Interreg France-Wallonie-Vlaanderen

UNION EUROPÉENNE EUROPESE UNIE

GRASS

Université de Lille

IFATCC

Improvement of the flame retardancy of cork by phosphorylation

Application to artificial turf structures

XXV[th] IFATCC INTERNATIONAL CONGRESS
27 – 29
APRIL 2021
ENSAIT-FRANCE

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TUESDAY 27[th] APRIL 2021

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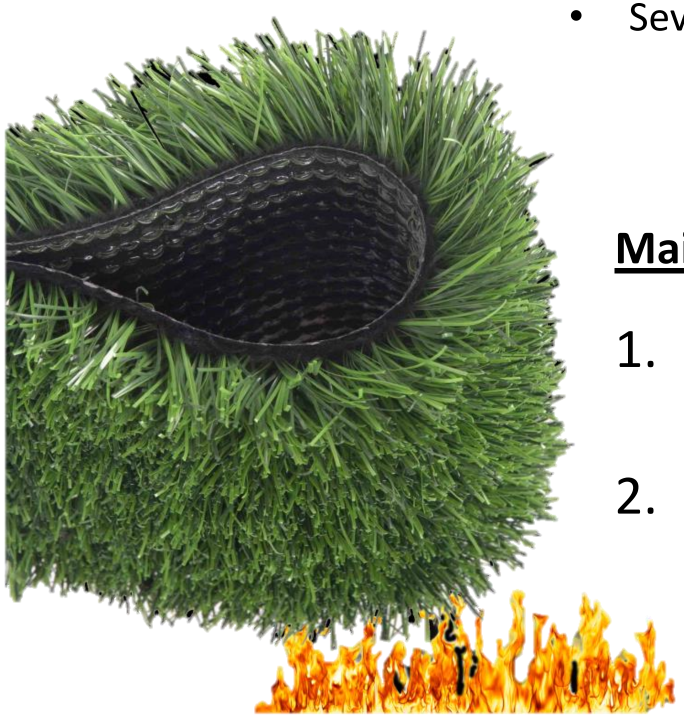
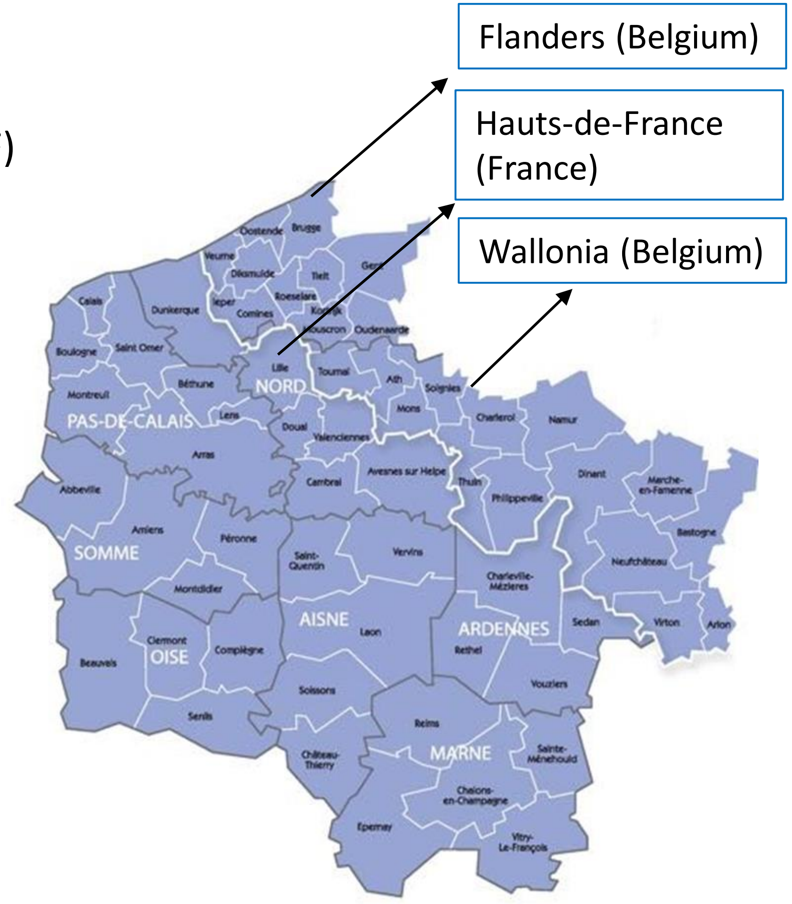
Context – GRASS Project

What is the GRASS project?

- European cross-border project France - Belgium
- Co-financed by the European Regional Development Fund (ERDF)
- 4 main partners
- Several associated partners





Main goals:

1. Increase awareness of public and stakeholders about the difference between natural and artificial grass
2. Improve the fire retardancy and eco-friendliness of artificial turf

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Context – GRASS Project

European artificial turf market: 45 million m²/year.

Sports fields

Landscaping (outdoor, balconies,…)

Indoor use (playground, event hall, …)

Advantages:

- Less maintenance
- Usable in all weather conditions
- Durability
- No need to use pesticides

Context – GRASS Project

Playground, Alaska, April 2017

Disadvantage: **High fire hazard**

Mainly composed of **organic materials**
→ Highly flammable
→ Dense smoke

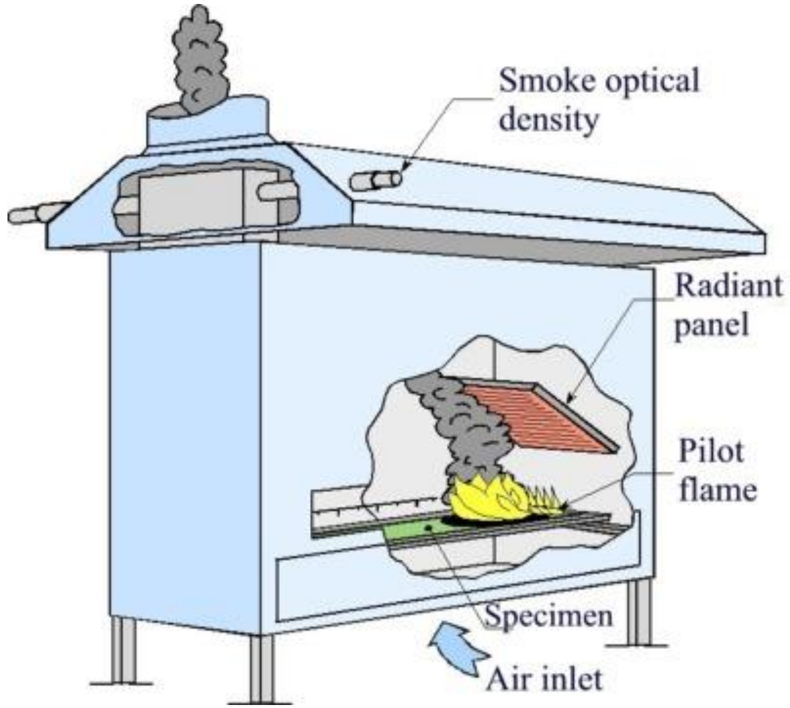
Warehouse, Marseille, October 2020

Synthetic sport turf, Westfields, March 2011

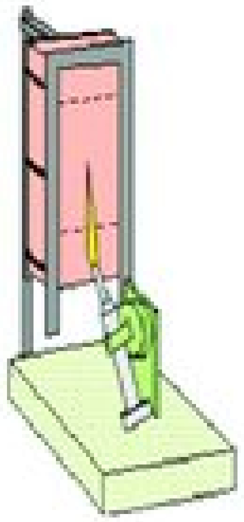
Regulations: Floorings

Evaluation of the fire behaviour of floorings:

