical and structural) without impairing the filler retention. However, paper strength was improved only to a small extent (increase in the tensile index of 8 % for a filler content of ca. 27.5 %). On the other hand, when used at the paper surface, remarkable improvements in the gamut area of >25 % in comparison to the base paper and of >40 % in comparison to starch-only coated papers were achieved for a formulation having 50 % BNC and 50 % of carboxymethylcellulose. Overall, the present results highlight the possibility of using BNC as a paper component, particularly when applied at the paper substrate as a coating agent aiming at improving printing quality.

1. Introduction

Bacterial cellulose or bacterial nanocellulose (also called biocellulose or microbial cellulose), hereafter abbreviated as BNC, is an extracellular, chemically pure-glucan produced from the glucose units by certain *Gluconacetobacter* strains (Abdul Khalil et al., 2014; Eichhorn et al., 2010; Gardner et al., 2008). The gram-negative and strict aerobic bacteria are cultivated in common aqueous nutrient media and, under static culture, the BNC is excreted to the air/liquid interface resulting in a highly swollen network of entangled cellulose fibrils (fibril diameters between 10 and 40 nm) with a distinct tunnel structure with interconnected pores (Klemm et al., 2006). This type of nanocellulose possesses high molecular weight, crystallinity and good mechanical stability.

The most studied species of bacteria for production of cellulose is *Gluconacetobacter xylinus*. During cellulose biosynthesis, these bacteria are kept at the surface of culture media, being entrapped inside a gelatinous, skin-like BNC membrane (Gama et al., 2016). Along with its unique properties, the advantage of bacterial derived cellulose nanofibrils is that it is possible to adjust culturing conditions to alter the nanofibril formation and crystallization (Moon et al., 2011).

BNC has been studied as reinforcing agent in papermaking. For instance, Gao et al. (2011) reported improvements in the tensile, tear and burst indices and in stiffness, when adding BNC to produce paper sheets based on softwood pulp. Increasing dosages in the range of 1–5 % typically increased the values of these properties. On the other hand, porosity, as measured by the air permeance (Bendtsen), decreased, as it would be expected. Further, the ability of the sheet to absorb water was reduced by the addition of BNC. Chen et al. (2017) used BNC as an additive in the production of chemithermomechanical pulp-based paper sheets. The mechanical strength of the sheets was improved using BNC produced in static culture. Remarkable achievements were found in the

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https://doi.org/10.1016/j.carbpol.2023.120915
Received 4 February 2023; Received in revised form 26 March 2023; Accepted 10 April 2023
Available online 13 April 2023

tensile index (increase of 49 % for 10 % BNC) and tear index (increase of 140 % for 10 % BNC), compared to the sheets produced without BNC. In another study, Xiang, Jin, et al. (2017) analysed the reinforcement effect of BNC in handsheets produced with different types of woody and non-woody fibre sources (softwood pulp, *Eucalyptus* pulp, sugarcane bagasse pulp, bamboo pulp). The maximum improvement in the tensile properties (tensile index) was achieved at the BNC level in the furnish of 0.5–1.5 %. Under these conditions, tensile index improved 5–25 %, the variation depending on the type of cellulosic fibres used. The authors concluded that for a good reinforcement effect, a proper dispersion of BNC is important, rather than a high BNC addition or retention rate in the paper sheets. Xiang, Liu, et al. (2017), also proved a positive effect of the cationization of BNC by (3-chloro-2-hydroxypropyl) trimethylammonium chloride at a very low degree of substitution for the purpose of strength reinforcement of paper sheets. Unmodified BNC, at <1 % level, could improve tensile by 25 % for sheets prepared with bleached sugarcane bagasse pulp, but the addition of cationized BNC improved even more the tensile index (increase of 32 %).

