Cellulose micro and nanofibrils as coating agent for improved printability in office papers

Ana F. Lourenço, José A. F. Gamelas, Pedro Sarmento & Paulo J. T. Ferreira

Cellulose

ISSN 0969-0239

Cellulose
DOI 10.1007/s10570-020-03184-9

Springer

Cellulose
https://doi.org/10.1007/s10570-020-03184-9

ORIGINAL RESEARCH

Cellulose micro and nanofibrils as coating agent for improved printability in office papers

Ana F. Lourenço · José A. F. Gamelas · Pedro Sarmento · Paulo J. T. Ferreira

Received: 28 November 2019 / Accepted: 23 April 2020

Abstract The use of nanocelluloses is being conducted for the most diverse applications. Their performance as coating agent has been mainly explored to improve barrier properties, as they emerge as perfect candidate for plastic substitution, but it is also important to explore their potential to improve printing quality. In the present work, the influence of different nanocelluloses, obtained through mechanical, enzymatic, TEMPO-mediated oxidation and carboxymethylation treatments, in the coating process and inkjet printability of office papers was assessed. The results revealed that the cellulose nanofibrils are better for printability than the microfibrils. But the size and charge of the former must be taken into account, since fibrils of very small size penetrate the paper structure, dragging the pigments from the surface, and very anionic nanofibrils can also have negative influence on the optical density. Besides, an interesting synergy between surface-sizing starch and the cellulose nanofibrils was found to occur as the latter closed the paper structure, which prevented starch from penetrating, while potentiating both of their positive effects on ink pigment entrapment. An additional study of characterization of inkjet pigments was also performed.

Keywords Cellulose micro/nano fibrils · Gamut area · Inkjet printing · Paper · Print-through

Introduction

Research concerning nanocelluloses has increased exponentially in the last years. New methodologies for their production, optimization of the existing processes and insight on the material characterization have been the main focus of the available publications. Due to the proven great potential of the nanocellulosic materials, a deep investigation of their possible applications has also been the subject of an increasing number of articles and patents. If on the one hand they have been tested and efficiently used in small-volume applications, such as medicine or electronics industries (Torvinen et al. 2012; Lin and Dufresne 2014;

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s10570-020-03184-9) contains supplementary material, which is available to authorized users.

A. F. Lourenço (✉) · J. A. F. Gamelas (✉) · P. J. T. Ferreira
University of Coimbra, CIEPQPF, Department of Chemical Engineering, Pólo II, R. Sílvio Lima, 3030-790 Coimbra, Portugal
e-mail: analourenco@eq.uc.pt

J. A. F. Gamelas
e-mail: jafgas@eq.uc.pt

P. Sarmento
The Navigator Company, Lavos - Apartado 5, 3081-851 Figueira da Foz, Portugal

Published online: 08 May 2020

Placket et al. 2014; Bacakova et al. 2019; Zhang et al. 2019), on the other it has been proved that the use in high-volume industries, such as papermaking, is very challenging due to the required high loadings, which has delayed their immediate use. In fact, recent reports have stated that more than twenty thousand tonnes of nanocelluloses are necessary to fulfil the annual needs of the papermaking industry (Miller 2019), while the current industrial facilities for their production generate much less than this.

In papermaking, nanocellulose has the potential to be used either at the furnish to improve the dry and wet strength properties and filler flocculation (Lourenço et al. 2017, 2019a, b) or at the paper surface. Regarding the latter approach, the research has been focused mainly on the improvement of the barrier properties, since nanocellulose is able to create a cohesive film, which results in high resistance to air, oxygen, grease and in some cases to water vapour (Hubbe et al. 2017a), making this material the perfect candidate as an environmentally-friendly substitute for plastics. The application of nanocellulose at the paper surface is usually performed by coating or spraying. Considering that paper is porous, a high degree of penetration is likely to occur, which can be beneficial to increase paper strength and air resistance (Syverud and Stenius 2009). However, this means that the hold-out of the material is not as high as expected (Aulin et al. 2010; Lavoine et al. 2014; Kumar et al. 2017) and therefore several authors have proposed to pre-treat the paper surface before the nanocellulose coating (Luu et al. 2011; Nygårds 2011; Ridgway and Gane 2012; Kumar et al. 2017). The results usually report that the higher uniformity and improved smoothness of the surface, along with hydrophilic nature promote the nanocellulose adhesion.

