Improvement of the flame retardancy of cork by phosphorylation

Application to artificial turf structures

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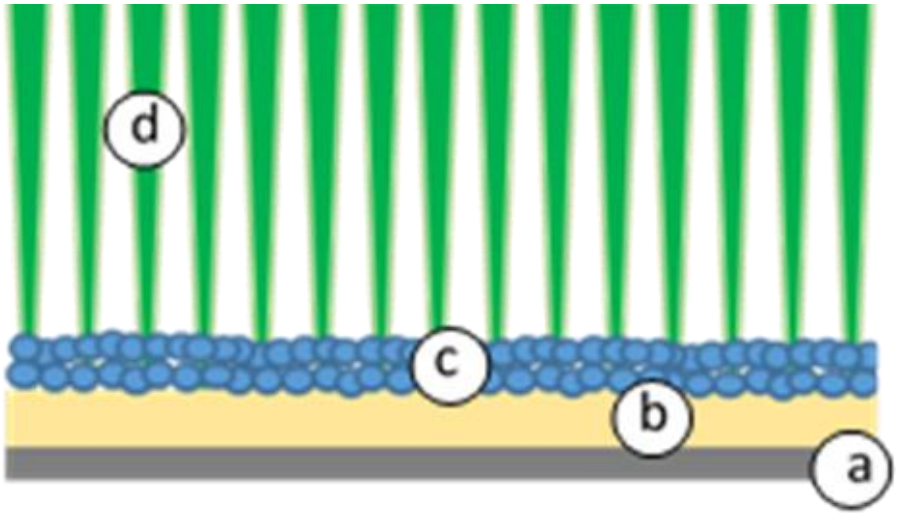
29ÈMES JOURNÉES
DU **GDR FEUX**

1st & 2nd JULY 2021

Artificial turf: Sports structures



Complex and multilayered material:

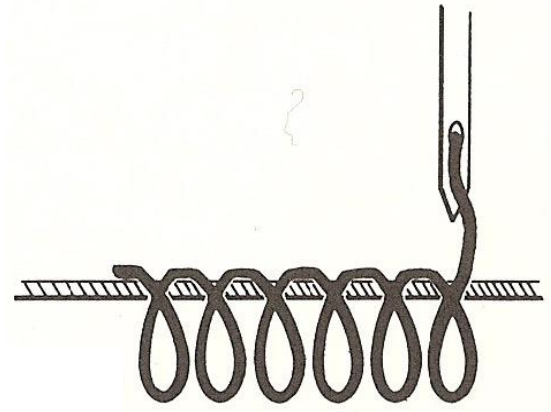
a : Backing (PP)

b : Sand

c : Performance layer (infill)

d : Straight pile (PE)

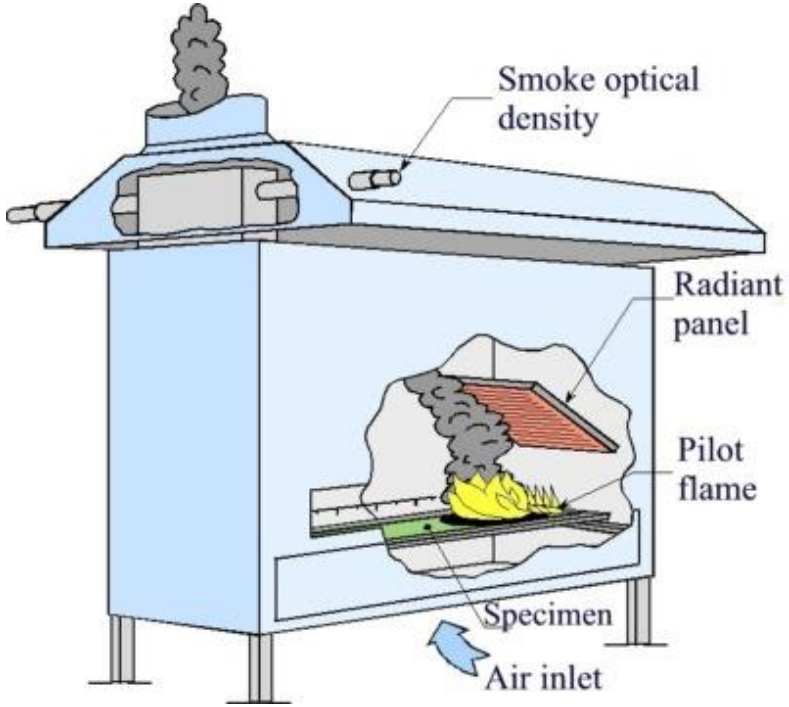
Designed by tufting process:



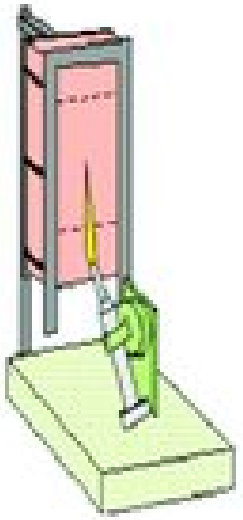
Regulations: Floorings

Evaluation of the fire behaviour of floorings:

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



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

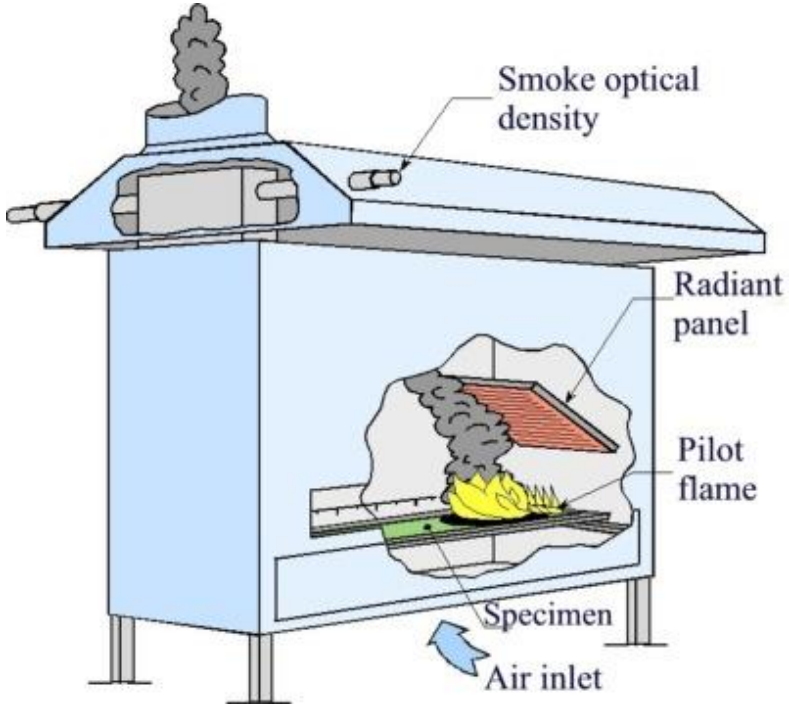


- Vertically positioned sample
- Determination of the flame height

Regulations: Floorings

Evaluation of the fire behaviour of floorings:

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

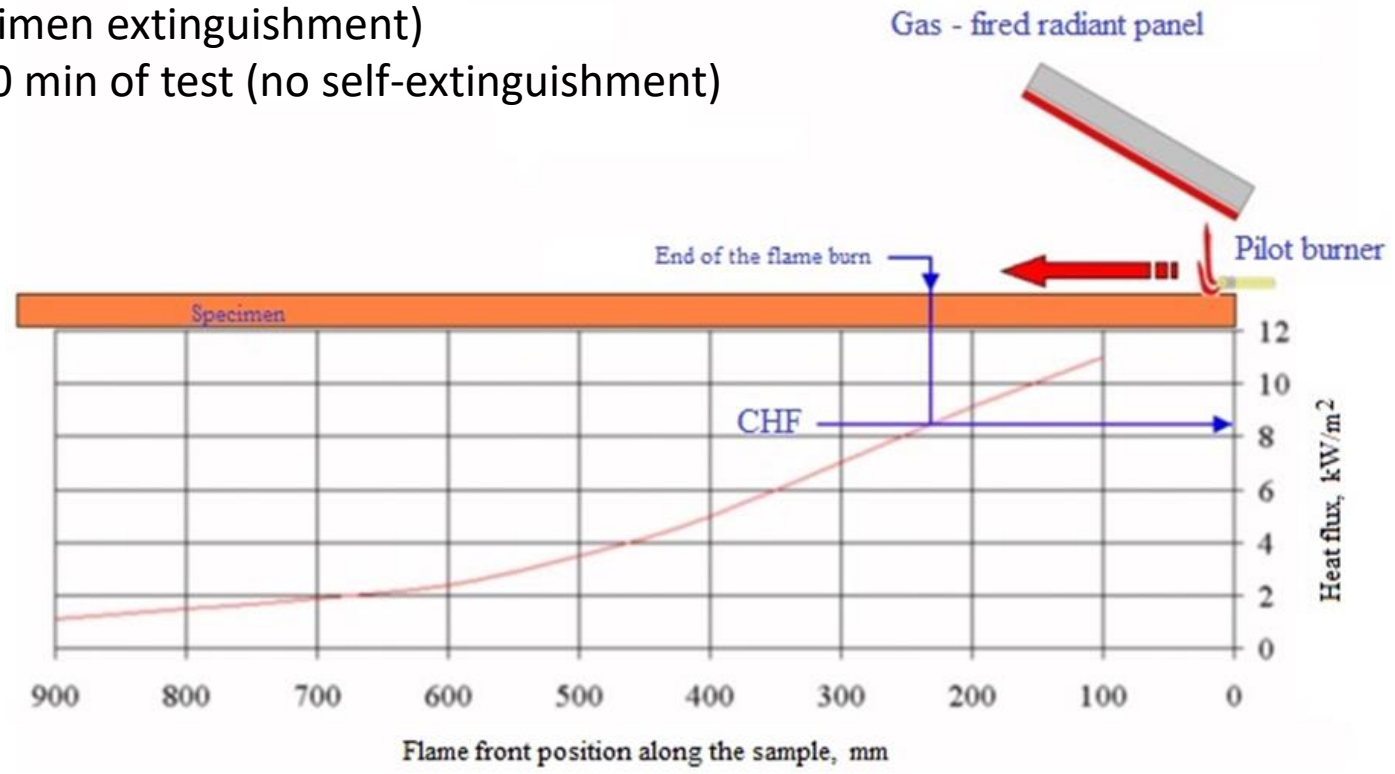


- **Energy heat flux gradient**
- **Flame propagation** (burnt length)
- Test duration: **30 min maximum**
- Specimen size : (1050 x 230) mm²
- Smoke density (additional requirement)

Regulations: Radiant panel test EN ISO 9239–1

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

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



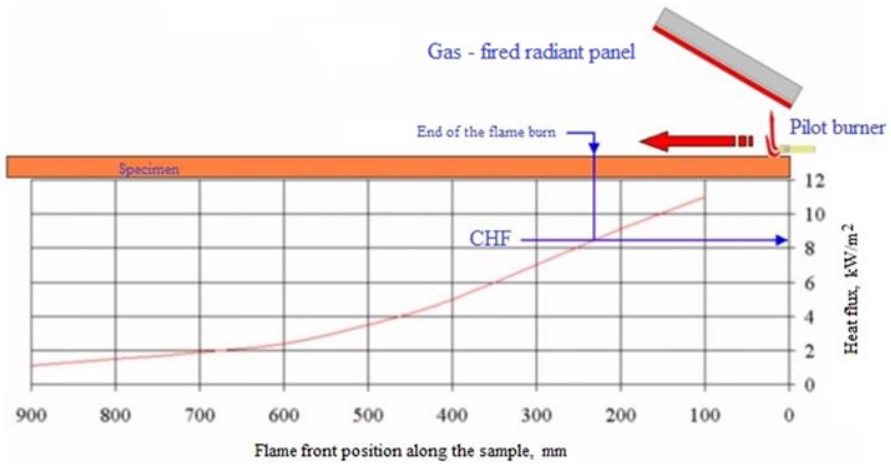
Heat flux distribution

Classifications : EN ISO 13501 – 1

Rating 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 C_{FL} : CHF ≥ 4.5 kW/m²
→ Burnt length about 420 mm max
→ Smoke rate S1 ≤ 750 %.min

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)

Lab scale radiant panel test

<u>Reproduced at **1/3 scale**:</u>

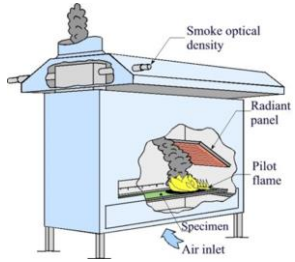
- Faster and cheaper experiment
- **Smaller sample size: (350 x 77) mm²**
- **Validated** by testing reference samples on the standardised test*