These studies mainly focused on the effect of the addition of BNC to formulations containing cellulose fibres from different sources on the strength and structural properties of the produced sheets. Only a few have considered the addition of mineral fillers. The influence of BNC in filler-containing handsheets has been mentioned briefly by Tsuchida and Yoshinaga (1997). The authors reported that the incorporation of BNC as a wet-end additive improved significantly both the tensile strength and filler retention. The improvements in filler retention were higher using the BNC from agitated culture. Recently, BNC was added to pulp from recycled office wastepaper (5–15 %). The addition of BNC failed to improve the most relevant paper strength properties. However, it promoted an increased retention of filler (calcium carbonate). Since the latter interferes negatively in the bonding between fibres, impairing strength, the expected effect of a reinforcement by BNC was obscured by the increased retention of filler, as stated. On the other hand, air resistance and water absorption were enhanced by the presence of BNC (Kalyoncu & Pesman, 2020). Campano et al. (2018a) reported an increase in both the tensile and tear indices of 12.2 % and 14.2 %, respectively, when using recycled paper pulps modified by *in situ* production of BNC in agitated culture. The authors mentioned that static culture failed at improving paper strength. In agitated culture, bacteria were found to grow on the surface of the cellulosic fibres, providing a coating of BNC on the surface of the fibres. In another study, the filler retention was quantified for handsheets produced using the same recycled pulps as above (Campano et al., 2018b). With the addition of up to 3 % of low-fibrillated BNC, the filler (kaolinite + calcium carbonate) retention was roughly the same compared to the blank experiment without BNC. The addition of 3 % BNC promoted an increase in both the tensile (11 % increment) and tear (8 % increment) indices.

A review on the use of BNC in papermaking was presented (Skocaj, 2019). The author compiled prospective applications of BNC in the papermaking industry, which include its use i) as a paper-reinforcing agent, ii) to improve the properties of paper made from low-grade fibre resources, iii) for application at the paper surface (as coating) in the restoration of damaged paper or to increase the barrier properties of paper, and iv) to improve fire resistance of paper. A review of the potential of nanocelluloses for industrial application in papermaking was also presented recently (Balea et al., 2020).

There are several studies reporting the use of BNC for coating the paper surface, but none regarding the effects on the printing properties of paper (Skocaj, 2019). Interestingly, BNC was evaluated for its suitability in restoring degraded old papers (Santos et al., 2016). The authors concluded that the papers lined with BNC were as good for the mechanical properties as those obtained with Japanese paper, commonly used by paper conservators. However, letters in books lined with BNC were more legible. Overall, BNC was proposed as a promising material for the restoration of paper. Additionally, Gómez et al. (2017) analysed the use of BNC for restoring papers printed with offset inks, and concluded that the lining with BNC provided only minor decrements in the print density and CIE L*a*b* color coordinates, most of them imperceptible to the human eye. The lining with Japanese paper, on the other hand, notably affected the values of these properties.

In this work, it was hypothesized that BNC, used as a wet-end additive in the production of fine papers, can improve the filler retention and paper's strength, optical and structural properties, and, when incorporated in coating formulations to coat paper surface has potential to improve the paper printing quality. As shown above, previous works on the use of BNC as a reinforcing agent/filler retention aid for paper were limited mostly to recycled paper/pulp and no studies are available regarding office papers. Regarding paper coating with BNC, to the authors' best knowledge, no studies have been presented to date concerning printing quality.

2. Materials and methods

2.1. Bacterial nanocellulose production and characterization

BNC was kindly supplied by Satisfibre, S.A., Portugal. According to the supplier, *Komagataeibacter xylinus*, strain BPR 2001 (ATCC 700178), purchased from American Type Culture Collection, was used. The strain was maintained in a Hestrin-Schramm culture medium in solid state with 2 % (*w/v*) agar. BNC was produced by static culture and purified as described in Rodrigues et al. (2019). The sample was designated as "BNC". Besides, a mixture with carboxymethylcellulose (CMC, 90 kDa, degree of substitution of 0.7) at a ratio of 1:1 (*w/w*), prepared as described in Martins et al. (2020), was also supplied, with sample designation "BNC:CMC". CMC was used as a rheology modifier. Both samples were subjected to high-pressure homogenization (HPH) in a GEA Niro Soavi homogenizer (model Panther NS3006L) with 2 passes at ca. 500 bar (first pass) and 1000 bar (second pass), and the samples with designation "BNC-HPH" and "BNC:CMC-HPH", respectively, were obtained.

The BNC sample had a high particle size heterogeneity and it was not possible to completely disperse it in water. However, after treatment by HPH, both samples (BNC-HPH and BNC:CMC-HPH) were more homogeneous.

Table 1 presents some characteristics of the BNC samples. The degree of fibrillation or "yield" of nanofibrillar material (percentage amount of nanosized material in the nanocellulose sample) was determined in duplicate by gravimetry of centrifuged 0.2 wt% suspensions (at 9000 rpm, for 30 min) (Lourenço et al., 2017). Zeta potential was measured in triplicate by electrophoretic mobility in a Malvern instrument (Zetasizer Nano ZS). The degree of polymerization was calculated based on

Table 1
General characterization of the BNC samples.

