

Inkjet printing on moulded cellulose with bio-based inks

Élise Jacachoury¹, William Pierron², Anne Blayo¹

¹Univ. Grenoble Alpes, CNRS, Grenoble INP*, LGP2, 38000 Grenoble, France

* Institute of Engineering Univ. Grenoble Alpes

²Centre Technique du Papier, 59500 Douai, France

E-mail: elise.jacachoury@lgp2.grenoble-inp.fr, william.pierron@webctp.com, anne.blayo@grenoble-inp.fr

Short abstract

In recent years, moulded cellulose has attracted increased interest from the scientific and industrial community and is being used exponentially in many fields, with rapidly growing interest as a replacement for plastic in the packaging sector. It is, therefore, imperative to analyse the processes by which it would be possible to customise this material as a printing substrate, and the objective of this project is to demonstrate its feasibility using 100% biobased ink with inkjet printing. For the sake of consistency with regard to sustainability and environmental protection, the study focused on the formulation of water-based inks using bio-based soluble dyes. Several natural dyes appeared to be promising, and inks formulated produced interesting colours and sharp printing.

Keywords: Bio-based inks, natural dyes, inkjet printing, moulded cellulose

1. Introduction and background

The packaging sector has a century-long history with a familiar form of moulded cellulose, almost exclusively used to manufacture egg cartons. However, in the current ecological landscape, where there is a pressing need to reduce the high plastic content of packaging, moulded cellulose has attracted significant renewed interest due to its renewable potential and inherent advantages (Semple et al, 2022).

Nevertheless, the widespread adoption of moulded cellulose in the packaging sector faces technological challenges, particularly related to customisation and printing. In order to compete with the current dominance of plastic solutions, it is essential to develop compatible printing technologies that ensure optimal visual quality and durability, while also aligning with eco-design principles. This project is a follow-up to a previous study, which demonstrated the feasibility of pad printing on moulded cellulose objects with bio-based inks [Jacachoury et al., 2024]. Despite the roughness of the substrate, small texts could be printed with reasonable readability, thus showing that it is possible to print complex patterns, text and even QR Code, which is promising for broadening material applications. The results obtained in terms of optical density and colorimetry, however, were not comparable to industry benchmarks, because natural pigments and dyes still underperform synthetic ones in these respects. Due to their larger particle size and their chemical characteristics, it is difficult to achieve the colorimetric and optical density performances of standard synthetic pigments using soluble dyes alone. However, a set of coloured inks, with a simple bio-based formulation, can be developed and a new colour gamut defined.

In this new phase, the focus is now on inkjet printing. Indeed, since moulded cellulose is a three-dimensional substrate, it is relevant to study the feasibility of formulating and printing 100% bio-based inks for inkjet printing. In contrast to the previously studied pad printing, inkjet is a direct printing process based on the controlled and precise projection of micro-droplets of ink onto a substrate (Le et al, 1998). The challenges of inkjet printing, especially when applied to substrates such as moulded cellulose, are ejectability and ink/substrate interaction. The behaviour of the

inks formulated in the context of this study was assessed by calculating the ejectability, a dimensionless number, Z , defined as follows (Cao et al, 2024):

$$Z = \frac{1}{Oh} = \frac{\sqrt{\rho \cdot \sigma \cdot d}}{\eta} \quad (1)$$

As a reminder, the Ohnesorge number, Oh , is defined as:

$$Oh = \frac{\sqrt{We}}{Re} \quad (2)$$

where the Reynolds number $Re = v \cdot d \cdot \rho / \eta$, and the Weber number $We = v^2 \cdot d \cdot \rho / \sigma$, with

ρ : density, in $\text{kg} \cdot \text{m}^{-3}$

σ : surface tension, in $\text{N} \cdot \text{m}^{-1}$

d : nozzle diameter, in m

η : viscosity, $\text{Pa} \cdot \text{s}$

Several authors have interpreted and discussed the ejectability through evaluation of Z :

- According to Fromm, if $Z > 2$, ejection is possible.
- According to Derby & Reis, if $1 < Z < 10$, then ejection is possible, but if $Z > 10$, then satellite droplets form.
- According to Jang & Moon, if $4 < Z < 14$, then ejection is possible; if $Z < 4$ then long filaments form and positioning accuracy deteriorates; and if $Z > 14$, possible satellite droplets form within the original droplet at or after ejection.