Considering the aforementioned, it also becomes very interesting to study the potential of the nanocellulose-coated surfaces for printing quality. Only a few reports have addressed this theme (Hamada et al. 2010; Nygårds 2011; Hamada and Mitsuhashi 2016; Gómez et al. 2017; Imani et al. 2019), as most of the available research only reports on the nanocellulose ability as binder or thickener replacer in coating formulations (Aspler et al. 2013; Dimic-Misic et al. 2013; Rautkoski et al. 2015). In particular, Nygårds (2011) tested cellulose microfibrils (CMFs) in formulations with ground calcium carbonate (pigment) and latex (binder) for offset printing, and stated that the coatings possessed relatively high surface energy, which is theoretically good for printing with water-based inks. However, in the study performed, CMFs highly diminished the paper surface strength, which is not favourable for offset printing. Gómez et al. (2017) analysed the use of bacterial cellulose (BC) for restoring paper printed with offset inks, and concluded that the lining with BC provided only minor decrements in the print density and CIE L*a*b* colour coordinates, most of them imperceptible to the human eye. Imani et al. (2019) used cellulose nanofibrils (CNFs) produced by TEMPO-mediated oxidation pre-treatment of unbleached and bleached fibres to coat paper, and evaluated the quality of the coatings for offset printing. Better results were obtained for the paper coated with CNFs obtained from bleached fibres; these CNFs provided a stronger coating layer with smoother surface and better offset printing quality. Hamada and Mitsuhashi (2016) coated woven and nonwoven fabrics with CNFs and evaluated the coated substrates for inkjet printing. Substantial improvements were achieved in the printability, as evaluated by the decreases of lightness (L*) and luminous reflectance (Y) of the prints. According to the work of Hamada and colleagues (Hamada et al. 2010; Hamada and Mitsuhashi 2016) the optical density is improved, since more ink pigment can be captured at the surface, and low ink absorption is noticed when low amounts of CNFs are applied. Besides the optical density, other properties of relevance to the printing performance, such as *dusting* and *linting*, could be improved by using CNFs at the paper surface (Hamada et al. 2010; Song et al. 2010; Ankerfors 2012).

Nanocellulose, especially cellulose nanofibrils, can present high viscosity even at low solids content (Nechyporchuk et al. 2016; Hubbe et al. 2017b). This fact poses a great challenge to the coating processes, not only due to the inherent technical difficulties of achieving a homogeneous coating, but also due to the large amount of water that cannot be removed without disturbing the quality of the suspension. Nonetheless, their pseudoplastic behaviour, as already evidenced by several authors (Nazari and Bousfield 2016; Nechyporchuk et al. 2016; Hubbe et al. 2017b) can contribute to ease of handling. When in aqueous suspension, CNFs form an interconnected network, which gives the sample a gel-like behaviour. The strength of this network depends on the nanocellulose production

process and, consequently, on the fibrillation degree of the sample, and therefore, when discussing the subject, it is of utmost importance to assess the distinct impact that different nanocelluloses will have in paper coating.

The present study intends to assess the influence of different nanocelluloses on the coating process and printing quality of office papers, by using a commercial inkjet printer. The results are always compared with starch surface-sized papers, the most common solution used in the industry. To our knowledge, no previous work has been published on the evaluation of inkjet printing quality of office papers coated with nanocelluloses.

Materials and methods

Materials

CNFs and CMFs were produced from an industrial bleached eucalyptus kraft pulp (BEKP), according to methodologies reported elsewhere (Lourenço et al. 2019a, b). Briefly, the never dried BEKP was refined up to 4000 PFI rev. and used as basis for the different enzymatic or chemical pre-treatments. For the production of the CMF-Mec sample, a total of 15,000 PFI rev. were applied to the BEKP (3 × 5000 PFI). For the CMF-Enz samples, an enzymatic hydrolysis, based on the procedure developed by Tarrés et al. (2016), was used. 300 g of a commercial enzyme (endocellulase, 10% of exocellulase and 5% of hemicellulase) were used for each tonne of the base pulp. The hydrolysis was conducted at a consistency of 3.5%, at 50 °C and pH 5, for 2 h, under mechanical stirring. Two CNF-TEMPO samples were obtained based on oxidation with NaClO (3 and 9 mmol per gram of pulp, respectively assigned T3 and T9), according to the methodology of Saito et al. (2007), in an aqueous medium with NaBr and TEMPO catalysts, controlled to pH 10 with NaOH, for 2 h. Finally, CNF-Carb was produced by reaction with monochloroacetic acid (9% relative to fibres) in a medium constituted by isopropanol, methanol and NaOH, for 3 h at 60 °C, according to the methodology published by Wagberg et al. (2008). The samples CMF-Mec, CMF-Enz-2P, CNF-TEMPO T3 and T9, and CNF-Carb were obtained by thorough washing with demineralized water to remove remaining chemicals and passing twice in a high-pressure homogenizer (HPH, GEA Niro Soavi, model Panther 115 NS3006L), first at 500 bar and second at 1000 bar. Besides, another sample produced with the same enzymatic hydrolysis conditions was obtained by passing 6 times in the HPH (first pass at 500 bar and the other passes at 750 bar), which was named CMF-Enz-6P.

The CNFs and CMFs produced were fully characterized for their nanofibrillation yield (gravimetry of centrifuged suspensions), content of carboxyl groups (C_{COOH}, conductometric titration), intrinsic viscosity (viscosimetry in cupriethylenodiamine) and charge (zeta potential, electrophoretic mobility) as detailed elsewhere (Lourenço et al. 2017). The degree of polymerization (DP) was calculated from the intrinsic viscosity values by applying the Mark-Houwink equation with the parameters defined by Henriksson et al. (2008), namely K = 2.28 and a = 0.76 (DP > 950) or K = 0.42 and a = 1 (DP < 950). A modified centrifugal water retention value (WRV) was measured according to the procedure detailed by Dimic-Misic et al. (2018), on mixtures containing BEKP and 3% of CNF/CMF. Finally, field emission-SEM images were acquired in air-dried films of aqueous suspensions of each CNF/CMF. The films were sputter-coated with gold and analysed in a Carl Zeiss Merlin microscope, in secondary electron mode.

