

CHALLENGES AND CONTEXT OF CELLULOSE VALORIZATION – FUNCTIONALIZATION TO PRODUCE HIGH-PERFORMANCE MATERIALS

Spalletta Alexis, Joly, N., De Clerck, K., Dropsit, S., Gosselin, I., Van Rie, J., Martin, P.

OBIWAN Guest lectures

28/04/2026

Context



- Reduce net greenhouse gas emissions in the EU by at least 55% by 2030 (compared to 1990 levels)
- Carbon neutrality by 2050

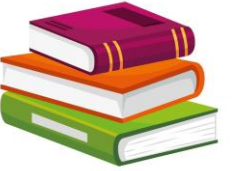
- Petroleum-based products → packaging / textiles / insulation materials / additives for biopolymers
- Environmental impact

Finding alternatives with abundant biomass using green chemistry processes

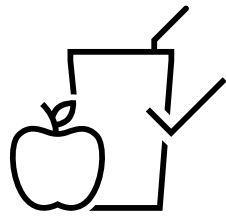
Short history of the cup



It all began in the 21st century



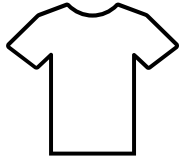
Coating / plastic film



Same challenge in food packaging ...

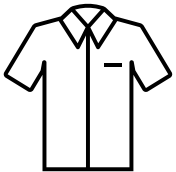


And textile ?



- Who doesn't have at least one piece of clothing made with synthetic/oil-based fibers?
- Mixed fibres

fast consumption and increasingly urgent environmental, economical and social challenges



- Technical textiles...



Big history of composite



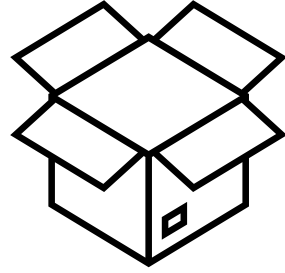
Worldwide application

Composites offer excellent performance (lightweight, high strength), but they pose a major challenge in terms of:

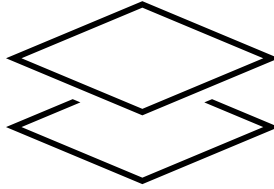
Recyclability
environmental impact
waste management

--> mixed composites made from petroleum-based materials / petroleum-based resins / biomass

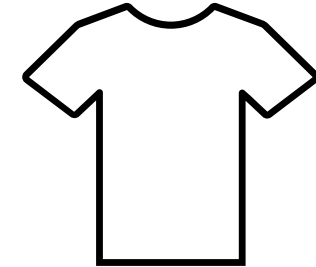




Green Deal: towards 100% recyclable packaging in the EU by 2030. However, cellulose packaging presents certain limits, in particular insufficient protective properties, which prevent it from fully competing with plastic packaging.



The increasing complexity of composite formulations leads inevitably to new recycling problems; and the products often contain non-degradable additives to fully preserve their intrinsic properties.



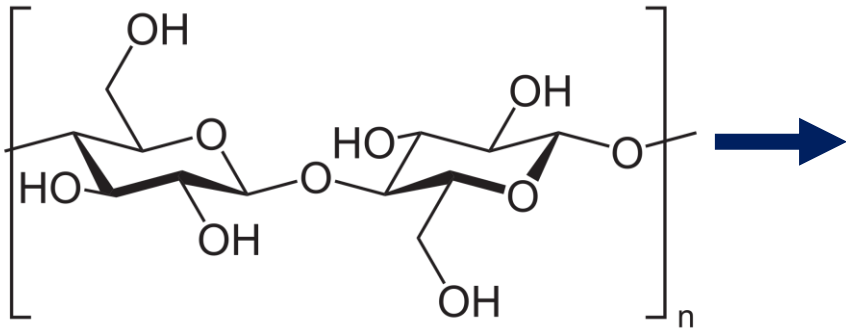
The EU's strategy for sustainable textiles by 2030 provides that all textiles commercialized in the EU should be sustainable, repairable, and recyclable, made primarily from natural and/or recycled fibers, and free from hazardous substances.





Budget total : 2 752 108,45 €
Budget FEDER: 1 651 265,06 €
10/2024 – 09/2028 | 48 month