1. ***Radiant panel test EN ISO 9239-1***



2. ***Single-flame source test EN ISO 11925-2***

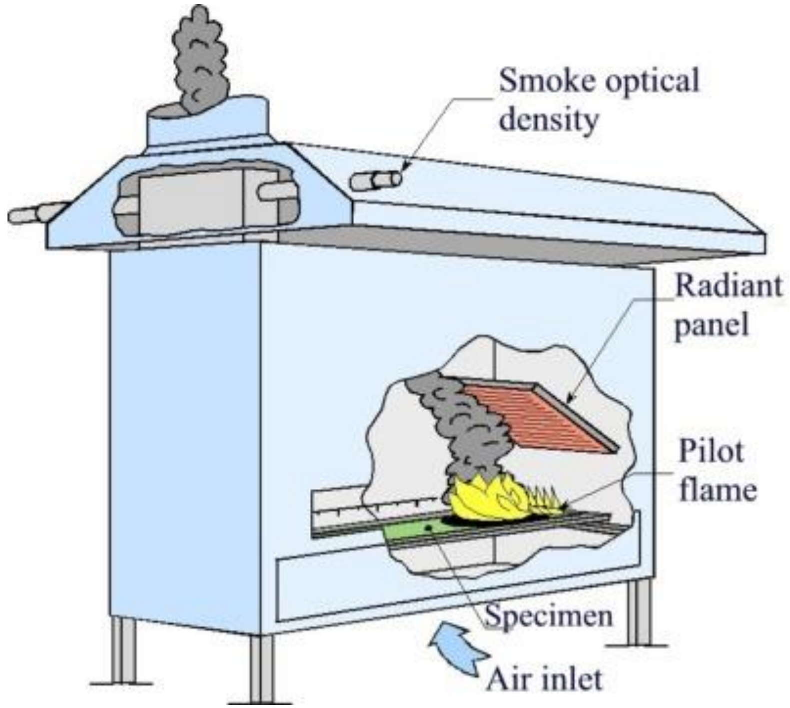


- Vertically positioned sample
- Determination of the flame height

Regulations: Floorings

Evaluation of the fire behaviour of floorings:

1. ***Radiant panel test EN ISO 9239-1***

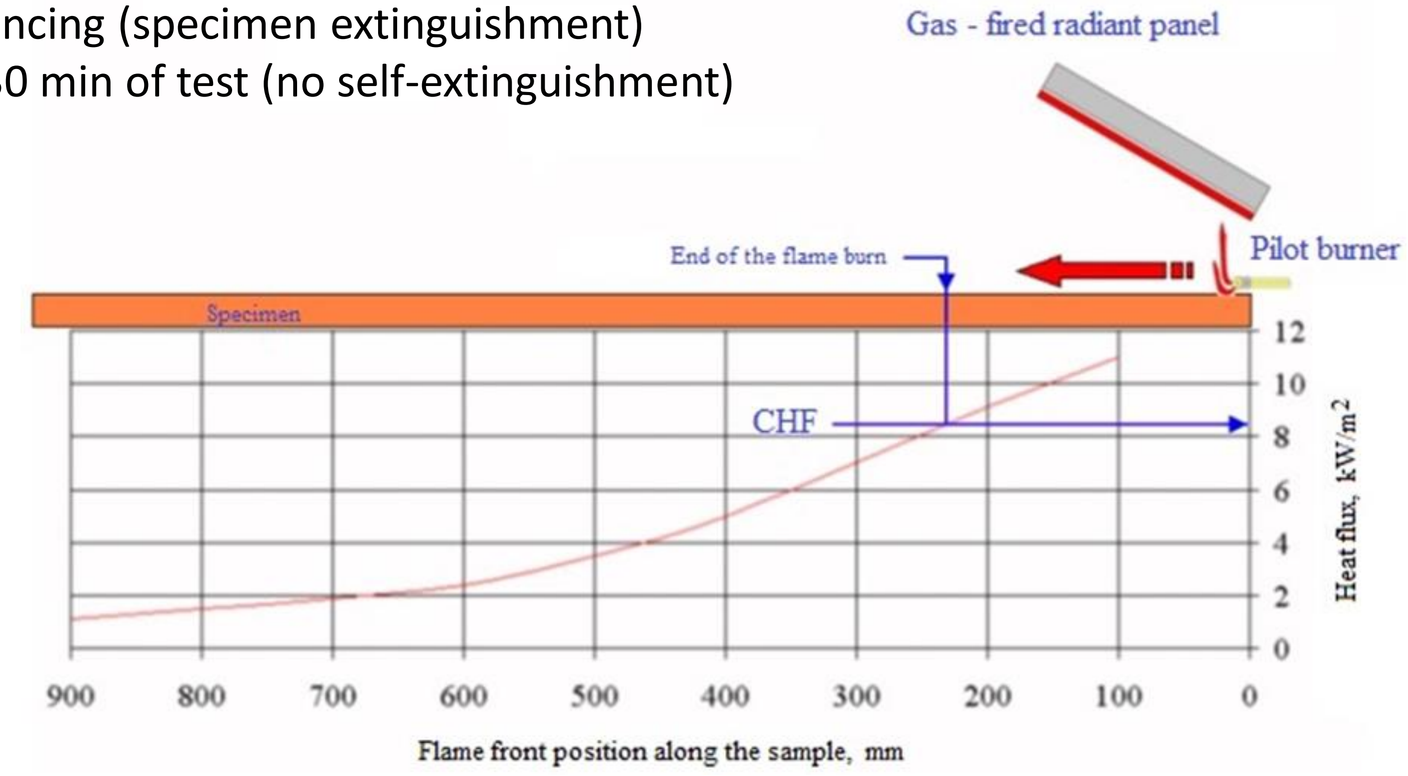


- **Energy heat flux gradient**
- **Flame propagation** (burnt length)
- Test duration: **30 min maximum**
- Specimen size : (1050 x 230) mm²
- Smoke density (additional requirement)

Regulations: Radiant panel test EN ISO 9239–1

Determination of the **critical heat flux (CHF):**

- Point where the flame stops advancing (specimen extinguishment)
- Position of the front flame after 30 min of test (no self-extinguishment)



Heat flux distribution

Classifications : EN ISO 13501 – 1

Class of reaction to fire performance for floorings:

Class	Radiant panel test *EN ISO 9239 – 1*	Single – flame source test *EN ISO 11925 – 2**	Additional requirements
B_{FL}	CHF ≥ 8 kW/m²	Fs ≤ 150 mm within 20 s	Smoke ≤ 750%.min (s1)
C_{FL}	CHF ≥ 4.5 kW/m²	Fs ≤ 150 mm within 20 s	Smoke ≤ 750%.min (s1)
D_{FL}	CHF ≥ 3 kW/m²	Fs ≤ 150 mm within 20 s	Smoke ≤ 750%.min (s1)
E_{FL}	No requirements	Fs ≤ 150 mm within 20 s	No requirements
F_{FL}		No requirements	