Paper coating and characterization

An industrial, calendered, uncoated, and woodfree base paper (BP) produced from BEKP and without any surface treatment, with a basis weight of 78 g m^{-2}, was used as substrate. This paper was coated with (1) native starch, (2) nanocellulose or (3) a mixture of starch with nanocellulose (the latter ranging from 10 to 50%). Before use, the nanocellulose was homogenized in a Dispermat equipment (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).

The coatings were performed using a Mathis laboratory coating device (SVA-IR-B) at 6 m min^{-1}. Different steel bars (plain or drilled drawdown) were used to control the coating thickness. The drying process was performed simultaneously 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 basis weight was determined according to ISO standard 536:1995. The total surface pickup was calculated by the difference from the basis weight of the original BP used for each coating.

Printing quality

The different paper samples were printed in a HP Officejet Pro 6230 printer using a specific mask set to print the CMYK system colours. After conditioning (23 °C ± 1, RH 50% ± 2), several printing quality attributes were measured, as follows. 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. Accordingly, the CIE L* lightness was also used for calculation of the gamut volume. The CIE L*a*b* colour coordinates were measured in duplicate with a spectrophotometer (Eye-One UVcut, X-Rite Inc.). The optical colour density was measured using the digital microscope PIAS II (QEA Inc., Billerica, MA, USA). The absolute printing optical density (POD) was calculated as the difference between the printed and unprinted areas of the samples. The print through (PT) was calculated for black according to Eq. (1) defined by Eriksen and Gregersen (2005).

$$PT = \sqrt{(L_p^* - L_u^*)^2 + (a_p^* - a_u^*)^2 + (b_p^* - b_u^*)^2} \quad (1)$$

where L*, a* and b* are the CIE values, and u and p denote the unprinted area and backside of solid print, respectively. The line quality was evaluated with the same equipment, through the black and white feathering (mean of the lead and trail raggedness's of the printed black line). Finally, the circularity of black and magenta printed circles was measured from the perimeter and area, in which a perfect circle has a circularity = 1. Measurements were always performed in duplicate.

The pigment-based inks used (cartridges with commercial designation "HP 934 XL" and "HP 935 XL") were characterized for their particle size and composition, by dynamic light scattering (Zetasizer Nano ZS, Malvern Instruments) and FTIR spectroscopy (FT/IR-4200, Jasco), respectively. The measured sizes (Z-average, intensity weighted diameter) were 113, 105, 83 and 72 nm for black, magenta, yellow and cyan, respectively. The FTIR spectra can be consulted in the Supplementary Material. Additionally, the zeta potential of the inks was also measured, and was found to be highly negative (around − 50 mV).

Results and discussion

Nanocelluloses characterization

The characterization data of the nanocellulose samples produced are depicted in Table 1. Two main groups of nanocelluloses were produced and used in this work: (a) cellulose microfibrils obtained by mechanical treatment or with the aid of enzymatic hydrolysis and (b) functionalized cellulose nanofibrils obtained with the aid of TEMPO-mediated oxidation or by carboxymethylation. The very different characteristics of the samples will obviously lead to very different behaviour when applied as coating in paper products. The samples produced in this work presented very distinct nanofibrillation yields, with the functionalized samples showing more than 70% of the fibrils at the nanometric scale. These values are explained due to the higher content of carboxyl groups on the latter, that aided the homogenization step, and are in accordance with the small intrinsic viscosity and corresponding small degree of polymerization, and very negative charge of the TEMPO and carboxymethylated CNFs. On the other hand, the cellulose microfibrils, Mec and Enz-2P, possessed only a small number of small fibrils, and the mean DP was much higher than measured for the functionalized samples, with the DP of CMF-Mec being only slightly smaller than that of the original pulp used for its production (Lourenço et al. 2019b). Besides, the HPH effect was quite perceptible on the enzymatic samples, since after 6 passes in the equipment the DP diminished from 1834 (2 passes) to 1496, probably allowing more hydroxyl groups to be available. The zeta potential of CMFs was relatively low, whereas highly negative values were found for the CNFs. As for the WRV values, it was noticed that the functionalized CNFs present about 4 times the network swelling level of the mechanical and enzymatic CMFs, with the highest value measured for CNF-T9, as expected.

Table 1 Characterization of the nanocelluloses produced

Sample	Designation	Yield (%)	C_{COOH} (μmol g^{-1})	Intrinsic viscosity (mL g^{-1})	DP	ζ Potential (mV)	WRV
BEKP	Ref	–	145	905	2628	− 26	1.3
CMF-mechanical treatment	Mec	8	123	817	2296	− 25	2.2
CMF-enzymatic hydrolysis	Enz-2P	20	186	689	1834	− 29	2.2
	Enz-6P	23	ND	590	1496	− 33	ND
CNF-TEMPO oxidation	T3	81	885	164	390	− 69	9.2
	T9	99	1498	114	273	− 82	10.8
CNF-carboxymethylation	Carb	72	403	544	1345	− 59	8.7