Cellulose



Most abundant biopolymer on earth,
recyclable/biodegradable

Modification/New features
using sustainable chemical
processes

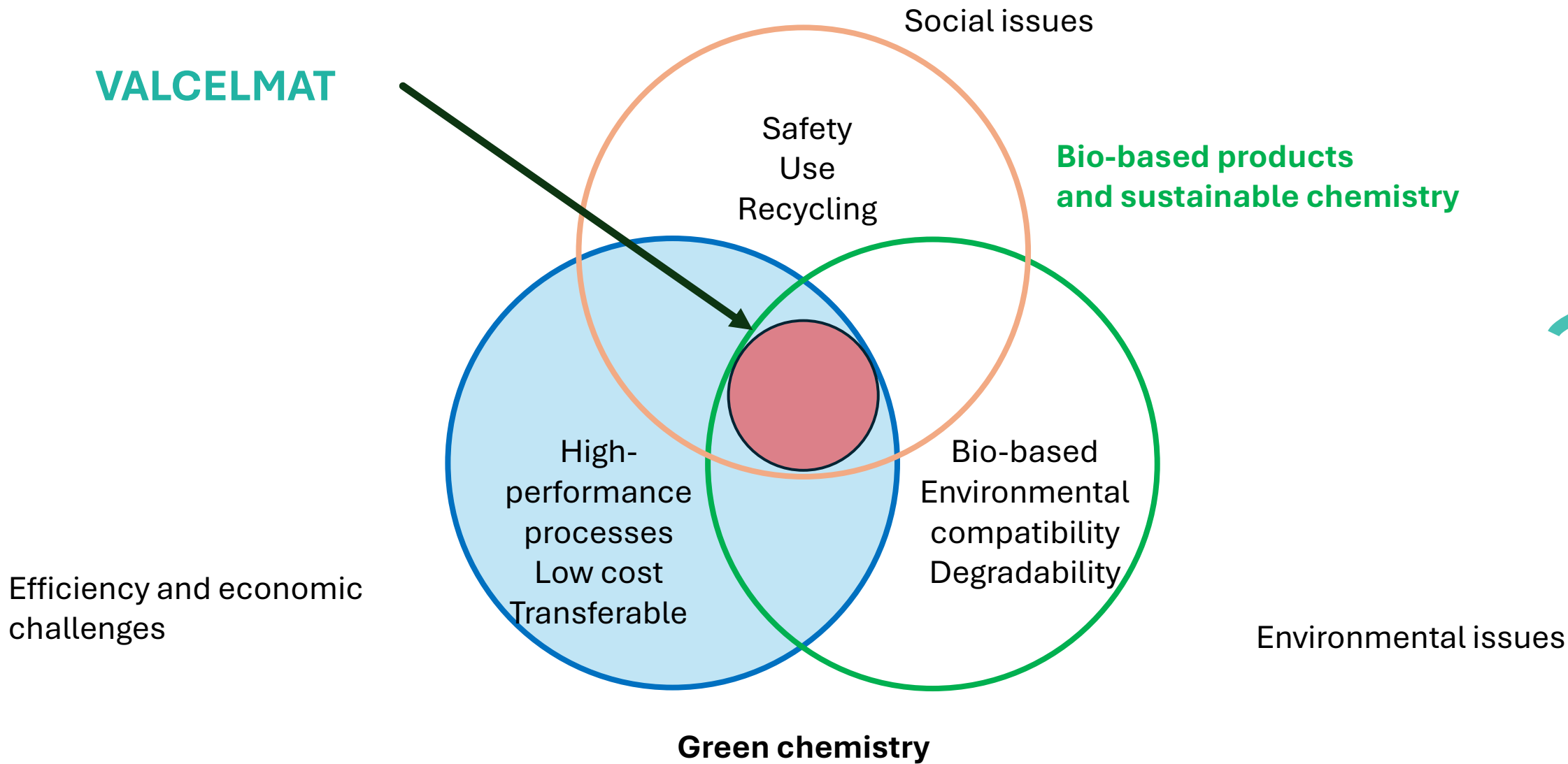
Packaging products,
food packaging, textiles,
materials, additives,
“bioplastics”

Circular and Sustainable Economy

4-year objective: to offer viable products and processes, at prototype/pilot scale, that can be transferred to manufacturers for all targeted areas.

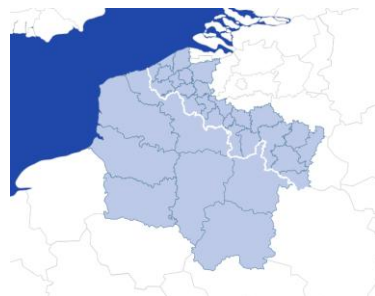


VALCELMAT



Who ?

5 partners



Interreg



Cofinancé par
l'Union Européenne
Medegefinancierd door
de Europese Unie

France - Wallonie - Vlaanderen



VALCELMAT



UArtois

Batch - Characterization



MaNo

Processes - Extrusion - Continuous



UPJV

Biological properties -
degradability



**HO
GENT**

HOGENT

Spinning - textiles-
coatings



**UNIVERSITEIT
GENT**

UGent

Electrospinning -
textiles

8 Associated partners

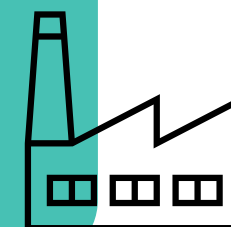
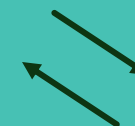
EuraMaterials