**S. Duquesne, Comportement au feu de gazons synthétiques à différentes échelles, 28èmes journées du GDR Feux 03 et 04 décembre 2020, Laboratoire Energies & Mécanique Théorique et Appliquée*

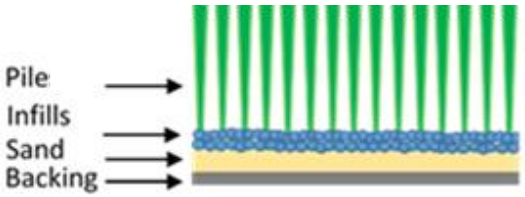
Fire behaviour: Lab – scale radiant panel test*

*at 1/3 scale

1. Fire retardant performance of artificial grass structures



Recorded parameters	S – SBR	S – Cork	S – TPE	S – EPDM	S – FR EPDM
Burnt length at extinction (%)	100	54	63	51	20
Burning time	27 min 05 s	13 min 22 s	30 min	15 min 38 s	10 min 19 s
CHF (kW/m²)	0.9	2.7	1.9	3.0	9.4
Ignition time (s)	0	0	8	5	5
Class	E_{fl}	E_{fl}	E_{fl}	D_{fl}	B_{fl}



Objective:

Focus on cork-based structure:

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

Flame retardant EPDM:

- Suitable for indoor use
- Not an environmentally friendly solution

Strategy:

Improvement of the fire behaviour of cork to meet the fire safety regulation for indoor use (C_{FL} class).