Sample	Fibrillation yield (%)[a]	ζ potential (mV)	Intrinsic viscosity (mL/g)[b]	Degree of polymerization[c]
BNC	<5	−19 (1)	411 (20)	1765 (44)
BNC-HPH	12	−27 (1)	528 (12)	2005 (27)
BNC:CMC	63 (3)	−81 (1)	–	–
BNC:CMC-HPH	97 (3)	−69 (2)	–	–

[a] Yield of nanofibrillar material, i.e., the percentage amount of nanosized material in the nanocellulose sample.
[b] Intrinsic viscosity in cupriethylenodiamine.
[c] Degree of polymerization estimated based on the intrinsic viscosity values. For the BNC:CMC and BNC:CMC-HPH samples, due to the presence of CMC, the degree of polymerization of cellulose could not be evaluated. Standard deviation values are shown within parentheses.

intrinsic viscosity measurements in cupriethylenodiamine (ISO 5351:2010, duplicate measurements), using the Mark–Houwink equation with the parameters defined by Tsouko et al. (2015): K = 1.65×10^{-4} and a = 1.97. Field emission-SEM images of films sputter-coated with gold were acquired in a Carl Zeiss Merlin microscope, in secondary electron mode.

2.2. Bacterial nanocellulose as a wet-end additive in papermaking: handsheet production

The BNC samples were used in the production of laboratory handsheets containing mineral filler in two distinct formulations: i) a formulation comprising the cellulosic pulp, the mineral filler, different additives and BNC and ii) a formulation comprising the cellulosic pulp, the mineral filler and BNC (without additives). Their influence on filler retention and on paper's mechanical, optical and structural properties was assessed.

Bleached *Eucalyptus globulus* kraft pulp (BEKP, industrially refined up to 33 °SR) was used as the cellulosic fibre source for the handsheet production. The handsheets were produced in a semi-automatic batch laboratory sheet former (300-1 model, LabTech) equipped with a 120-mesh screen using formulations prepared with the refined fibre, precipitated calcium carbonate (PCC) and BNC. A mixture of cationic starch with alkenyl succinic anhydride (ASA), and a linear cationic polyacrylamide (CPAM) were also used in the formulation comprising all additives. All the additives were supplied by a paper production mill.

Previously to the mixture, the different paper components were prepared, as follows. After disintegration, the refined pulp was diluted to a consistency of 0.4 % in demineralized water. Aqueous suspensions of BNC (0.2 wt%) were magnetically stirred for 1 h. Aqueous suspensions of PCC (1 wt%) were stirred magnetically (20 min) and sonicated (15 min, 50 KHz). For the handsheet preparation with additives, a 3 wt% starch suspension standing at 60 °C was also prepared according to a procedure detailed elsewhere (Saraiva et al., 2010). ASA was used as internal sizing agent; it was firstly stabilized by mixing with the cooked starch suspension, standing at 60 °C, before mixing with the other components of the furnish. The CPAM (commercial Percol 47, from BASF) with a high molecular weight and a low charge density was diluted in water to 0.025 wt% and used as retention agent.

The handsheets were made according to the procedure described in detail by Lourenço et al. (2017). The amounts of each component added to the paper formulations are listed in Table 2. Briefly, the PCC suspension was mixed with the BNC dispersion at a PCC/BNC ratio of 10 (*w/w*). The PCC-BNC mixture was added to the BEKP. For the formulation containing all additives, the starch-ASA mixture was subsequently added after 120 s and CPAM after 265 s of magnetic stirring. The furnish was then transferred into the sheet former after a total time of 270 s. In the former, at solids concentration of ca. 0.02 wt%, air agitation and decantation (5 and 10 s, respectively) were succeeded by drainage. For each preparation series, 8–10 handsheets were prepared.

The sheets were collected from the web and pressed, dried, and conditioned according to the ISO 5269-1 standard. The structural, optical and mechanical properties were measured according to the corresponding ISO standards. Additionally, the dried handsheets were calcined at 525 °C for 16 h to determine the effective PCC content, according to the TAPPI Standard T211 om-93.

Table 2
Amounts of each component added in the production of laboratory handsheets.

Component	Amount added (wt%)			
	Without additives		With additives	
	Ref.	BNC	Ref.	BNC
BEKP	70	67	69	66
PCC	30	30	30	30
BNC[a]	–	3	–	3
Cationic starch	–	–	1	1
ASA	–	–	0.12	0.12
CPAM	–	–	0.02	0.02

[a] Four BNC samples were used to produce handsheets, namely BNC, BNC:CMC, BNC-HPH, and BNC:CMC-HPH.