PLASTIWIN



artevelde
hogeschool



Industrial

Currently – Scientific activities - Functionalization



Hydrophobisation / Esterification

1

Ignifugation / fireproofing

2

Conclusion & Perspectives

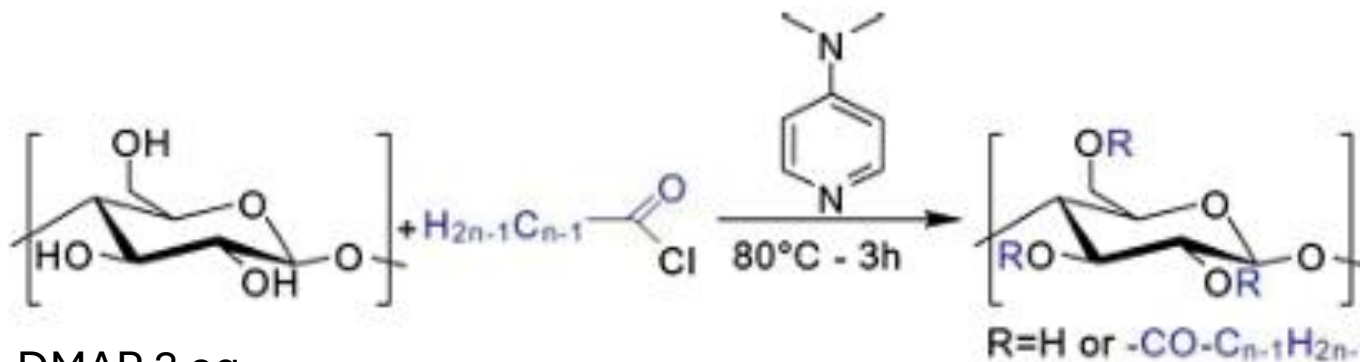
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1 Functionalization of cellulose

Hydrophobisation / Esterification



20 g/L cellulose solution 6.7%
LiCl/DMAc (v/w) system



- DMAP 3 eq
- Fatty acyl chloride (2-10eq)

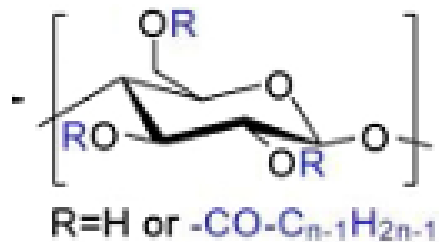
C8-C18: caprylate – caproate – laurate – myristate – palmitate - stearate

Reaction efficiency controled by FT-IR spectroscopy
Purity and DS determined by ^1H NMR spectroscopy

FACE name	C10				C12				C14				C16			
Fatty acid chloride (eq.)	5.5	6	8	9	5	5.5	7.5	9	4.5	5	6.5	8	4.5	5	6.5	8
DS (± 0.1)	1.7	2	2.5	3	1.7	2	2.5	3	1.7	2	2.5	3	1.7	2	2.5	3

1 Functionalization of cellulose

Hydrophobisation / Esterification



Casting



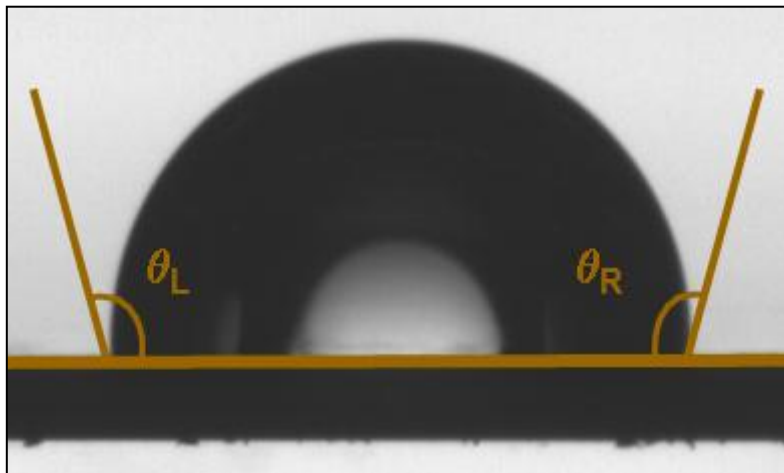
Analyses



Hydrophobicity
Resistance to acids and alkalis
Mechanical behavior (uniaxial tests)
Thermal properties (DSC)
Structural analyses (WAXS)
Solubility

1 Functionalization of cellulose

Hydrophobisation / Esterification



Microcrystalline cellulose : $\theta \approx 30^\circ$

FACEs : $92^\circ < \theta < 107^\circ$

➡ $\theta > 90^\circ$ = hydrophobic materials.