**Ignition time: 15 s*

Outdoor applications

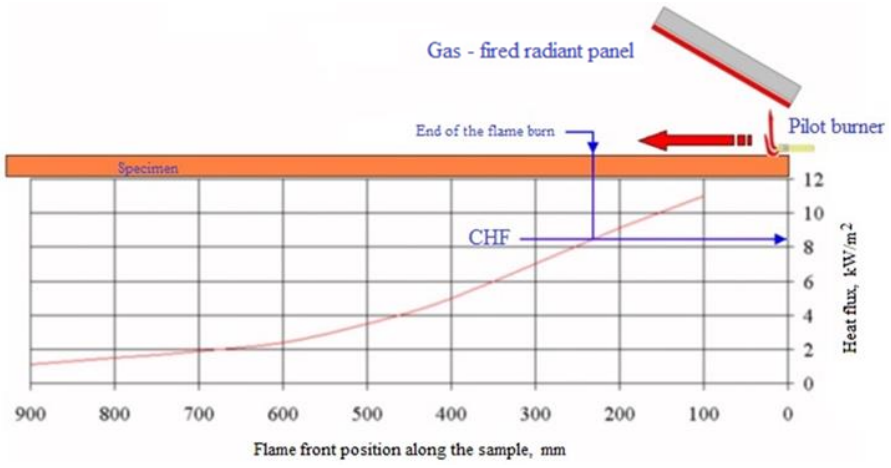
Indoor applications

<u>For indoor applications:</u>

Minimum $\mathbf{C_{FL}}$: CHF ≥ 4.5 kW/m²

→ Burnt length about 420 mm max

→ Smoke rate S1 ≤ 750 %.min



Objective

Current solutions to meet the regulation:

	Indoor / lanscaping	Sports fields
Current solution	Incorporation of sand	Use of fire retarded rubber
Reality	Almost always used without sand	Mainly rubber from recycled tyres

Objectives:

• Develop **new fire retardant solutions** taking into account the **durability** and **ecological aspect** as well as the **industrial feasibility**

•Meet the **CFL class for indoor use.**

Regulations: Radiant panel test EN ISO 9239–1

Evaluation of the fire behaviour of floorings exposed to an energy heat flux gradient

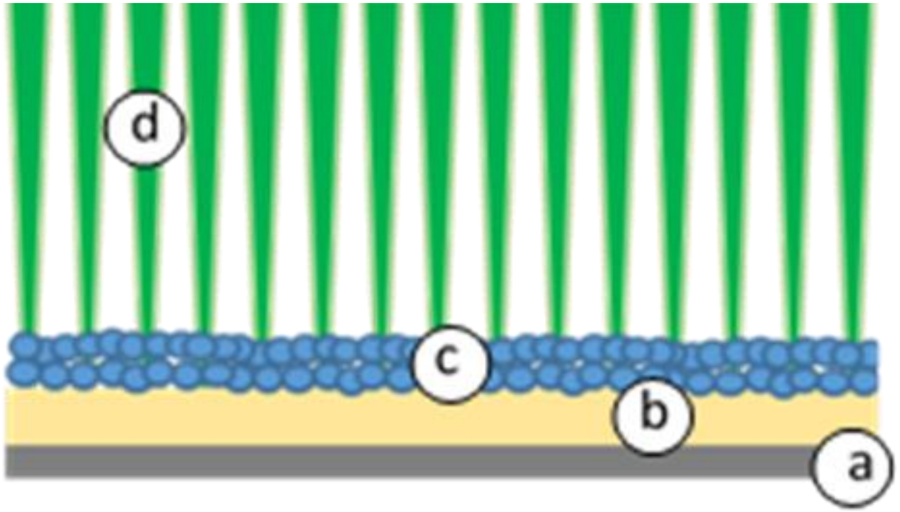
- Flame propagation (burnt length)
- Test duration: **30 min maximum**
- **Specimen size: (1050 x 230) mm²**
- Smoke density (additional requirement)

Reproduced at 1/3 scale:

- Experiment faster and cheaper
- **Smaller sample size: (350 x 77) mm²**
- **Validated** by testing reference samples on the standardised test

Lab scale radiant panel test

Artificial turf: Sports structures



Complex and multilayered material:

a : Backing (PP)

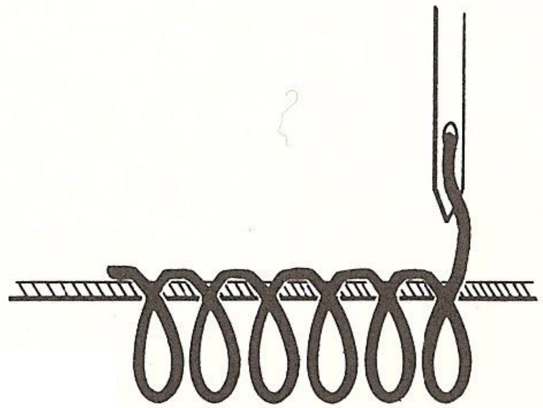
b : Sand

c : Performance layer (infill)

d : Straight pile (PE)

SBR **EPDM** **TPE** **Cork**

Designed by tufting process:



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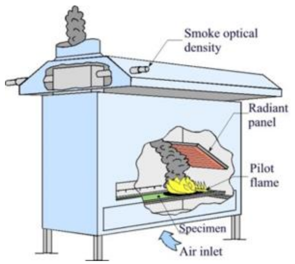
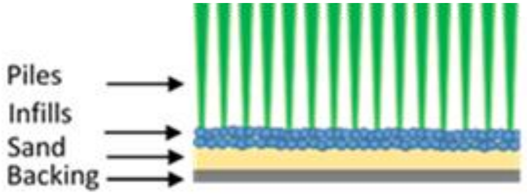
Fire behaviour: Lab – scale radiant panel test*

**at 1/3 scale*

1. Fire retardant performance of artificial grass structures



Recorded parameters	S – SBR	S – Cork	S – TPE	S – EPDM
Burnt length at extinction (%)	100	54	63	51
Burning time	27 min 05 s	13 min 22 s	30 min	15 min 38 s
CHF (kW/m²)	0.9	2.7	1.9	3.0
Ignition time (s)	0	0	8	5
Class	E_{fl} / F_{fl}	E_{fl} / F_{fl}	E_{fl} / F_{fl}	D_{fl}



Objective:

Focus on cork-based structure:
- ECHA: Ban of microplastics under debate
- Eco-designed approach

Strategy:

- **Improvement of the fire behaviour of cork to meet the fire safety regulation for indoor use.**