ND not determined

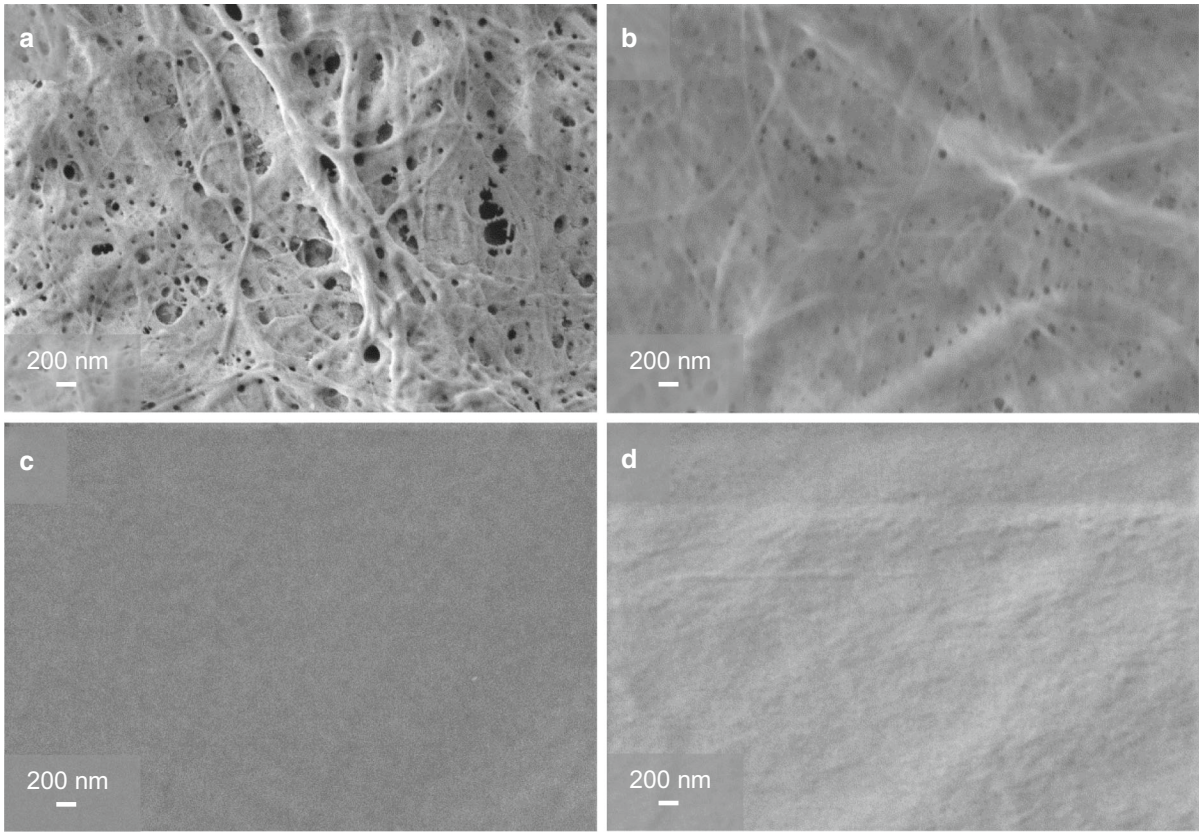

Fig. 1 FE-SEM images (×20.000 magnification) of films made of **a** CMF-Mec, **b** CMF-Enz, **c** CNF-TEMPO and **d** CNF-Carb

FE-SEM observations of the samples produced are also helpful in differentiating the two main groups of nanocelluloses (Fig. 1). In fact, for the cellulose microfibrils (Fig. 1a, b) it was possible to observe the different fibrils, while for the cellulose nanofibrils (Fig. 1c, d) only a spider-web-like structure was observable, without the possibility to distinguish fibrils. This tight network is well-known (Nemoto et al. 2015; Chen et al. 2017) and is of utmost importance for the foreseen applications.

Printing quality

The assessment of the printing quality in papers coated with nanocellulose is of utmost importance, especially considering that this material is being widely explored

as coating for the most diverse substrates. The gamut area and gamut volume are typically used to quantify colour rendition since they usually correlate with the end users perception. Figure 2 presents the gamut values measured in the papers coated with the different nanocelluloses (100% CMF/CNF) or with formulations of starch and nanocellulose (0, 10 and 50% of CNF/CMF). The final pickup of all the coated papers was 2.4 g m^{-2} (SD 0.9). The first observation is that the behaviour of the cellulose microfibrils (CMF-Mec and CMF-Enz) is different from that of the cellulose nanofibrils (CNF-TEMPO and CNF-Carb). For the former, the gamut area and volume increased with the CMF incorporation in the coating formulation, with maximum values being obtained for the papers coated with 100% of CMF.

Besides, either at 10%, 50% or at 100% of the CMFs, both types of CMFs (Mec and Enz) led to similar gamut area and gamut volume, if only 2 passes are used in the HPH; the CMF-Enz-6P, provided, in general, lower gamut values, probably due to the weakening of the fibril structure caused by excessive pressure in the homogenizer, as previously reported (Lourenço et al. 2019b). Nonetheless, when comparing with the performance of the uncoated base paper, none of the CMFs used were able to significantly improve the printing quality. Additionally, the paper surface-sized with only starch presented a smaller gamut area (as previously reported by Sousa et al. 2013). Starch is usually modified (Lee et al. 2002; Li et al. 2019) or used in combination with other compounds (polyvinyl alcohol, styrene acrylate latex, among others) (Moutinho et al. 2007; Saraiva et al. 2010; Sousa et al. 2014) to succeed as printing quality enhancer. However, when the functionalized CNFs were used, an interesting result was obtained, since the formulations containing 50% of starch and 50% of CNFs led to better results than those obtained for the papers coated only with CNFs. It seems that there is a positive synergy between starch and the anionic CNFs. Besides, the much higher surface density of hydroxyl groups typical of these samples is creating a cohesive entangled network, as evidenced by the FE-SEM images (Fig. 1), which is probably entrapping the ink pigments at the surface of the coated papers, contrary to the base paper which is very porous, as observed in previous work (Hamada et al. 2010; Hamada and Mitsuhashi 2016). SEM images were taken on the surface of the coated papers and compared to base paper, but due to the very low coating pickup achieved, no structural differences could be observed (data not shown).