$\theta(^{\circ})$	C10		C12		C16	
	DS1.7	DS3	DS1.7	DS3	DS1.7	DS3
Control sample	93	97	95	100	97	107

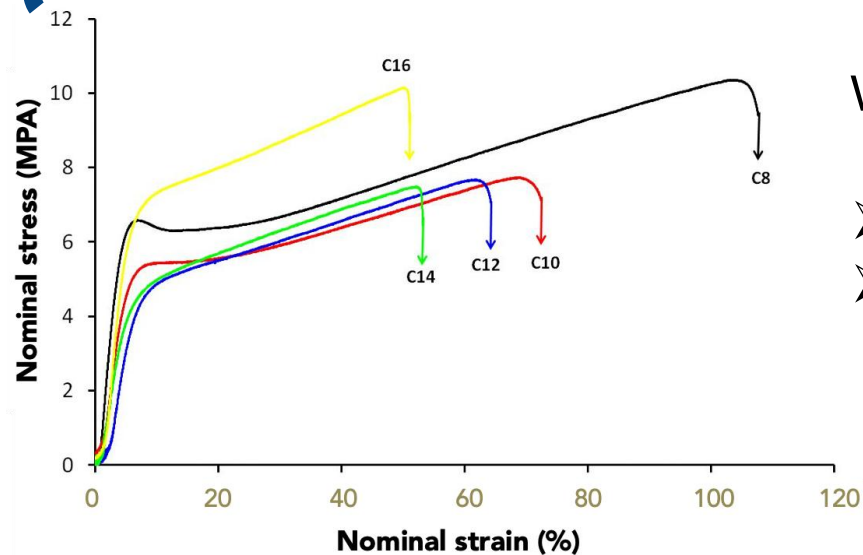
Resistance confirmed by FT-IR
and ^1H NMR spectroscopies

Mineral deposit at the
surface, confirmed by EDX

L. Duchatel-Crépy, N. Joly, P. Martin, A. Marin, J.-F. Tahon, J.-M. Lefebvre, V. Gaucher. *Carbohydr. Polym.*, **2020**, 234, 115912.

1 Functionalization of cellulose

Hydrophobisation / Esterification

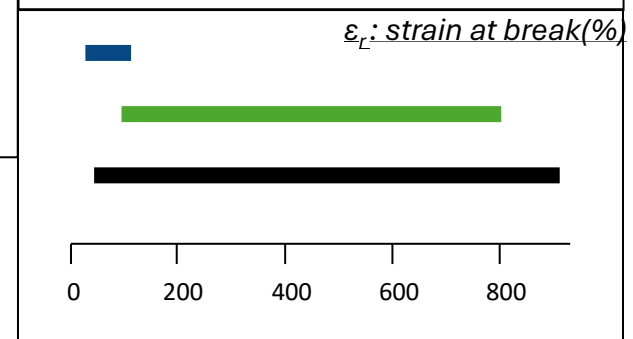
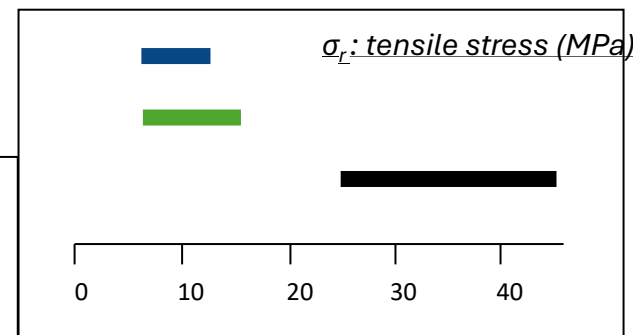
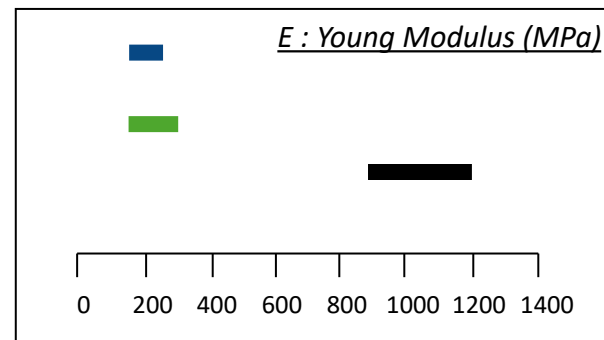


When fatty chain length increases:

- Tensile strength tends to decrease with $\uparrow n_C$
- No clear evolution of the yield stress is evidenced

Comparison with petrosourced commodity plastics

- ➡ E (MPa) lower: internal plasticizing effect of fatty chains. Flexible
- ➡ σ_r (MPa) : equivalent to LDPE.
- ➡ ε_r (%) : at the beginning of LD- and HDPE range.



■ FACES
■ LDPE
■ HDPE

L. Crépy, L. Chaveriat, J. Banoub, P. Martin, N. Joly. *ChemSusChem*, **2009**, 2(2), 165-170.
L. Crépy, V. Miri, N. Joly, P. Martin, J.-M. Lefebvre. *Carbohydr. Polym.*, **2011**, 83, 1812-1820.