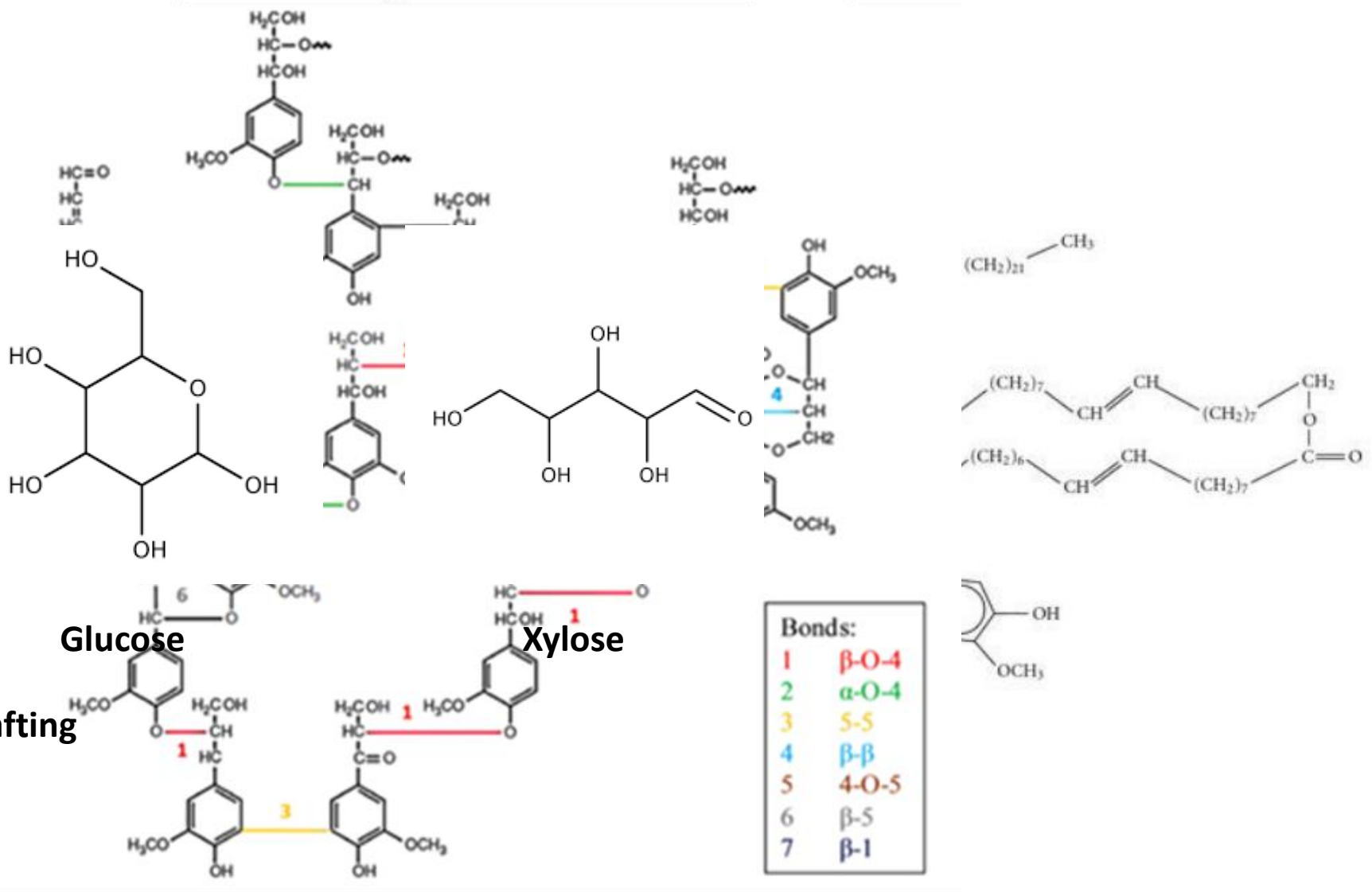
Cork modification

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 through grafting of phosphorus moities demonstrating high performance

Strategy:

Impregnation ✗

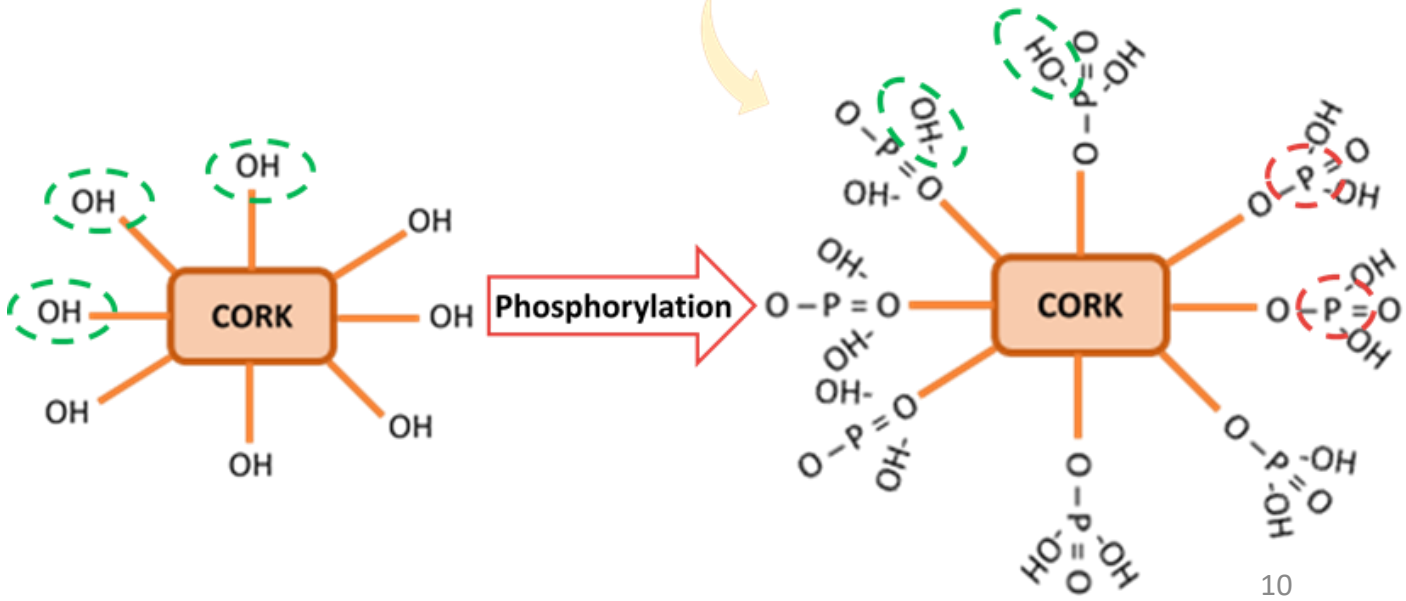
Low durability, risk of leaching, …

Grafting ✓

Grafting phosphorus moieties onto cork

→ reactions with the **free hydroxyl groups**

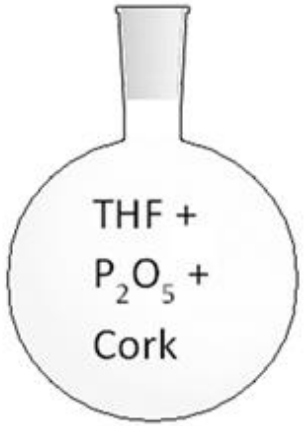
P_2O_5 , PCl_3 , $POCl_3$, …



Cork modification: Phosphorylation

3. Cork phosphorylation protocol

First protocol[1]:

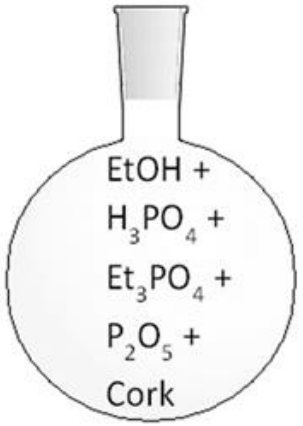