In this sense, the printing optical density (POD) was measured for the coated papers. Table 2 depicts the POD for cyan, magenta, yellow and black measured in the papers coated with 100% of nanocellulose and in the reference paper coated with starch, as a relative increase in relation to the base paper POD values. Generally, for the mechanical CMF-coated paper, a slight increase of the cyan and black POD was

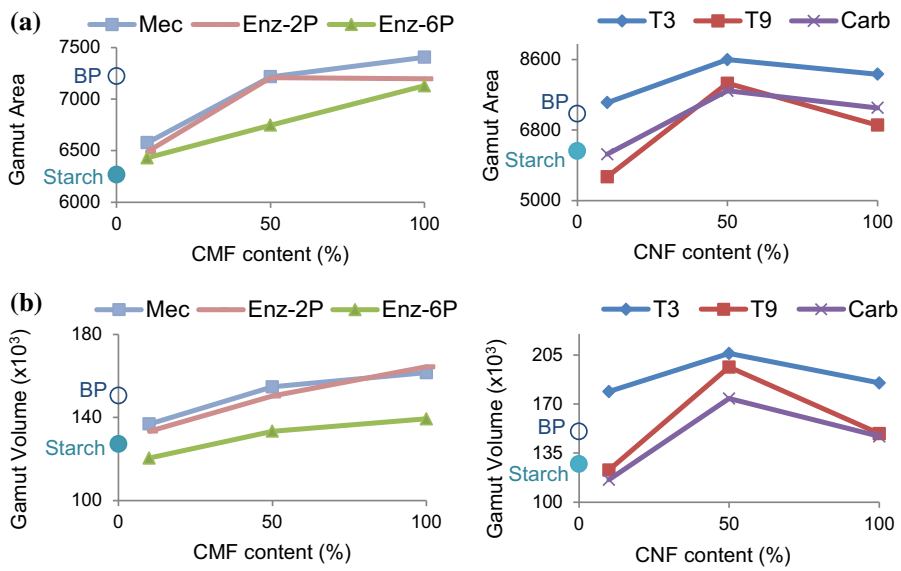

Fig. 2 Gamut area (a) and gamut volume (**b**) of papers coated with starch and different contents of nanocellulose. The values for base paper (BP) and paper coated with only starch are presented for comparison. The standard deviation of the results was always inferior to 400

observed when comparing to the base paper. The enzymatic CMFs did not significantly influence the POD values, as similar results were obtained, except for the black POD with the CMF-Enz-6P, which was very low.

For the CNF-T9 and CNF-Carb coated papers the values of the optical density were generally worse than those of the base paper, except for the POD of black which slightly increased with CNF-T9. It is very likely that the very small fibrils, specifically those of CNF-T9, are penetrating into the paper structure; moreover, since this is the most hydrophilic sample (Table 1), it is expected to attract in a higher extent the water-based inkjet inks into the sheet bulk, instead of entrapping them at the paper surface, causing therefore the printing optical density to be even worse than that of the base paper. On the other hand, with CNF-T3, a great increment of the black POD, and also (in a minor extent) of the yellow POD, was found.

To better evaluate the values obtained, the composition of the pigments of the ink formulations was analysed. From the FTIR spectra available in the Supplementary Information, it can be concluded that all the pigments are similar and based on azo compounds, with sulfonic groups and carboxylic acid groups, as common in inkjet dyes (Yuen et al. 2005; Hubbe et al. 2012). It is expected that the negatively charged sulfonic acid groups are negatively interfering with the highly anionic CNFs, which can be one explanation to why the CNF-T9, the most anionic and charged of the CNFs, is deteriorating POD. This effect was much less pronounced with CNF-T3, which could even improve POD, as mentioned.

As for the starch-coated papers, generally the POD values revealed a better performance. In fact, the POD of starch-coated papers seems not to be in line with the gamut values obtained, but it must be taken into account that the gamut was computed using the optical density of more than the three colours presented in Table 2.

Since the most striking differences were observed for the black pigment, the black POD was measured on the coated papers for all the formulations tested (Fig. 3) and compared to that obtained for the reference papers (base paper and starch-coated paper, indicated as horizontal lines in Fig. 3). As previously concluded for the gamut values, the tested CNFs presented, overall, a better performance than the CMFs. If for the CMF-coated papers (Mec and Enz), the amount of CMFs in the formulation seems not to be so relevant, as 10, 50 or 100% of their content leads to similar POD, for the CNFs the used amount had a significant impact. Just as previously concluded, a mixture of 50% starch and 50% nanocellulose led to the highest POD, with values superior to those obtained for starch-sized papers.

