Laboratoire de Génie des Procédés pour la Bioraffinerie, les Matériaux Bio-sourcés et l'Impression Fonctionnelle

Laboratory of Process Engineering for Biorefinery, Bio-based Materials and Functional Printing

UMR 5518

YEAR BOOK 2024

lgp²

lgp2.grenoble-inp.fr

Few words from the head of the lab

Anne BLAYO,
Head of the LGP2 lab

We are delighted to present the 2024 edition of the LGP2 *Yearbook*. As in previous years, the *Yearbook* is made up of mini-posters created by the laboratory's doctoral and post-doctoral students, which summarize the topic of their thesis or post-doctoral research, as well as the progress of their work.

The *Yearbook* is therefore not an annual activity report in the traditional sense, but rather a snapshot of the subjects currently being studied within the laboratory.

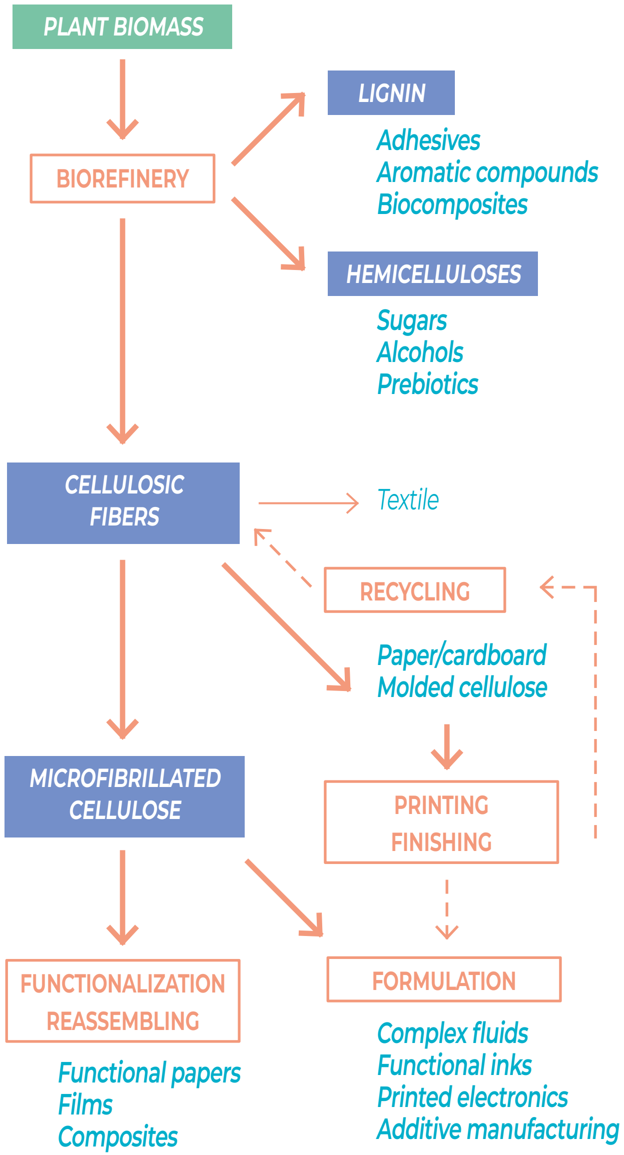
The 2024 *Yearbook* is based on summaries of more than 30 current research projects, organized in chronological order. It illustrates the fact that LGP2's areas of specialization are now strongly rooted in the field of biobased materials, the valorization of lignocellulosic materials and functional printing, with increasing importance placed on sustainable development, recycling and eco-design.

The *Yearbook* also offers an overview of the breadth of collaboration between LGP2 and its partner laboratories and companies.

I would like to thank all the young researchers who agreed to contribute to the *Yearbook* and who endeavored to make their work accessible in a concise format. Special thanks must also go to Aurore Denneulin, Deputy Director of LGP2 and head of the Funprint team, who encourages our researchers to contribute each year and collects their mini-posters, and to Antoine Julien, LGP2's Communications Manager.

I hope you enjoy reading this new edition and exploring LGP2's latest research topics.

An overview of the LGP2



At the very heart of sustainable development

LGP2 has built up a reputation in France and abroad for its research in the **valorization of plant biomass**, the development of **biobased materials** (paper, cardboard, composites), recycling processes, **nanocelluloses**, **printing processes for surface functionalization** and printed electronics.

In line with the **principles of eco-design** and **the challenges of sustainable development**, these research projects help to reduce the impact of human activities on the environment.

High-quality collaborative research

European projects, **ANR**, Idex and numerous direct industrial partnerships.

Member of the **LabEx Tec21**, **Institut Carnot PolyNat** and **Bioeconomy for Change** networks.

Strong synergies with the **Grenoble INP - Pagora, Graduate School of Engineering**.

Quality, Safety and Environment certified (ISO 9001, ISO 14 001, BS-OHSAS 18 001).

60 PUBLICATIONS EACH YEAR | **2 / 3 PATENTS EACH YEAR** | **2 RESEARCHERS ARE MEMBERS OF THE INSTITUT UNIVERSITAIRE DE FRANCE** | **60 RESEARCHERS AND PH.D STUDENTS** | **10 PH.D THESES EACH YEAR**

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Organization : 3 research groups

BioChip

Biorefinery: chemistry and eco-processes

Dr N. Marlin (HDR)

- Plant biomass fractionation processes
- Valorization of plant biomass fractions

MatBio

Multi-scale bio-based materials

Pr J. Bras

- Building blocks extracted from plant biomass
- Suspensions & blends: material process engineering
- Composites and fiber-based materials for packaging, healthcare and transport

FunPrint

Surface functionalization by printing processes

Dr A. Denneulin (HDR)

- Formulation and characterization of complex fluids
- Design and characterization of structured functional systems and components

Young Researcher's research project description

Ph.D. students

Elise BESSAC
Ph.D. thesis (2022-2025)
LGP2 (A. Blayo; N. Reverdy-Bruas)
BeFC (B. Demir)

Coupling biofuel cells and physiological sensors with printing technologies for the development of autonomous devices

Couplage de bio-piles à combustibles et de capteurs par des technologies d'impression pour la mise au point de dispositifs autonomes

Context / Objectives

Legacy technology

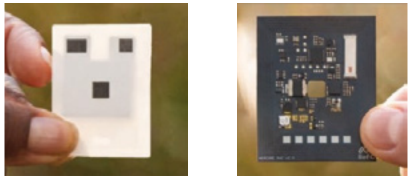
- Bio-enzymatic fuel cell

Stack of 7 layers (carbon, paper)

- Electronic platform

Flexible substrate and component implementation (e.g. sensors)

BeFC Bio-enzymatic fuel cell (left) and associated electronic platform (right)



Printing technologies advatanges

For bio-inks and sensor inks

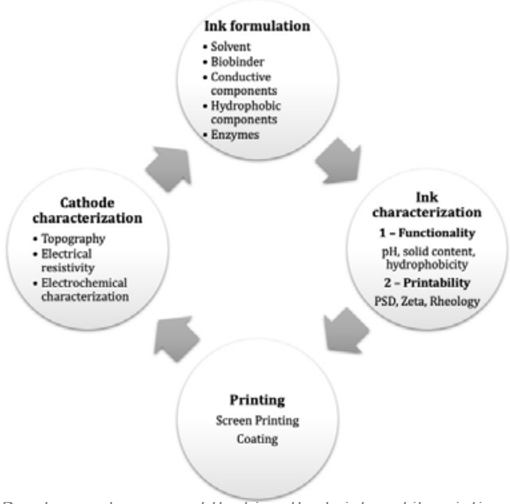
- Upscale (10 million unit a year) + high throughput
- Production cost's improvement
- Eco-friendly components
- Hybridization on common substrates

Funded by: ANRT

In collaboration with BeFC

Methods

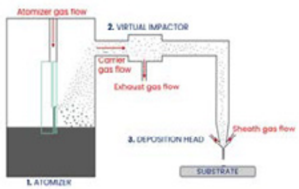
Enzymatic biocathode formulation



Development process of the biocathode ink and its printing

Printed Temperature Sensors

Ink Formulation

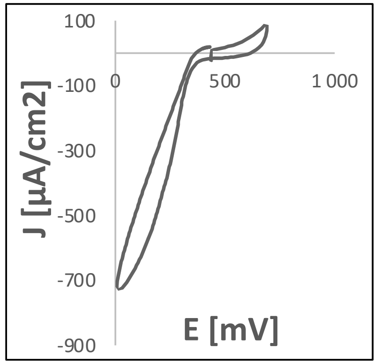


AJP Process

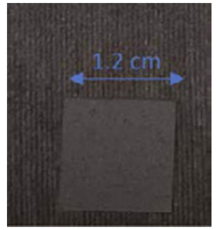
Climatic Chamber

Results

Printed biocathode performances

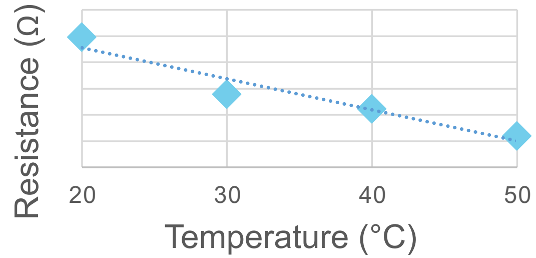


Cyclic voltametry (1mV/s)



Printed cathode

Printed temperature sensor performances



Conferences:
Bessac, E & al. (2023).*Iarigai*. Wuppertal, Germany.

Emilien FREVILLE
Ph.D. thesis (2021-2024)
LGP2 (J. Bras; E. Mauret)
CTP (E. Zeno)

Use of twin screw extruder (TSE) for innovative cellulose based packaging by thermocompression

Utilisation de l'extrusion biVis pour obtenir des emballages cellulosiques innovants par thermocompression

Context / Objectives

Single Use Plastic Directives and PPWR

- 1st of January 2022plastic bags, packaging for fruits and vegetable, tea bag not biodegradable
- 1st of January 2025, non recyclable packagings of styneric polymere, microwaved plastic food packaging

Exisiting solutions

Cellulose molded fibers
Dry molded fibers
Thermocompressed molded fibers
→ Specific properties brought by coating or a lamination of a petroleum based polymer
Limits in recyclabilty

Industrial context

- Looking for energy efficient alternative processes to produce microfibillated cellulose (mfc)
- Growing interest in thermocompressed molded cellulose

Funded by:

In collaboration with CTP

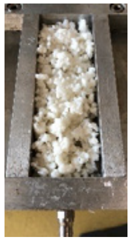
Methods

Produce new recyclable cellulosic packagings with high specific properties.

Formulation by TSE

Produce cellulosic material at high concentration

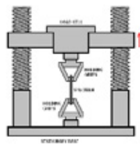
Pulp distribution



- Rheological study of highly concentrated suspension. (20-50%wt)
- Water vacuum before thermocompression

Thermocompression and applications

- Optimisation
- 2D and 3D object
- Mechanichal, barrier tests
- Application

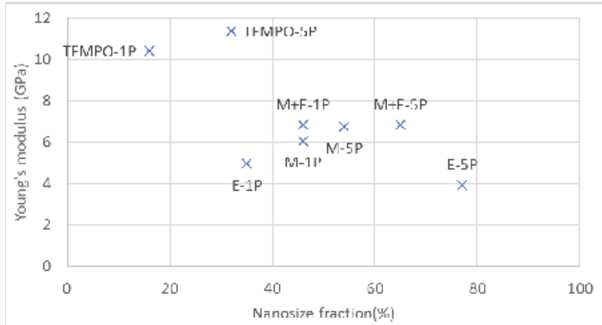


Results

- Experimental model of friction forces in TSE during nanofibrillation

$$\dot{E}_{f,i} = q_m . cp_m . (T_i - T_{i-1}) - \dot{E}_{c,i}$$

- Impact of pretreatments on TSE-CNF quality and TSE process



→ Combination of enzymatic hydrolysis and refining results in:

- Stable process (torque, mass flow, temperature, solid content)
- Higher quality index[1]

1- Desmaisons *et al.* « A New Quality Index for Benchmarking of Different Cellulose Nanofibrils ». *Carbohydrate Polymers* 174 (15 octobre 2017)

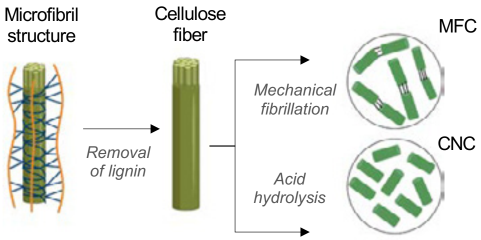
Laura GIRALDO ISAZA
Ph.D. thesis (2021-2024)
LGP2
(E. Mauret, G. Mortha, N. Marlin, A. Dufresne)

New use of chlorine dioxide for conversion processes of lignocellulosic fibers into microfibrillated cellulose and cellulose nanocrystals

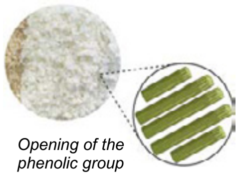
Nouvelle utilisation du dioxyde de chlore pour des procédés de conversion des lignocelluloses en cellulose microfibrillée et nanocristaux de cellulose

Context

Microfibrillated cellulose (MFC) and cellulose nanocrystals (CNC) production



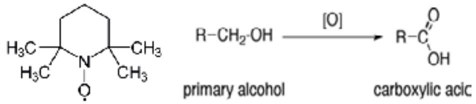
Chlorine dioxide delignification stage



T: 50 °C, 20-60 min, pH: 2-3 (acid)