In accordance with the eco-design objective for moulded cellulose packaging mentioned above, this study aims to formulate 100% bio-based inks that are directly printable on this substrate following the criteria indicated, thus opening up new applications for moulded cellulose in challenging sectors such as food packaging and cosmetics.

2. Materials and methods

2.1. Characterisation of substrates

Moulded cellulose is made from a suspension of pressed cellulose fibres. Different types of pulp can be used: recycled, virgin fibre or kraft pulp; wood, bamboo, bagasse, wheat or hemp pulp (Didone et al., 2017). Two moulded cellulose sheet substrates were produced by dewatering and compression against a backing fabric at the Centre Technique du Papier (CTP, Grenoble), named CM1 and CM2, having the same fibre mixture (long and short fibers (50:50), but CM2 being less compressed during moulding. The three-dimensional object used during this study is a food tray. The roughness of the substrate affects dot definition. If the surface is smooth, the print will be more precise. The surface profile was obtained optically from an Alicona profilometer (Bruker Alicona, Austria), from which R_a (the arithmetic average of the absolute deviations of surface peaks and valleys from the mean) was calculated (μm).

2.2. Selection of the raw materials

Conventionally, inkjet inks are formulated with 4 key elements. The solvent or vehicle (60-90%), generally water, transports the dyes and additives to the print head. A humectant co-solvent is added (5-30%), usually an organic solvent (glycerol, glycol, alcohol) to prevent the ink from drying too quickly on the print head nozzles, preventing clogging, while allowing it to dry quickly on the substrate. The colouring agent (1-10%) determines the ink's optical properties and their durability. Dye-based colorants are fully soluble in the liquid vehicle. They provide bright, vivid colours. However, they are often less resistant to water and light. In contrast, pigment-based

colorants are finely ground solid particles that are dispersed (not dissolved) in the vehicle. They offer better resistance to water and light. Finally, additives (surfactants, pH regulators, biocides, etc.) play a crucial role in optimising printability, stability, and shelf life of the ink.

In the food industry, regarding dyes, there is a distinction between 'natural colours' and 'colouring ingredients'. Natural colours are derived from plant, mineral or animal sources and involve the selective extraction of the colouring molecules. But ingredients with colouring properties, on the other hand, are made exclusively from plant materials and involve non-selective extraction from plants, fruits or vegetables. In this study, the formulations were simplified and dyes rather than pigments are used in the inks. The inks are formulated from water, monopropylene glycol, ethanol and natural dyes.

2.3. Formulation and printing

The inks were formulated using a Speedmixer (Hauschild SpeedMixer, Germany) using 2 mixing cycles, 800 rpm for 5 minutes and 1200 rpm for 5 minutes.

The printing tests were conducted using a DIMATIX DMP-2850 inkjet printer (Fujifilm, USA).

2.4. Characterisation of inks for inkjet

Surface tension was determined with a Sigma700 Tensiometer (Attension, Finland) utilising the Du Noüy ring method. The surface tension was measured 10 times over 180 s and averaged to provide a single mean value. This procedure was then repeated 5 times.

Viscosity was measured with an MC 302 Rheometer (Anton Paar, Austria). All measurements were conducted at 20°C by measuring viscosity at 6 shear rate intervals, 0.01 s⁻¹, 0.1 s⁻¹, 1 s⁻¹, 10 s⁻¹, 100 s⁻¹ and 1000 s⁻¹.

Density was measured by using a precision weight scale. All measurements were conducted 10 times. The density is calculated as follows:

$$\rho = 1000 \cdot \frac{m_{\text{measured}}}{V_{\text{ink}}} \quad (3)$$

ρ : density, in kg.m⁻³

m_{measured} : weight of ink, un kg

V_{ink} : weighed ink volume, in mL

UV-visible spectrometry allows the concentration of an absorbing molecule to be measured in a spectral range, in this case between 200 and 800 nm. The absorbance was measured with a Shimadzu UV-1800 spectrometer (Shimadzu Corporation, Japan). The proportional relationship between absorbance and concentration is based on the Beer-Lambert Law:

$$A = \varepsilon \cdot l \cdot C \quad (4)$$

where A: absorbance, dimensionless

ε : molar spectral absorption coefficient specific to each species, in L.mol⁻¹.cm⁻¹

l : cuvette width (path length of light transmission), in cm

C : solution concentration, in mol/L

2.5. Characterisation of prints

The prints were first observed with the naked eye and then under a microscope DigiMicro Profile USB optical microscope (DNT, Germany) using MicroCapture Plus software. Prints were

characterised with a spectrophotometer eXact 2 (X-Rite, USA) in the conditions D50, 2°. The $L^*a^*b^*$ values and optical densities were measured.