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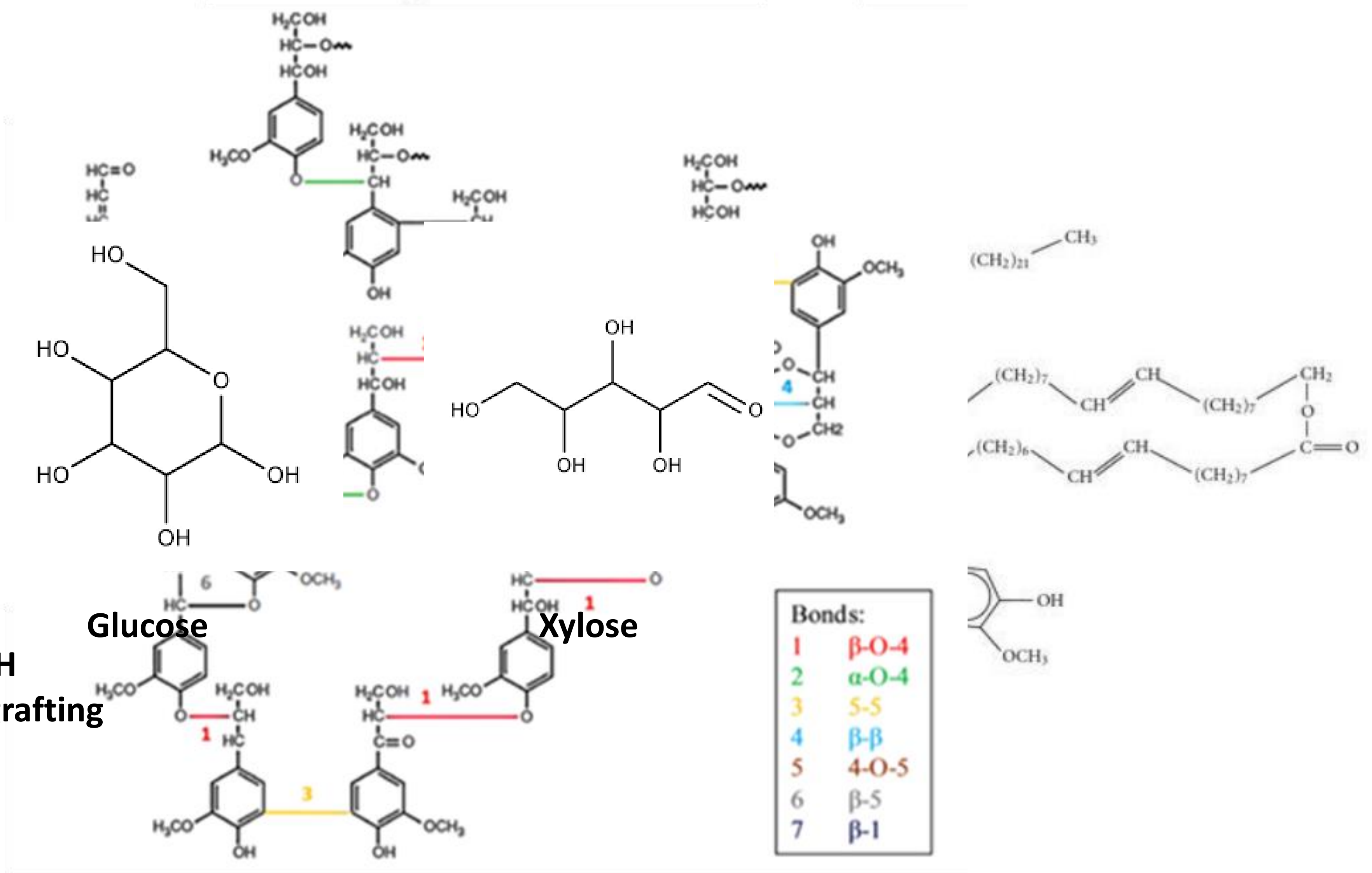
Cork modification

2. Cork modification process

Cork composition:

- Suberin: 42%
- Lignin: 22%
- **Polysaccharides: 15%**
- Extractives: 14%
- Ash: 2%

Presence of **hydroxyl groups –OH**
→Reactive groups suitable for grafting



Cork modification

Objectives:

- Enhance the fire behaviour of cork granules
- Increase the charring phenomenon of cork

Limitation:

- Avoid toxic compounds, especially halogenated flame retardants

Litterature review:

- No paper on cork flame retardancy
- Flame retardancy of lignins or cellulose

Strategy:

Impregnation

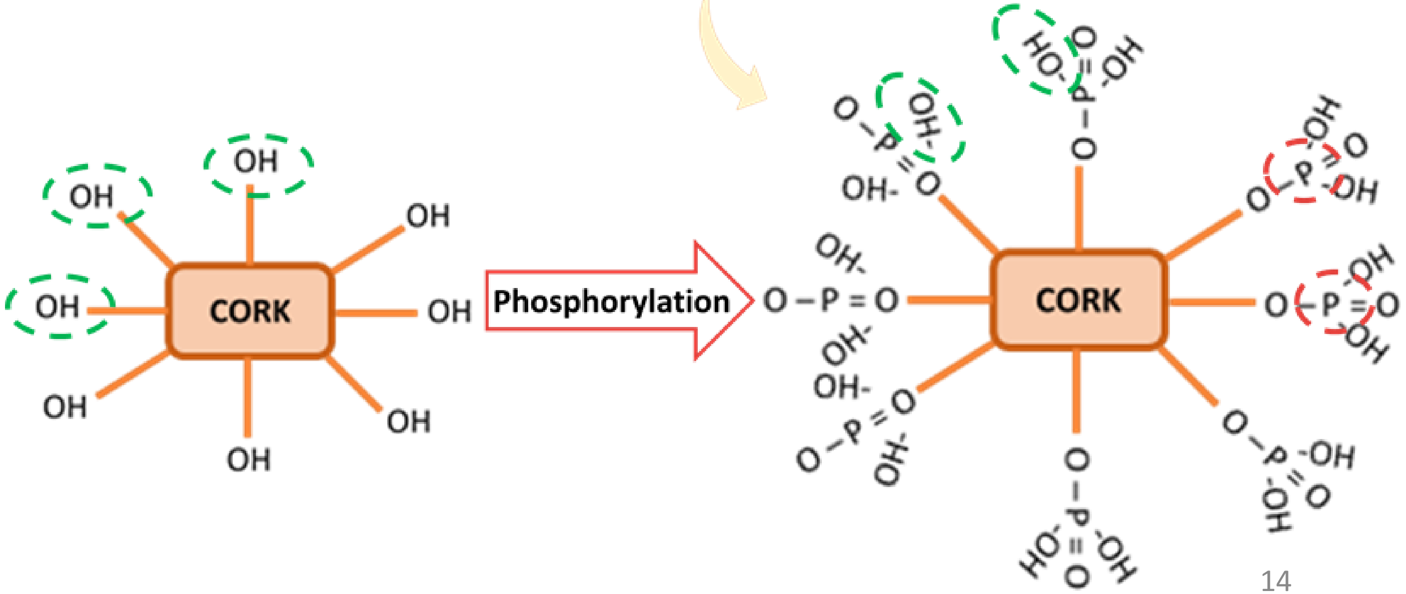
Low durability, risk of leaching, …

Grafting

Grafting phosphorus moieties onto cork

→ reactions with the **free hydroxyl groups**

P_2O_5, PCl_3, $POCl_3$, …



Cork modification: Phosphorylation

3. Cork phosphorylation protocol

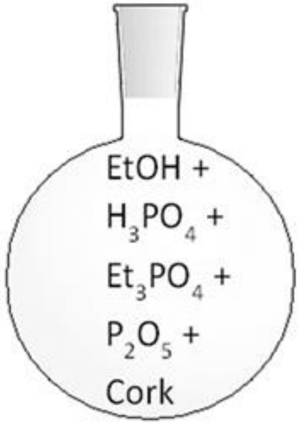
First protocol[1]:

- Tetrahydrofuran
- Phosphorus pentoxide
- Cork

Minor improvements ✗

THF  ✗

Second protocol[2]:



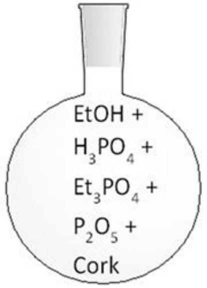
- Ethanol
- Phosphoric acid
- Triethyl phosphate
- Phosphorus pentoxide
- Cork