2.3. Bacterial nanocellulose in the paper coating

An industrial calendered, uncoated, and woodfree base paper produced from BEKP and without any surface treatment, with a grammage of 78 g/m^2, was used as substrate. This paper was coated with different aqueous formulations containing BNC, typically with 6–8 wt% solids content. Three main series of experiments were conducted, namely the paper coating with: i) BNC, ii) a mixture of starch with incorporation levels of BNC ranging from 3 to 10 % or iii) a formulation containing starch, BNC, optical brightening agent (OBA), alkyl ketene dimer (AKD) and salt, according to Table 3. CMC (90 kDa, degree of substitution of 0.7) was added in order to control the rheology of the BNC suspensions and aid in the dispersibility. Different BNC/CMC ratios were tested, but ratios higher than 5 were impossible to prepare due to the difficulty in dispersing the BNC bundles; additionally, and only for this ratio, a CMC with 250 kDa (degree of substitution of 0.7) was used, as shown in Table 3. Before use, the BNC:CMC mixture was homogenized in a Dispermat (model CV3-Plus-E, VMA-Getzmann GmbH) at speeds between 2000 and 5000 rpm, depending on the sample and consistency used. The native starch suspension was prepared as reported elsewhere (Saraiva et al., 2010). A commercial premium fine paper (80 g/m^2, uncoated, woodfree) was used as reference.

The coatings were performed using a Mathis laboratory coating device (SVA-IR-B) at 6 m/min. Different steel bars (plain or drilled drawdown) were used to control the coating thickness. The drying process was performed by an IR drier coupled to the applicator roll (1.0 kW drying intensity), followed by air drying. The base paper was attached to a metallic plate before coating, in order to avoid curling during the coating and drying processes.

The coated samples were cut into A5 size and the grammage was determined according to ISO standard 536:1995. The total surface pickup was calculated by the difference from the grammage of the original base paper used for each coating. Final pickups of all the coated papers were 3.4 g/m^2 (standard deviation of 1.0).

The different paper samples were printed in a HP Officejet Pro 6230 printer using a specific mask set to print the CMYK (cyan, magenta, yellow and black) system colours (Lourenço et al., 2020). After conditioning (23 °C ± 1, RH 50 % ± 2), several printing quality parameters were measured: the gamut area was calculated as the area of the hexagon whose vertices are the CIE a*b* coordinates obtained for cyan, yellow, magenta, green, blue and red areas of the printed mask; the CIE a*b* colour coordinates were measured in duplicate with a spectrophotometer (Eye-One UVcut, X-Rite Inc.).

Table 3
Amounts (wt%) of each component used in the coating formulations with BNC.

	BNC	CMC	BNC/CMC ratio	Starch	OBA	AKD	Salt
i	50	50	1	–	–	–	–
ii	3	0.6[a]	5	96.4			
		1.5	2	95.5	–	–	–
		3	1	94			
	5	1[a]	5	94			
		2.5	2	92.5	–	–	–
		5	1	90			
	10	10	1	80	–	–	–
		2[a]	5	88			
iii	5	5	1	66.7	6.2	0.4	16.7

[a] CMC with 250 kDa was used.

3. Results and discussion

3.1. General characterization of the BNC samples

From the yield values of nanofibrillar material (Table 1) it may be suggested that the sample with CMC after the HPH is the most fibrillated, with a yield value apparently close to those measured for TEMPO-oxidized cellulose nanofibril samples (Lourenço et al., 2017). However, the yield values obtained for the samples containing CMC are most probably overestimated, since according to the method used for their determination, the supernatant could contain some amount of CMC, in addition to the fibrillated matter, thus increasing the apparent amount of fibrillated material (yield). For the BNC sample (without CMC), even after the physical treatment in the homogenizer, the yield is still very low. The zeta potential is very negative for the BNC-CMC and BNC:CMC-HPH samples due to the incorporation of CMC, as expected. The intrinsic viscosity values determined are high, showing BNC samples with a high degree of polymerization of cellulose. From the FE-SEM images (Fig. 1) it is possible to clearly distinguish between fibrils with diameters as low as 10 nm and fibrils with large diameters, above 200 nm.

3.2. Influence of bacterial nanocellulose on filler-containing handsheets

The incorporation of BNC in filler-containing handsheets was performed both in the presence and in the absence of additives (Tables 4 and 5, respectively). BNC samples before (BNC) and after the mechanical treatment (BNC-HPH), and with CMC before and after the mechanical treatment (BNC:CMC and BNC:CMC-HPH, respectively) were used.

