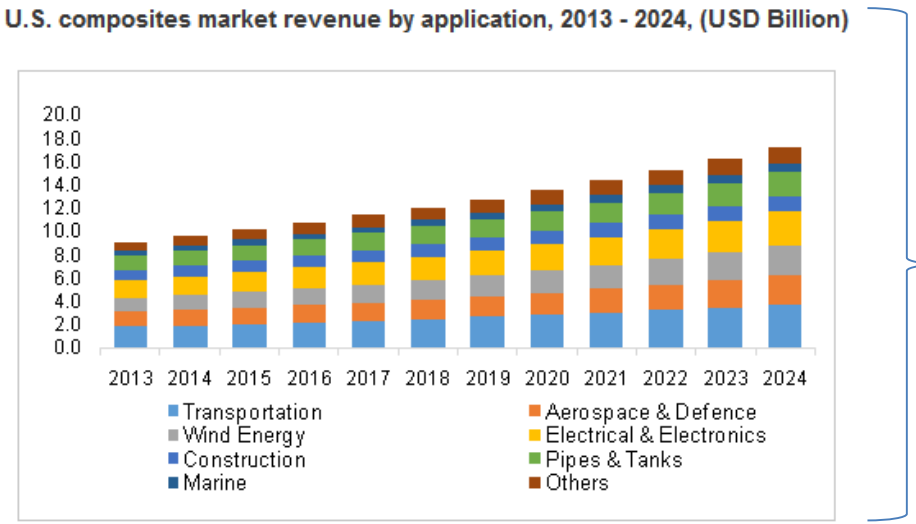
Approches innovantes d'ignifugation de bio-composites thermoplastiques

Fabienne SAMYN, Oscar GALVIS, Sophie DUQUESNE, Séverine BELLAYER

Unité Matériaux Et Transformations, UMR CNRS 8207, Ecole Nationale Supérieure de Chimie de Lille, Villeneuve d'Ascq, France
Fabienne.samyn@ensc-lille.fr

Context



http://www.grandviewresearch.com/industry-analysis/composites-market

Composites is an increasing market

Durables

High Performance

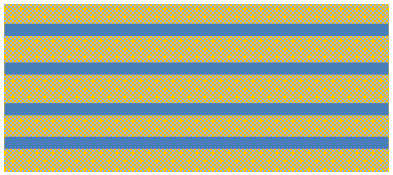
Need to be flame retarded

Context

Classical approaches to flame retard composites

- ✓ ***Modification of the resin***

  Incorporation of FR additives (loading15 to 40% FR)

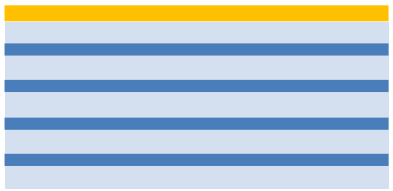


- ✓ ***Treatment on the fibres***

  *Padding of fibres with **FR solutions***

- ✓ ***Protection from the surface***

  Insulative materials like intumescent/ ceramic coatings or fabrics



Drawbacks

Not suitable for some of the processing technologies used

Modification of the interface fibres/matrix and decrease of the mechanical properties

Adhesion problems

Additional processing step

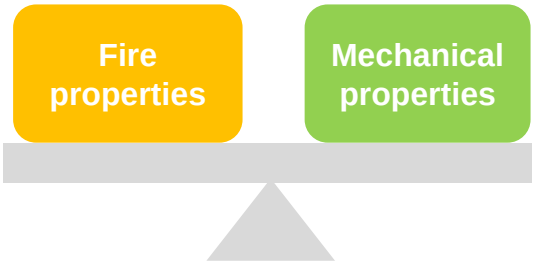
Context

How to balance FR/mechanical properties?

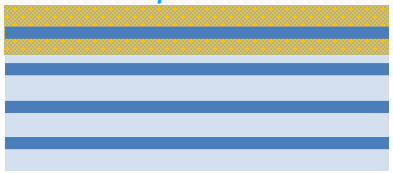
- ✓ ***Protection from the surface***
- ✓ ***Modification of the resin***
- ✓ ***Treatment on the fibres***

Localize the FR on the surface

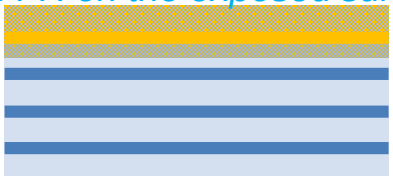
Preserve as much untreated materials as possible



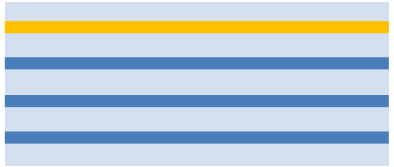
First approach: *Partial modification of the resin with FR on the exposed surface*



Second approach: *Partial modification of the resin + fibres with FR on the exposed surface*



Third approach: *Partial modification fibres with Si-N or Si-P on the exposed surface*



Focus on flame retarded thermoplastic bio-composites

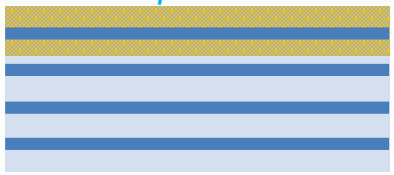
Thermoplastic matrix: PLA

Flame retardant Thermoplastic bio-composite

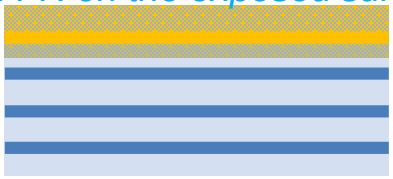
Natural Fibres: Flax

Potential carbonization agent

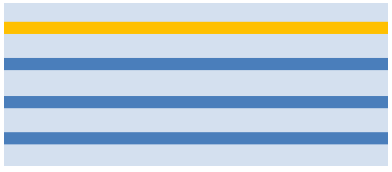
First approach: *Partial modification of the resin with FR on the exposed surface*



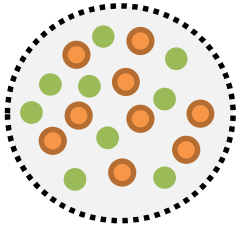
Second approach: *Partial modification of the resin + fibres with FR on the exposed surface*



Third approach: *Partial modification fibres with Si-N or Si-P on the exposed surface*



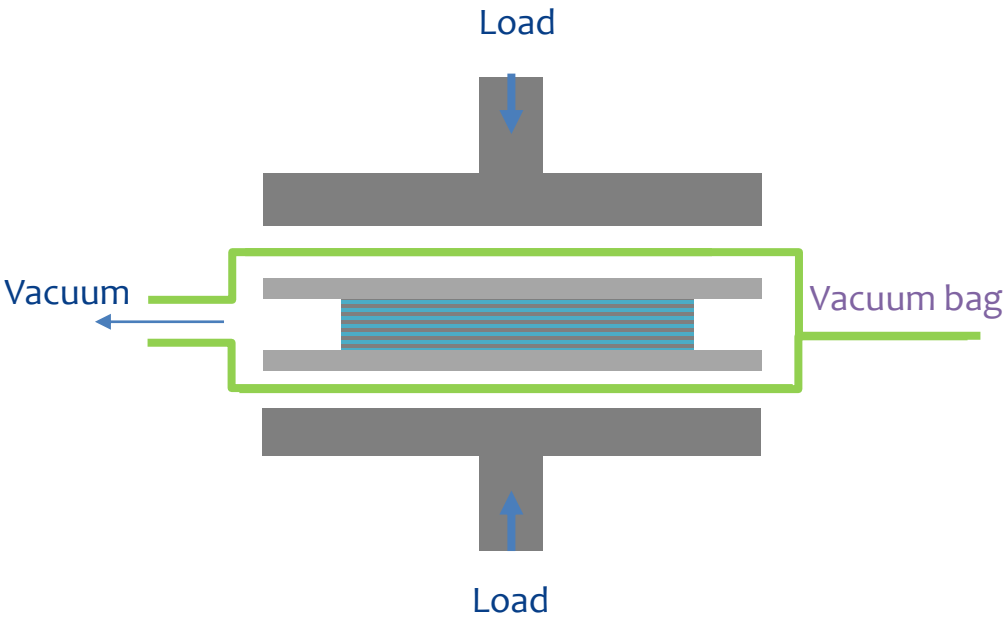
3plis
Use of PLA films + Flax fabrics
Additive approaches



50% wt. PLA / 50% wt. Flax

4plis
Use of comingled fabric
Reactive approach

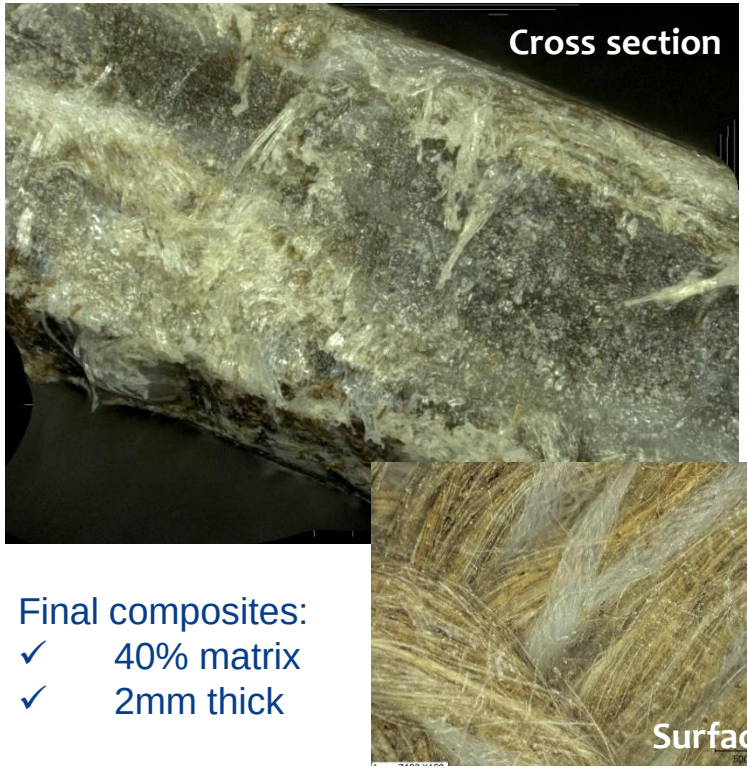
Consolidation = vacuum bagging



Optimized conditions for the impregnation:

- ✓ Temperature: 175 to 190°C
- ✓ Pressure: 40KN
- ✓ Time: 6min

Example of optical microscopy pictures of the laminate

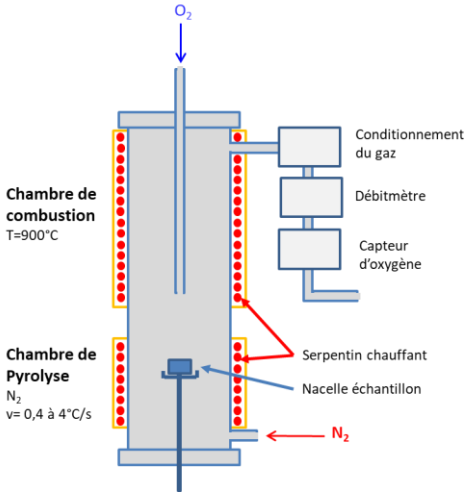


Final composites:

- ✓ 40% matrix
- ✓ 2mm thick

Characterizations

Pyrolysis-Combustion Flow Calorimetry (PCFC)



Sample: ~5mg fibres
Flux: 35kW/m²

Evaluation of the composites in terms of:
- ✓ HRR versus temperature
- ✓ THR

Mass loss cone calorimeter

Sample 10x10cm² ;

Flux: 35kW/m²

Evaluation of the composites in terms of:
- ✓ HRR versus time
- ✓ Mass loss versus time
- ✓ Time to ignition
- ✓ THR

Deposit / fibres characterizations

^{29}Si NMR: level of condensation of Si
ATR- FTIR: evolution of the group present on fibres
GPC: molar weight evolution

Uniaxial tensile test (composite)

Sample 12x2cm²

Evaluation of the composites in terms of:
- ✓ Maximal stress
- ✓ Maximal force
- ✓ Strain at break
- ✓ Young modulus

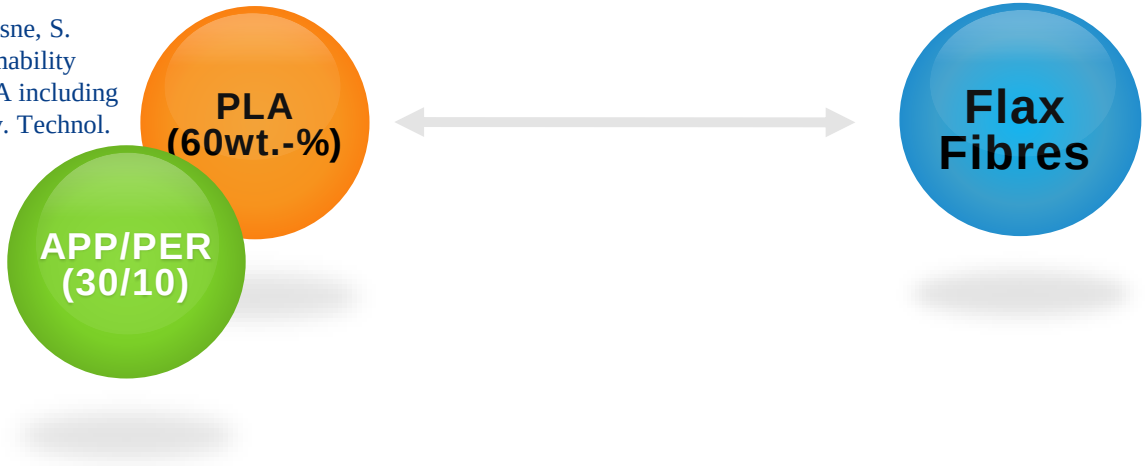
Microscopy

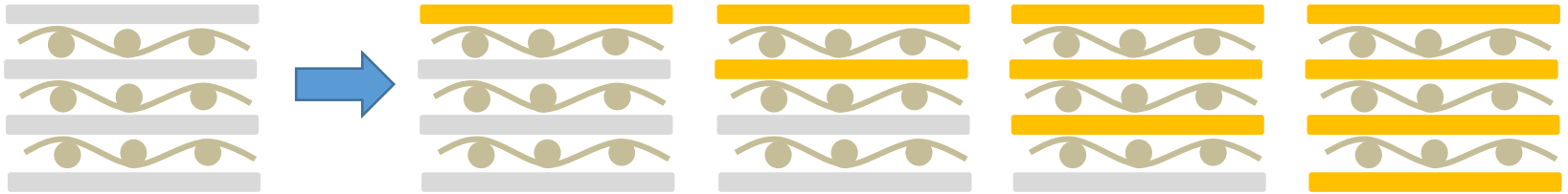
Digital microscope: Keyence VHX-1000 microscope: observation of the samples after cone experiments

SEM: HITACHI S-3400N microscope in which a voltage of 10 kV was applied to the metalized samples

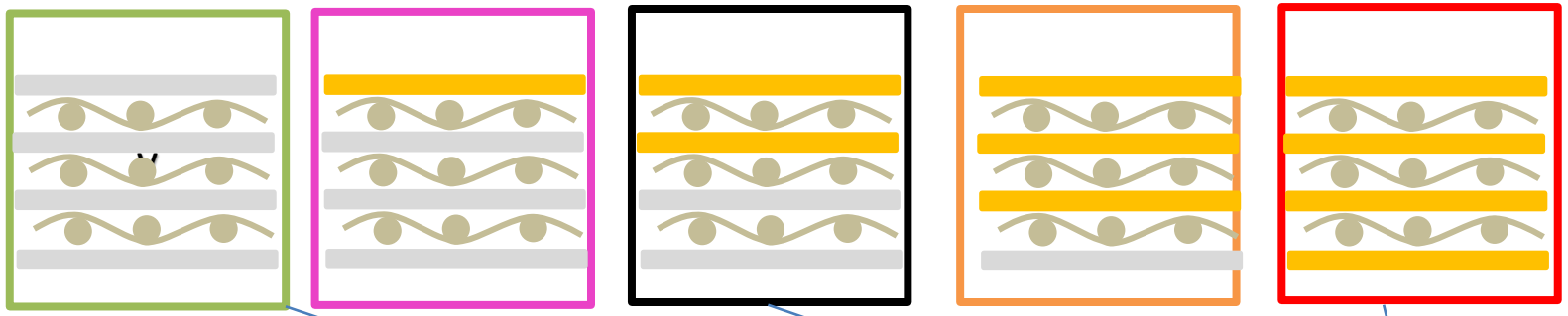
1st approach

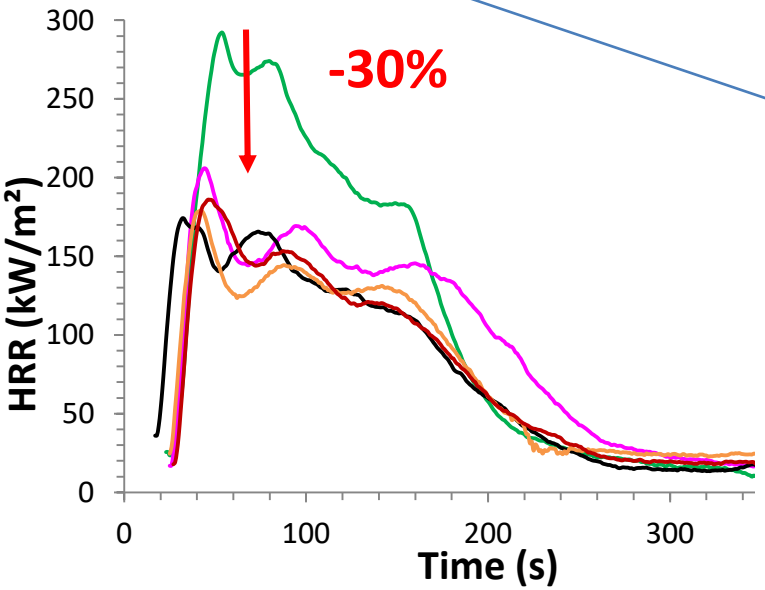
C. Réti, M. Casetta, S. Duquesne, S. Bourbigot, R. Delobel, Flammability properties of intumescent PLA including starch and lignin, Polym. Adv. Technol. 2008; 19: 628–635