Significant improvements ✓

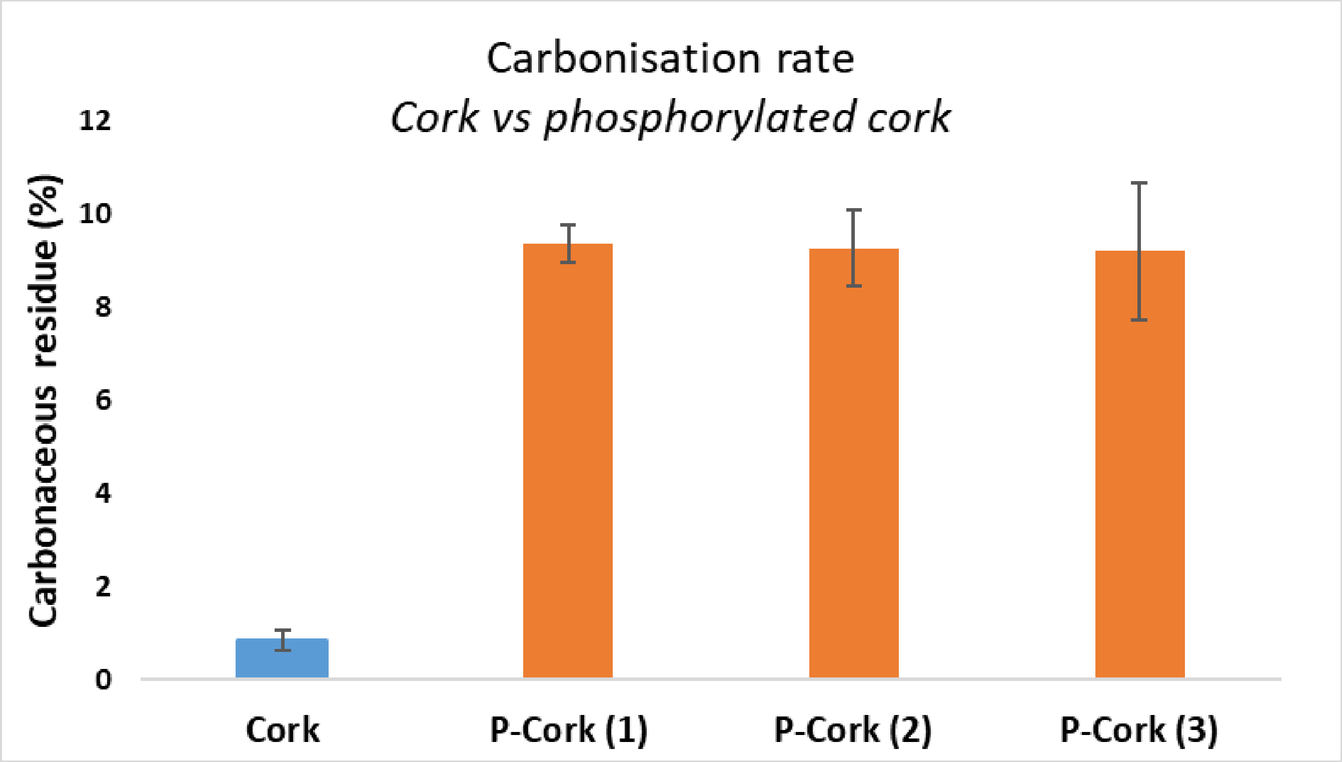
→ **3 phosphorylated corks** (P-Cork):
- **Process repeatability confirmed**

[1] B Prieur et al. "Phosphorylation of lignin: characterization and investigation of the thermal decomposition", RSC Advances, 2017.
[2] PL Granja et al. "Cellulose Phosphates as Biomaterials. I. Synthesis and Characterization of Highly Phosphorylated Cellulose Gels", Journal of Applied Polymer Science, 2001.

Cork modification: Characterizations



- **Carbonaceous residue at 600°C (Oven)**



→3 phosphorylated corks:
- P-Cork (1)
- P-Cork (2)
- P-Cork (3)

Up to +9% of carbonaceous residue
→Improvement in the amount of residue
→Significant improvement in charring phenomenon

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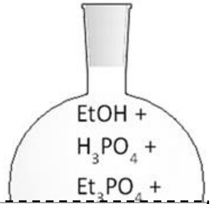
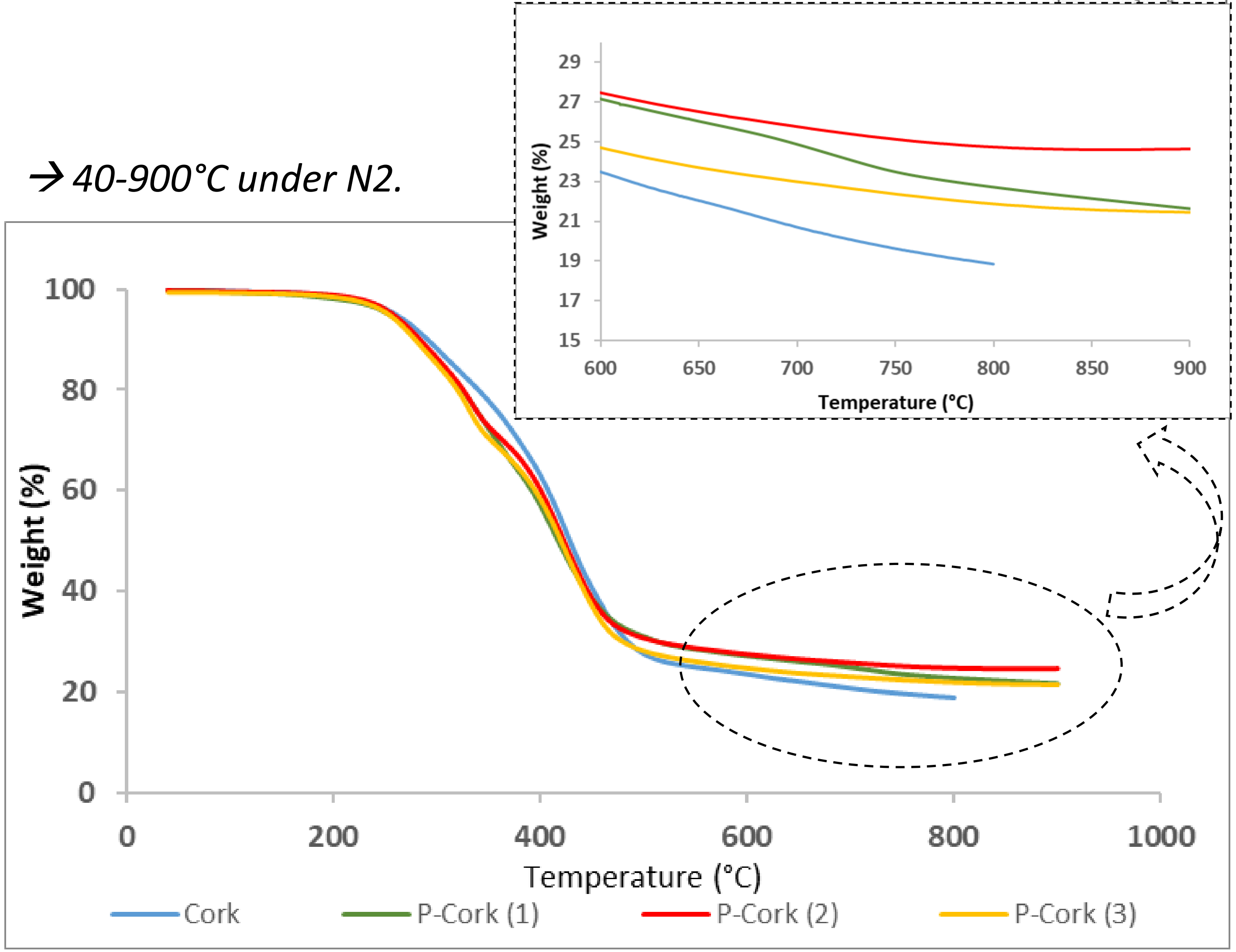
Cork modification: Characterizations



Thermogravimetric analysis (TGA):
→Thermal Stability

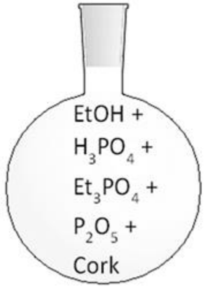
→ 40-900°C under N2.