- Widely used industrially
- Hazard and ecological concerns for application

TEMPO-mediated oxidation

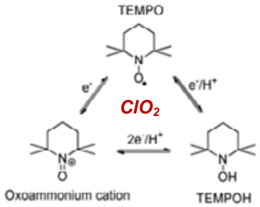


- High selectivity, proceeds under mild conditions, TEMPO commercially available and stable
- High cost of TEMPO, important depolymerization of cellulose fibers, ecological impact (AOX disposal)

Funded by: GRENOBLE INP UGA, UGA Collège Doctoral, ED I-MEP²

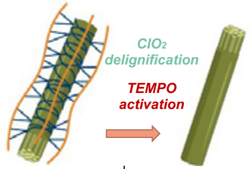
Methods

Kinetic modelling



Understand kinetic dynamics between TEMPO oxidation states and ClO_2

- Electron paramagnetic resonance
- UV- Vis spectroscopy
- Iodimetric titration

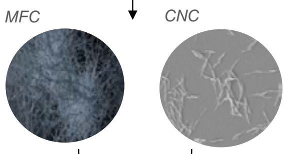


Integrated delignification and TEMPO oxidation

1. Delignification and TEMPO activation
2. TEMPO oxidation
3. Residual aldehyde conversion

Mechanical disintegration

Fiber disruption conditioning a reduced energy consumption



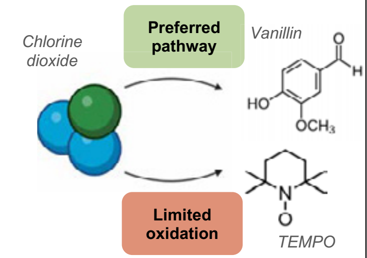
MFC and CNC production

Milder acid hydrolysis conditions for CNC derivatization

Applications → Composites, films, foams, aerogels

Preliminary results

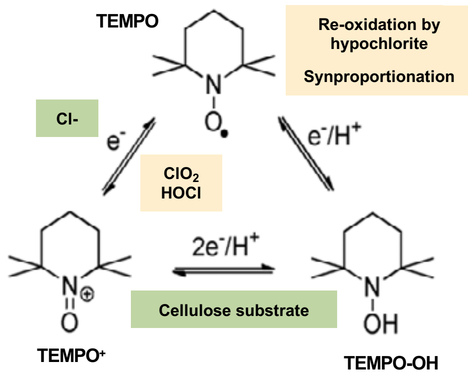
TEMPO activation in the presence of lignin



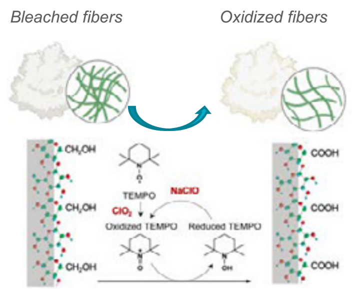
No conversion in the presence of vanillin

Competition between oxidation and delignification in a mixed system

Redox model for a ClO_2 –mediated TEMPO oxidation



Preliminary results for TEMPO-ClO_2 oxidation of bleached eucalyptus fibers



- COOH content (mmol/g pulp): 0.75-1.3
- Limited degree of depolymerization loss
- Effective oxidation of cellulose fibers
- Low affectation on the fiber's surface
- Fiber consistency and TEMPO amount directly affect the COOH content and DPv loss

Points to evaluate

1. Fibers consistency
2. TEMPO: mmol/g pulp
3. TEMPO/ClO2 molar ratio

MFC production by Masuko grinding

Julia PESCHEUX-SERGIENKO

Ph.D. thesis (2021-2024)
LGP2 (J. Bras; N. Belgacem)

New cellulose engineering for high barrier specialty papers and 3D cellulosic materials

Développement d'une nouvelle matière cellulosiques pour des papiers spéciaux et des objets 3D à hautes propriétés barrières

Context

Single use plastics problematics

- EU restrictions' severity increases
  - 2040 : Final prohibition in France
- Petroleum resource decreases
- Social green initiatives flourishment

Cellulose as a great alternative

- Most abundant bio-polymer
- Attractive mechanical featuring
- Prone for chemical modifications

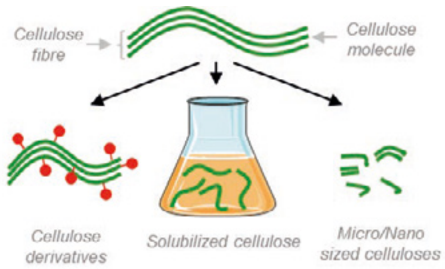
Cellulose Valley chair

- Ambition to find practical solutions for efficient bio-based packaging.
- Combination of research, education and industrial contributions.

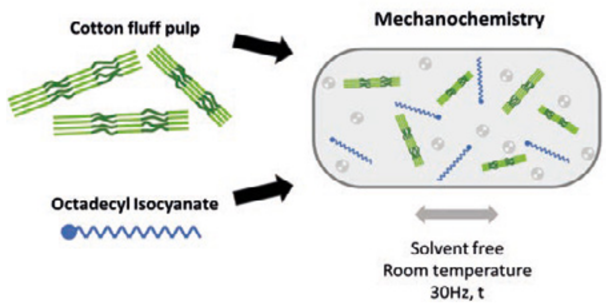
Funded by: Fondation Grenoble INP, lgp², AHLSTROM, DS Smith, ALPHA Form · by Guillin, Aptar, CHANEL, DECATHLON, Marie, CITEO

Methods

Cellulose-sourced materials



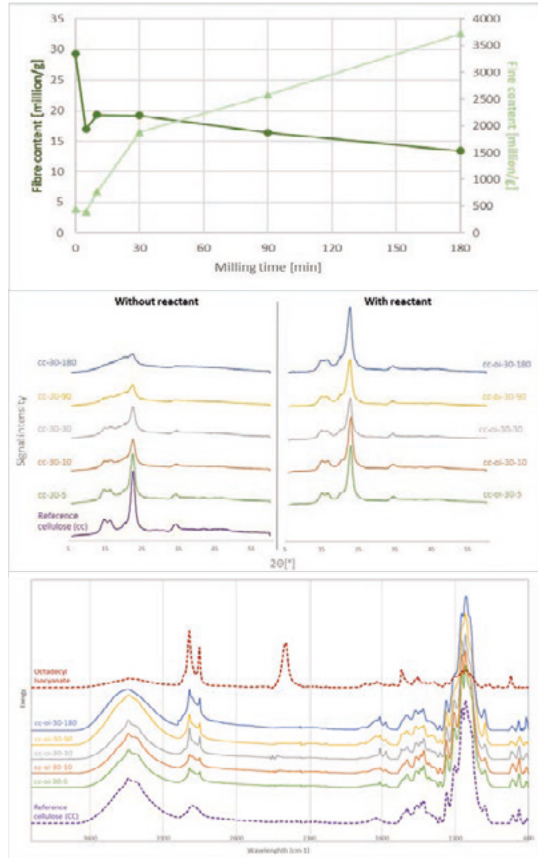
Innovative chemical modification



Morphology and chemistry characterization

- MorFi and granulometry
- Microscopes (optical, SEM)
- XRD, NMR
- FTIR
- Elemental analysis
- XPS, NMR
- Contact angle

Results



Fragmentation

Amorphization

Chemical modification

Erwan TROUSSEL
Ph.D. thesis (2022-2025)
LGP2 (D. Beneventi; A. Denneulin)
PCCEI (J-C. Brès)

Fabrication of a full-paper point of care platform by additive manufacturing

Elaboration d'un dispositif de diagnostic médical en papier par procédé de fabrication additive

Context / Objectives

Actual nucleic acid amplification tests (NAATs) :

- Performed in centralised laboratories
- Requires equipment and trained personnel

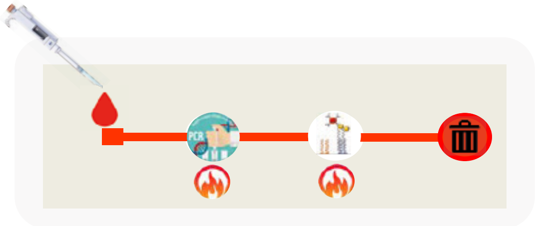
→ Bottleneck for a rapid disease diagnostic

Point of care testing (POC) :

- Defined as a test performed near or at the patient's place of residence
- Rapid results requiring minimal user intervention
- Production of plastic waste

CareFab project :

The objective is to develop a **printed microfluidic paper-based device** (µPAD) integrating all unit operations necessary for **nucleic acid amplification tests** and of the associated **fabrication process**.



Funded by: anr

In collaboration with AlpRobotic

Methods

Printing processes

6 axis robot

- Multiple printing tools :
  - Dispenser printing
  - Spray deposition
  - Jetting
- 3D substrates
- Various shape of design

Cellulose µ-particle aqueous inks:

porous cellulose based materials with high capillary suction can be elaborated using cellulose-nanofibers (CNF), -µparticles and SiO2 as inert filler obtainded by moulding

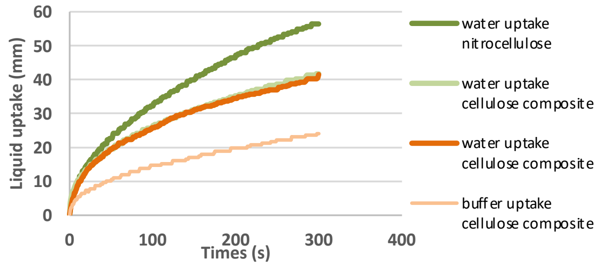
MFC spray encapsulation

Encapsulation of the path by spray of MFC to manage the air permeability. Modification of the hydrophilicity to hydrophobicity of the cellulose by addition of AKD emulsion

Results

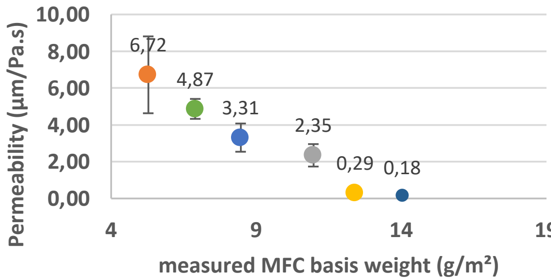
Capillarity path

- Cellulose composite with a comparable water uptake than nitrocellulose
- Increase of the accessible porosity with ethanol solvent exchange



MFC encapsulation

- Decrease of the permeability with the increase of the MFC basis weight



- Increase of the water contact angle with the increase of the amount of AKD

Arnel BRZOVIC

Ph.D. thesis (2023-2026)

N. Reverdy-Bruas; N. Marlin (LGP2)

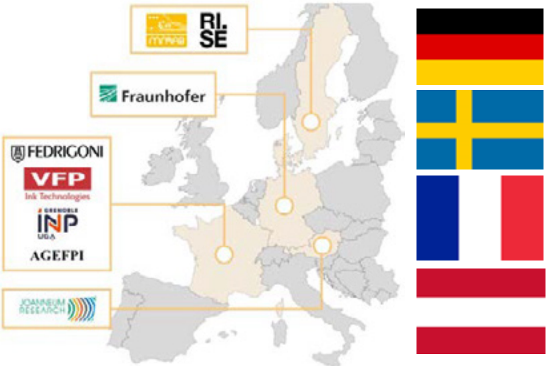
L.Svecova (LEPMI)

Recycling of multilayered electronic devices printed on cellulosic substrates

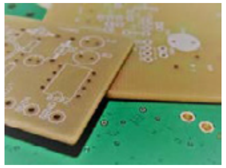
Etude de le recyclabilité de modèles complexes d'électronique imprimée sur papier par adaptation de lignes de recyclage papier existantes.

Context / Objectives

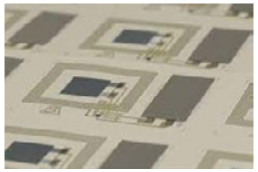
European Circel-paper project



Only **17.4 %** of the e-waste is documented to be collected and formally recycled worldwide.



FR4 PCB



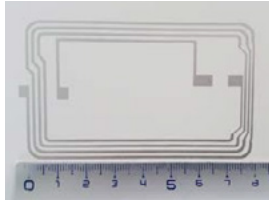
Paper PCB

- Challenges:

1) Recover the fiber fraction with minimum contaminants.
2) In a second fraction recover functional materials.

Methods

1. Paper printed electronics



Powercoat XD200
- Silver conductive Ink
- Coated paper
- 200 g/m^2

2. Conventional paper recycling line

Pulping → Screening → Centrifugal cleaning → Flotation →

Units are optimized individually and tested sequentially as part of the process.

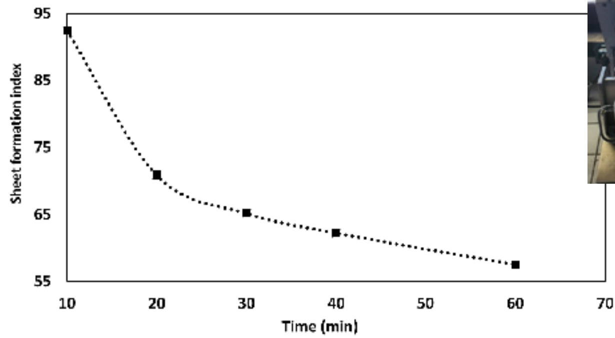
3. Atomic Absorption Spectroscopy (AAS)

Objective: silver tracking

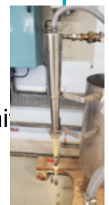
Ash + silver → Leaching in Nitric acid → Solvated silver Ag^+ → (AAS)

Results

1. Pulping optimization



The optimization involves monitoring the properties of handsheets as they vary with several parameters.



2. Silver Recovery

Centrifugal cleaning emerges as a highly promising unit operation for the separation of silver from fibers.