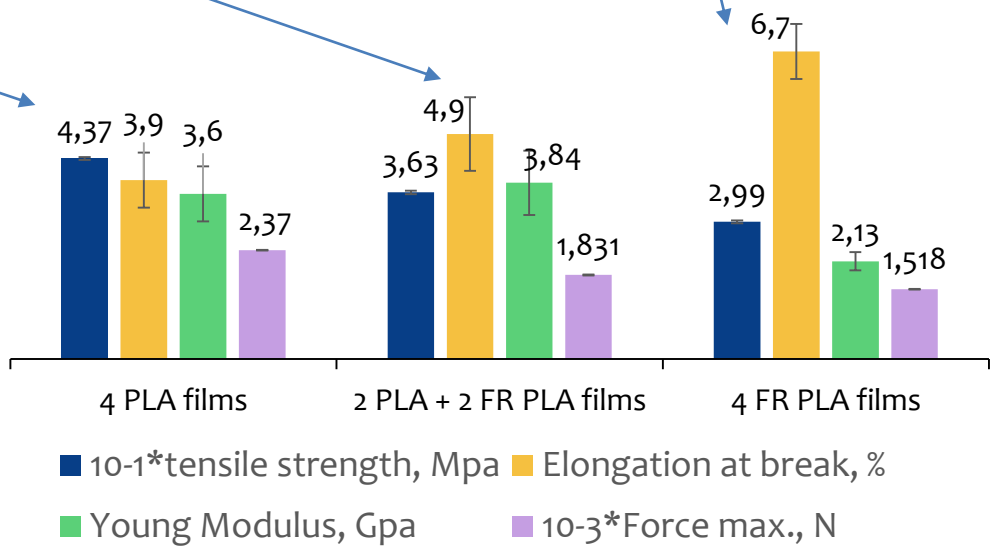




Performances according to the number of FR films used

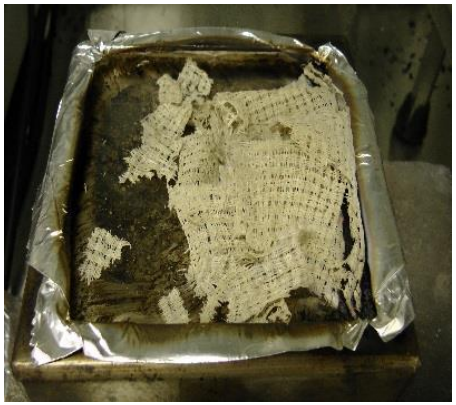


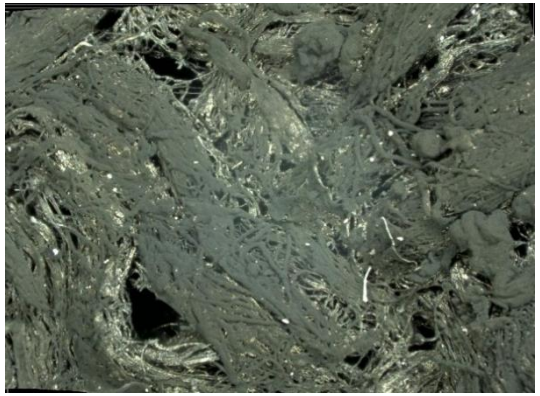




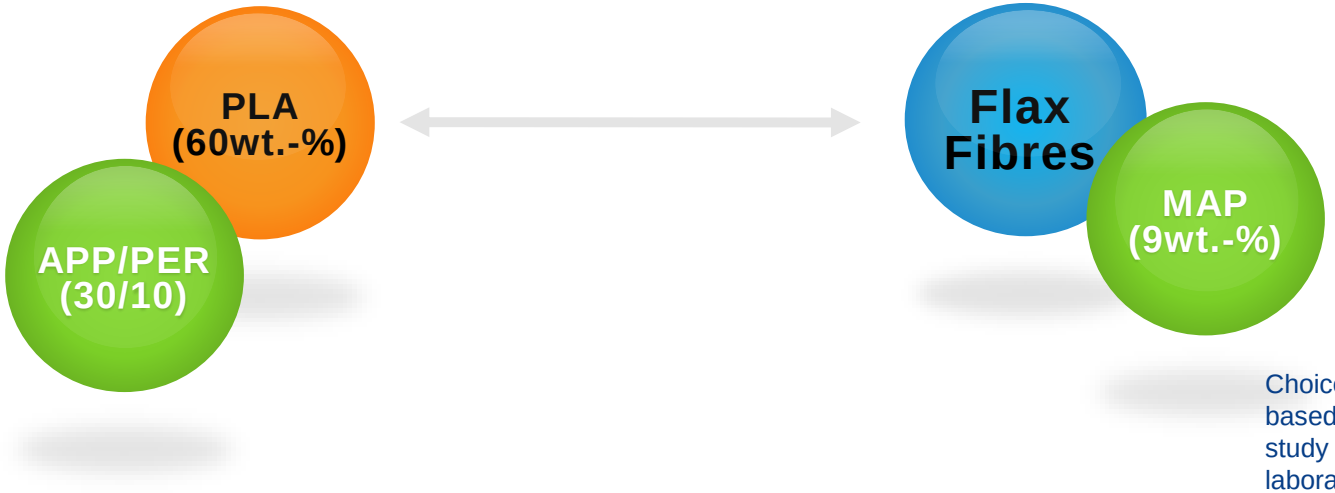
Before MLC

After cone calorimeter experiment

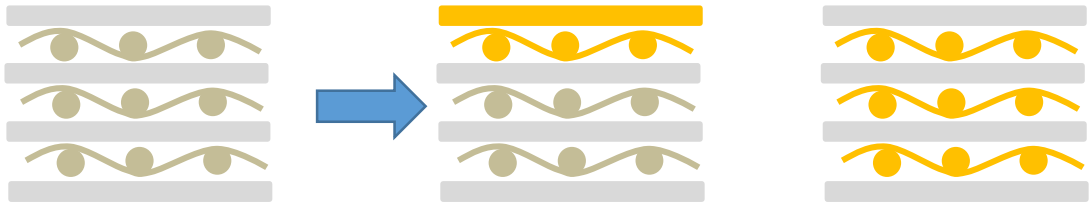




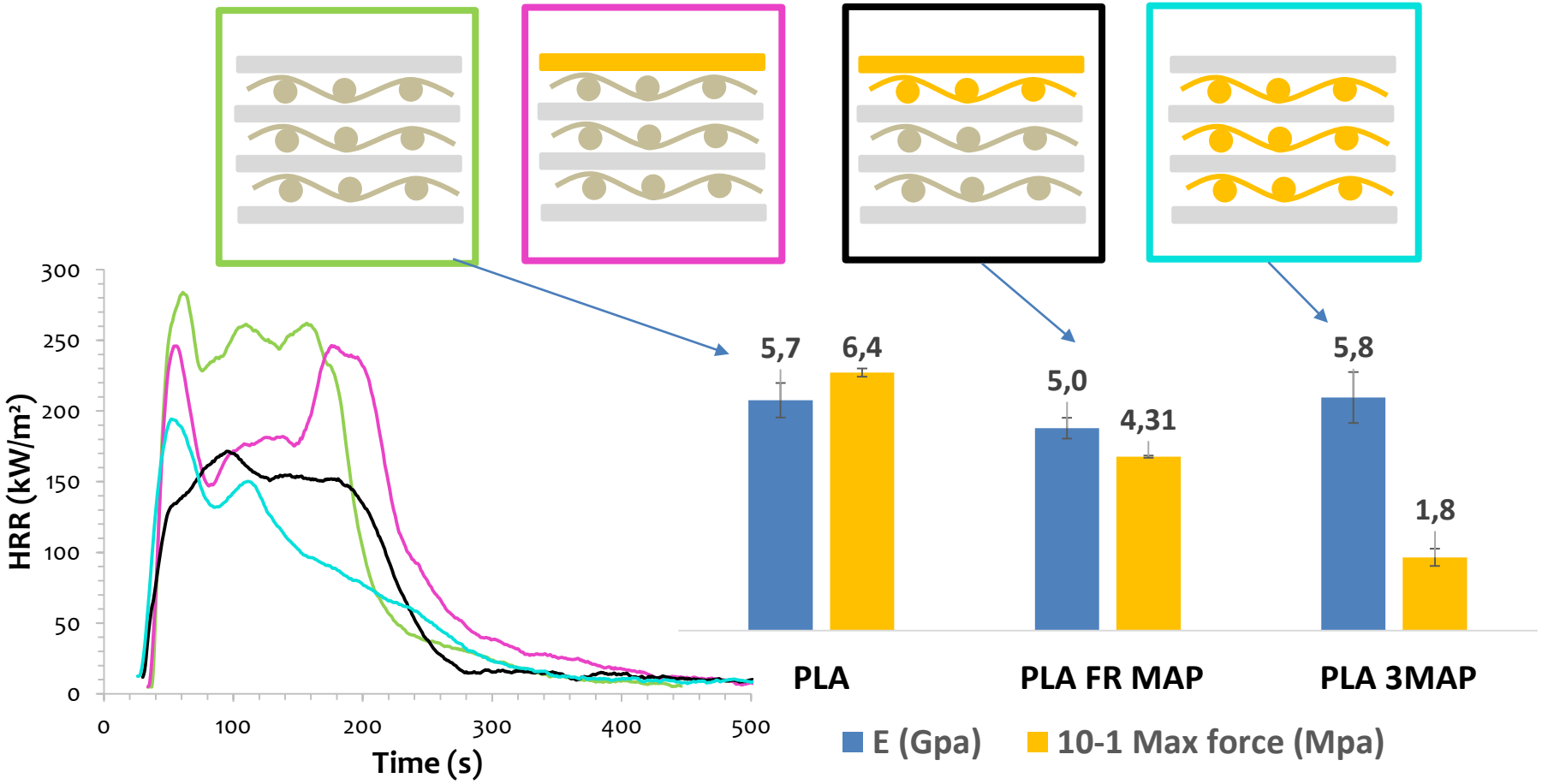
2nd approach



Choice of the MAP based on a preliminary study done at the laboratory



Performances of MAP treated fabrics



UMET
Unité Matériaux Et Transformations

R2Fire

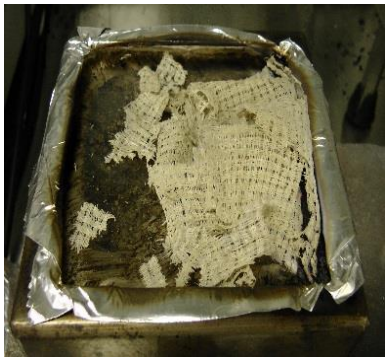
Université de Lille 1 SCIENCES ET TECHNOLOGIES