3. Results and discussion

3.1. Properties of the moulded cellulose

The properties of the 2 substrates are summarised in Table 1. The roughness was measured on both sides (*fabric side and opposite side*). As expected, this substrate is quite rough, especially on the fabric side. The properties of these substrates are comparable to those of cardboard. The fabric side is particularly marked, as illustrated in Figure 1. Additionally, it is observed that CM2 exhibits fibres protruding from the fabric, which could be detrimental for inkjet printing.

Table 1: Example of physical properties of moulded cellulose

	CM1	CM2
Grammage (g.m ⁻²)	443.68	454.48
Thickness (μm)	574 ± 10	1370 ± 16
Ra (μm) – <i>fabric side</i>	6.5 ± 0.9	10.9 ± 0.8
Ra (μm) – <i>opposite side</i>	1.8 ± 0.3	5.4 ± 0.7

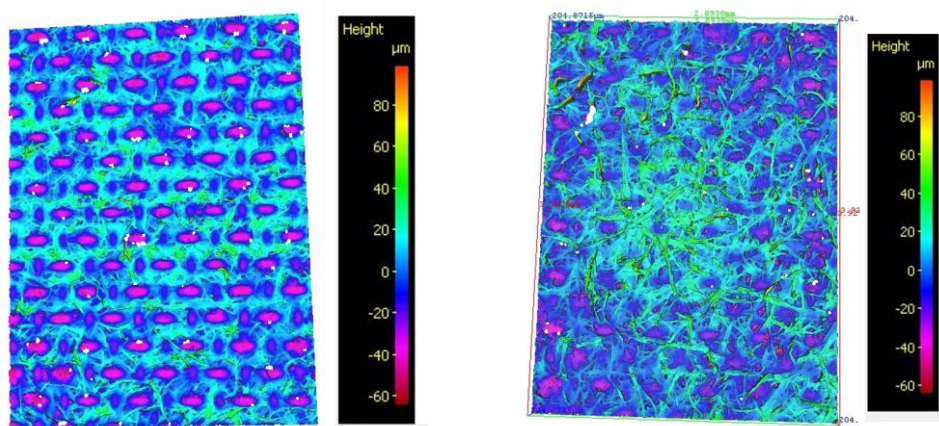


Figure 1: Example of topography of moulded cellulose surface on fabric side - left: CM1; right: CM2 (obtained from Alicona profilometer on 2.9x3.9 cm² samples)

3.2. Selection of the natural dyes

The next step is the screening and selection of the natural dyes. These dyes must fulfil the following requirements: solubility in water, absence of toxicity, permanence properties compatible with inkjet criteria and ejectability of the ensuing inks. The objective is to achieve a four-colour printing process, thereby producing a large range of colours. A total of 80 dye references were classified, of which 17 were selected for experimental testing.

Table 2 shows the molar spectral absorption coefficients of the tested dyes at the maximum absorption wavelength λ_{max} . It is interesting to note that several of these dyes appear to possess significant colouring power.

It is noteworthy that these tests demonstrated colour variations depending on the pH of the substrate (CM1 is more acid than CM2) for certain dyes, as shown on Figure 2. Exploration of this aspect has been limited [Dimić-Mišić et al., 2024]. However, instead of considering it a disadvantage of natural dyes, these pH-sensitive dyes could be used to formulate ink that reacts to the pH of its substrate.

Table 2: Molar spectral absorption coefficients of the tested dyes

	λ_{max} (nm)	ϵ (L.mol ⁻¹ .cm ⁻¹)
Logwood	449	4.8x10 ⁵
Chestnut tree	-	-
Cochineal	520 and 555.5	5.10 ⁶ and 3.7x10 ⁶
Purple Sweet Potato	543	5.5x10 ⁴
Red radish	464 and 493	1.7x10 ⁶ and 1.6x10 ⁶
Red madder	-	-
Annatto	352.5 and 482	2.6x10 ⁶ and 1.4x10 ⁶
Black carrot	532	1.5x10 ⁵
Purple corn	526	1.1x10 ⁵
Blueberry	522	6.6x10 ⁴
Beetroot + Safflower	528	1.5x10 ⁶
Safflower	406	5.7x10 ⁶
Coreopsis	427	3.9x10 ⁴
Chlorophyll	398.5 and 626	9.7x10 ⁶ and 9.7x10 ⁶
Genipa	592	8.4x10 ⁵
Blue spirulina	615	1.3x10 ⁶
Squid ink	-	-