Ag= 100 % —inlet→ **Centrifugal cleaning** —accepts→ Ag= 2-3%

Centrifugal cleaning —rejects→ Ag= 90 %

→90 % of the silver can be recovered from the pulp.

Maxime FAUREAU-TILLIER
Ph.D. thesis (2022-2025)
LGP2 (A. Blayo; A. Denneulin)
Chomarat (J. Maupetit)
Thèse confidentielle

Modification of the properties of polymer surfaces by an environmentally friendly printable coating

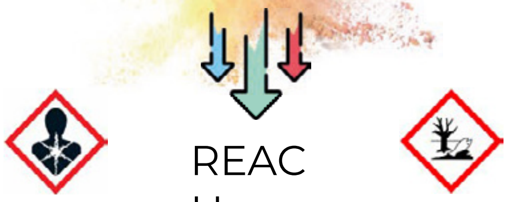
Modification des propriétés de surfaces polymères par un vernis imprimable respectueux de l'environnement

Context / Objectives

Coatings industry – Textile field
Textile personnalization

- Demand used to grow up the last decade
- Customers always want new design in every area
- Clothing manufacturers are looking for new solutions

Printable coating offer an unlimited way of personnalization



Use of a lot of dangerous products for both human health and environment

Objectives : Create a new coating that respect :

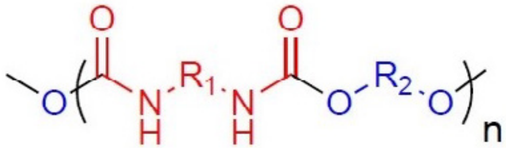
- the same requirements and industrial constraints
- the environment, labels, laws and human health

Funded by: ANRT CHOMARAT

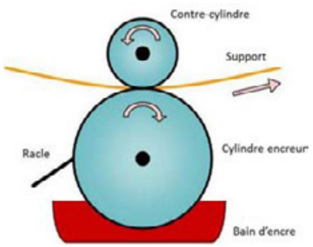
In collaboration with Chomarat Textiles Industries

Methods

Formulation with polymer and additives



Rotogravure/reverse coating
Transfert with heat and pressure on textile



Printing by inkjet

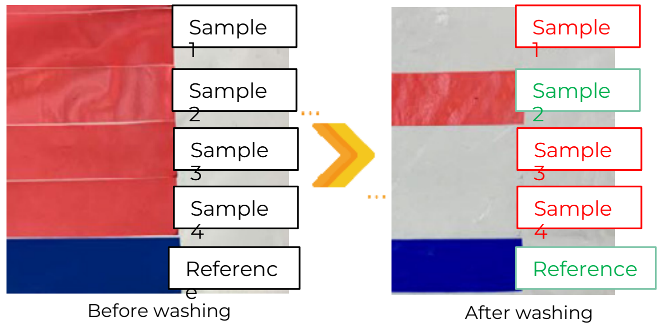
Surface/interface/interphase characterizations

- Contact angle measurements
- Washing test
- Mechanical properties
- X-Ray photoelectron spectrometry

Results

Washing test

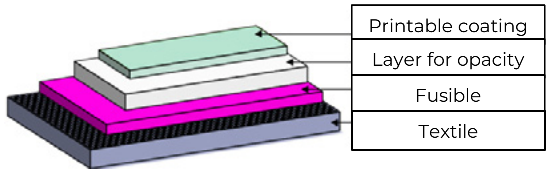
- Selection of CMR-free products that resist to the washing test (main requirement)



- Delamination of the coating from the textile : **KO**

Why does a coating works and resist the washing test ?

- Contact angle measurements proved that it not related to polarity
- Next step : another theory of adhesion, the diffusion



Emma COLOMBARI
Ph.D. thesis (2022-2025)
LGP2 (J. Bras)
CRAterre (T. Joffroy; A. Misse)

DESICELL : Design approach for new recyclable cellulosic based materials in building industry

Nouveaux procédés d'obtention de matériaux cellulosiques et terre crue recyclable pour architecture

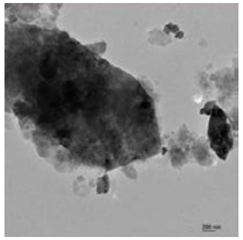
Context / Objectives

Recyclable cellulosic and earth-based panel

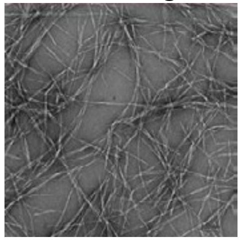
Lowering the environmental impact of building industry

- 23% of the French carbon footprint [1]
- 86,8 Mt of inert waste in France in 2020 [2]
- 2/3 of down-cycled waste and 1/3 landfilled [3]

Blend of earth, fibers and MFCs for finishing elements



TEM picture of the FAC



TEM picture of MFCs

- Low thermal conductivity [4]
- Hygroscopic behavior: passive cooling [4]
- Increase of mechanical properties [5]

References:
1. *Ministère de la transition écologique - **2022***
2. SDES, ***2020***
3. *Bastin A. Flux - **2019***
4. *Giada G. et al., Hygrothermal Properties of Raw Earth Materials – **2019***
5. *Stanislas T.T. et al., Effect of cellulose pulp fibres on the physical, mechanical, and thermal performance of extruded earth-based materials - **2021***

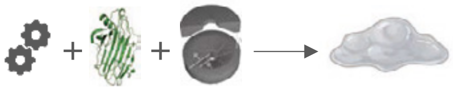
Funded by: Glyco@Alps Université Grenoble Alpes; France 2030

Methods

Production process

1. MFCs production

The production of MFCs is perfomed by refining, enzymatic hydrolysis and mechanical fibrillation.



2. Formulation

Mixture of cellulose fibers, micro-fibrillated cellulose and earth (FAC) in various proportion is made.

3. Mixing process

4. Compression process

Hydraulic press:
100 kN, 25°C

5. Drying process

Drying in standard room:
23°C, 50% RH, 72h

6. Recycling process

The final composite will be recycled following a protocol. The recovered mixture should be usable to produce a new material with the same level of properties.

Scheme: BioRender

Results

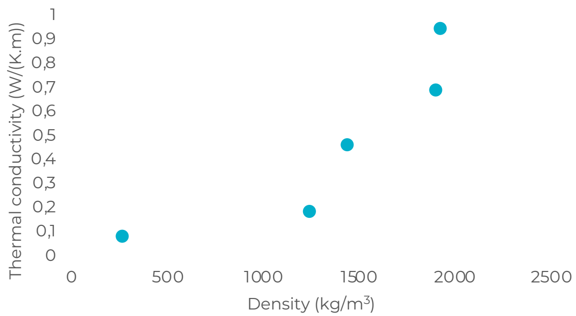
Mechanical properties

Sample	Modulus of Elasticity (MPa)	Modulus of Rupture (MPa)
FAC	711 ± 205	0.6 ± 0.5
FAC + fibers	903 ± 227	0.6 ± 0.2
FAC + additive	2824 ± 893	1.3 ± 0.1

3 point bending

The addition of fibers increases MOE but the MOR stays the same. Moreover, the addition of an additive increased significantly the MOE as well as the MOR.

Thermal conductivity



The addition of fibers decreases the density and so the thermal conductivity.

Mathilde DAVID
Ph.D. thesis (2022-2025)
LGP2 (Q. Charlier, J. Bras)

Manufacturing of bio-based materials using ultra-sonic compression molding

Élaboration de matériaux biosourcés par compression ultrasonore

Context / Objectives

Manufacturing of 100% biosourced materials

Environmental footprint reduction

Bio-sourced materials can have a significant environmental impact :

- Use of petroleum-based resins (wood panels)
- High energy consumption during production (papers and boards)
- Low recyclability (bio-based composites)

New process and material development

1. Use of Bio-waste as raw material in order to get into a *circular economy model*
2. Dry process in order to *reduce water and energy consumption*
3. Manufacturing of molded composites via powder compression using ultrasonic vibrations

→ 100% Composite materials made derived from cellulosic fibers and natural binder (lignin and others)

Funded by: GRENOBLE INP UGA; UGA COLLÈGE DOCTORAL ED I-MEP²

Methods

Ultrasonic compression

High frequency acoustic vibration under compression

Compaction of dry powder into bulk

Composites materials

Figure : Ultrasonic Press - Sonimat

Characterization methods

Analysis :

- *Microstructural*
- *Resistance to water and humidity*
- *Thermal and insulation properties*
- *Mechanical properties*
- *Energy consumption*

Impact assessment

Multicriteria analysis to associate material properties and energy footprint

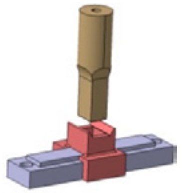
Toward scale up (TRL 4+)

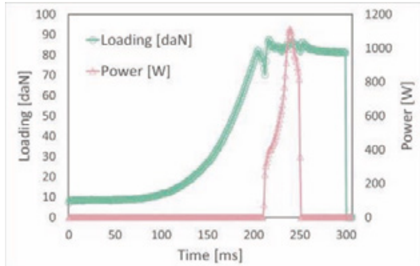
Life Cycle Assessment

Results

Key process parameters :

- Power and transmitted energy
- Pressure





Process development :

- Molds (for dry materials)
- Spring tooling system for US molding
- Temperature monitoring

In-situ monitoring of material formation

Key raw material characteristics :

- Influence of chemical composition
- Shape and Size of bio-elements
- Influence of humidity content

Conference:
David M. Et al. (2023), Journée Nationale sur les Composites (JNC). *Besançon*

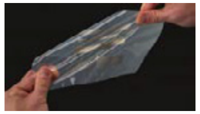
Marie GOIZET
Ph.D. thesis (2022-2025)
LGP2 (A.Deneulin; J.Bras)
Thèse confidentielle

Development of stretchable conductive inks

Développement d'encres conductrices étirables

Context / Objectives

Stretchable electronics field



- Growing market
- Applications in

healthcare, safety, e-textile…

Most of current stretchable conductive inks :

- Are only flexible
- Have a high resistance increase under stretching
- There is an uniformity of used materials (PDMS, PU)

Challenges:

- Formulation of a stretchable printable fluid
- Adapt and optimize the printing process
- Maintain a good adhesion and functional properties of the ink while stretching the printed pattern
- Ecodesign: use of biobased alternatives for the matrix and decrease of the amount of metallic material

Funded by: ANRT Association Nationale Recherche Technologie; Encres DUBUIT

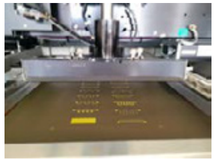
Methods

Formulation of stretchable fluids

- Silver particles with different morphologies
- Biobased matrix
- Water and co -solvent
- Additives

Printing process

Screen-printing



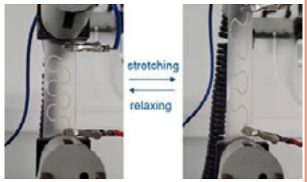
Speed: medium
90-grade mesh
Thickness : 10 µm
Substrates: PET, TPU

Electrical characterization under stretching

Records electrical resistance of the conductive sample while being deformed

Parameters:

- Sample shape (pattern, size, line width)
- Elongation rate
- Speed of deformation
- Unique or cyclic deformation

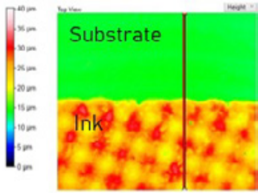


Results

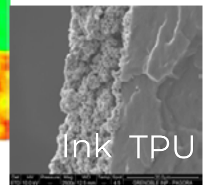
Imagery of the printed pattern

Morphological analysis of the ink at different scales (surface and inside the layer)

Binocular magnifier



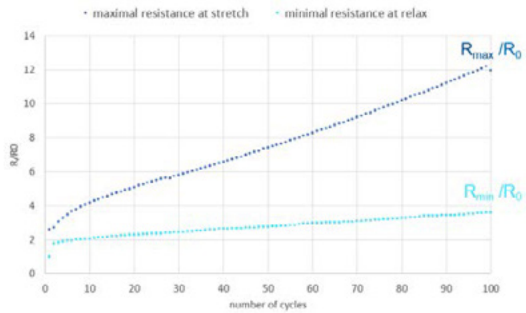
Optical profilometer



MEB images

Performances of conductive inks under streching

- Inks are still conductive after 100 cycles at 25% elongation
- Observation of a hysterisis phenomenon



Jérémy MANIFACIER
Ph.D. thesis (2022-2025)
LGP2 (A. Blayo; A. Boyer)

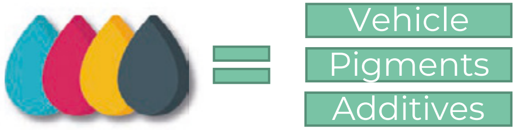
Bio4Inks: Formulation of 100% biobased 4-colored inks for press printing

Formulation d'encres offset quadrichromiques 100% biosourcées pour la presse

Context / Objectives

Need for sustainability

Replacing pigments in offset ink



- Several biobased vehicles are already used
- Very few research on biobased pigments in inks

Finding suitable pigments for ink formulation

- Compatibility with oil-based vehicles and fountain solution
- Color strength
- Low ΔE compared with the standard values
- Stability (light, pH)

Obtaining ink with suitable properties

- Rheological properties
- Tack
- Permanence properties

End of life (recyclability, biodegradation)

Funded by: MINISTÈRE DE LA CULTURE, CITEO

In collaboration with Écograf, Sun Chemical & Grakom

Methods

Pigment grinding

Dry grinding using bead mill (~60 balls of Ø2 cm)
Wet grinding using three-roll mill / bead mills