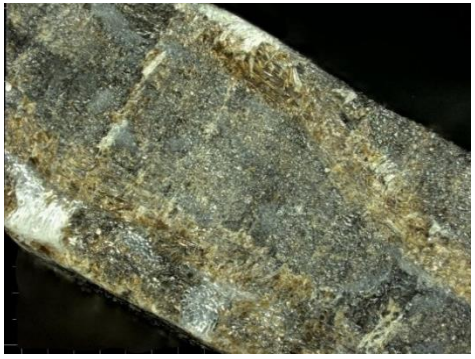
cnrs

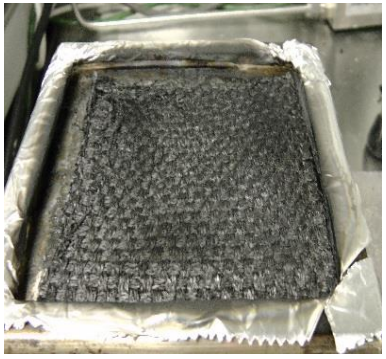
Chimie Lille
ÉCOLE NATIONALE SUPÉRIEURE DE CHIMIE

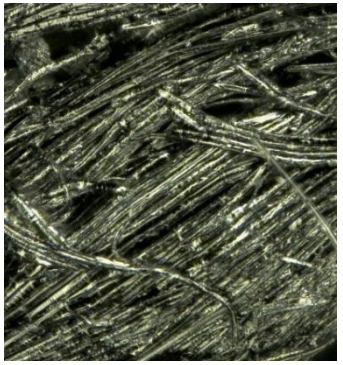
Before MLC

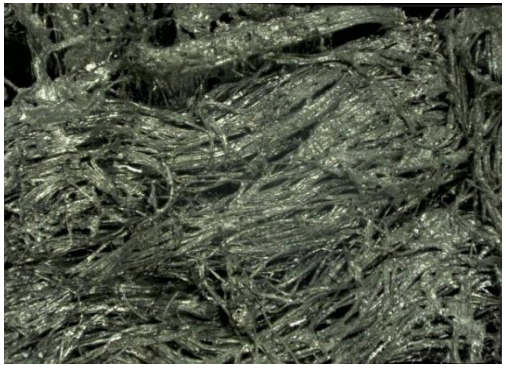
After cone calorimeter experiment

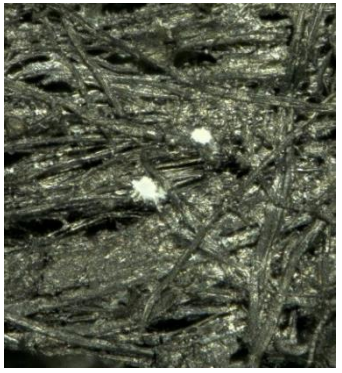








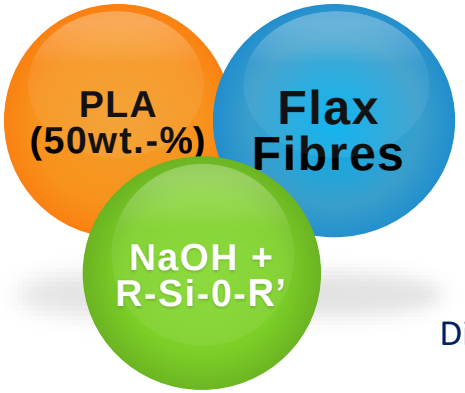




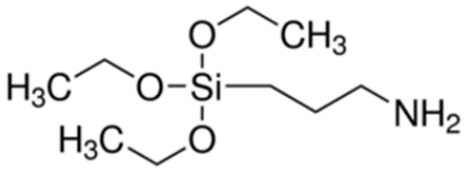
Performances of the different composites

%FR	0	2.77 ± 0.03	5.5 ± 0.4	4.38 ± 0.07
ti (s)	37 ± 1	34 ± 1	26 ± 1	31 ± 1
PHRR (kW/m²)	280 ± 6	247 ± 2	188 ± 9	172 ± 0.8
MAHRE (kW/m²)	187 ± 6	153 ± 9	108 ± 7	123 ± 0.6
THR (MJ/m²)	43.8 ± 0.1	45.1 ± 0.2	28 ± 2	34 ± 2
Residual weight (%)	2.8 ± 0.1	2.3 ± 0.1	15.50 ± 0.05	7.5 ± 0.4

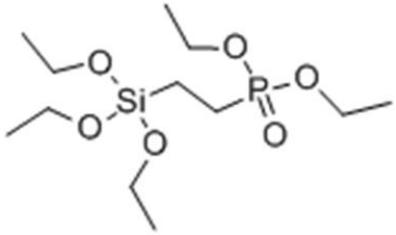
3rd approach

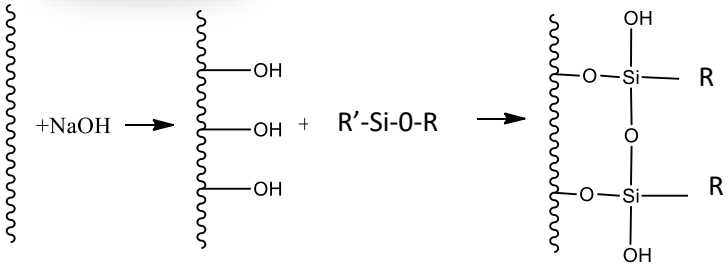


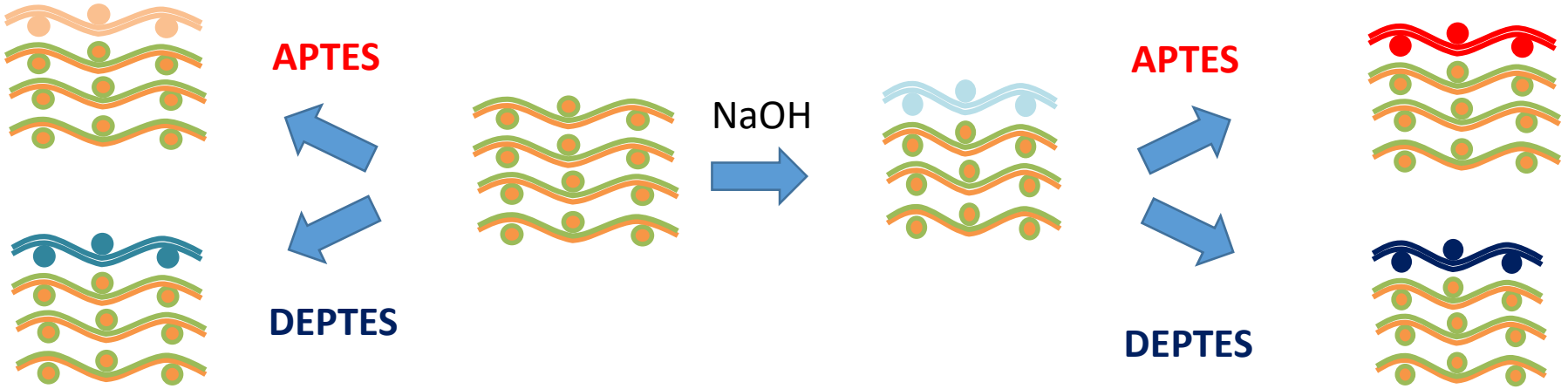
Aminopropyltri-ethoxysilane (APTES)



Diethylphosphatoethyltri-ethoxysilane (DEPTES)







Details on the treatments

Pre-treatment with NaOH

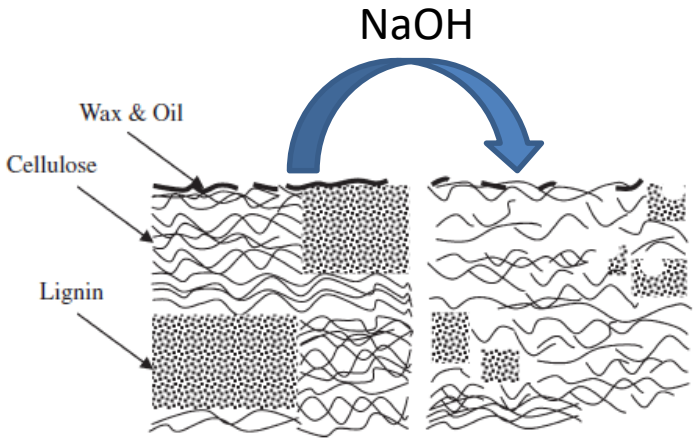
3h
5% wt.
Under stirring
Neutralization with tap water
Dry at 50°C for 48h