	Carbonaceous residue (%)	
	600°C	800°C
Cork	**23.2**	**18.5**
P-Cork (1)	27.5	22.7
P-Cork (2)	**27.4**	**24.7**
P-Cork (3)	24.6	21.8



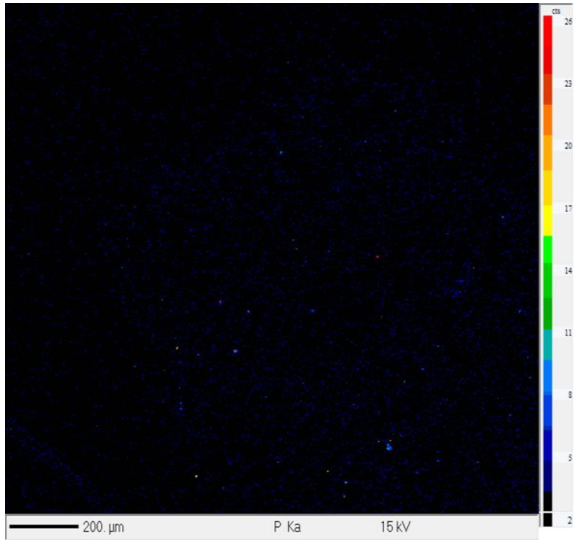
→Improvement in thermal stability

Cork modification: Characterizations

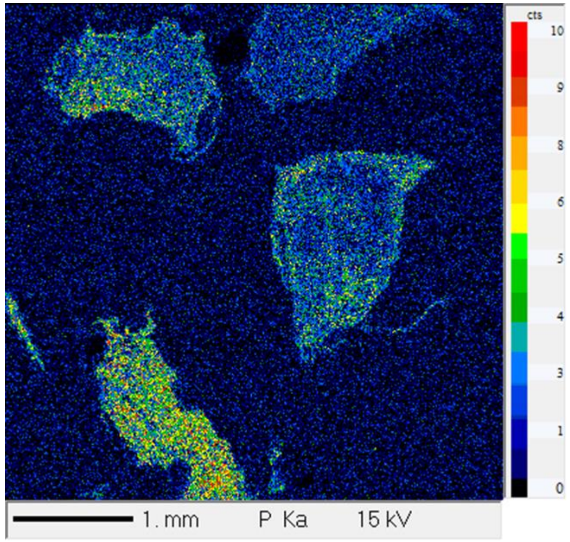


- **Electron probe micro analysis (EPMA):**

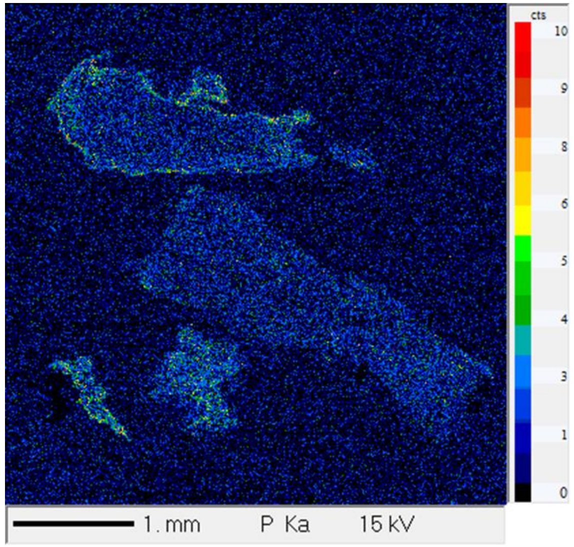
→ Phosphorus element mapping.



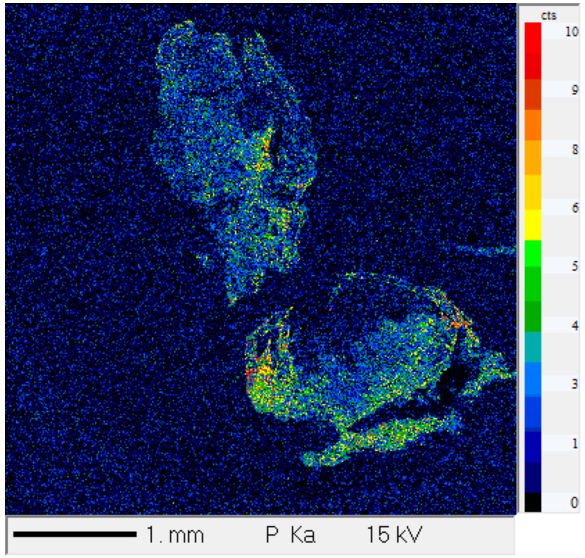
Cork



P-Cork (1)



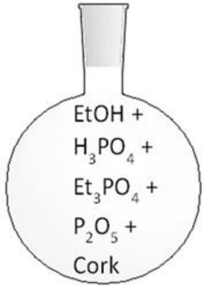
P-Cork (2)



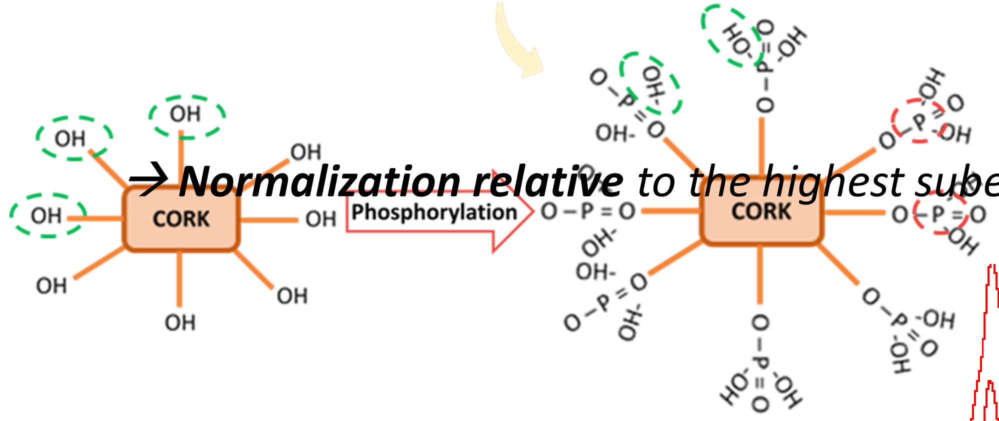
P-Cork (3)