The print-through of the coated papers (Fig. 4) is in line with the assumption that the CNFs are forming an entangled network that is entrapping the ink pigments at the surface. In fact, for the CNF-coated papers, the print-through is much smaller than for the CMF-coated papers or starch-coated papers (except with 10% CNF-Carb). Differences between CNF incorporation levels of 50% and 100% were not significant; however, the print-through for these addition levels in the coating formulations was smaller than that corresponding to 10% of CNFs. The air resistance, as measured by the Gurley method (Fig. 5) confirms this theory. The CNFs are closing the paper structure in

Table 2 Increase, relative to base paper, of the printing optical densities (POD) of papers coated with starch or with different nanocelluloses

	Cyan	Magenta	Yellow	Black
Starch	2.1	6.2	− 2.3	8.5
Mec	3.3	0.1	0.1	5.0
Enz-2P	1.2	− 0.2	− 1.5	− 0.2
Enz-6P	− 1.5	− 3.0	− 1.3	− 14.0
T3	− 0.4	− 0.5	5.5	17.4
T9	− 10.2	− 7.9	− 0.6	3.7
Carb	− 11.7	− 8.5	1.7	− 5.1

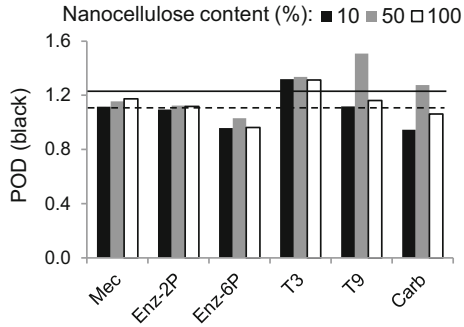

Fig. 3 Black printing optical density (POD) of papers coated with different contents of nanocellulose and starch. The horizontal lines depict the POD of the base paper (dashed) and of the paper coated with only starch (full)

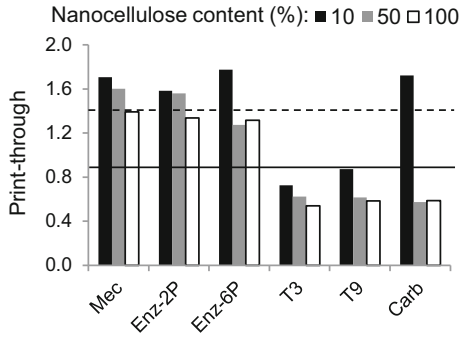

Fig. 4 Print-through of papers coated with different contents of nanocellulose and starch. The horizontal lines depict the print-through of the base paper (dashed) and of the paper coated with only starch (full)

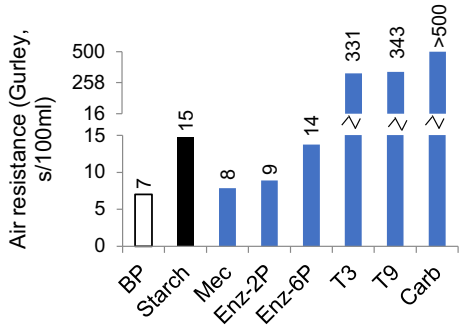

Fig. 5 Air resistance (Gurley) of papers coated with different nanocelluloses. The results for the base paper (BP) and paper coated with starch are presented for comparison

such a way that the air does not even pass through the paper (for CNF-Carb it was not even possible to measure the air resistance value).

The black and white feathering (Fig. 6a) of the printed papers showed that, despite the very closed structures, the ink vehicle was able to penetrate into the structure, since a good line quality was obtained. The results help defining the formulations that are more appropriate for the printing quality improvement, since (1) the CMFs always led to higher feathering than starch-sized papers, which was not evident with CNFs and (2) the CNF content highly influenced the results, with the 10% incorporation providing always higher values than the reference ones. As for the circularity (Fig. 6b), no improvements were found by using nanocelluloses in comparison to the base paper.

Conclusions

The impact of different nanocelluloses on the coating process and inkjet printability of office papers was assessed. Six different nanocelluloses were produced by using mechanical, enzymatic, TEMPO-mediated oxidation and carboxymethylation techniques. The different treatments and conditions used led to distinct nanocellulose characteristics, namely of size and charge. The nanofibril (CNF) films revealed a very compact web-like structure, contrary to what happened with the microfibrils (CMFs).

The different nanocelluloses were applied on base papers without any previous surface treatment, individually or combined with native starch. From the printability results it was possible to conclude that, overall, CNFs are better for printing quality than CMFs, as higher gamut area and volume, higher black optical density and lower print-through could be obtained with CNFs. This is due to the higher fibrillation of the former, that promoted accessibility to hydroxyl and carboxyl groups, generating an entangled network at the paper surface that entraps

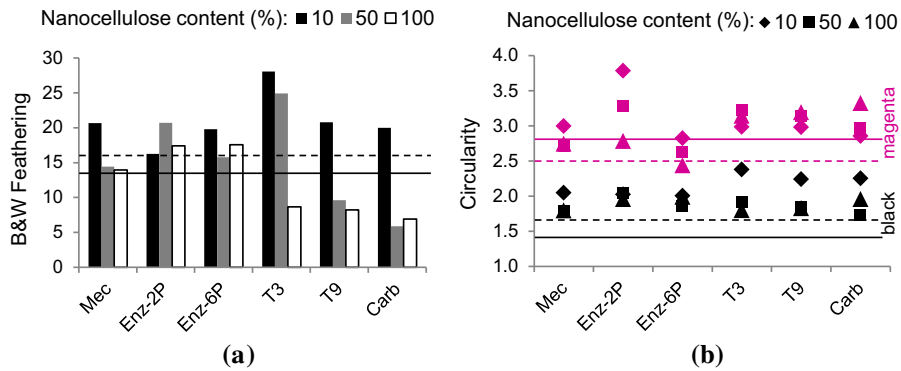

Fig. 6 Black and white feathering (**a**) and circularity (black and magenta) (**b**) of papers coated with different contents of nanocellulose and starch. The horizontal lines depict the values of the base paper (dashed) and of the paper coated with only starch (full)