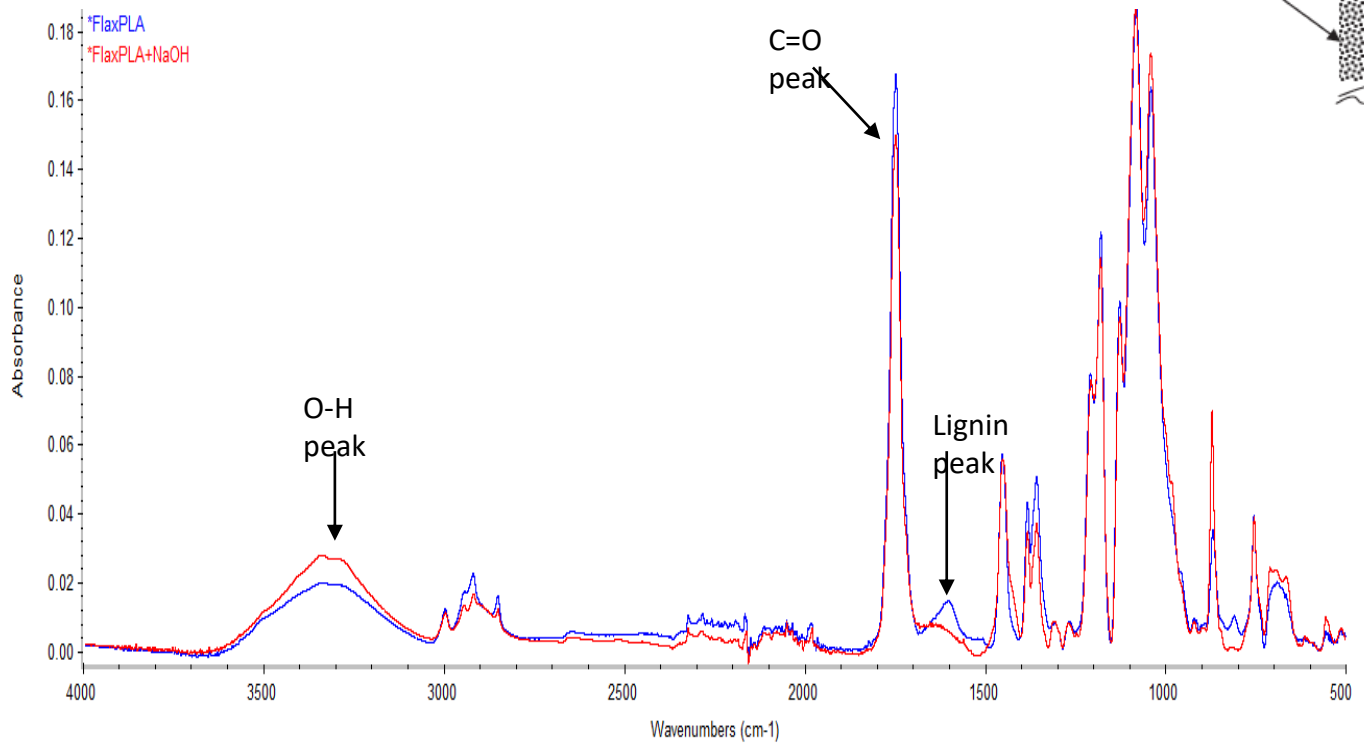
Treatment with R'-Si-O-R

1h
70/30 v/v Ethanol/Water
10% wt.
Under stirring
Dry at 50°C for 48h

Effect of these treatments on PLA fibres?

Effect of the pre-treatment on PLA/flax fabric (3h)

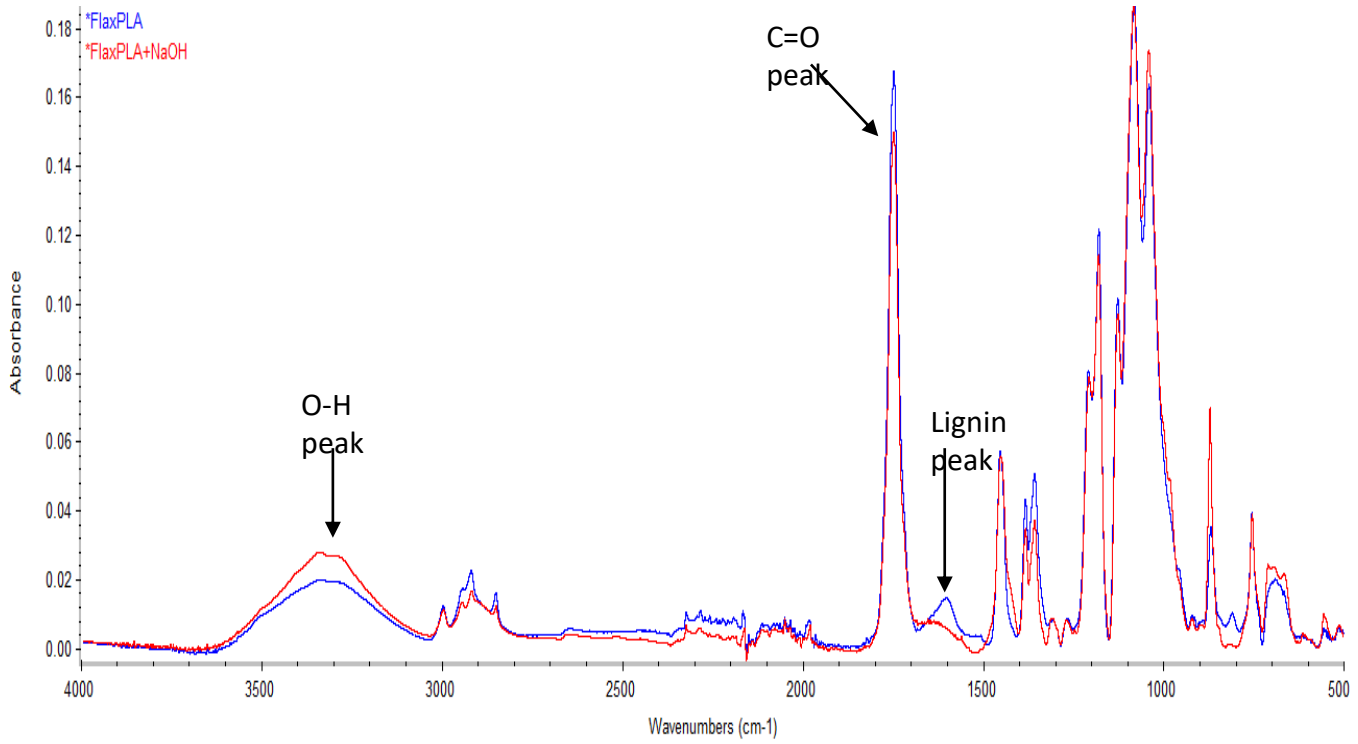




Iran Polym J DOI 10.1007/s13726-015-0395-3

Effect of the pre-treatment on PLA/flax fabric (3h)

Sample	Increased/Decreased mass after treatment [%]
FlaxPLA	0.00
FlaxPLA+NaOH	-25.16

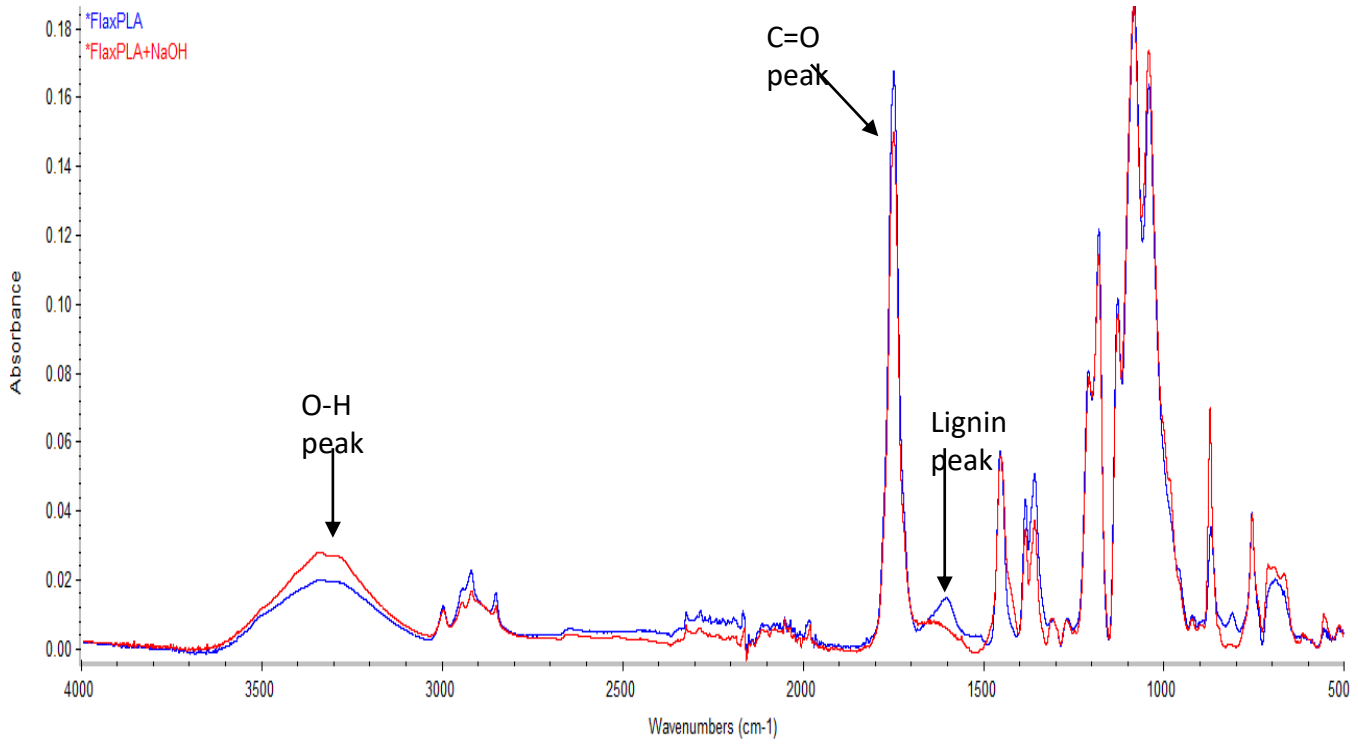


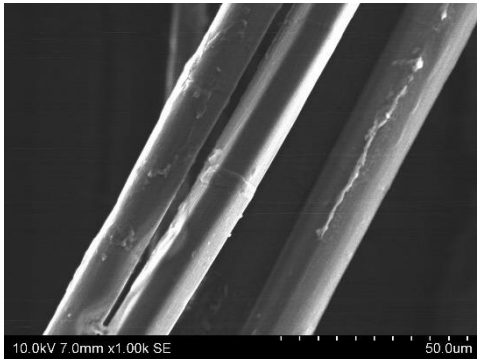
Iran Polym J DOI 10.1007/s13726-015-0395-3