1 Functionalization of cellulose Hydrophobisation / Esterification

- Structural characterization of FACEs
 - Hydrophobic plastics ($\theta > 92^\circ$)
 - Can be processed using conventional plastic processing methods
 - Mechanical properties comparable to those of LDPE
-
- Applications?



→ UPJV / HOGENT / UGent



1 Functionalization of cellulose

Hydrophobisation / Esterification

Additional properties?

Addition of a biomolecule (bio-based additive): 0.1% (w/v) during casting



ATG
Antioxidant activity

Currently – Scientific activities - Functionalization



Hydrophobisation / Esterification

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Ignifugation / fireproofing

2

Conclusion & Perspectives

3

Phosphorylation of Microcrystalline Cellulose (MCC) via Ball Milling

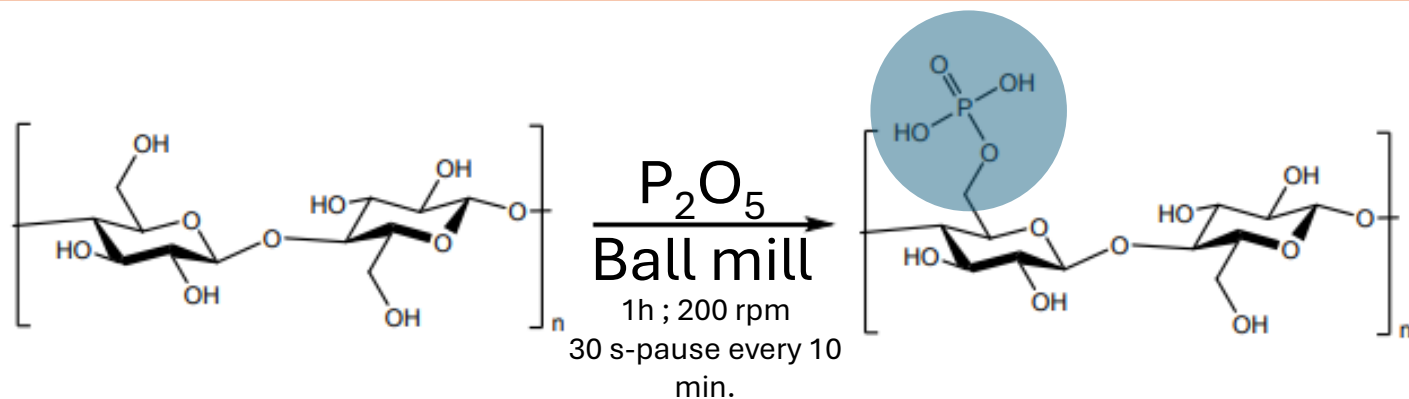
- A more **environmentally friendly** alternative to traditional chemical processes (low energy consumption)
 - Solvent-free process
 - **Good reactivity:** mechanical activation enhances cellulose reactivity, enabling faster reactions and effective phosphate group grafting.
-
- Phosphorylation of MCC via ball milling
 - Evaluation of structural properties of phosphorylated celluloses (MCC-P)
 - Preparation of Polypropylene/MCC-P composites (PP/MCC-P) using internal mixer
 - Evaluation of fire and mechanical properties of PP/MCC-P composites



Phosphorylation of MCC via Ball Milling

Formulations

- **MCC-P1** : ratio cellulose/ P_2O_5 90/10 w/w (0,25 eq P par AGU)
- **MCC-P2** : ratio cellulose/ P_2O_5 70/30 w/w (1 eq P par AGU)
- **MCC-P3** : ratio cellulose/ P_2O_5 43/57 w/w (3 eq P par AGU)



Phosphorylation of MCC via Ball Milling

MCC-P1 :

MCC/P₂O₅ 90/10 w/w

MCC-P2 :

MCC/P₂O₅ 70/30 w/w



MCC-P3 : MCC/P₂O₅ 43/57 w/w

The excess of P₂O₅ caused side reactions:

- Expansion et porous structure formation
- Color change
- Heat release
- Vapor emission

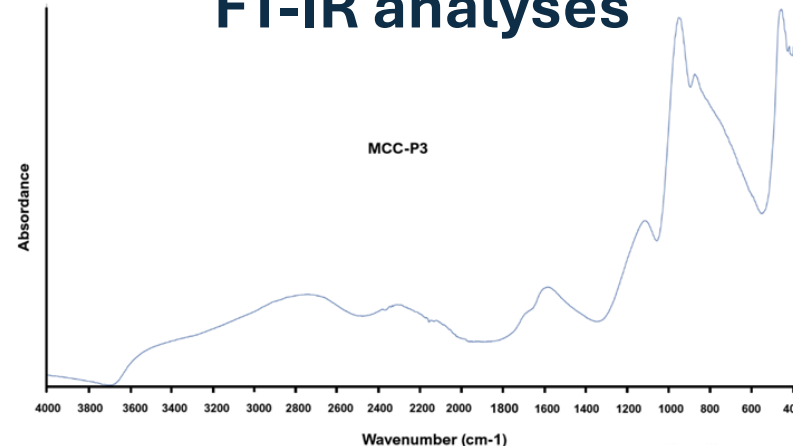
ICP MCC-P

Reference	MCC/P ₂ O ₅ (w/w)	P (w%)	DS
MCC-P1	90/10	1,1	0,06
MCC-P2	70/30	3,6	0,21
MCC-P3	43/57	17,3	1,97

$$DS = \frac{M_{\text{cellulose}} \times P\%}{100 \times M(P) - \Delta M \times P\%}$$