As it is possible to observe for the results of the paper properties for the tests performed with addition of common paper additives (starch, ASA and CPAM), shown in Table 4, the reference handsheets (without BNC) present a high filler retention (filler content approaching the maximum of 30 %, Table 2). With the addition of the BNC samples, a further increase in the PCC content was noticed, when using BNC:CMC. This trend was not exhibited when using BNC or BNC:CMC-HPH, and using the BNC-HPH the filler content was roughly the same of that of the reference handsheets. By the comparison of the results obtained for the BNC samples, without and with HPH, it seems that the higher content of nano-size fibrils (Table 1) was beneficial for the filler retention with the BNC-only samples but not with the BNC:CMC samples.

As known, the mechanical properties of paper are much dependent on the content of filler, which is known to disturb the bonding between fibres, thus reducing paper strength. In order to better understand the influence of the effective PCC content on the paper properties, a filler-tensile factor (Eq. (1)) was applied to the tensile index values depicted in Table 4. Values higher than 1 correspond to handsheets with a normalized tensile index superior to that of the reference handsheets (Lourenço, Godinho, et al., 2019). A filler-tear factor was calculated in a similar manner from the values of the tear index and filler content. The results of the filler-tensile and filler-tear factors, together with the filler content variation vs. reference, are presented in Fig. 2. The BNC sample (without HPH) showed no positive effect in the filler retention and tensile factor, although some slight improvement in the tear factor was obtained. BNC-HPH sample led to slight increases in the paper strength in comparison to the reference handsheets, without affecting filler retention. The BNC:CMC sample favoured the filler increase but harmed the paper strength. BNC:CMC-HPH was not good in retaining PCC, and no positive effects were observed in the strength factors either. As previously concluded for TEMPO-oxidized cellulose nanofibrils with high negative charge (Lourenço et al., 2017), there is the possibility of repulsion phenomena between the BNC containing CMC in their composition and the cellulosic fibres, as well as preferential bonding with the cationic additives (starch and CPAM), which hinders its positive effect. In the case of BNC-HPH, this did not occur and a positive effect of the use of BNC in enhancing paper strength could be observed.

$$\text{Filler} - \text{tensile factor} = \frac{(\text{Tensile Index} \times \text{Filler content})_{\text{with BNC}}}{(\text{Tensile Index} \times \text{Filler content})_{\text{without BNC}}} \quad (1)$$

The evaluation of the optical properties showed that improvements can be obtained, even if the filler content did not increase (note that a lower filler amount is usually translated into lower light scattering and opacity values of the produced handsheets). As for the structural properties, air resistance and smoothness were always improved in comparison to the reference handsheets, as it would be expected.

In sum, BNC demonstrates a positive effect in all the measured paper properties in the presence of additives, if no CMC is used. With BNC-HPH, the filler content was roughly similar, from 27.2 (±0.2 %) to 27.7 % (±0.4 %), tensile index increased slightly from 30.1 to 32.5 N·m/g, light scattering and opacity increased from 69.3 to 75.8 m^2/kg and from 90.6 to 91.6 %, respectively. Additionally, the air resistance (Gurley) increased greatly from 2.8 to 18.7 s/100 mL and surface roughness decreased from 194 to 123 mL/min, due to the effect of nanocellulose in closing the paper structure.

Interestingly, there was a positive effect of BNC samples in improving the handsheet optical properties operating with additives. It is not to be discarded that the BNC fibrils increase the number of air/paper interfaces in the cellulose-filler network, by leading to a more intricate/entangled 3D structure, thus providing greater light scattering. This was also observed previously for some carboxymethylated and TEMPO-oxidized cellulose nanofibrils under specific conditions (Lourenço, Godinho, et al., 2019).