Effect of the pre-treatment on PLA/flax fabric (3h)

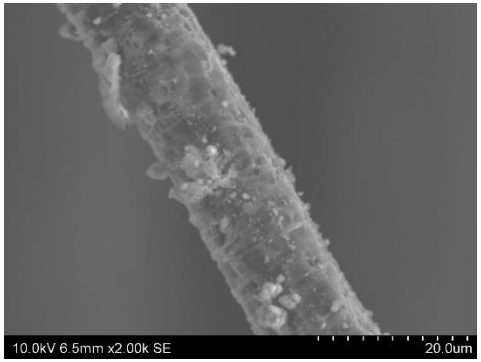
Flax diameter [µm]		Reduction percentage [%]
Before treatment	After treatment	
23.99	23.79	0.83
PLA diameter [µm]		Reduction percentage [%]
Before treatment	After treatment	
18.41	16.91	8.15

Sample	Increased/Decreased mass after treatment [%]
FlaxPLA	0.00
FlaxPLA+NaOH	-25.16





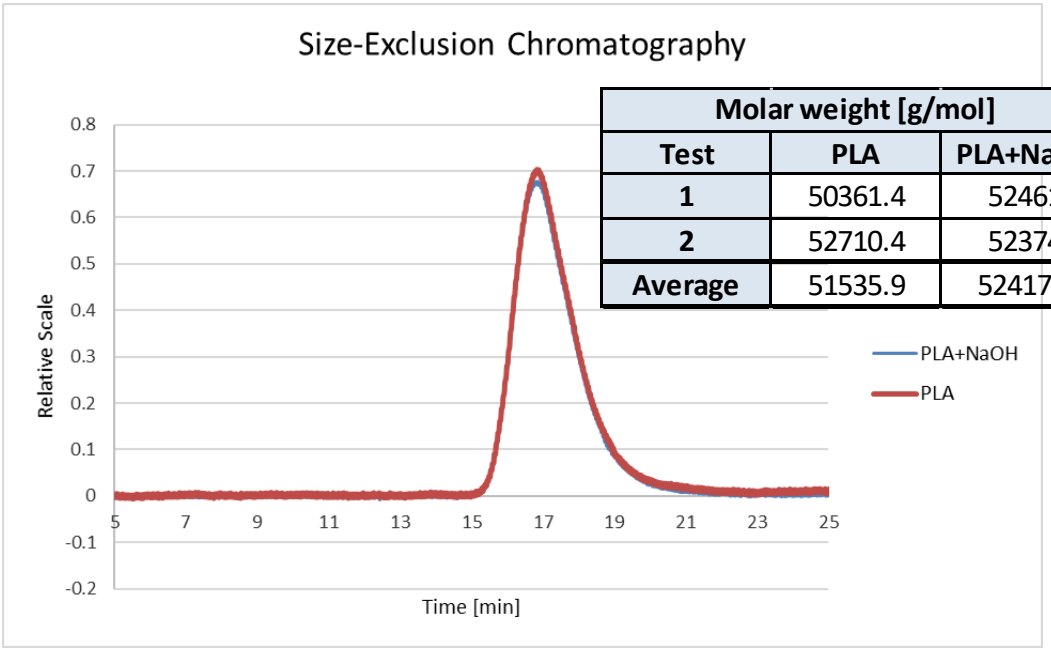
Virgin FlaxPLA



FlaxPLA + NaOH

Iran Polym J DOI 10.1007/s13726-015-0395-3

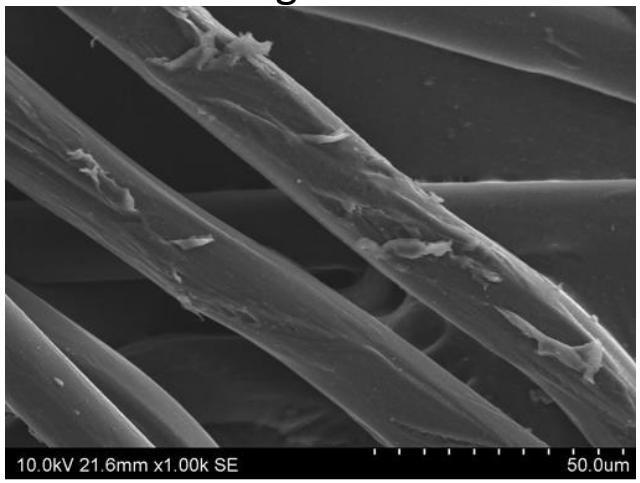
Effect of the pre-treatment on PLA/flax fabric (3h)



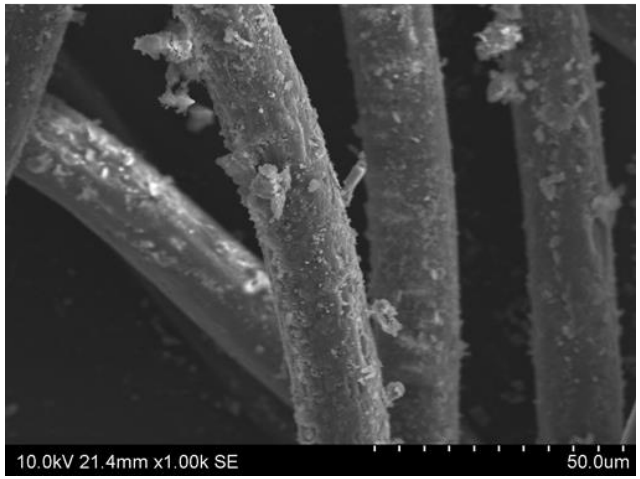
Molar weight [g/mol]		
Test	**PLA**	**PLA+NaOH**
1	50361.4	52461
2	52710.4	52374
Average	51535.9	52417.5

- Lignin of flax fiber was dissolved in NaOH solution
- PLA is affected by the NaOH treatment
- Erosion of PLA fibers is observed