the ink pigments; however, extremely negative nanofibrils, as the case of CNF-T9 (with ca. 1500 μmol/g^{-1} of carboxyl's and zeta potential of -82 mV), can negatively interfere with the ink's sulfonic groups; besides, the nanofibrils small size (> 90% in the nanometric scale and a DP < 300) leads to their penetration into the bulk of the paper structure. Surprisingly, when starch and CNFs were used together, a good synergy was found, as the CNF suitability to close the structure prevented the starch penetration, which helped in retaining the ink pigments at the paper surface thus improving printing quality (higher gamut area and black optical density).

With the study performed, it was possible to define the nanocellulose types that most improve printability, as well as their synergistic effects with starch, commonly used for the surface sizing of office papers.

Supplementary information

FTIR spectra of the pigment-based inks and the corresponding peaks attribution can be consulted.

Acknowledgments This work was supported by Fundacão para a Ciência e a Tecnologia (FCT), Portugal [SFRH/BDE/108095/2015]. Some of the work was conducted under Project inpactus—innovative products and technologies from eucalyptus, Project No. 21874 funded by Portugal 2020 through European Regional Development Fund (ERDF) in the frame of COMPETE 2020 no 246/AXIS II/2017.

References

Ankerfors M (2012) Microfibrillated cellulose: energy-efficient preparation techniques and key properties. Litentiate thesis presented to Innventia AB and KTH Royal Institute of Technology

Aspler J, Bouchard J, Hamad W, Berry R, Beck S, Drolet F, Zou X (2013) Review of nanocellulosic products and their applications. In: Dufresne A, Thomas S, Pothan LA (eds) Biopolymer nanocomposites: processing, properties, and applications, 1st edn. Wiley, Hoboken, NJ

Aulin C, Gällstedt M, Lindström T (2010) Oxygen and oil barrier properties of microfibrillated cellulose films and coatings. Cellulose 17:559–574

Bacakova L, Pajorova J, Bacakova M, Skogberg A, Kallio P, Kolarova K, Svorcik V (2019) Versatile application of nanocellulose: from industry to skin tissue engineering and wound healing. Nanomaterials 9:164

Chen YW, Lee HV, Hamid SBA (2017) Investigation of optimal conditions for production of highly crystalline nanocellulose with increased yield via novel Cr(III)-catalyzed hydrolysis: response surface methodology. Carbohydr Polym 178:57–68

Dimic-Misic K, Puisto A, Paltakari J, Alava M, Maloney T (2013) The influence of shear on the dewatering of high consistency nanofibrillated cellulose furnishes. Cellulose 20:1853–1864

Dimic-Misic K, Vanhatalo K, Dahl O, Gane P (2018) Rheological properties comparison of aqueous dispersed nanocellulose derived from a novel pathway-produced microcrystalline cellulose or by conventional methods. Appl Rheol 28:64474

Eriksen Ø, Gregersen ØW (2005) The influence of ink pigment penetration and paper structure on print through. Nord Pulp Pap Res J 20(2):242–246

Gómez N, Santos SM, Carbajo JM, Villar JC (2017) Use of bacterial cellulose in degraded paper restoration: effect on visual appearance of printed paper. BioResources 12(4):9130–9142

Hamada H, Mitsuhashi M (2016) Effect of cellulose nanofibers as a coating agent for woven and nonwoven fabrics. Nord Pulp Pap Res J 31(2):255–260

Hamada H, Beckvermit J, Bousfield DW (2010) Nanofibrillated cellulose with fine clay as a coating agent to improve print quality. In: Paper conference and trade show 2010 (PaperCon 2010) TAPPI Press, Atlanta, Georgia, USA, pp 854–880

Henriksson M, Berglund LA, Isaksson P, Lindstrom T, Nishino T (2008) Cellulose nanopaper structures of high toughness. Biomacromolecules 9:1579–1585

Hubbe MA, Beck KR, O'Neal WG, Sharma YC (2012) Cellulosic substrates for removal of pollutants from aqueous systems: a review. 2. Dyes. Bioresources 7(2):2582–2687

Hubbe MA, Ferrer A, Tyagi P, Yin Y, Salas C, Pal L, Rojas OJ (2017a) Nanocellulose in thin films, coatings, and plies for packaging applications: a review. BioResources 12(1):2143–2233

Hubbe MA, Tayeb P, Joyce M, Tyagi P, Kehoe M, Dimic-Misic Pal L (2017b) Rheology of nanocellulose-rich aqueous suspensions: a review. BioResources 12(4):9556–9661

Imani M, Ghasemian A, Dehghani-Firouzabadi MR, Afra E, Gane PAC, Rojas OJ (2019) Nano-lignocellulose from recycled fibres in coatings from aqueous and ethanolic media: effect of residual lignin on wetting and offset printing quality. Nord Pulp Pap Res J 34(2):200–210

Kumar V, Koppolu VR, Bousfield D, Toivakka M (2017) Substrate role in coating of microfibrillated cellulose suspensions. Cellulose 24:1247–1260