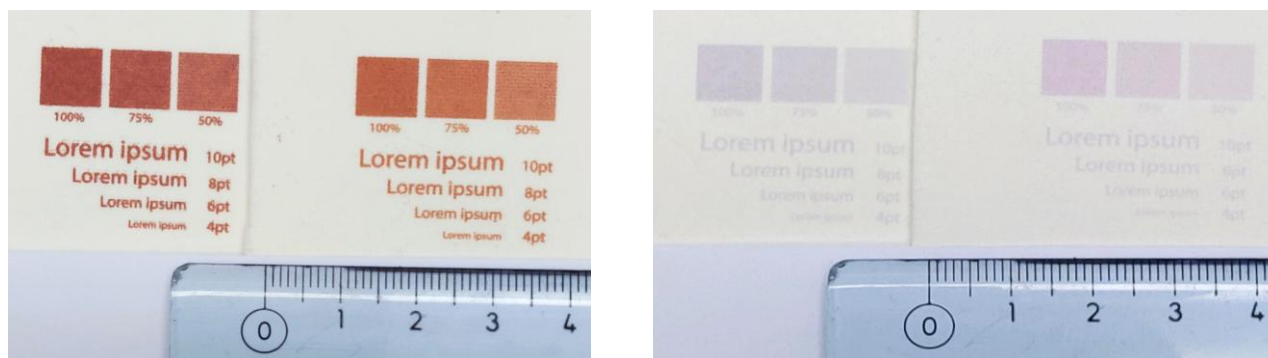


Figure 2: Examples of colour variations depending on the pH of the substrate (left: logwood-based ink printed on CM2 and CM1; right: purple sweet potato printed on CM2 and CM1)

3.3. Properties of the bio-based inks

In this section, the focus is made on the analysis of the properties of four inks. The dyes used in the formulations are presented in Table 3.

Table 3: Dyes used in the four analysed inks

	Dye(s) used
Black ink	Chlorophyll + Cochineal
Blue ink	Blue Spirulina
Red ink	Cochineal
Yellow ink	Safflower

Table 4 shows the ejectability number Z of these inks. It is important to note that, in accordance with the theory proposed by Jang and Moon, the inks are ejectable.

Table 4: Ejectability of the bio-based inks printed on moulded cellulose

	Z
Black ink	9.6 ± 0.4
Blue ink	10.9 ± 0.5
Red ink	13.6 ± 0.7
Yellow ink	10.7 ± 0.4

3.4. Prints characterisation

Prints were first assessed with a simple visual evaluation. Despite the substrate's roughness, the prints are remarkably accurate, as shown in the previous Figure 2 and in further detail here in Figure 3.



Figure 3: Examples of prints on moulded cellulose (yellow, blue, red, black)

Tables 5 and 6 show the colorimetric values and optical densities of the coloured prints, respectively. Finally, Figure 4 shows the colour gamut defined during this study. In comparison to conventional prints, those colours are obviously less saturated and their optical density is not as high. However, these results can be further improved by increasing the proportion of dye, a process which is currently in progress.

Table 5: Colorimetric values of the bio-based inks printed on moulded cellulose (in the D50, 2° conditions)

	L*	a*	b*
Black ink	45.38	1.40	4.69
Blue ink	89.44	-6.89	-4.29
Red ink	57.17	39.14	-0.50
Yellow ink	89.73	0.27	55.46

Table 6: Optical density of the bio-based inks printed on moulded cellulose

	D _{Black}	D _{Cyan}	D _{Magenta}	D _{Yellow}
Black ink	0.95	0.90	0.99	1.17
Blue ink	0.10	0.15	0.06	0.02
Red ink	0.57	0.33	0.94	0.58
Yellow	0.06	0.03	0.10	0.71