- Tetrahydrofuran
- Phosphorus pentoxide
- Cork

Minor improvements ❌

THF  ❌

Second protocol[2]:



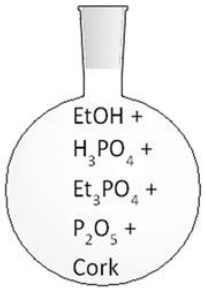
- Ethanol
- Phosphoric acid
- Triethyl phosphate
- Phosphorus pentoxide
- Cork

Significant improvements ✅

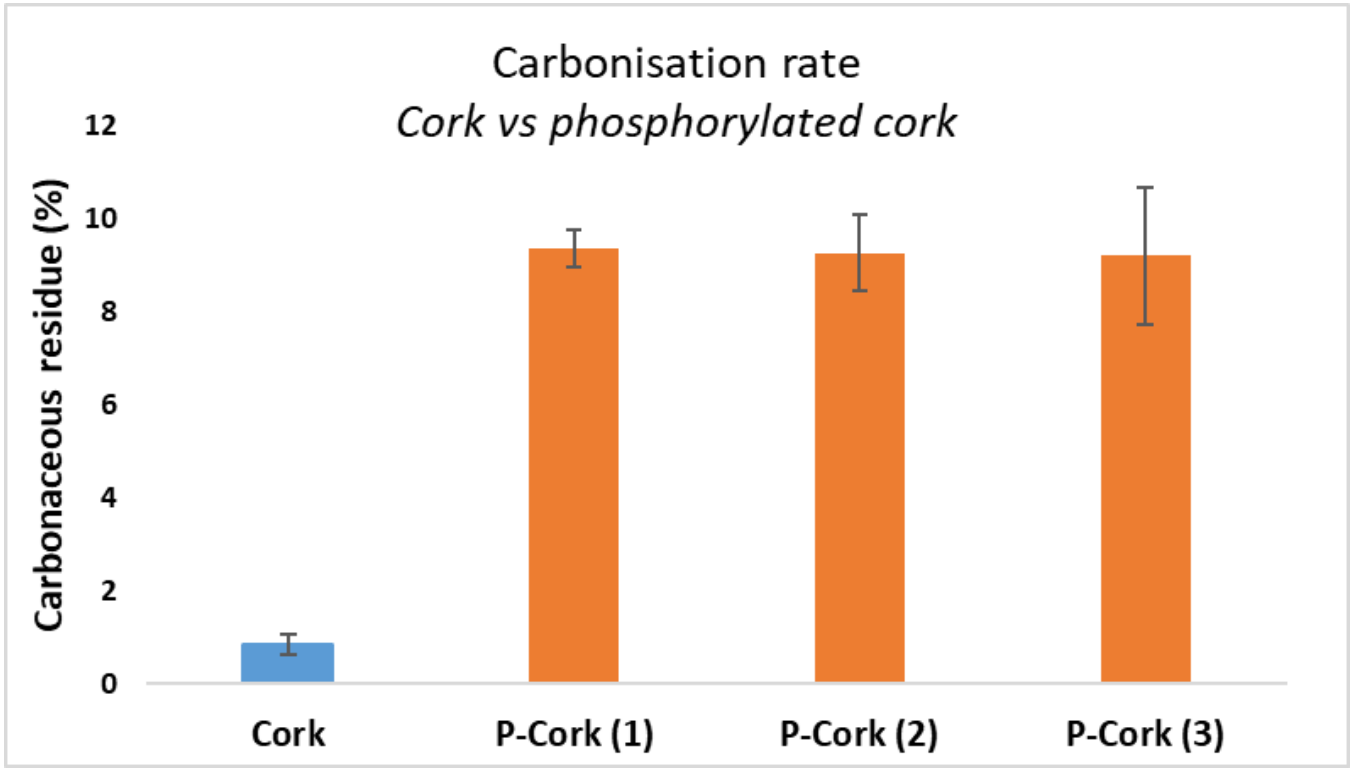
→ **3 phosphorylated corks** (P-Cork):
- **Process repeatability confirmed**