→ Uniform thin layer grafting of phosphorus

Cork modification: Characterizations

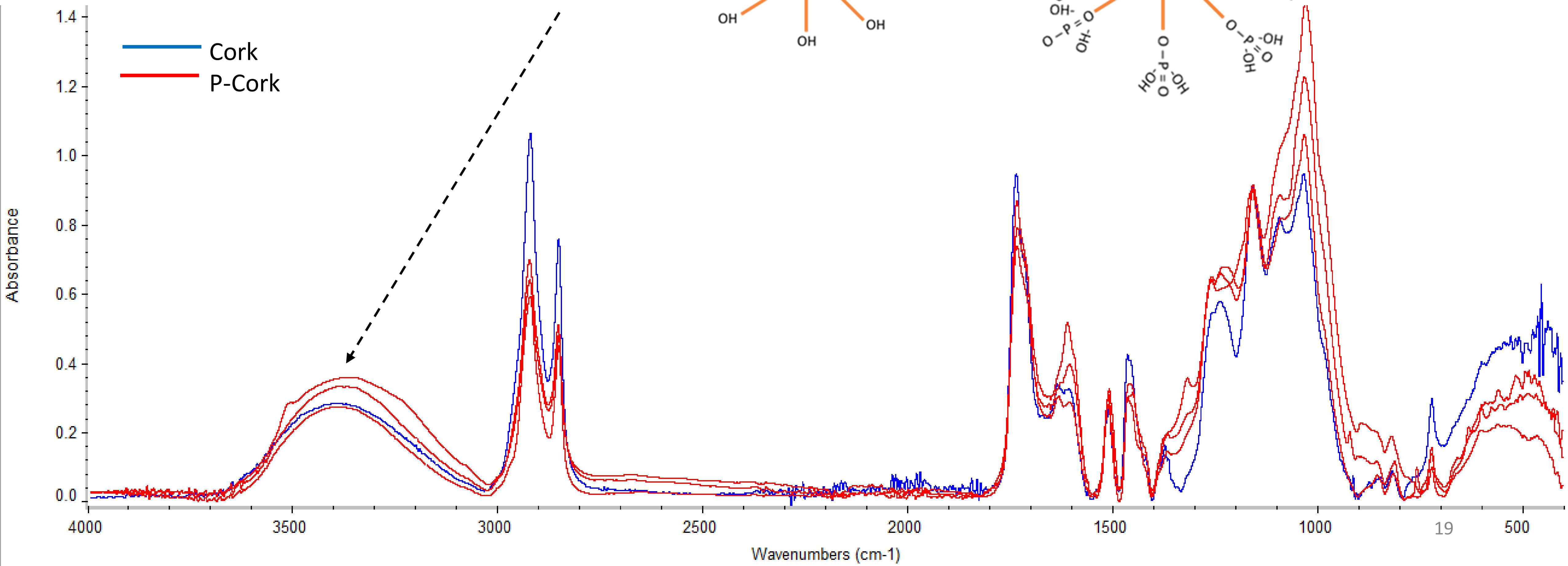


- **Infrared spectroscopy**



→ ***Normalization relative*** *to the highest suberin peak (**1160 cm^{-1}**)*

– OH à 3400 cm^{-1}



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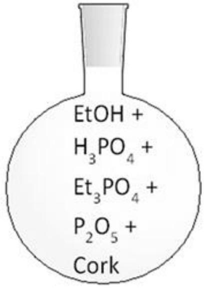
Cork modification: Characterizations

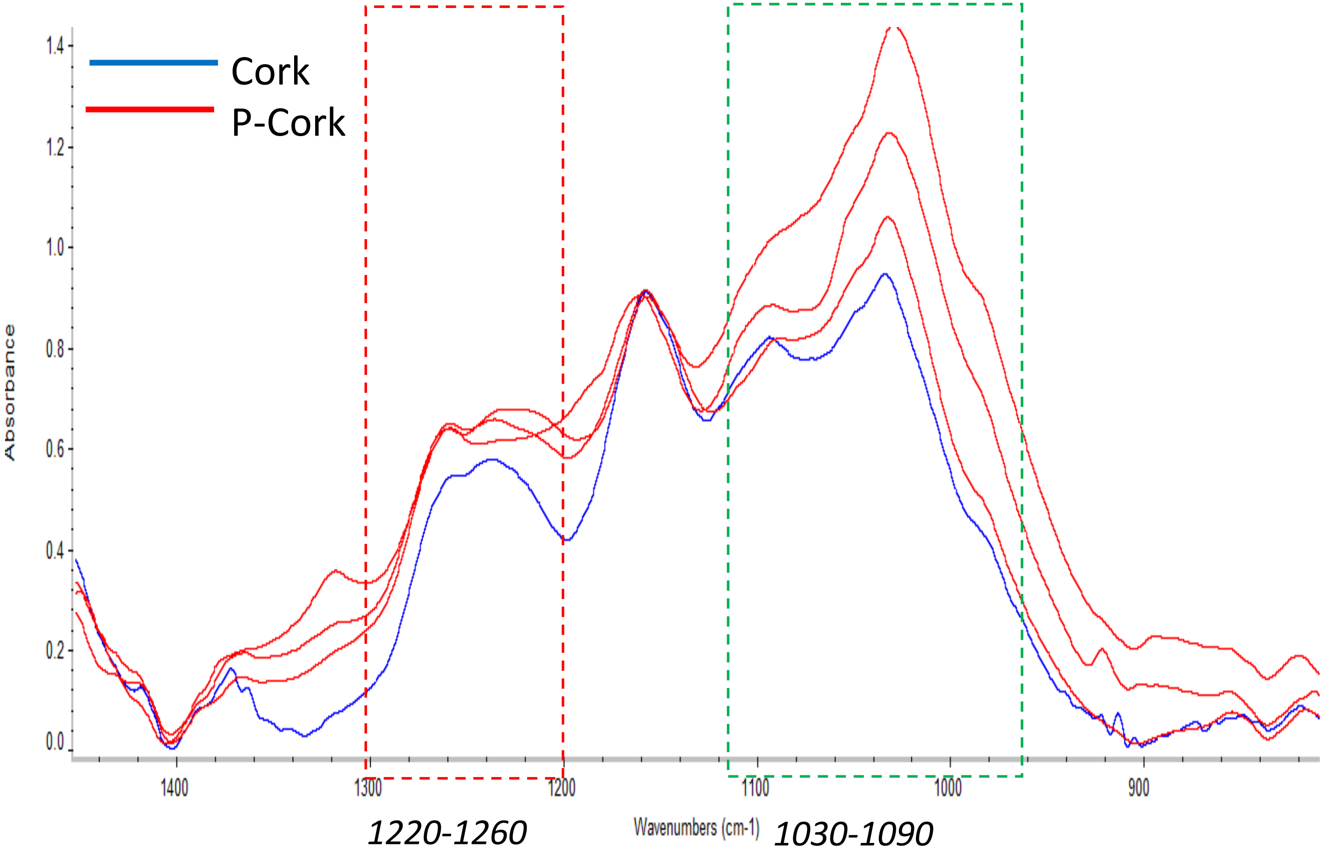


- **Infrared spectroscopy**

$\tilde{\nu}$ (cm^{-1})	Assignment	Phosphorus bonds
1220-1260	ν CO	Aromatic ethers (formed during the phosphorylation reaction)
1030-1090	ν PO-R	PO-R bonds of phosphate groups (respectively $\nu_{as}PO_4$ and ν_sPO_3)