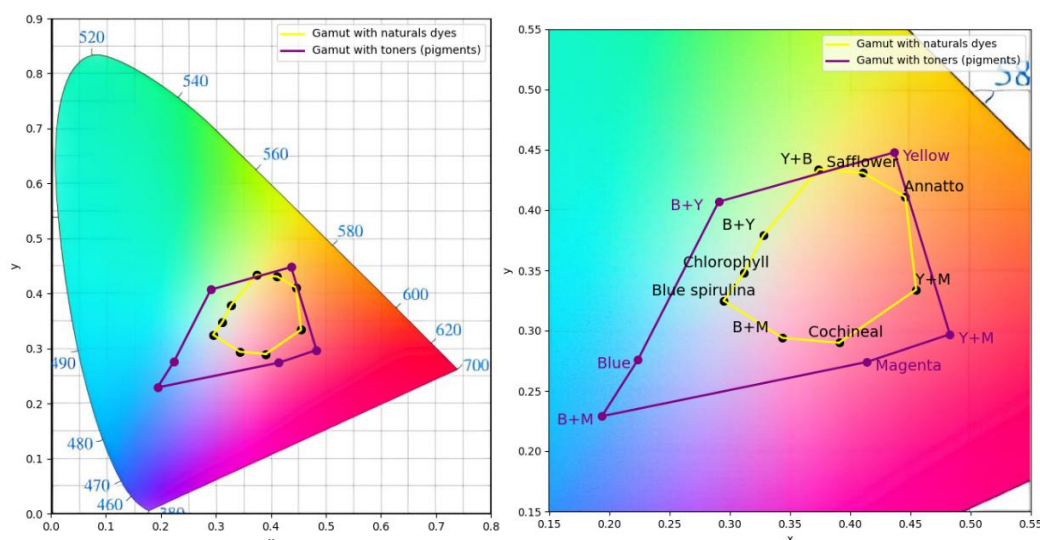


Figure 4: Colour gamut of the combination of the biobased inkjet inks the CIE 1931 chromaticity diagram, compared to the gamut of an electrophotographic print (toners)

4. Conclusions

This project demonstrated the feasibility of bio-based inks for inkjet printing on moulded cellulose substrate and provided the opportunity to conduct a screening of natural dyes convenient for this process. A key challenge the project encountered was the selection of natural soluble dyes. In comparison with synthetic dyes, they are typically more expensive, possess a more limited selection of standard colours, and are more sensitive to heat, pH, light, and oxidation. However, it is important to note that nature offers a wide range of colours (Gosh et al, 2022) even if the utilisation of these dyes remains limited. This study provided an evaluation of various natural dyes, assessing their colour and colouring power. The results obtained in terms of colorimetry and optical density are not comparable to industry benchmarks, but they reveal a variety of colours that could be produced. In addition, the stability of these inks and their deinkability are currently being studied more thoroughly.

Acknowledgements

This work has been partially supported by the PolyNat Carnot Institute (Investissements d'Avenir-grant agreement n°ANR-16-CARN-0025-01).

References

- Cao, T., Yang, Z., Zhang, H., and Wang, Y. 2024. Inkjet printing quality improvement research progress: A review. *Heliyon*, 10(10), e30163.
- Didone M., Saxena P., Brilhuis-Meijer E., Tosello G., Bissacco G., Mcaloon T.C., Pigosso D. C. A. and Howard T.J. 2017. Moulded Pulp Manufacturing: Overview and Prospects for the Process Technology, *Packaging Technology and Science*, 30(6), pp. 231–249.
- Dimić-Mišić K., Imani M. and Gane P. 2024. Natural plant dye inks set new challenges: analysing the interaction of anthocyanin-rich dye with modern calcium carbonate containing substrates. *J. Print Media Technol. Res.* 13(3), 145–159.
- Ghosh, S., Sarkar, T., and Chakraborty, R. 2023. Underutilized plant sources: A hidden treasure of natural colors. *Food Bioscience*, 52, 102361.

Jacachoury E., Monteil-Ochs Z., Pierron W. and Blayo A. 2024. Formulation of bio-based inks for pad printing on molded cellulose. *iarigai Proceedings*, 2024.

Le, H. P. 1998. Progress and Trends in Ink-jet Printing Technology. *Journal of Imaging Science and Technology*, 42(1), 49-62.

Semple K. E., Zhou C., Rojas O. J., Nkeuwa W. N., and Dai C. 2022. Moulded pulp fibers for disposable food packaging: A state-of-the-art review, *Food Packaging and Shelf Life*, 33, 100908.