Virgin PLA

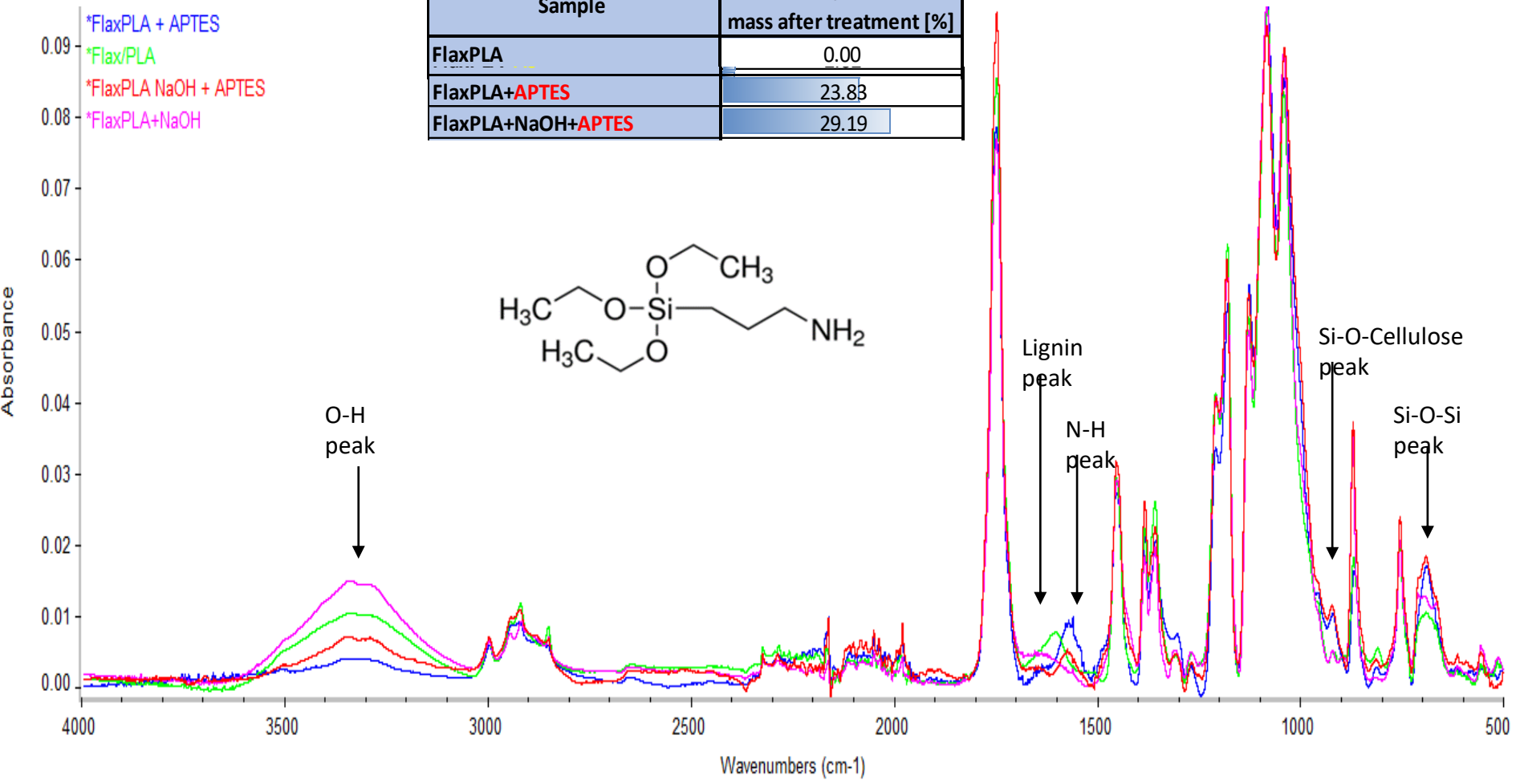


PLA + NaOH



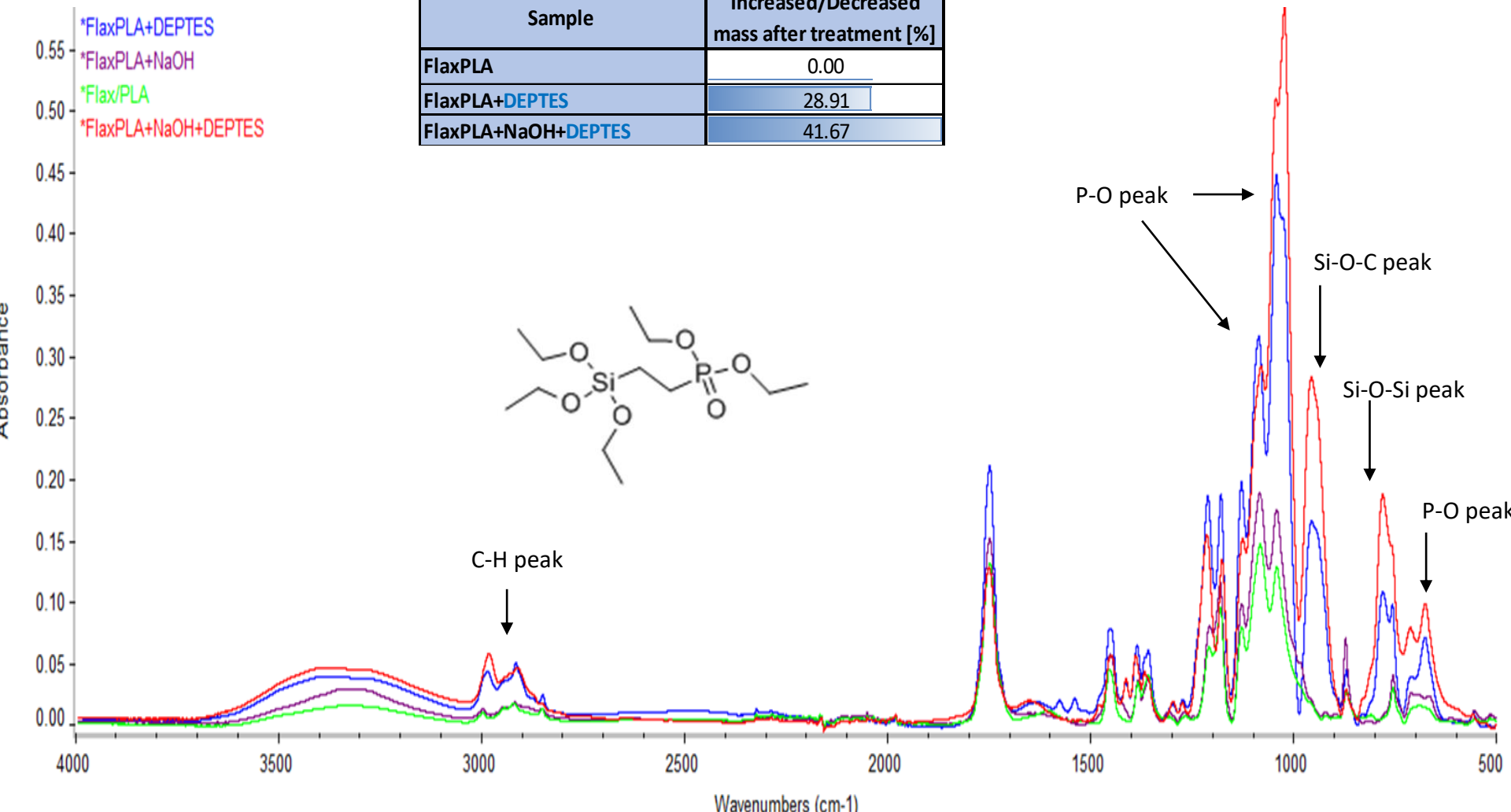
Characterization of APTES treated PLA/flax fabric

Sample	Increased/Decreased mass after treatment [%]
FlaxPLA	0.00
FlaxPLA+APTES	23.83
FlaxPLA+NaOH+APTES	29.19

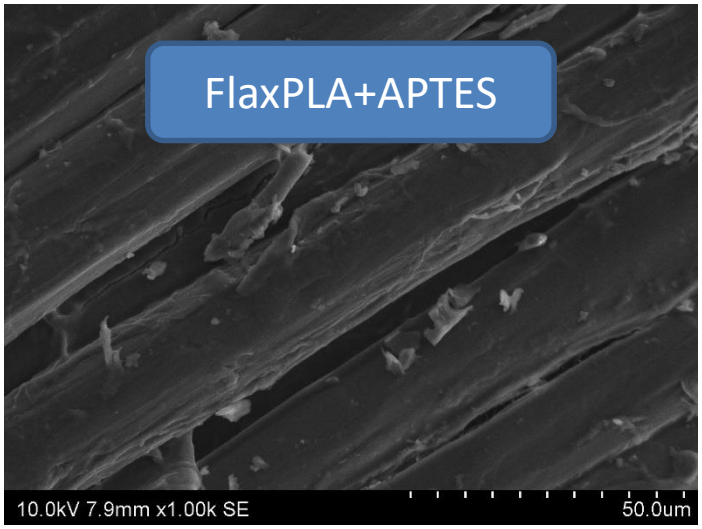


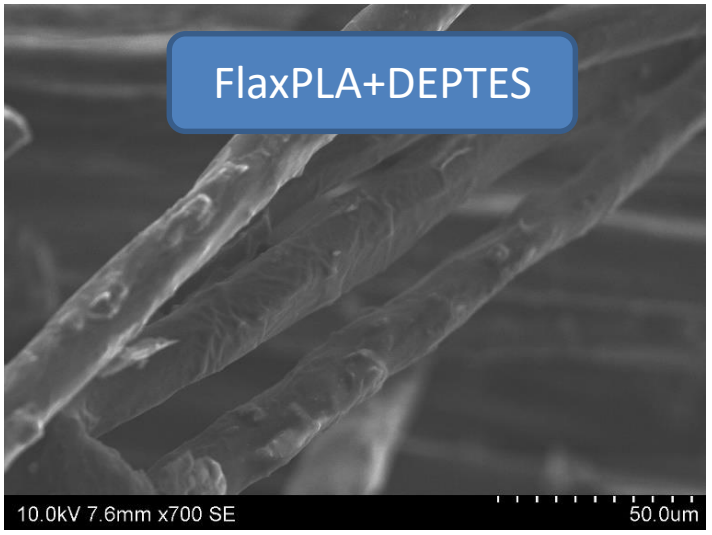
Characterization of DEPTES treated PLA/flax fabric

Sample	Increased/Decreased mass after treatment [%]
FlaxPLA	0.00
FlaxPLA+DEPTES	28.91
FlaxPLA+NaOH+DEPTES	41.67

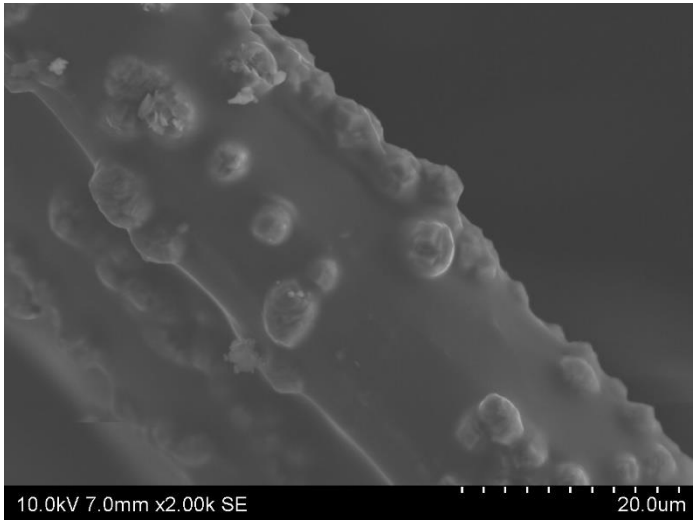


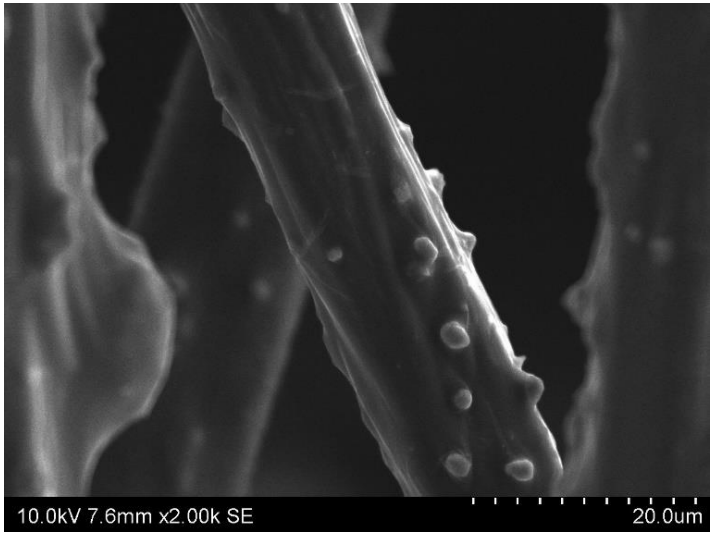
Characterization of treated PLA/flax fabric