Mixing

Mixing using a SpeedMixer device

Printing

IGT C1-5 on paper
Printing force: 750 N
Ink volume: 0,5 cm^3
10 successive prints

Pigment characterization

- Pigment size (granulometer)
- Surface energy (tensiometer)
- BET Specific Surface Area
- Composition (proximate and elemental analysis)

Ink characterization

- Tack
- Rheological properties (thixotropy, viscosity)
- Colorimetric properties (optical density, color)
- Lightfastness (Xenotest)

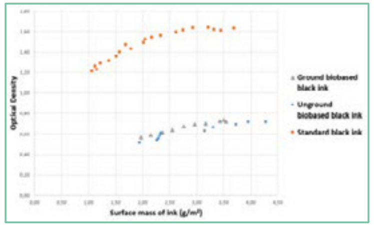
Results

Selection of biobased pigments

Lookout for pigments through literature and known historical biobased pigment

Black inks

Inks formulated with biobased pigments (1) are lighter than industrial black inks (2)
→ Need to optimize pigments dispersion via grinding, better dispersion or increase of carbon content

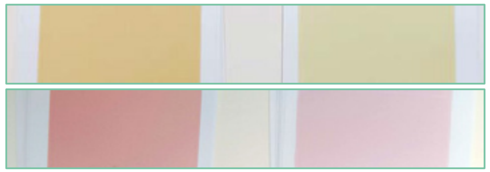


(1)

(2)

Colored inks

Promising results for yellow inks
Some good leads for magenta inks
Only few biobased pigments for cyan inks



Léopold OUDINOT
Ph.D. thesis (2022-2025)
LGP2 (J.Viguié)
3SR(F.Dufour; A.Naillon; L.Orgeas)

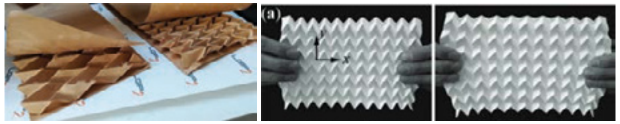
Comprehension and characterization of the impregnation and drying of bio-based hydrogel for self-folding of architectured paper structures

Compréhension et caractérisation de l'imprégnation et du séchage d'un hydrogel biosourcé pour l'autopliage de structures papier architecturés

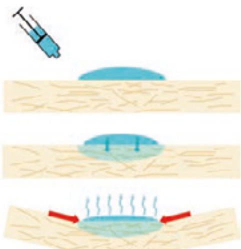
Context / Objectives

Architectured paper structures

- Developp new paper based sandwich pannel (folded core improving mechanical performances)
- Industrial production via self folding technologies



Self folding mechanism using a cellulose hydrogel



(1) Hydrogel printing

(2) Paper impregnation

(3) Drying and folding

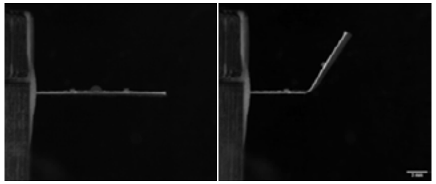
- Understand non newtonian fluid impregnation in fibrous media (2)
- Characterize stress and strain during drying (3)
- Find key physical parameters to predict angle and local curvature of fold

Funded by: GRENOBLE INP UGA; UGA COLLÈGE DOCTORAL ED I-MEP²

Methods

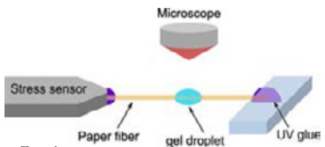
Macro-scale experimentations

Using lab paper and automatic gel dispenser



- Different papers/gels/printing parameters
- Measuring angle and curvature of fold

- **Model system approach**



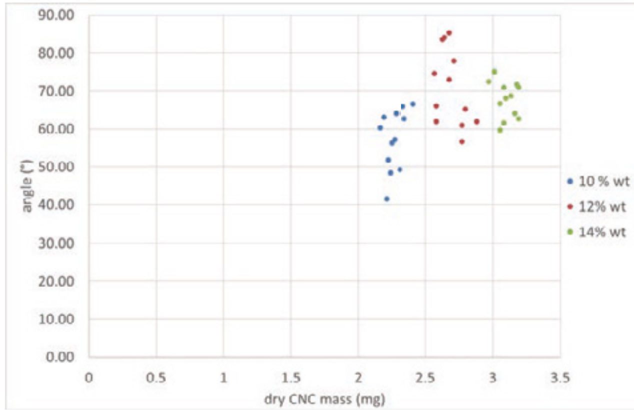
- *System example*
- Separate impregnation and drying phases
- Characterise separately gel and paper behavior
- **Determine specific physical law**

- **Meso-scale observation**
- Using X-ray tomography
- Observe impregnation phase and characterize impregnated area
- Measure strain field during drying

Results

Macro-scale expérimentations : influence of gel concentration

- 150 g/m² bleached soft wood paper
- Dispenser delivers 0.9 mm³ of gel with 1.37mm nozzle
- Using 10%, 12%, 14% concentrated CNC gels
- Measuring angle and curvature of samples



- The mechanism works on high basis weight papers (150g/m²)
- High result variability under the same experimental conditions
- Explaining variability requires local caractérisations of paper heterogeneities

René ROMERO LEZAMA
Ph.D. thesis (2022-2025)
LGP2 (J. BRAS; I. DESLOGES, J. VIGUIE)

Multilayer Biomaterial Processing to produce high value-added active cellulose packaging solution.

Context

European directive on single use plastics

New legislations pushing the transformation of the packaging industry:

- New required sustainable solutions.
- Recyclable packaging.

Cellulosic Materials

- Bio-based and Biodegrable.
- Most abundant material on earth.
- Most recycled material in Europe.

Chaire Cellulose Valley

An organisation working to:

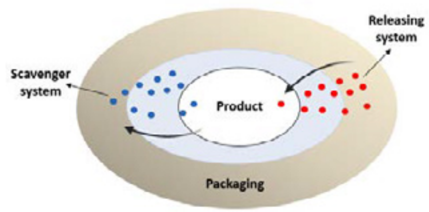
- Upgrade cellulosic materials.
- Propose new innovative and high performance solutions.

Funded by: INP Fondation, AHLSTROM, Aptar, CHANEL, Marie, CITEO, DECATHLON, DS Smith, GUILLIN

Objectives

➡ Create a multilayer structure for active packaging.

- Extend shelf life product's.
- Ensure barrier properties during storage.



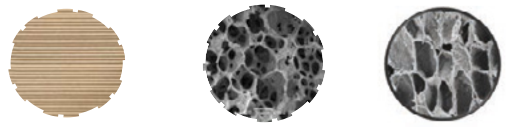
Active packaging mechanisms

Three different main targeted properties:

- Antimicrobial and antioxidation protection.
- Moisture protection.
- Barrier shift.

Methods

Cellulosic materials

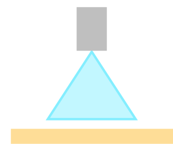


Cardboard *Foams* *New cellulose forms*

Processing

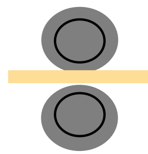
➡ Preparation of active layers

Foaming processes

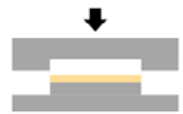


Spray coating

➡ Manufacturing processes



New assembly cardboard process



New 3D thermoforming

Panagiota RIGOU
Ph.D. thesis (2023-2026)
LGP2 (N. Marlin; G. Mortha; D. Lachenal)

Clean process for dissolving wood cellulose for the production of textile yarn

Procédé propre de dissolution de cellulose de bois pour la production de fil textile

Context

Dissolving pulps

- Expanding market for dissolving pulp (textile production, cellulose derivatives and nanocellulose)
- Wood pulp or cotton linters with high cellulose content (>90 %) and distinct properties
- Main methods to obtain dissolving pulps: Kraft pre-hydrolysis (PHK), and acid bi-sulphite (AS)

Regenerated cellulose

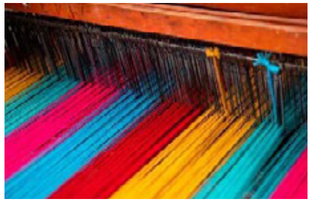
- Chemically modified cellulose deriving from dissolving pulps or cotton linters
- Cellulose derivatives that can be obtained: viscose, lyocell, cupro and acetate

Natural fibers

- Viscose: polluting production process (use of CS_2)
- Lyocell – Cupro: expensive production processes
- Cotton: high consumption of water, demand for more arable land, use of pesticides

Synthetic fibers

- Fossil-based derivatives
- 64 % of the global fiber market
- Release of microplastics even if recycled

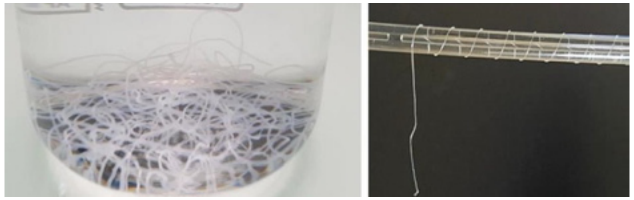


Funded by: Grenoble INP – ANR RegenCell project
In collaboration with CTP, UniLaSalle, Gemtex

Objectives

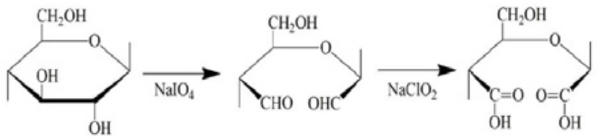
Optimization of cellulose oxidation and dissolution to produce textile yarns

- Optimization of $NaIO_4$ – $NaClO_2$ oxidations to produce oxidized cellulose with high amount of COOH groups and without severe degradation of DPv
- Enhancement of cellulose dissolution in alkaline medium
- Increase cellulose accessibility by using pre-treatments (mercerization, mechanical refining, high consistency mixing)
- Recycling of $NaIO_4$, replacement of $NaClO_2$ to chlorine free oxidant
- Regeneration of dissolved cellulose to yarns with properties comparable to viscose yarns

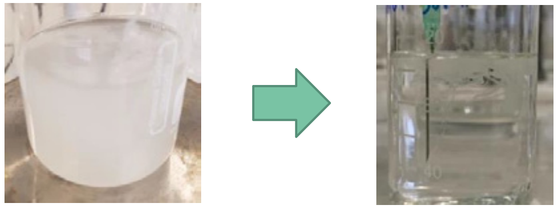


Methods

Two-step oxidation, $NaIO_4$ – $NaClO_2$

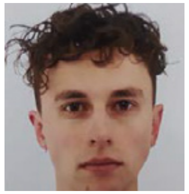


Cellulose dissolution | **Regeneration of dissolved cellulose to yarns**



Chacterization methods :

- Carbonyl (HCO) measurement by titration
- Carboxyl (HCOOH) content by conductometric titration
- Viscosity – degree of polymerization (DPv) of the oxidized cellulose
- Dissolution yield



Clément TURPIN
PhD thesis (2023-2026)
LGP2 (N. Reverdy-Bruas, J. Viguié)
3SR Lab (L. Orgéas)

Architecturing papers and boards with bio-based grid printing: a low-cost approach to lightweight packaging

Papiers et cartons architecturés par impression de renforts bio sourcés : développement d'une approche à bas coût pour alléger les emballages.

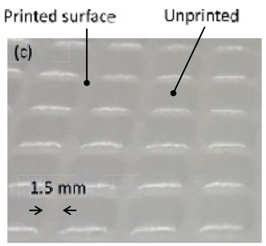
Context & Objectives

Reducing the weight of paper-based packaging

- Paper production demands substantial ressources:
  - ✓ 15-25 m³/ton of water,
  - ✓ 2.9 MWh/ton of energy,
  - ✓ 2-3 ton/ton of wood

Idea: architecturing papers and cardboards

- Embossing paper sheets to increase their bending stiffness
- Low cost biodegradable route:
  - ✓ Printing patterns with starch suspensions
  - ✓ Sheet embossing induced during suspension drying



Thesis objectives

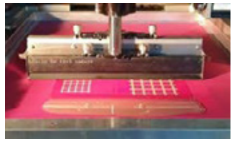
- Optimization of the printing process
- Multiscale analysis of :
  - ✓ Drying, shrinkage, buckling phenomena
  - ✓ Induced meso and microstructures
  - ✓ Induced hygro-mechanical properties

Funded by:

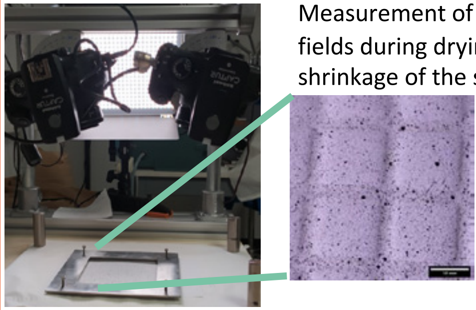
Materials & Methods

Materials & Processing route

- Handmade model paper sheets:
  - ✓ Softwood kraft bleached pulp
  - ✓ Rapid Köthen former
  - ✓ Basis weight: 80-120g/m²
- Aqueous suspension with 40 wt% of low molecular weight corn starch
- Screen printing



Monitoring the drying/embossing



Measurement of meso kinematic fields during drying and shrinkage of the starch.