When added to the fibrous matrix, in the absence of additives, the HPH-treated BNC samples led to distinct papermaking results (Table 5). Contrary to the results shown above in Table 4, the reference handsheets (without BNC) present a low filler retention. The addition of the BNC sample with CMC led even to a greater loss of material through the web and therefore the filler content was less than half of the one measured in

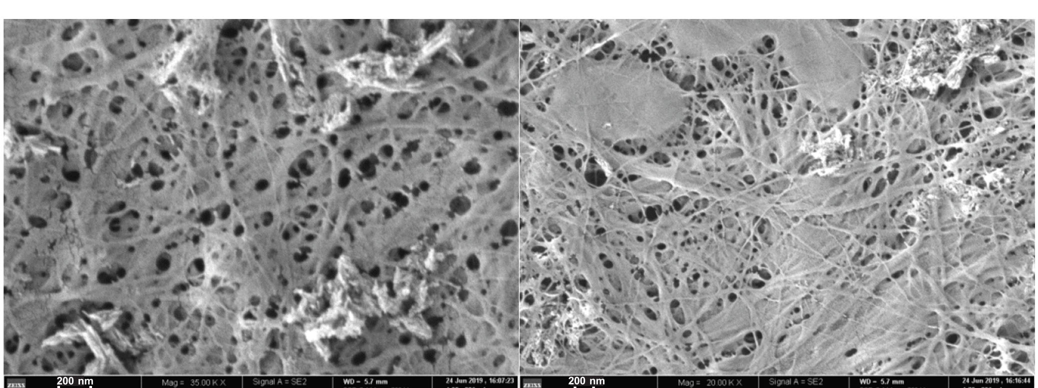

Fig. 1. FE-SEM images of bacterial nanocellulose before (left) and after (right) high-pressure homogenization. The scale bar denotes 200 nm.

Table 4
Papermaking properties of handsheets containing PCC and additives (starch, ASA and CPAM), produced without BNC (Ref.) and with different BNC samples[a].

	Ref.	BNC	BNC-HPH	BNC:CMC	BNC:CMC-HPH
Filler content (%)	27.2 (0.2)	25.5 (0.3)	27.7 (0.4)	28.9 (0.1)	23.6 (0.2)
Grammage (g/m^2)	82.2 (0.4)	81.1 (1.4)	82.7 (0.7)	82.6 (0.3)	76.5 (0.2)
Bulk (cm^3/g)	1.62 (0.01)	1.64 (0.06)	1.52 (0.03)	1.57 (0.04)	1.52 (0.02)
Tensile index (N·m/g)	30.1 (0.7)	29.3 (1.3)	32.5 (1.0)	25.3 (0.5)	34.9 (1.2)
Burst index (kPa·m^2/g)	1.9 (0.1)	2.0 (0.2)	2.2 (0.1)	1.4 (0.1)	2.2 (0.05)
Tear Index (mN·m^2/g)	5.0 (0.4)	5.8 (0.2)	5.3 (0.4)	3.8 (0.2)	4.7 (0.3)
Light scattering (m^2/kg)	69.3 (0.8)	nd	75.8 (0.8)	82.3 (1.1)	70.7 (1.0)
Opacity (%)	90.6 (0.1)	nd	91.6 (0.1)	92.0 (0.1)	89.4 (0.2)
Air resistance (Gurley, s/100 mL)	2.8 (0.3)	16.2 (0.4)	18.7 (2.5)	31.2 (2.5)	16.4 (1.0)
Roughness (Bendtsen, mL/min)	194 (16)	187 (21)	123 (17)	105 (12)	90 (7)

[a] Standard deviation within parentheses; nd: not determined. The average values and the corresponding standard deviations correspond to the measurement of a minimum of five replicates (up to ten replicates) for each property, expect for the filler content, which was determined in duplicate.

Table 5
Papermaking properties of handsheets containing PCC, produced without BNC (Ref.) and with HPH-treated BNC[a].

	Ref.	BNC-HPH	BNC:CMC-HPH
Filler content (%)	13.8 (0.1)	12.6 (0.04)	6.5 (0.01)
Grammage (g/m^2)	69.0 (0.6)	68.2 (0.5)	62.0 (0.6)
Bulk (cm^3/g)	1.58 (0.02)	1.47 (0.03)	1.47 (0.01)
Tensile index (N·m/g)	41.0 (1.5)	47.4 (1.0)	55.0 (1.8)
Burst index (kPa·m^2/g)	2.5 (0.1)	3.1 (0.2)	3.5 (0.1)
Tear index (mN·m^2/g)	5.1 (0.3)	6.2 (0.5)	6.8 (0.5)
Light scattering (m^2/kg)	57.7 (1.6)	54.7 (1.1)	43.8 (0.6)
Opacity (%)	86.1 (0.5)	84.6 (0.4)	79.3 (0.3)
Air resistance (Gurley, s/100 mL)	4.6 (0.4)	46.6 (5.4)	9.8 (1.0)
Roughness (Bendtsen, mL/min)	122 (8)	67 (6)	92 (6)