Lavoine N, Desloges I, Khelifi B, Bras J (2014) Impact of different coating processes of microfibrillated cellulose on the mechanical and barrier properties of paper. J Mater Sci 49:2879–2893

Lee HL, Shin JY, Koh C-H, Ryu H, Lee D-J, Sohn C (2002) Surface sizing with cationic starch: its effect on paper quality and papermaking process. Tappi J 1(1):34–40

Li H, Qi Y, Zhao Y, Chi J, Cheng S (2019) Starch and its derivatives for paper coatings: a review. Prog Org Coat 135:213–227

Lin N, Dufresne A (2014) Nanocellulose in biomedicine: current status and future prospect. Eur Polym J 59:302–325

Lourenço AF, Gamelas JAF, Nunes T, Amaral J, Mutjé P, Ferreira PJ (2017) Influence of TEMPO-oxidised cellulose

nanofibrils on the properties of filler-containing papers. Cellulose 24:349–362

Lourenço AF, Godinho D, Gamelas JAF, Sarmento P, Ferreira PJT (2019a) Carboxymethylated cellulose nanofibrils in papermaking: influence on filler retention and paper properties. Cellulose 26:3489–3502

Lourenço AF, Gamelas JAF, Sarmento P, Ferreira PJT (2019b) Enzymatic nanocellulose in papermaking—the key role as filler flocculant and strengthening agent. Carbohydr Polym 224:115200

Luu W, Bousfield D, Kettle J (2011) Application of nano-fibrillated cellulose as a paper surface treatment for inkjet printing. In: Paper conference and trade show 2010 (PaperCon 2010) TAPPI Press, Atlanta, Georgia, USA, pp 2222–2233

Miller J (2019) Nanocellulose: packaging applications and markets. RISI

Moutinho IMT, Ferreira PJT, Figueiredo ML (2007) Impact of surface sizing on inkjet printing quality. Ind Eng Chem Res 46:6183–6188

Nazari B, Bousfield DW (2016) Cellulose nanofibers influence on properties and processing of paperboard coating. Nord Pulp Pap Res J 31(3):511–520

Nechyporchuk O, Belgacem MN, Pignon F (2016) Current progress in rheology of cellulose nanofibril suspensions. Biomacromolecules 17:2311–2320

Nemoto J, Saito T, Isogai A (2015) Simple freeze-drying procedure for producing nanocellulose aerogel-containing, high-performance air filters. ACS Appl Mater Interfaces 7(35):19809–19815

Nygårds S (2011) Nanocellulose in pigment coatings—aspects of barrier properties and printability in offset. Dissertation presented to Linköping University, Sweden

Placket DV, Letchford K, Jackson JK, Burt HM (2014) A review of nanocellulose as a novel vehicle for drug delivery. Nord Pulp Pap Res J 29(1):105–118

Rautkoski H, Pajari H, Koskela H, Sneck A, Moilanen P (2015) Use of cellulose nanofibrils (CNF) in coating colors. Nord Pulp Pap Res J 30(3):511–518

Ridgway CJ, Gane PAC (2012) Constructing NFC-pigment composite surface treatment for enhanced paper stiffness and surface properties. Cellulose 19:547–560

Saito T, Kimura S, Nishiyama Y, Isogai A (2007) Cellulose-nanofibres prepared by TEMPO-mediated oxidation of native cellulose. Biomacromolecules 8:2485–2491

Saraiva MS, Gamelas JAF, de Sousa APM, Reis BM, Amaral JL, Ferreira PJ (2010) A new approach for the modification of paper surface properties using polyoxometalates. Materials 3(1):201–215

Song H, Ankerfors M, Hoc M, Lindström T (2010) Reduction of the linting and dusting propensity of newspaper using starch and microfibrillated cellulose. Nord Pulp Pap Res J 25(4):495–504

Sousa S, Gamelas JA, Mendes AO, Fiadeiro PT, Ramos A (2013) Interactions of ink colourants with chemically modified paper surfaces concerning inkjet print improvement. Mater Chem Phys 139:877–884

Sousa S, Sousa AM, Reis B, Ramos A (2014) Influence of binders on inkjet print quality materials. Science Medziagotyra 20(1):1392

Syverud K, Stenius P (2009) Strength and barrier properties of MFC films. Cellulose 16:75–85

Tarrés Q, Delgado-Aguilar M, Pèlach MA, González I, Boufi S, Mutjé P (2016) Remarkable increase of paper strength by combining enzymatic cellulose nanofibers in bulk and TEMPO-oxidized nanofibers as coating. Cellulose 23:3939–3950

Torvinen K, Sievänen J, Hjelt T, Hellén E (2012) Smooth and flexible filler-nanocellulose composite structure for printed electronics applications. Cellulose 19:821–829

Wagberg L, Decher G, Norgren M, Lindström T, Ankerfors M, Axnäs K (2008) The build-up of polyelectrolyte multilayers of microfibrillated cellulose and cationic polyelectrolytes. Langmuir 24:784–795

Yuen CWM, Ku SKA, Choi PSR, Kan CW, Tsang SY (2005) Determining functional groups of commercially available ink-jet printing reactive dyes using infrared spectroscopy. Res J Text Appar 9(2):26–38

Zhang H, Dou C, Pal L, Hubbe MA (2019) Review of electrically conductive composites and films containing cellulosic fibers or nanocellulose. BioResources 14(3):7494–7542