Mechanical test:

Cantilever strip of paper

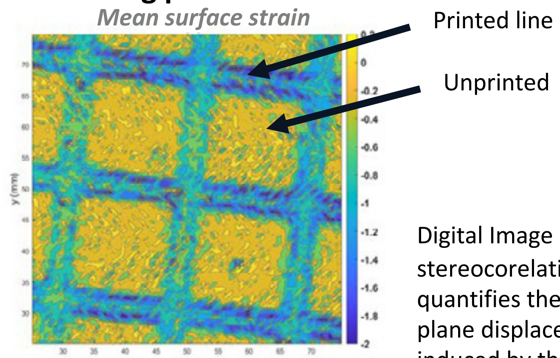
Bending stiffness measurement based on image analysis

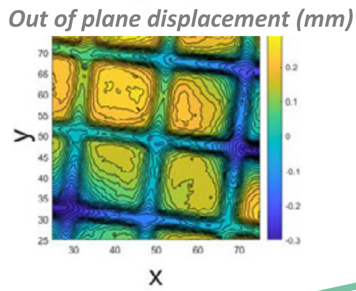
Microstructure observations :

ESEM

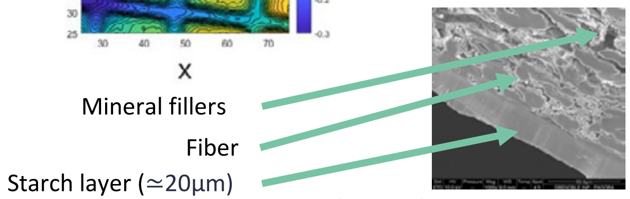
First Results

Embossing phenomenon





Digital Image stereocorelation quantifies the out of plane displacement induced by the strains due to the shrinking of starch



Printed starch presents good adhesion, homogeneous thickness and many cracks due to its britleness

Conferences: Turpin, C et. al. (2023). 8th EPNOE International Polysaccharide Conference, Graz

Océane AVERTY
Ph.D. thesis (2023-2026)
LGP2 (C. Martin; J. Bras;
Q. Charlier)

<u>**Confidential**</u>

Cellulose substrate functionalization for barrier & sealing solutions in beauty packaging

Fonctionnalisation de substrat cellulosique pour des emballages barrières et scellables dans le domaine cosmétique

Context

Single Use Plastic pollution

- SUPD in Europe, more and more regulations around the world
- Society expectations to have less plastic packaging

Today's water vapor barrier papers

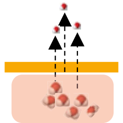
- Not recyclable
- Petrosourced layers
- Migration issues

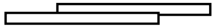
Funded by / in collaboration with : Unilever

Objectives

Replace flexible plastic packaging by paper packaging barrier to water vapor with bio-based coating

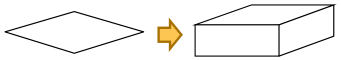
Reach the **barrier performance** required for high moisture products





Be **sealable**

Be **recyclable**



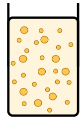
Converting resilience

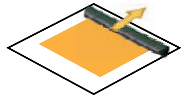
- Bio-based suspension formulation
- Coating and drying processes
- Surface design
- Other barrier developement

Go towards industrialisation

Methods

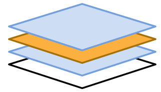
1. Suspension formulation





2. Monitoring coating and drying parameters

3. A multilayer strategy for a better recyclability



4. Characterisations of the material:

- Barrier performance
- Mechanical performance
- Sealability

5. Recyclability test

Mathilde BERNARD-CATINAT
Ph.D. thesis (2023-2026)
LGP2 (J. Bras; E. Mauret)

Development of innovative process for 3D cellulosic materials

Développement de procédés innovants pour l'obtention de matériaux cellulosiques tridimensionnels

Context

Single use plastics: a modern issue

New legislation pushing manufacturers to find alternatives to plastic

- SUP (Single Use plastic) legislation: deposit in 2018.
- AGEC (Anti-Gaspillage pour une Économie Circulaire) law: deposit in 2019.
- PPWR (Packaging and Packaging Waste Regulation): deposit in 2022.

Cellulosic Materials

- Bio-based and biodegradable.
- World's most naturally produced biobased polymer.
- Production and recycling chain well managed.

Chaire Cellulose Valley

- An organization dedicated to finding high performance alternatives to cellulose-based single-use plastics.
- Linking research, education and industry across the cellulose packaging value chain.

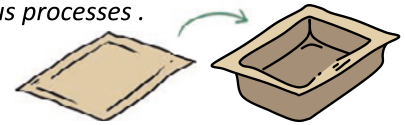
Cellulose Valley

Funded by: Fondation Grenoble INP, Ahlstrom Munksjö, Aptar, Chanel, Citeo, Decathlon, DS Smith, Guillin, Marie

Objectives

3D shaping of a cellulosic material

Obtaining a three-dimensional fibrous material and understanding the technical challenges associated with the various processes .

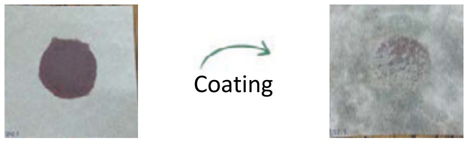


Ex: Laboratory 3D samples.

Surface functionalization

Binging specific properties (barrier properties, recyclability, …) to a substrate with different processes.

Ex: Colored cobb oil of paper samples without and with coating.

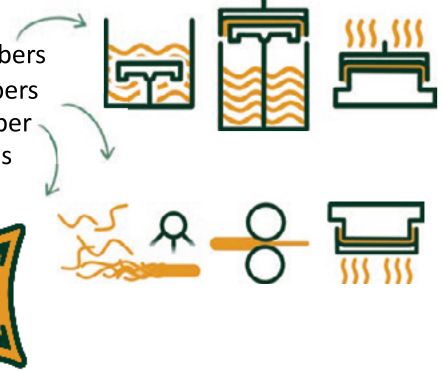


Methods

3D shaping of a cellulosic material

Understanding different processes by varying parameters (temperature, pressure, etc.) and comparing them.

- Wet Molded Fibers
- Dry Molded Fibers
- Stretchable paper
- Other strategies



Surface functionalization

Comparing surface functionalization methods adapted to substrates (2D then 3D) and developping new ones.

- Spray coating
- Screen printing

Eliott BONNET MARTIN
Ph.D. thesis (2024-2027)
LGP2 (D. Beneventi; A. Denneulin)
FCBA (M. Lecourt)

Set-up of an innovative wood-based biocomposite for processing by 3D LDM printing and wood panel adhesion

Elaboration d'un biocomposite innovant à base de bois et développement de sa mise en forme par procédés d'impression 3D LDM et thermopressage

Context

Substitution of Phenol-Formaldehyde Resins

- Widely spread polymer.
- Formaldehyde in the resin : SVHC.
- Imperative need of a bio-based, non toxic replacement.

Applications targeted :

Wood based panels

- Used in furniture and construction
- Production volume doubled in 20 years

3D printing

- Disrupting technology
- Broad range of techniques and applications
- Market doubled in 6 years
- Large-scale 3D printing in progress

Funded by: FCBA Institut Technologique; ANRT Association Nationale Recherche Technologie

Objectives

To replace phenol formaldehyde resins by fully bio-based ones

- Bio-based phenols : Lignin, tannins…
- Bio-based dialdehydes : HMF, furfural…

To increase the commercial value of lignin products

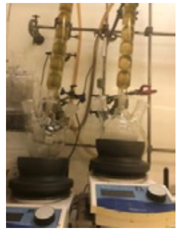
- By creating new sustainable and non-toxic biomaterials.
- By developing new applications for lignin in wood-based panel and as an additive for 3D printing.

To produce demonstrators

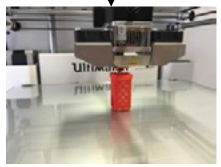
- 5m² of wood panels made from 100 % bio-based adhesives.
- > 100 printed objects produced with 3D printing with more than 50 % bio-based resin.

Methods

Solubilization of lignin → Resin formulation → Thermopressing with wood / 3D printing



Wood based panels (Particleboard)



Extrusion-based prints

Laura BERNARD
Ph.D. thesis (2023-2026)
LGP2 (A.Denneulin; N. Reverdy)
CEA-Leti DTIS (P. Mailley;
P. Marcoux)

Printed electronics for early detection of bloodstream infections

Electronique imprimée pour le dépistage rapide des infections sanguines

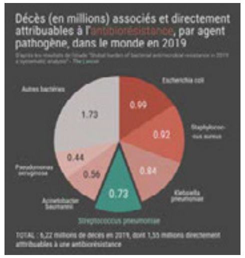
Context

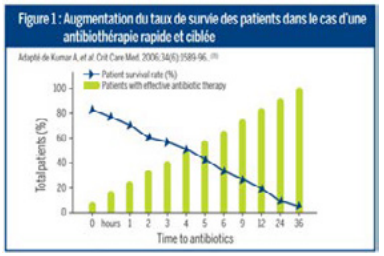
Bloodstream infections

Statistics

- 48,9 million cases 2017
- 11 million deaths in 2017 (20% of worldwide deaths)

Antibiotic resistance





- Increase in antibiotic resistance, leading to the leading cause of death by 2050.
- The longer is the time of effective medication, the lower the survival rate.

This project follows T. Babin's thesis work.

Funded by: anr® cea leti CHU Grenoble Alpes

In collaboration with LGP2

Objectives

Industrialization of the manufacturing process

Handmade to a standardized product

Requirements :

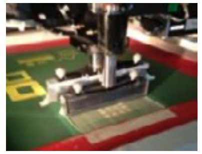
- **Autoclave-proof** (130°C/18 min/2 bar)
- **Rigid**, resistant to breakage during septum perforation
- **Biocompatible**
- **Electrically insulating**
- **Electrochemical sensor**, based on T.Babin device

Perspectives: Connected smart bottle to improve patient care.

Methods

Printing processes

More precise printing. Control of film homogeneity and quantity of inks applied.



Perforation study

Testing different needle geometries using 3D printing to verify optimum shape before injection molding

Materials Characterization

Study of materials which would fit the best to the requirement.

Annabelle JULIEN
Ph.D. thesis (2024-2027)
LGP2 (J. Bras; Q. charlier)

Dry processing methods to manufacture low environmental-footprint bio-based materials

Fabrication en voie sèche de matériaux biosourcés à empreinte environnementale diminuée

Context

1 Environmental issues - Plastic industry

- CO_2 emission during production
- Not biodegradable so a lot of wastes finds itself in landfill or ocean (6900 Mt[1])

2 Scientific advances in our understanding of cellulosic biomass

- **Paper and carboard**
  - Hight energy and water consumption
- **Wood panel**
  - Petroleum-based adhesives with formaldehyde, VOCs and health issues
- **Bioplastic from biomass**
  - Low biodegradability or recyclability

New challenge : How to substitute plastic with bio-based material that uses less energy, less water, no petroleum based adhesives and that can be biodegradable ? …

[1] Tony R. Walker et al. Trends in Analytical Chemistry 2023

Funded by:
Drybiomat - ANR-23-CE43-0002
https://anr.fr/Projet-ANR-23-CE43-0002
anr agence nationale de la recherche AU SERVICE DE LA SCIENCE

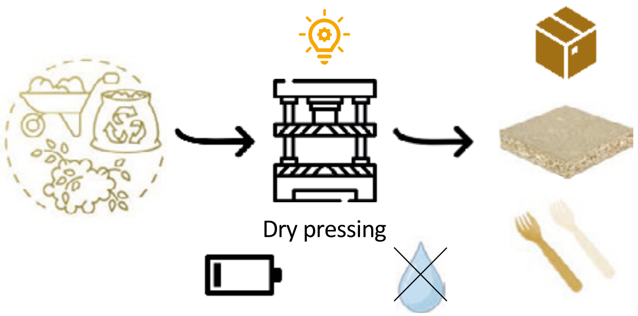
Objectives

… Development of more sustainable dry processes to make material from biomass in order to substitute plastic

Environnemental
- Reduced carbon footprint
- Sustainable
- Circular economy

Process
- Low energy and water consumption
- Scalable

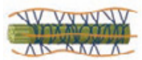
Product
- High-performance
- Low-cost



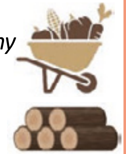
Understanding adhesion phenomena is key
Use of bio-based binders to enhance mechanical performances

Methods

"Pure" Material
- to control and understand
- Lignin
- Cellulose
- Hemicellulose

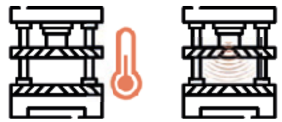


Byproduct
- for circular economy
- Agricultural
- Wood industry



→ Different type of material shaping (powder, chip, fiber)

Dry process
- Thermocompression
- Ultrasonic compression molding



→ Different process parameter

→ Adjust input parameters to tailor final properties

Iterative work

Multi-criteria analysis
Creation of a global performance index

Performance
- Mechanical properties
- Thermal properties
- Specific product requirements

Environmental
- Dry recyclability
- Fragmentability
- Biodegradability
- Energy consumption
- LCA

Amélie LEFEVRE
Ph.D. thesis (2023-2026)
LGP2 (N. Marlin; G. Mortha)
CERMAV (L. Heux)

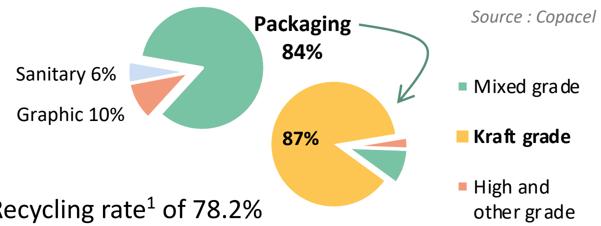
Oxidative processes for recycled fibers upcycling

Procédés oxydants pour la valorisation des fibres recyclées

Context

- **EU laws on reduction of the impact of plastic products on the environment**
- **Paper and Board recycling in France in 2022**