[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)**

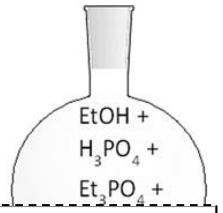


→3 phosphorylated corks:

- 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

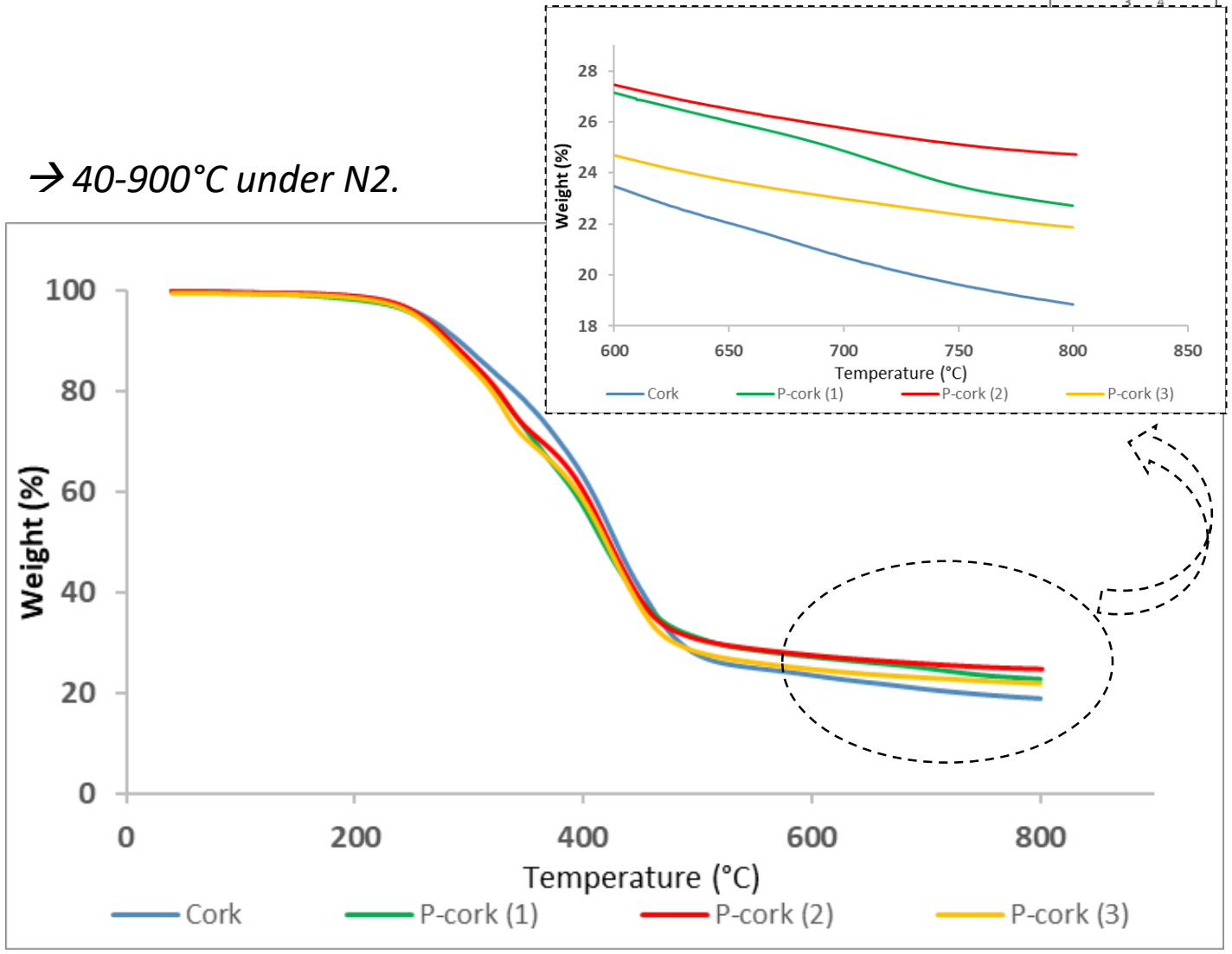
Cork modification: Characterizations



Thermogravimetric analysis (TGA):
→Thermal Stability

	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

→ *40-900°C under N2.*

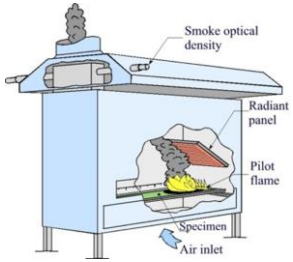


→**Improvement** in **thermal stability**
→Improvement in the **final residual mass**

Fire behaviour: Lab – scale radiant panel test*

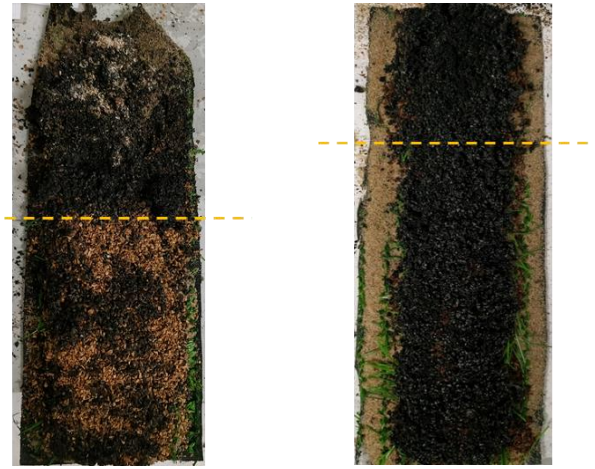
*at 1/3 scale

4. Fire performance of phosphorylated cork based structure



Indoor applications

Recorded parameters	S – Cork	S – Phosphorylated Cork
Burnt length at extinction (%)	54	**100 / 29**
Burning time	13 min 22 s	10 min 23 s
CHF (kW/m²)	2.7	0.9 / 7.1
Ignition time (s)	0	0
Class	E_{fl}	**E_{fl} / C_{fl}**



"Flame run" at the surface

Considering only the deeply degraded part:

- **Significant improvement in fire performance**
- Burns over a shorter distance in a shorter time
- **Meeting of C_{FL} class** → suitable for indoor use

Considering the whole burnt length:

- Significant improvement in charring but significant flame spread
- **No improvement in fire performance**

Conclusion

Context

Focus on cork-based structure:

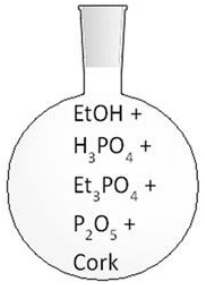
- ECHA: Ban of microplastics under debate
- Eco-designed approach

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

- **E_{fl} 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.



↗ charring
↗ thermal stability

Results

- Improvement of fire performances: **Reduction in burnt length + C_{FL} class at radiant panel test.**
- Significant flame spread.

Outlook

- Improve the phosphorylation protocol.
- Further improve fire properties of artificial turf structures by **also fireproofing the pile**.

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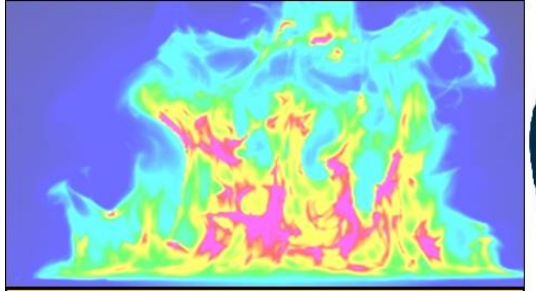

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Thank you for your attention.

Do you have any questions?

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