$M_{\text{cellulose}}$ = molecular weight of D-glucose unit (162 g/mol), $P\%$ = phosphorus weight %, $M(P)$ = molar mass of phosphorus (31 g/mol), ΔM = molar mass of substituent - leaving group ($H_3PO_4 - H = 97$ g/mol)

FT-IR analyses



MCC-P1 et MCC-P2 : **no significant difference from the MCC spectrum**

MCC-P3 : very **different spectrum**, similar to that of a **graphitic structure**.

Evaluation of properties of Polypropylene/Phosphorylated cellulose composites :

- Preparation of composites (PP/MCC-P) using internal mixer
- Samples preparation by thermocompression (100 x 100 x 3 mm³ plates)
- Fire testing: Mass Loss Cone (MLC)
- Mechanical testing: uniaxial tensile test

Formulations

- **PP+30 MCC** : ratio PP/MCC-P 70/30 w/w
- **PP+30 MCC-P1** : ratio PP/MCC-P1 70/30 w/w
- **PP+30 MCC-P2** : ratio PP/MCC-P2 70/30 w/w
- **PP+12,5 MCC-P3** : ratio PP/MCC-P3 87,5/12,5 w/w



Internal mixer

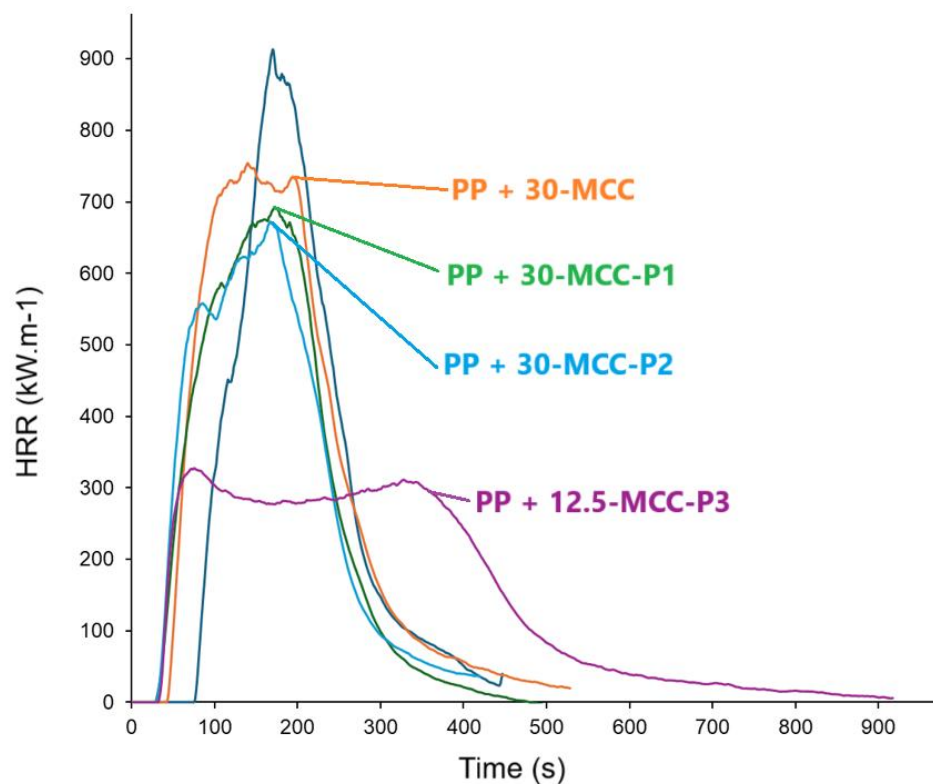


Thermopresse



MLC

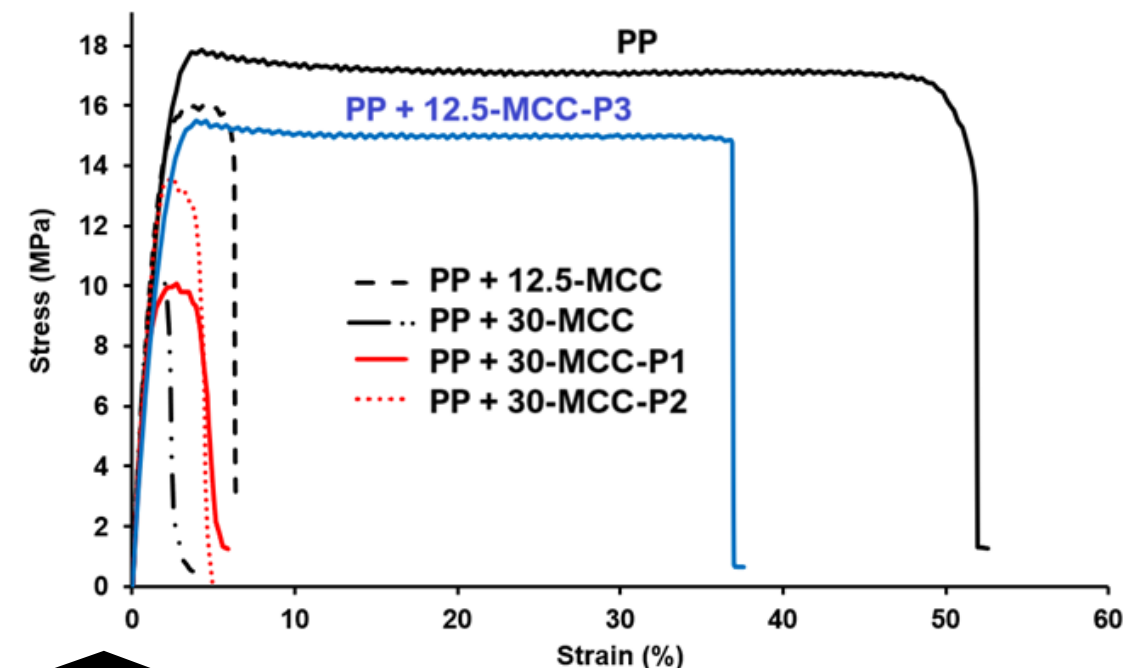
Evaluation of the flame-retardant effect of MCC-P in PP



Reference	P content (w%)	TTI (s)	pHRR (kW.m ⁻²)	pHRR change (%)
PP	-	62	922	-
PP + 30 MCC	0	41	757	-18
PP + 30 MCC-P1	1,1	28	715	-23
PP + 30 MCC-P2	3,6	28	675	-27
PP + 12,5 MCC-P3	17,3	30	336	-64

- **PP:** burns easily and exhibits rapid and intense combustion.
- **PP + 30% MCC:** the addition of MCC reduces the peak HRR of PP by 18%.
- **PP + 30% MCC-P1 and MCC-P2:** no additional effect compared to the addition of unmodified MCC. Flame-retardant effect is not significant (low phosphorus content).