Consumption of recovered paper and board



Recycling rate[1] of 78.2%
Recovery rate[2] of 70.2% and of 89.3% for packaging

Increased demand for recycled fibers ⇨ Lower fibers quality ⇨ Reduction of packaging strength properties

[1]Collection/Consumption
[2]Consumption of recovered papers/Production

- **PEPR PAC3R project**

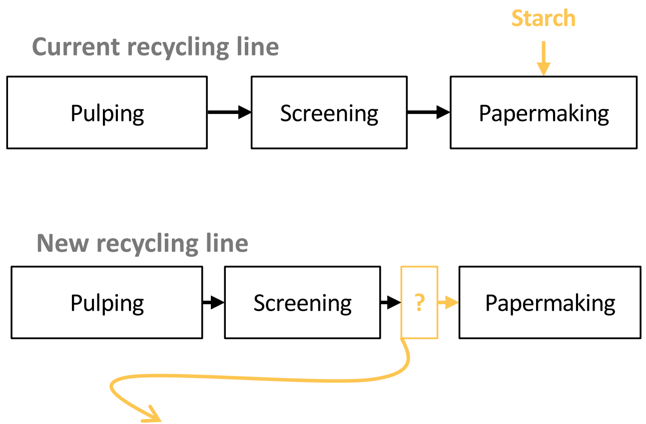
PACkaging, Recycling, Recyclability, Re-use of papers and carboards

Funded by: agence nationale de la recherche; France 2030 Programme de recherche Recyclage

Objectives

To develop new sustainable chemical process to upcycle recycled fibers for packaging applications

To improve the fiber properties originating from the recycling of cardboards

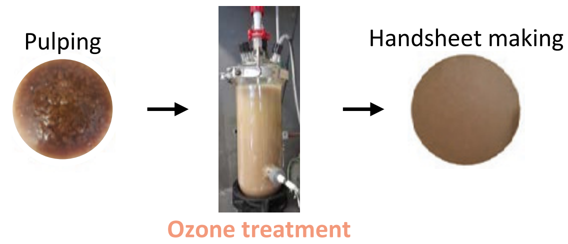


Fiber upcycling using chemical processes

- To increase the fiber bonding potential and water resistance
- To limit the use of additives (starch for example), responsible for process and wastewater treatment issues

Methods

Carboxyl groups creation on lignin and carbohydrates by oxidative process of the lignified recycled fibers



⇨ Promote the interfiber hydrogen bonds by increasing the lignin hydrophilic character and reducing its stiffness

Fiber hydrophilization by grafting process

Mechanical and chemical characterizations

Raw materials

Real recycled paper	Model paper
Industrial recycled corrugated paper - with contaminants	Unbleached refined kraft pulp - free of contaminant

Maxime LEGAY
Ph.D. thesis (2023-2026)
LGP2 (D. Beneventi; I. Desloges, J. Viguié)

Printing stiffeners on the surface of folding or corrugated boards: a bio-inspired approach to lighten packaging and optimize resource consumption

Impression de renforts à la surface d'emballages cartons: une approche bio-inspirée pour alléger les emballages et optimiser la consommation des ressources.

Context

Paper industry consumption

- 15-25 m^3 of water / ton of paper
- 2.9 kWh / ton of paper
- 2-3 ton of wood / ton of paper

→ Two approaches to reduce the use of resources :

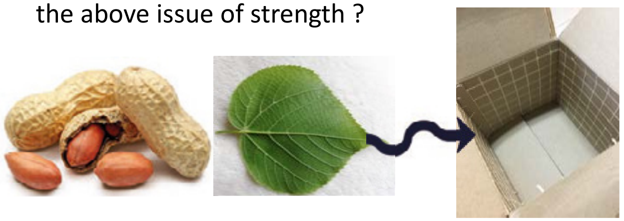
1. Lighten packaging
2. Increase the use of recycled pulps

→ Both raise an issue of mechanical strength

Ribbed structure

- High bending stiffness to weight ratio
- Ribs networks depend on the solicitation and geometry of the structure to reinforce

→ Could the printing of ribs of polymer on cardboard boxes be a virtuous way to stiffen them, addressing the above issue of strength ?



Funded by: UGA Collège Doctoral, ED I-MEP²

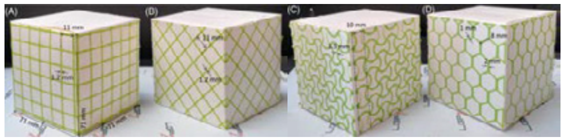
Objectives

1. Finding the best printing process & stiffening materials

- Lowest environmental impact
- Suitable adhesion of the printed patterns on boards
- Maximum mechanical properties, especially bending stiffness

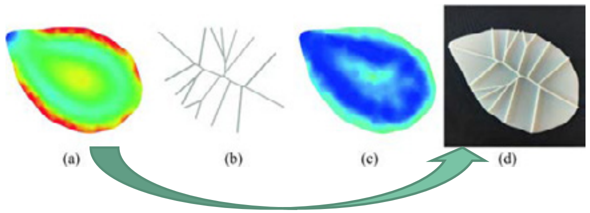
2. Characterizing the mechanical behavior of boxes

- Printing different types of rib pattern and identifying which one best stiffen a given geometry of box



3. Developing a numerical tool

- Optimizing the rib pattern to be printed depending on the geometry of the boxes



Methods

3D Printing

- Fused Deposition Modelling = 3D printing from a fused filament

→ Materials : PLA, Thermoplastic starch, …

- Liquid Deposition Modelling : 3D printing from a paste

→ Materials : cellulose ester suspension, potentially adding CNC / CNF, …

Characterizations

- On corrugated board plates :

→ 4 points bending, compression (ECT), DST

- On boxes :

→ Compression (BCT), cyclic loading, creep , digital image correlation (DIC) to measure the strain field on panel surfaces and observe how they are locally deformed

Towards the numerical tool :

- Calculation of stress maps from DIC strain maps using plate theory, then encoding an algorithm to calculate an optimized stiffening pattern from those maps

Julie LUNEAU
Ph.D. thesis (2023-2026)
LGP2 (R. Passas; C. Martin)

Influence of the drying conditions on the surface properties of end-products during Roll to Roll surface functionalisation : comparison between copper and fiber-based strips

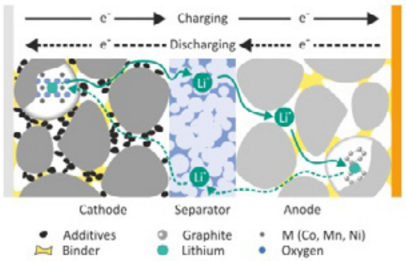
Influence des conditions de séchage sur les propriétés de surface des produits finis lors de la fonctionnalisation de surface Roll to Roll : comparaison entre les bandes à base de cuivre et de fibres

Context

Energetic transition

- Need to store the energy produced
- Increase in electric car production
- Need to improve the manufacturing process

Lithium-ion battery



Schematic drawing of the components and operation of a lithium-ion battery cell – Marcel Schmitt – slot die coating of lithium ion battery electrode

The electrodes are manufactured by coating an active material on the current collector

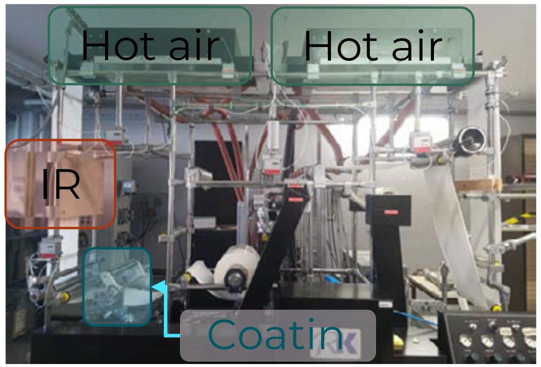
- Copper film for anode
- Aluminum film for cathode

Funded by:
AMI – CMA, L'école de la batterie, Grenoble-INP UGA

Objectives

Adaptation of a paper functionalization driver for the functionalization of a battery anode

Anode manufacturing

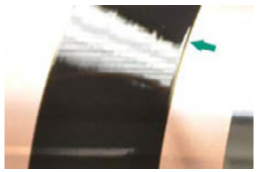


Functionalization driver

Study of anode drying

Optimisation of anode drying

- IR drying
- Hot air drying
- Surface defect detection



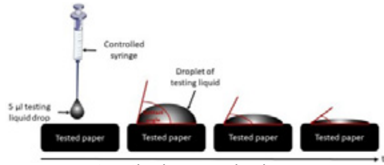
Battery anode - Marcel Schmitt – Slot die coating of lithium-ion battery electrodes

Methods

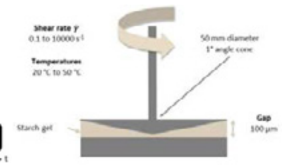
Comparision between copper and fiber-based strips

Ink characterisation

- Rheological characterisation
- Adhesion to the substrate



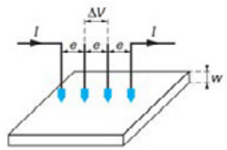
Sessile drop method test



Rotational rheological measurement with a cone-plan system

Copper film characterisation with and without functionalisation

- Electrical characterisation
- Electrochemical characterisation
- Surface characterisation
- Thermal characterisation
- Mechanical characterisation



Conductivity measurement with the four-probe system

Analogy humidity for paper and thermal dilatation for copper strip

Zelda MONTEIL-OCHS
Ph.D. thesis (2023-2026)
LGP2 (D. Beneventi)
STPE - CEA Liten (G. Furia ;
JF. Blachot ; M. Heitzmann)

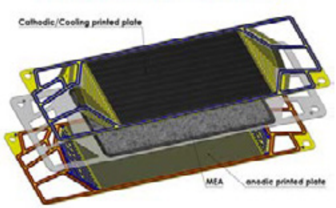
Development of conductive biosourced composites for PEMFC fuel cells

Développement de composites biosourcés conducteurs pour les cellules PEMFC

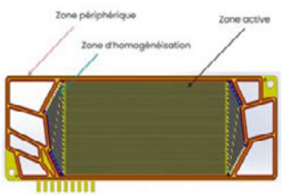
Context

Printed PEMFC developed by CEA

Objectives: offer a sustainable, ecological and economical technology.



Printed PEMFC



Printed bipolar plate

Advantages of printing: lightweight, compact, roll to roll industrialization and flexible in implementation

Printed bipolar plates in PEMFC cells

Printing of fluidic channels to distribute gases and cooling, conduct electrons, water management and mechanical strength of the cell

Carbon composites printed on carbon substrates
But based on harmful fluoropolymer incompatible with potential European legislation

Funded by: cea liten

Objectives

Replacing the fluoropolymer in the composite with a biobased polymer
To obtain a composite that meets specifications

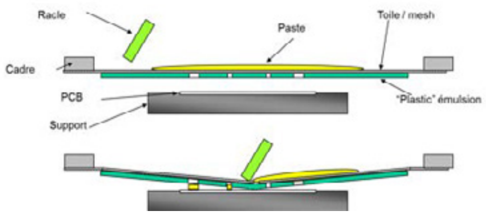
Composite specifications

- Composition: biobased binder + carbon fillers
- Compressive electrical conductivity, ICR < 10 mΩ.cm^2 under 1 MPa
- Resistant to heat (80 °C), water/moisture and acids (pH = 3)

Printing processes: Screen-printing

Resolution: 50 µm
Thickness: 200 µm

Screen-printing principle



Formulate inks compatible with the screen-printing process to shape the composite

Methods

Two types of composites

- Composites with discontinuous polymer matrix, cured (90-130°C)
- Composites with continuous polymer matrix, cured and carbonization (850°C)

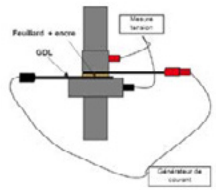
Find the optimum ink composition to obtain a composite that meets specifications

Ink characterization

- Rheological behavior ⟶ Rheometer
- Stability, homogeneity, aggregation ⟶ SEM

Printed composite characterization

- Structural properties ⟶ SEM, density measure, permeability measure
- Electrical properties ⟶ ICR test
- Thermo-mechanical properties ⟶ mechanical test in compression, DSC, TGA, DMA, etc.
- Surface properties ⟶ contact angle
- Resistance in stacked environment ⟶ ageing test



ICR test principle

Costin PANA
Ph.D. Thesis (2023-2026)
LGP2 (R. Passas; J. Viguié)
CTP (B. Carré)

Compression refining an innovative process for reducing energy consumption in the papermaking industry

Raffinage par compression, un procédé innovant permettant de réduire la consommation énergétique de l'industrie papetière

Context

Environmental impact

- high energy consumption in the production of papers and cardboards
- a significant reduction in the energy consumption of the paper industry and associated greenhouse gas emissions

New process and material development

- process in order to reduce energy and water consumption
- main method to create newly improved materials serving specifying needs

Funded by: ADEME Agence de la transition écologique; ctp centre technique du papier

Objectives

Objectives

- to evaluate the new technology
- the possibilities of the new strengthen development strategy to be implemented in the paper-making industry

Tasks

- to estimate the potential gain for specific paper & board grades
- effects of compression refining on the kinetics of water elimination at each of the stages of consolidation of the fibrous mattress
- evaluation of energy consumption at each stage (refining, draining, pressing, drying)
- study the effect of compression refining on surfacing operations (size-press, coating)
- to estimate potential technological costs

Methods

Process

- Characterization of the experimental set-up of refining process with adjustable parameters resulting in specialized paper for varied purposes
- New process has to be compatible with the conventional technological processes