[a] Standard deviation within parentheses. Due to difficulties of dispersion in water of the BNC samples that did not undergo a previous HPH treatment, no results are provided for these samples. The average values and the corresponding standard deviations correspond to the measurement of a minimum of five replicates (up to ten replicates) for each property, expect for the filler content, which was determined in duplicate.

the reference handsheets; using the BNC-HPH sample raised the filler content, but the values were still low with no improvement in comparison to the reference. These great filler losses in the handsheet production were reflected in the grammage of the handsheets, which was notably lower in the series of experiments without additives (<70 g/m^2) than in the series with additives (grammages >80 g/m^2). According to the lower levels of the filler content vs. reference handsheets, the

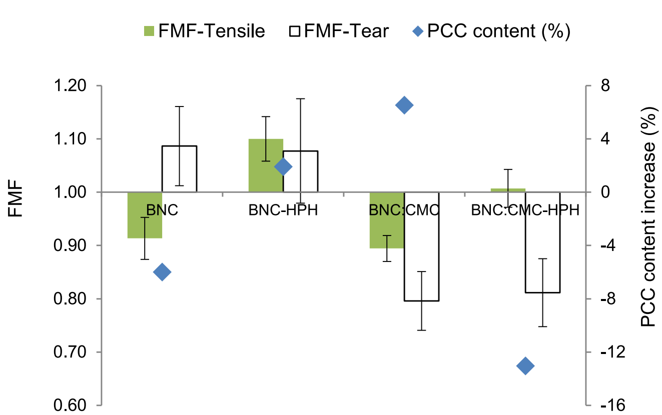

Fig. 2. Results of the filler-mechanical strength factor (FMF) for the tensile and tear indices, and PCC content increase in handsheets produced with different BNC samples. Bars upwards 1.0 and downwards 1.0 represent increments and decrements of the FMF, respectively.

strength properties were enhanced and the optical properties were impaired in both cases (BNC-HPH and BNC:CMC-HPH). Additionally, air resistance increased (more closed structure) and roughness decreased (smoother surface) as a consequence of the effect of nanostructured BNC in closing the paper structure, having been these effects more pronounced using BNC-HPH. The filler retention in the handsheets was lower than 50 % (filler content lower than 13 %, vs. the aim of 30 %) which is insufficient for a practical application of BNC under the conditions referring to Table 5. These results mean that BNC alone does not improve the filler retention and additional components are thus required for this purpose. Although common in the paper industry, where retention agents are added to the formulations, this contrasts to the behaviour previously described for other types of cellulose nanofibrils (enzymatic, TEMPO-oxidized and carboxymethylated) which were able to flocculate and retain PCC (Lourenço, Gamelas, et al., 2019; Lourenço, Godinho, et al., 2019).

3.3. Coatings with bacterial nanocellulose

Fig. 3 depicts the gamut area obtained for the BNC incorporation in sizing formulations composed of starch, as a relative increase from the value obtained for the base paper or for the starch-sized papers. Since the gamut area is highly influenced by the thickness of the applied coating, for the starch reference a trend line based on six experimental points with increasing thicknesses was defined. The value of the increase presented is based on the gamut area calculated for a starch coated sample with the same thickness of that coated with BNC. Incorporation values of BNC ranging from 3 to 50 % in the coating formulation were evaluated. As stated, BNC had to be mixed with CMC in order to control the rheology of the formulation, and, therefore, the results obtained for three different BNC/CMC ratios are presented.

From the results obtained, it is possible to define the minimum amount of BNC and the BNC/CMC ratio that improve printing quality. When compared to the base paper, papers coated with 3 % BNC presented always an inferior performance. However, the formulation with BNC:CMC mixed in equal parts (BNC/CMC ratio of 1) was able to improve the gamut area for higher BNC content. Improvements were also obtained using 10 % of BNC and 2 % of CMC250 (BNC/CMC ratio of 5). On the other hand, when compared with starch-surface sized papers, it is even possible to detect gamut area increases with 5 % BNC + 1 % CMC250. The highest improvement observed was obtained using the formulation comprising 50 % of BNC and 50 % of CMC, with which gamut area increases of >25 % compared to the base paper and of >40 % compared to starch-only coated papers were achieved.

When added to complete formulations (including starch, OBA, AKD and salt), it is possible to increase the gamut area by incorporating only 5 % of BNC, combined with 5 % of CMC (Fig. 4). By comparing the value obtained with that obtained for the commercial fine paper, an increase in the gamut area of ca. 350 was also observed (Fig. 4).