- **PP + 13% MCC-P3:** significant reduction in the pHRR of PP (-64%) with less MCC-P but more phosphorus.

Evaluation of the mechanical properties of phosphorylated PP/MCC composites (tensile testing)



Reference	E (MPa)	$\sigma_{\max}$ (MPa)	ϵ_{rupt} (%)
PP	1139 +/- 56	17,1 +/- 0,9	55,2 +/- 17,0
PP + 30 MCC	1254 +/- 78	9,8 +/- 0,8	2,8 +/- 0,3
PP + 13 MCC	1217 +/- 64	15,9 +/- 0,9	11,0 +/- 3,3
PP + 30 MCC-P1	1003 +/- 178	10,8 +/- 2,1	4,7 +/- 0,7
PP + 30 MCC-P2	1250 +/- 105	14,2 +/- 0,7	4,6 +/- 1,2
PP + 12,5 MCC-P3	918 +/- 10	15,2 +/- 0,2	35,6 +/- 3,2

- **PP: ductile behavior**
- **A decrease in mechanical properties** is observed for the **PP + 30% MCC** and **PP + 30% MCC-P1 and -P2** composites → numerous and heterogeneous particles lead to embrittlement of the material.
- The **mechanical properties of PP are preserved in the PP + 12.5% MCC-P3 composite** → lower amount of dispersed phase and more homogeneous distribution of particles within the PP matrix → less matrix/dispersed phase decohesion.



<https://doi.org/10.1016/j.polymdegradstab.2025.111632>



Application of phosphorylated PP/MCC composites

Main potential applications:

- **Aeronautics/aerospace:** panels, internal structures → strict fire safety requirements
- **Automotive:** dashboards, insulation, electric vehicle batteries
- **Construction:** sandwich panels, facades, building cladding
- **Textiles**
- **Packaging**



Currently – Scientific activities - Functionalization



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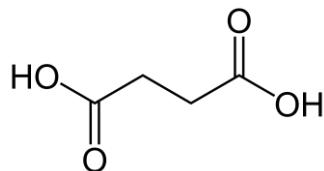
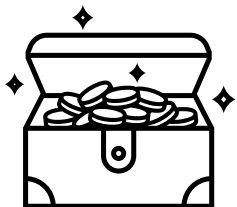
Conclusions & Perspectives