Investigations

- Effects of compression refining on fiber flexibility / flocculation, pressing and drying
- Effects of mixing temperature on pulp properties / energy requirement
- Forecasting mixing efficiency by modelling, measurement of pulp viscosity at high consistency

Chloé PARISI
Ph.D. thesis (2023-2026)
LGP2 (J.BRAS)
SIMAP (E.BLANQUET)
CILKOA (F.MERCIER)

ALD optimization for cellulosic substrate

Optimisation du traitement ALD (Atomic Layer Deposition) sur support cellulosique barrière et recyclable dans le domaine de l'emballage

Context

New legislation on plastic packaging

Reduce Reuse Recycle

- **44%** of the global plastics for packaging

And only **10%** recycled in 2021…

- Single Use Plastics Directive (2019)
- Packaging and Packaging Waste Regulation (2018)

Green alternative

Cellulosic materials

Most abundant biopolymer on earth
Recyclable, Biodegradable & Renewable

x But *Permeable, Low barrier & Hydrophilic*

CILKOA

Created in June 2022 in Grenoble

Develop an innovative hydrophobic barrier treatment for cellulose substrates with few nanometers of ceramic

Funded by:

In collaboration with

Objectives

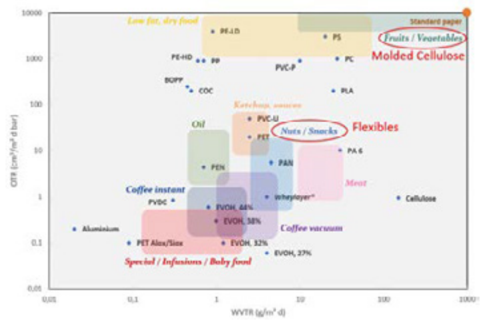
High barrier & mechanical properties

The requirements for a good packaging

3 applications

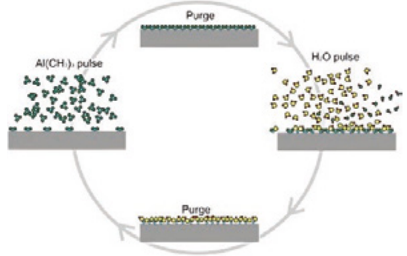
Flexible (High-performance & Green)
Water barrier molded cellulose
Foam

Depending on the application:
→ *Water, Water Vapor, Oxygen & Grease Barriers*
→ *Hydrophobic*
→ *Good wet and dry mechanical and thermal properties*

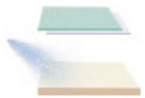


Methods

Atomic Layer Deposition



Protection strategy & New technologies



Ecoconception

Recyclability
Durability
Life Cycle Assessment

Suzy Ruano

Ph.D. thesis (2024-2027)
LGP2 (J. Bras ; N. Belgacem)
Gascogne Paper (J. Desmaisons ; A. Pinsolle)

<u>Thèse confidentielle</u>

Development of new biobased barrier solutions for flexible packaging

Développement de nouvelles solutions barrières biosourcées pour emballages flexibles

Context

Regulations

SUP directive – AGEC law

- Imminent need to find plastic-free solutions
- Solutions such as petro-based coatings or laminated papers are emerging, but at the expense of end-of-life issues

Cellulosed based materials and especially coated paper appear promising

- Their use is still limited due to their low barrier properties
- Force to use petro-based and controversial products (PVDC, BPA, PFAS…)

Funded by: Gascogne ANRT Association Nationale Recherche Technologie

Objectives

Formulation

- Functionalized biomaterials
- Nanocellulose
- Nanolignin

Coating

- Process optimization
- Multilayers

Characterization

- Barrier methods of characterization

Industrialization

- Upscaling
- Industrial adaptability

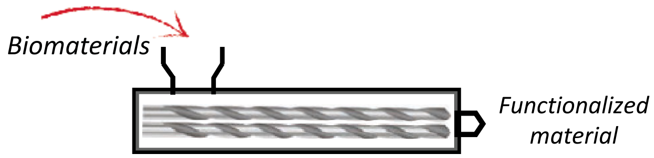
End of life

- Recyclability
- LCA

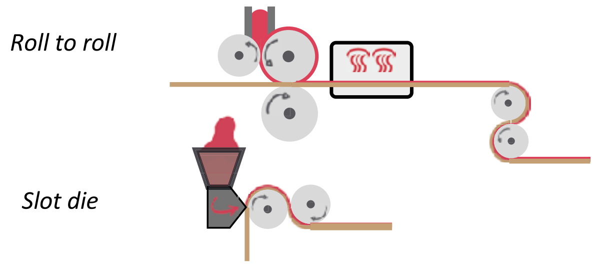
PAPER

Methods

Extrusion



Coating process



Barrier characterization

Niusha SAFARI
Ph.D. thesis (2023-2026)
LGP2 (C. Chirat)
TIMC (B. Toussaint; D. Hannani)

Study the Nature of Wood Oligosaccharides for their Prebiotic effects

Étude de l'effet de la nature des oligosaccharides d'hémicelluloses de bois sur leurs propriétés prébiotiques

Context

The establishment of biorefineries is crucial for enabling integrated production of food, feed, chemicals, materials, fuels, and energy in the future.

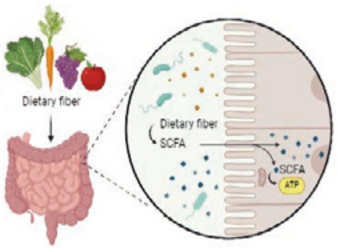
Hemicelullose valorization

valorizing hemicellulose plays a crucial role in maximizing:

- resource utilization
- diversifying product streams
- reducing waste
- promoting sustainability in biomass processing industries.

Prebiotics

Due to their structural resemblance to common dietary fibers, wood-based oligosaccharides exhibit prebiotic characteristics, providing advantageous effects on the host's health by selectively influencing the composition of the gut microbiota.[1]

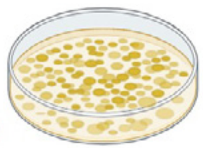


Funded by: GRENOBLE INP UGA; UGA COLLÈGE DOCTORAL; ED I-MEP²

Objectives

- **Purification and characterization of the Oligosaccharide solution's fractions with the possibility of having an immunomodulatory effect**

- **Finding the most relevant microbial consortium and system to initially screen the fractions**

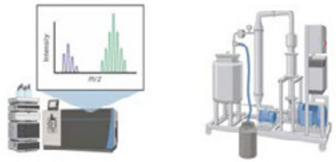


- **Study the promising fractions *in vivo*, to evaluate the immunomodulatory effect of the fractions**

Methods

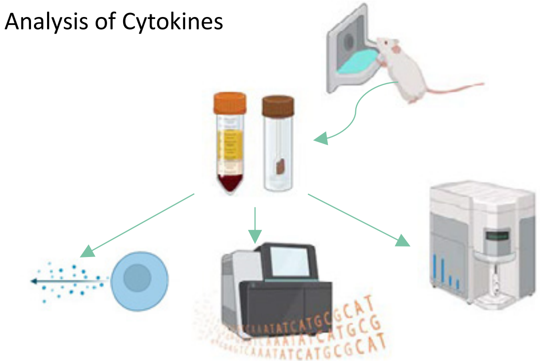
Oligosaccharides purification and characterization

- Ultrafiltrartion
- HPLC
- FTIR
- MALDI ToF



Prebiotic tests including *in vivo* and *in vitro*

- SCFA analysis
- Flow Cytometry
- Metagenomic study of caecal microbiota
- Analysis of Cytokines



Graphics created with BioRender.com

1.La Rosa, et al.(2019). Wood-derived dietary fibers promote beneficial human gut microbiota. MSphere, 4(1), 10-1128.

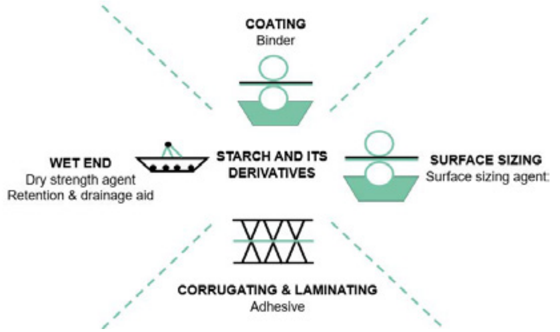
Alicia TESTON
Ph.D. thesis (2023-2026)
LGP2 (C. Chirat ; N. Marlin)

Biorefinery Integrated In Paper Recycling : Starch Extraction from Recycled Paper/Cardboard and its Valorization into High Value-Added Products

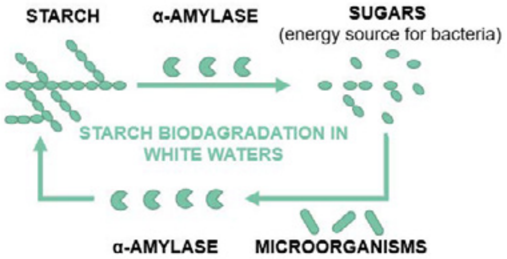
Bioraffinerie intégrée au recyclage des papiers/cartons récupérés : Extraction de l'amidon des fibres de récupération et sa valorisation en produits à haute valeur ajoutée

Context

Use of starch in papermaking : 40 – 60 kg/ton of paper



Environmental impact and runability issues related to starch release during paper recycling operations

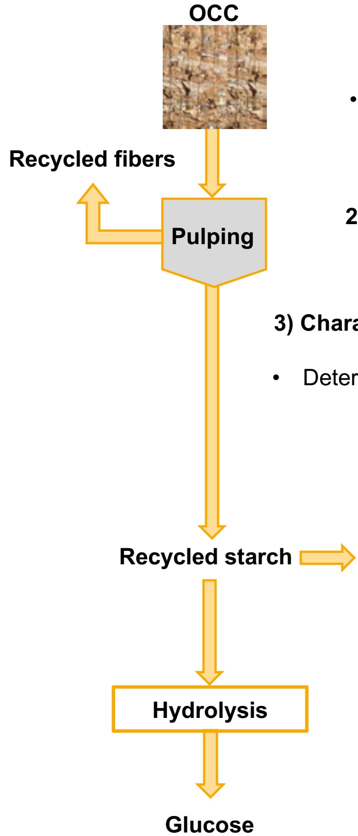


- **Microorganisms growth**
- **BOD/COD increase**
- **Odor and scaling issues**
- **Biocides overconsumption**

Funded by anr FRANCE 2030

In collaboration with UniLaSalle Institut Polytechnique

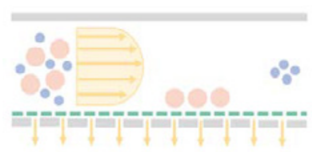
Objectives & Methods



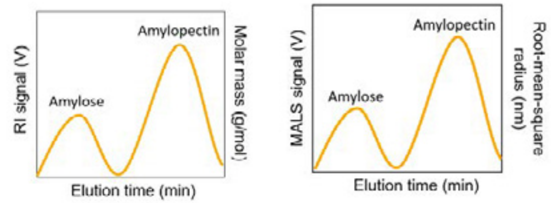
1) Determination of starch content in Old Corrugated Containers (OCC)
- Iodine Method (TAPPI Test Method : 419 om-91)
- Megazyme Total Starch Kit Assay : enzymatic hydrolysis of starch followed by glucose content measurement using glucose oxidase – peroxidase reagent / UV-vis.

2) Optimization of pulping operating conditions to maximize starch extraction from OCC
- pH, temperature, pulp consistency, duration, use of chemicals e.g. α-amylase.

3) Characterization of the recycled starch using Asymmetric Flow Field-Flow Fractionation with Multi-Angle Light Scattering and Refractive Index detection (AF4-MALS-RI)
- Determination of mass percentage and average weight-average molar mass of amylose (AMY) and amylopectin (AMP), AMY/AMP ratio.



AF4 Fractionation



AF4-MALS-RI fractograms

4) Optimization of starch depolymerization into glucose
- Acid hydrolysis : HCl and H_2SO_4.
- Enzymatic hydrolysis : α-amylase and amyloglucosidase.