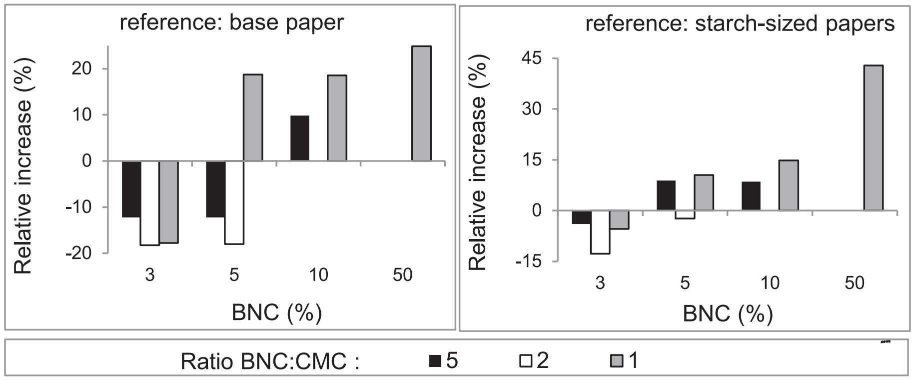

Fig. 3. Increase in gamut area, relative to base paper (left) or starch-sized papers (right), for papers coated with starch and different contents of BNC and CMC (see Table 3) and for a paper coated with a 50 % BNC formulation composed only of BNC and CMC (ratio 1:1). Bars upwards zero and downwards zero represent increments and decrements, respectively.

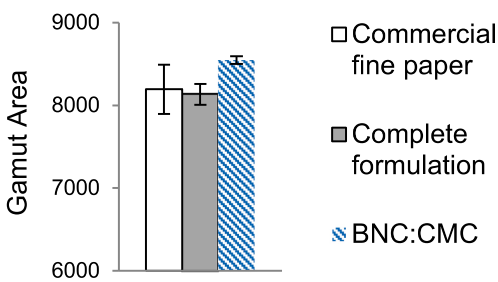

Fig. 4. Gamut area values for: commercial fine paper; paper coated with complete formulation (starch, OBA, AKD, salt); paper coated with complete formulation with 5 % of BNC (combined with CMC at 1:1 ratio).

4. Conclusions

Bacterial nanocellulose (BNC) from *Komagataeibacter xylinus*, after high-pressure homogenization (BNC-HPH), when used as a wet-end component for the production of filler-containing handsheets was able to improve slightly the paper strength without harming the filler retention in the presence of common additives typically used in the furnish of printing and writing papers. Light scattering coefficient and opacity, and even greatly, air resistance and surface smoothness also increased, showing an enhancement in all the measured paper properties.

The use of this type of nanocellulose brought remarkable benefits when it was applied at the paper surface as coating agent, using levels of at least 5 % of BNC in the coating formulations together with equivalent amounts of CMC (1:1, *w/w*). The most promising result was indeed obtained by coating the surface of an uncoated office paper with a formulation containing 50 % of BNC and 50 % of CMC, where an increase in gamut area of >25 % was achieved in comparison to the base paper. The results of applying BNC:CMC incorporated in more complete formulations (including starch, AKD, OBA and salt) also showed advantages when comparing to the results exhibited by commercial fine paper regarding printing quality, as evaluated by the gamut area of the printed mask.

Overall, the BNC is a good choice to be used for the paper coating. The present studies are, to our knowledge, the first ones in what concerns the use of BNC for the coating of a paper surface aimed at improving printing quality.

CRediT authorship contribution statement

Ana F. Lourenço: Methodology, Investigation, Writing – original draft, Writing – review & editing. **Daniela Martins:** Methodology, Investigation, Writing – review & editing. **Fernando Dourado:** Conceptualization, Writing – review & editing. **Pedro Sarmento:** Conceptualization, Writing – review & editing, Supervision. **Paulo J.T. Ferreira:** Conceptualization, Methodology, Writing – review & editing, Supervision, Funding acquisition, Project administration. **José A.F. Gamelas:** Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

Fundação para a Ciência e a Tecnologia (FCT), Portugal is acknowledged by SFRH/BDE/108095/2015 grant and Strategic Research Centre Project (UIDB/00102/2020). This work was also carried out under the Project Inpactus - innovative products and technologies from eucalyptus, Project N.° 21874 funded by Portugal 2020 through European Regional Development Fund (ERDF) in the frame of COMPETE 2020 n°246/AXIS II/2017.

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