Project Targets

- ✓ Development of cellulose **functionalization processes** that are **eco-efficient**
- ✓ **Industrially viable** processes, targeting **TRL 5-6**.



batch - hydrophobisation of cellulose
(grafting of chains) → **greener process**

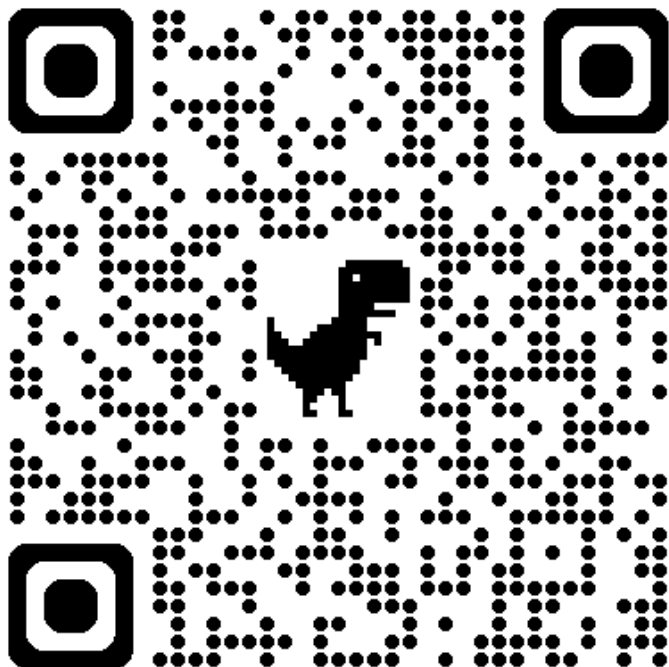


? To be continued....



Ball-milling - - fireproofing of cellulose via
phosphorylation





[Valcelmat](#)[Home](#)[Le Projet](#)[Partenaires](#)[Actualités](#)[Contact](#)

Cofinancé par
l'Union Européenne
Medegefinancierd door
de Europese Unie

France - Wallonie - Vlaanderen

VALCELMAT

Fonctionnalisation des substrats et fibres cellulosiques pour
obtention de nouveaux matériaux

Le projet ValCelMat vise à valoriser la cellulose dans de nouvelles applications (packaging, textiles et additifs pour matériaux composites). La cellulose sera modifiée chimiquement pour lui conférer de nouvelles fonctionnalités (résistance à l'humidité, au feu...) tout en conservant ses bonnes propriétés intrinsèques (absence de toxicité et biodégradation). Les modifications et la transformation ultérieure en applications finales seront réalisées à l'aide de procédés innovants et respectueux de l'environnement.

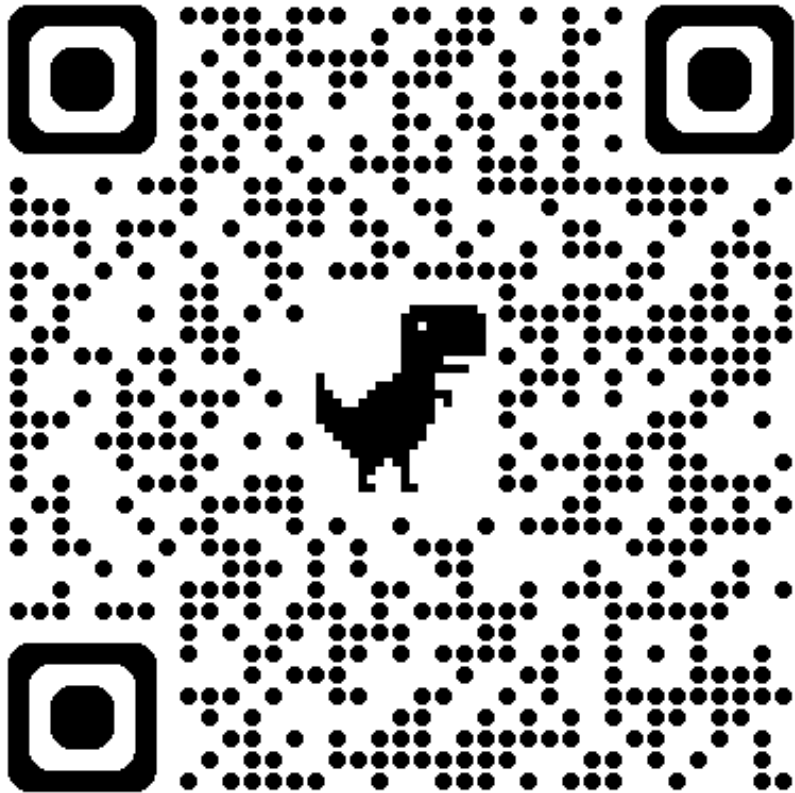
Le projet

A horizontal image showing various cellulose-based materials and fibers, including a roll of fabric, a pile of fibers, and a box of small wooden blocks.





To discover the latest developments in the project,
follow us on LinkedIn.



Internship next year



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