Arthur VALENCONY
Ph.D. thesis (2023-2026)
LGP2 (G. MORTHA; N. MARLIN)
FCBA (S. TAPIN-LINGUA)

Lignocellulosic biorefinery: Development of a new pulping process to produce high-quality fibers from underexploited resources

Bioraffinerie lignocellulosique : Développement d'un nouveau procédé de mise en pâte pour la production de fibres de haute qualité à partir de ressources sous-exploitées

Context

Underexploited biomass:

Huge quantities are available

- Wastes of industrial biomass
- Underexploited sources: hemp, nettle and poplar residues available in local areas

The Kraft process is a strongly alkaline process

Large plants with limited flexibility

- Soft alkaline pulping processes are in the trend
- Total Chlorine Free (TCF) bleaching sequence is a must
- Smaller cooking units for smaller biomass quantities

MicroFibrillated Celluloses (MFC) are in current development for their good properties

- Reinforcement in composites
- Packaging applications for barrier properties
- Textile utilization

Funded by: FCBA, Cifre, ANRT, Bio-LUSH

Objectives

Selection & analysis of biomass

- Chemical composition
- Prepare biomass for cooking

Development of an alternative, mildly alkaline pulping process

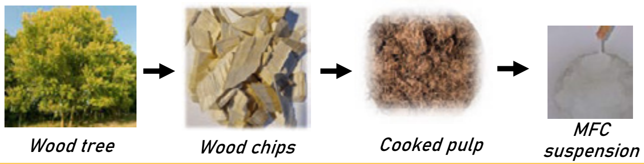
- Find a way to delignify the biomass with a limited quantity of chemicals
- Compare this pulping process with the Kraft process
- Understanding the impregnation phenomena

Fibers and pulp modification & analysis

- TCF bleaching sequences
- Refining steps
- Pulp, paper & fibers properties

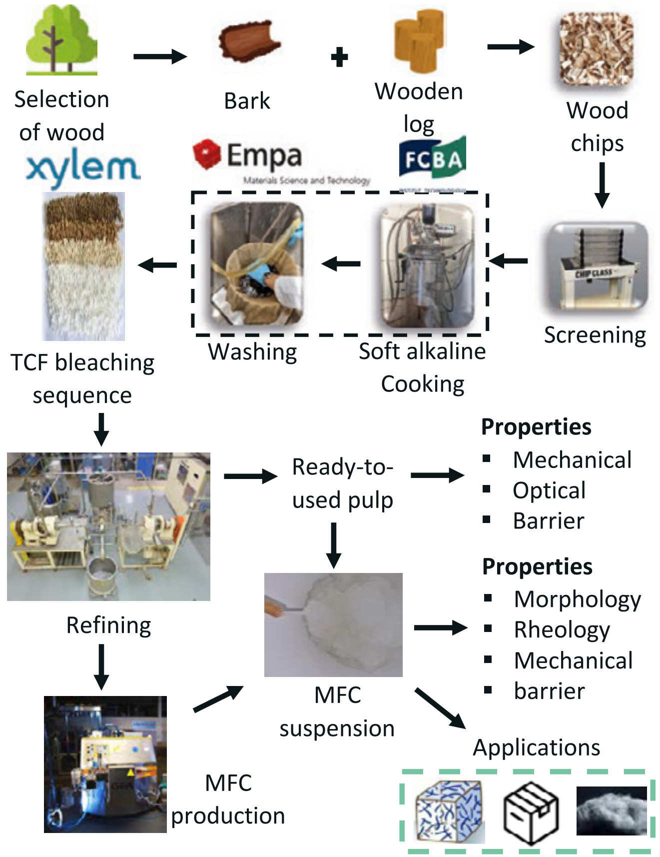
MFC production

- MFC production capabilities
- Analysis of their properties
- Impact on fiber morphology
- Controlling energy consumption during production



Methods

Process – at lab and/or pilot scale



Young Researcher's research project description

Post-doctorates and Research Engineers

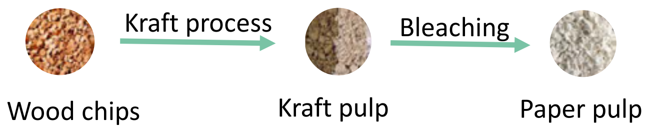
Karen AL HOKAYEM
Post-doc (2023-2024)
LGP2 (N. Marlin; M. Mortha)
CTP (A. Burnet)

PolyCell: New oxidative process for added-value celluloses production

PolyCell : Nouveau procédé d'oxydation pour la production de celluloses à valeur ajoutée

Context / Objectives

Conventional paper pulp production



Objectif: Synthesis of different types of pulps on the same bleaching line

- Increase the flexibility of paper pulp mills
- Develop an innovative oxidizing process to produce dissolving pulp in parallel to the production of the conventional bleached Kraft pulp

Bleaching/ Purification
Paper pulp ⟷ Dissolving pulp

Advantages of dissolving pulps

- Replace fossil-based sources by natural sources
- Bioproducts of high added value
- Large field of applications: textile, pharmaceuticals …

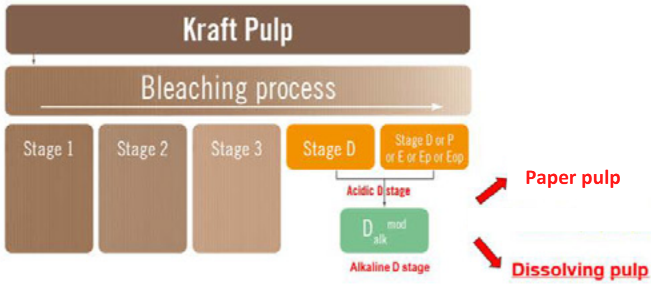
In collaboration and funded by CTP:

Methods

Step 1: Optimized D_{alk}^{mod} bleaching process

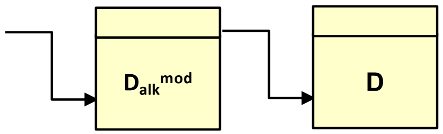
Patented process

- Modified alkaline bleaching
- Chlorine dioxide under revisited operating conditions to purify the pulp during bleaching
- 5min / 50°C – variation of chemical dosages



Step 2: Final bleaching step: D stage

Conventional chlorine dioxide bleaching



Results

Step 1: D_{alk}^{mod} bleaching process

- Decrease environmental impact (low AOX)
- Reduce production costs
- High pulp brightness (≈ 90%)
- Low hemicelluloses values (≈ 6%)
- Very low lignin and Kappa number (< 1)
- Possibility to recover the removed hemicelluloses from effluents

Step 2: Residual hemicelluloses removal process

Hemicelluloses content reduced to 4,5%

Lorette BRAULT
Post-doc (2024-2027)
LGP2 (N. Marlin, G. Morth
Cermav (L. Heux, S. Molina-Boisseau)

Valorization of the fibrous rejects from paper and cardboards recycling process

Valorisation des déchets fibreux issus de la filière de recyclage papier-cartons

Context

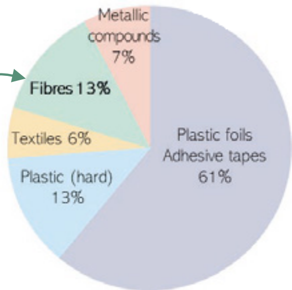
Paper and cardboards (PC) recycling process[1]

- 4.9 Mt of recovered PC in France/year, including

4 Mt for packaging sector (2020).
└93% recycled into PC
Among the 7% waste:

13% of fibrous rejects

= 36 kt of non-valorized fibres per year in France.



Lignocellulosic high value products

- EU directives (Green Deal) on reducing consumption and replacing of petroleum-based products.
- High demand of cellulose and lignocellulosic compounds for ubiquitous applications.

= high demand of virgin fibers and pure bio-compounds representing high energy and chemical consumption.

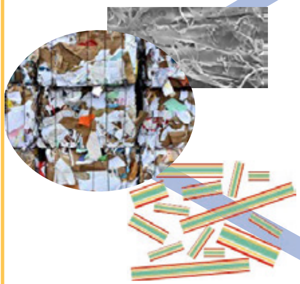
However, for some applications, non-pure and damaged cellulose from paper recycling process could be used.

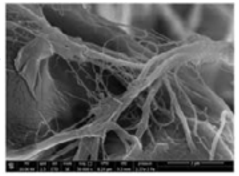
Funded by:
anr® agence nationale de la recherche
FRANCE 2030 PROGRAMME DE RECHERCHE RECYCLAGE
RECYCLAGE RECYCLABILITÉ RÉUTILISATION MATIÈRE PEPR

Objectives

Development of valorization methods tailored to the fibre quality and contaminant nature

Damaged fibres

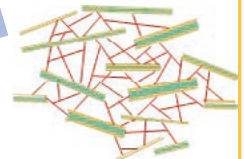




MFC

Applications
Mechanical reinforcement
(paper coating, composites)
Rheological additive

Resin



Caption:
Cellulose
Hemicelluloses
Lignin

Applications
Adhesives, sealing, coating, composites,...

Methods

Characterization of rejects

Chemical: %cellulose, %hemicelluloses, %lignin, %stickies,... functional groups analysis (COOH, CHO, phenol,...)
Physical: Fibres morphologies and specific areas.

MFC production[2]

Rejects or model compounds → Chemical fibrillation + delignification with TEMPO oxidation → Mechanical fibrillation

Resin production

Rejects or model compounds → Chemical depolymerization → Fractionation → Stickies elimination or dispersion / Cellulose and hemicellulose carbonylation / Lignin amination → Reticulation via drying

Characterization of MFC and resin

Mechanical, thermical, chemical and optical characterization.

[1] K. Guiltaux, et al., ADEME 2023. Perspectives d'évolution de la filière papiers-cartons en France. 79 pages
[2] L. Dollié, Thèse Université Grenoble Alpes, 2019

Jules
DE BARDONNECHE
Research engineer (2023-2025)
LGP2 (A. BOYER)

BIO-4-INKS: Life Cycle Assessment (LCA) of 100% bio-based inks for newspaper offset printing

Analyse de cycle de vie d'encres 100% bio-sourcées pour l'impression offset de la presse

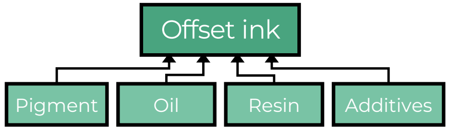
Context / Objectives

Context

- Limited recent available LCA data to guide industrials in their eco-design approach
- Environmental impacts of newly-used bio-based vehicles are little studied
- Bio-based pigments are being studied as substitutes for conventional petroleum-based colorants

Objectives

- LCA modeling of both conventional and 100% bio-based inks formulations in the European context



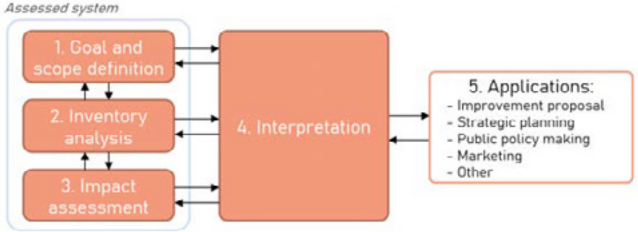
- Calculation of the environmental weight of pigment in current industrial offset inks
- Impact transfer assessment through comparative LCA
- Identification of possible future improvements

Funded by: MINISTÈRE DE LA CULTURE, CITEO

In collaboration with Écograf, SunChemical, Grakom

Methods

System definition



LCA framework (ISO 14 044)

Data collection

Primary data

- Industrial partners

Secondary data

- Ecoinvent
- Literature review

Conjunction with lab work and choice of FU

- Bio-based pigments: technical relevance of assessed solutions are validated in lab environment
- Functional Unit (FU) is linked with the optical performances (contrast, color, i.a.) of the formulated inks.

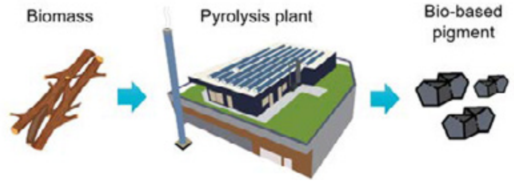
Need for multi criteria approach

LCA method: Environmental Footprint V3.1

Preliminary results

Modeling of bio-based black pigment

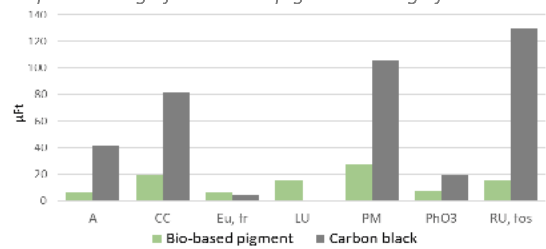
- Based on literature study and industrial data



Source: www.biochar-industry.com (adapted)

Comparative LCA of black pigments

Comparison 1kg of bio-based pigment vs 1kg of carbon black



A: Acidification, CC: Climate change, Eu, fr: Eutrophic., freshwater, LU: Land use, PM: Particulate matter, PhO3: Photochem. O_3 formation, RU, fos: Resource use, fossils

→ *Bio-based pigment shows a positive influence on 5 out of 7 of the main impact categories. Optical performances are to be validated in lab.*

- The overall ink formulation (pigment, vehicle and additives percentages) shall be considered to assess the total impact transfer.

Elise JACACHOURY
Engineer (2023-2024)
LGP2 (A. Blayo)
CTP (W. Pierron)

Formulation of bio-based inks for direct printing on molded cellulose

Formulation d'encres biosourcées pour l'impression directe sur cellulose moulée

Context / Objectives

Molded cellulose

- Sustainable material
- Alternative to singe-use plastics
- 3D objects

Properties of the inks

- Rheological properties
- Printability
- Stability

Properties of the prints

Optical properties

- Low ΔE compared with the standard values
- Color strength
- Low gamut variation

Resistance/durability

- Lightfastness
- Rub-fastness

Funded by: cnrs, INSTITUT CARNOT PolyNat

Methods

Raw materials selection

- Bio-based
- Binder, solvent(s), pigments

Pad printing

Formulation of inks

- Mixing (SpeedMixer)
- Grinding (Three-roll mill)

Testing

- Rheology
- Color

Manual Pad Printer

Inkjet

Formulation of inks

- Mixing
- Filtration

Testing

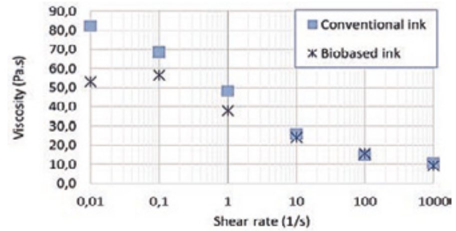
- Granulometry
- Rheology
- Surface Tensionr
- Color

Dimatix Printer

Results

Rheology

- Shear-thinning behaviour
- Similar to conventional ink

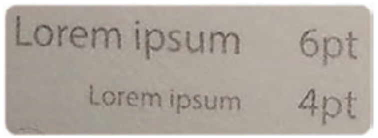


4 Colors

- Black
- Primary colors : Blue (Indigo), Magenta (Red Madder), Yellow (Gaude)

Readable, functional prints

- 4 pt font size
- Flashable QR Code



Laboratoire de Génie des Procédés pour la Bioraffinerie, les Matériaux Bio-sourcés et l'Impression Fonctionnelle

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