→ Higher peak intensities for P-Cork

→ ***Normalization relative** to the highest suberin peak (**1160 cm^{-1}**)*



Cork modification: Characterizations

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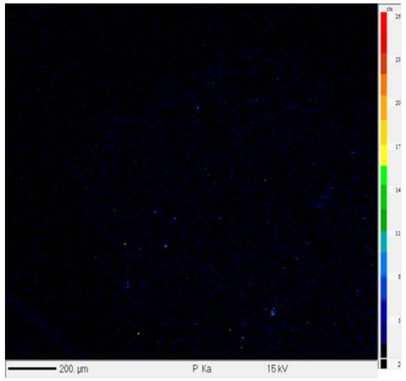
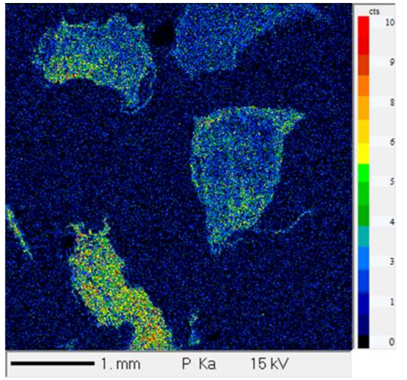
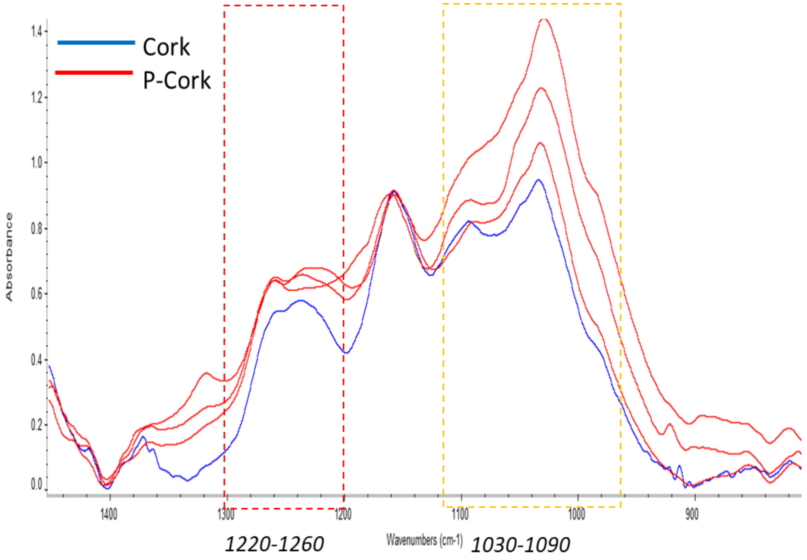
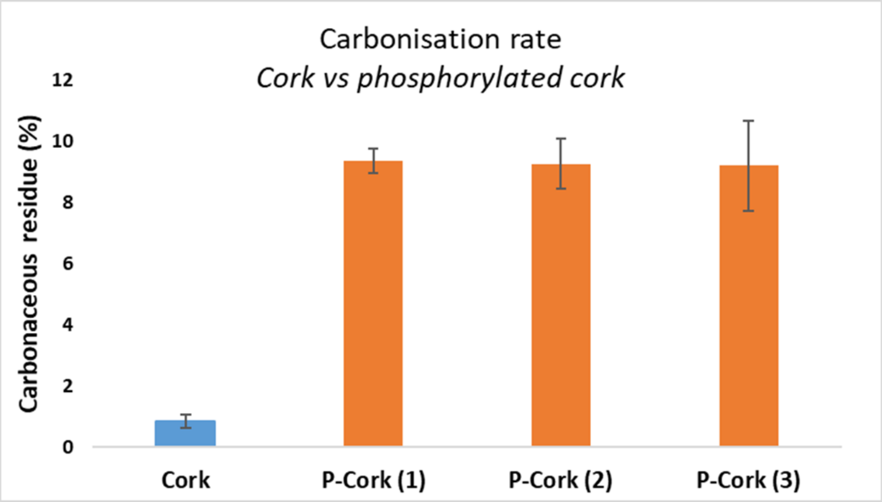
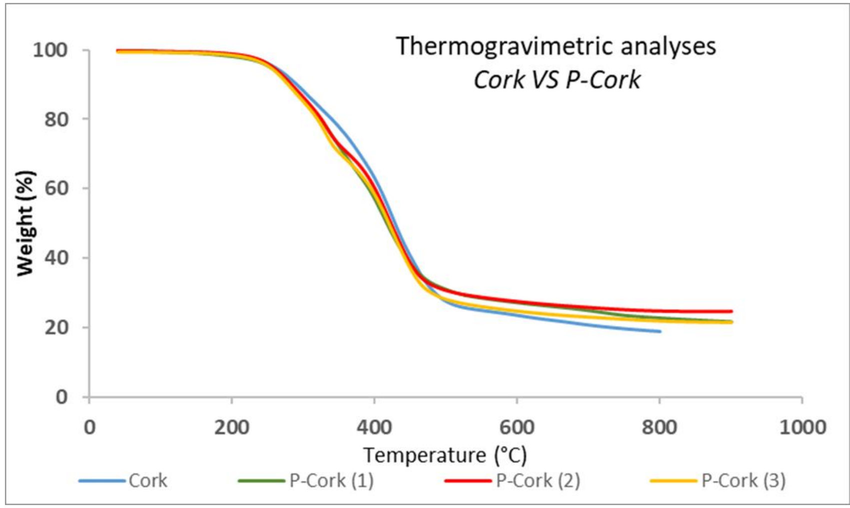
- → **Significant improvement in charring phenomenon**
- → Improvement **in thermal stability**
- → Uniform **thin layer grafting** of phosphorus
- → **Phosphorus bonds** in P-Cork





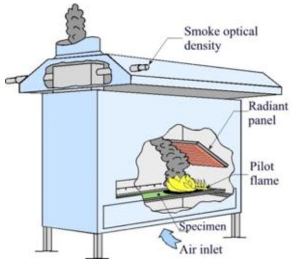






Fire behaviour: Lab – scale radiant panel test*

**at 1/3 scale*



4. Fire performance of phosphorylated cork based structure

Recorded parameters	S – Cork	S – Phosphorylated Cork
Burnt length at extinction (%)	54	**29**
Burning time	13 min 22 s	10 min 23 s
CHF (kW/m²)	2.7	7.1
Ignition time (s)	0	0
Class	E_{fl} / F_{fl}	**C_{fl}**

Indoor applications

Significant improvement in fire performance:

- Burns over a shorter distance in a shorter time
- **Meeting of CFL class** → suitable for indoor use

Observations of **residues after testing**:

- Piles/fibres melted
- **Backing preserved**

Conclusion

Context

Focus on cork-based structure:

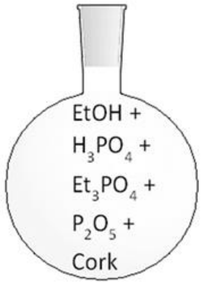
- ECHA: Ban of microplastics under debate
- Eco-designed approach

<u>Lab – scale radiant panel test:</u>

- **E_{fl} / F_{fl} class**: not suitable for indoor use.

Fireproofing strategy

- **Improvement of the fire behaviour of cork** (bulk modification) to meet the fire safety regulation for indoor use.
- Choice of a **phosphorylation** protocol + characterizations.



↗ carbonisation
↗ thermal stability
Uniform thin layer P-grafting
P-bonds in P-Cork

Results

- Improvement of fire performances.
- **Reduction in burnt length + CFL class at radiant panel test.**
- Backing preserved.

Outlook

- Further improve the fire properties of artificial turf structures by **also fireproofing the piles**.

Thank you for your attention.

Do you have any questions?

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