+NaOH

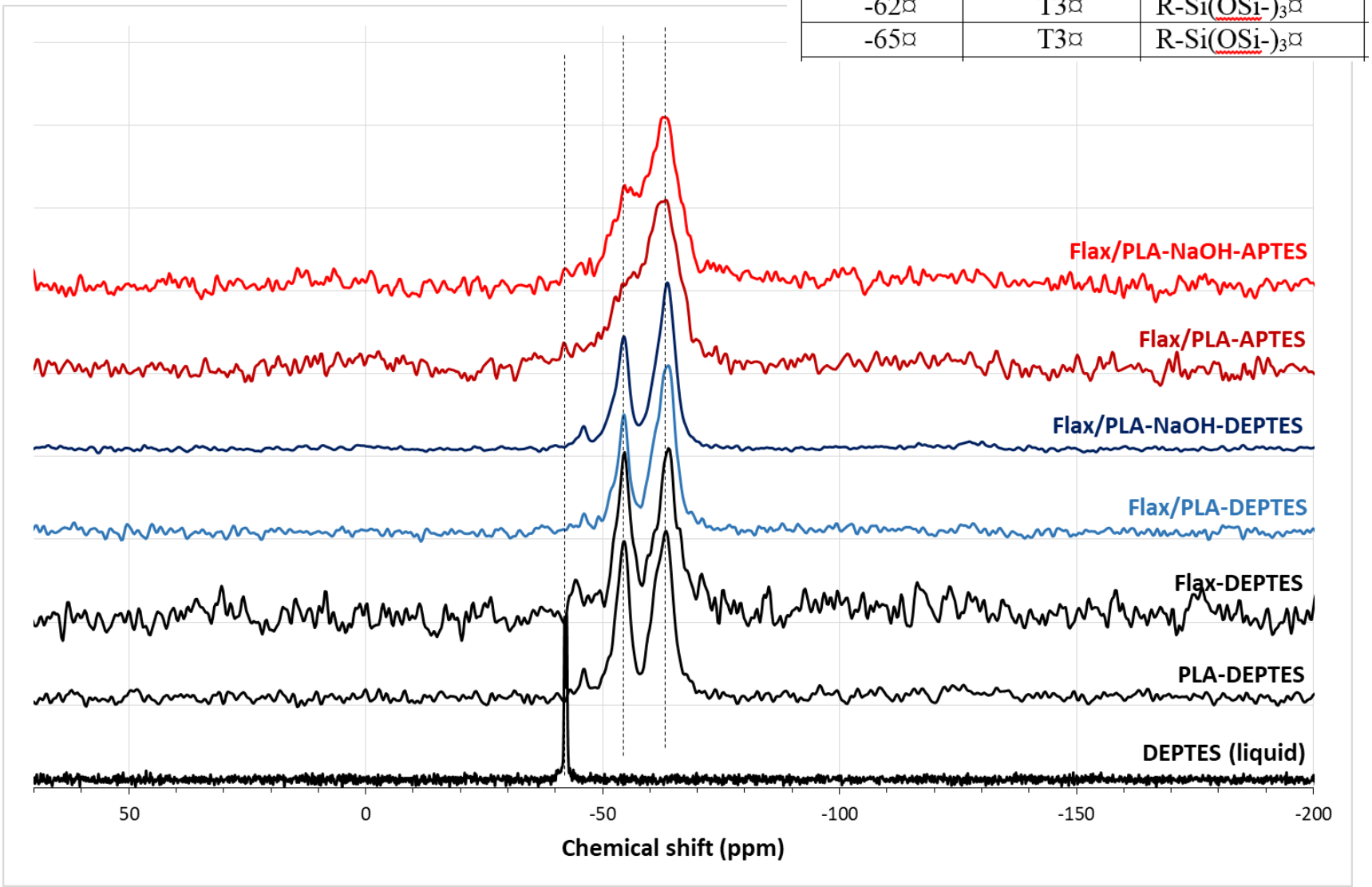




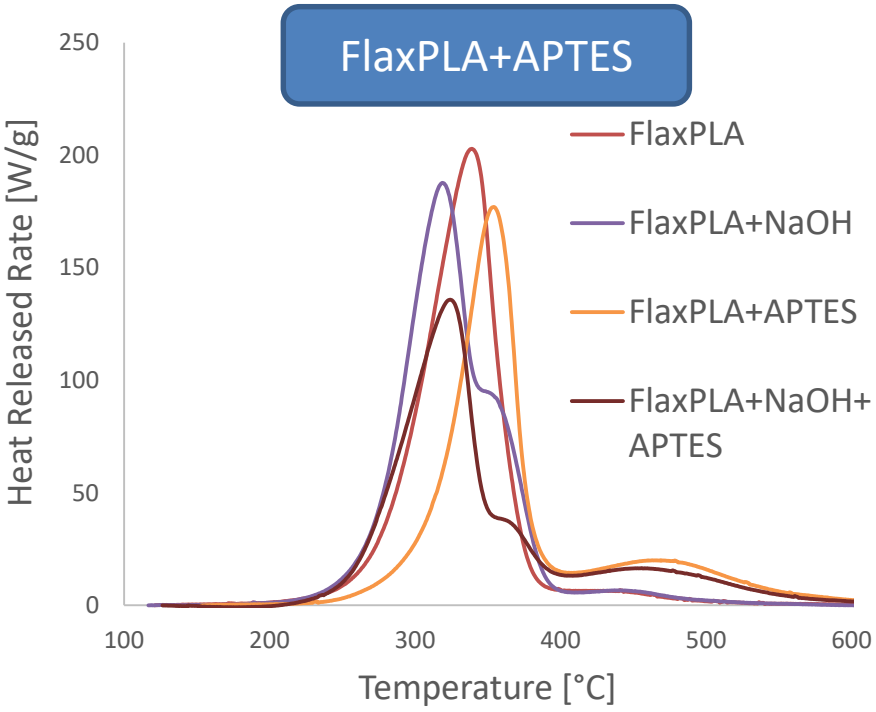
+NaOH

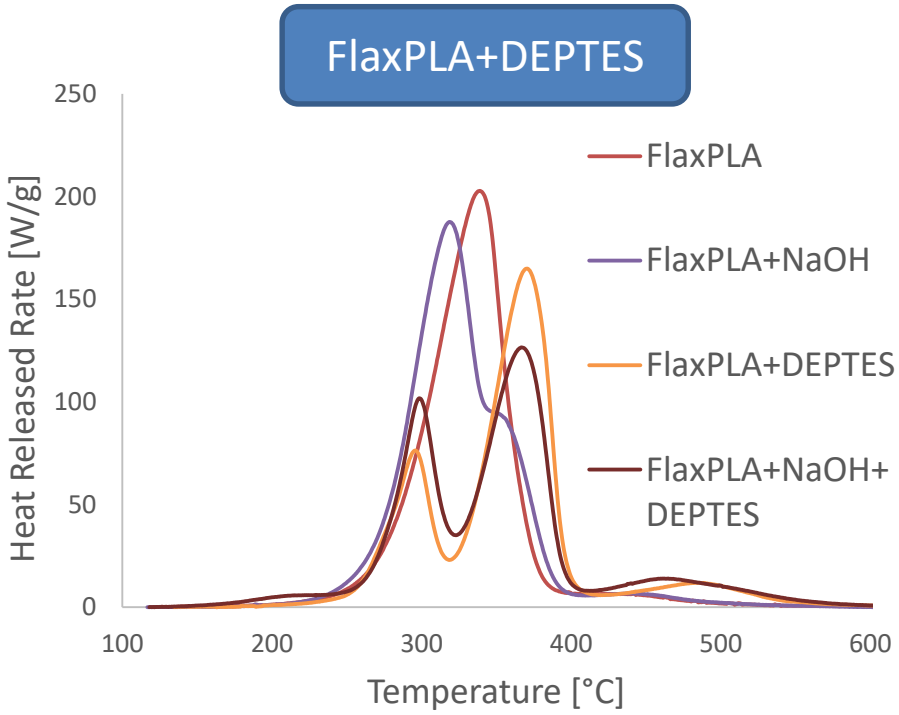
Characterization of treated PLA/flax fabric

^{29}Si·(ppm)¤	Assignment¤	Formula¤
-55¤	T2¤	R-Si(OH)(OSi-)$_2$¤
-62¤	T3¤	R-Si(OSi-)$_3$¤
-65¤	T3¤	R-Si(OSi-)$_3$¤



Fire retardant performance of FR fabrics



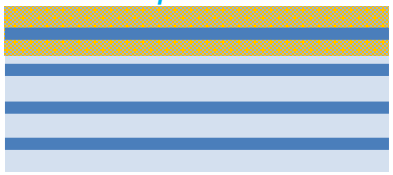


- APTES/DEPTES can be deposited on the surface of the fibres
- NaOH pre-treatment leads to higher add-on
- Promising effect of the treatment on the fire behaviour

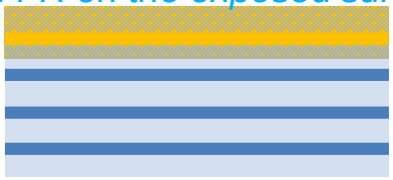
Conclusions and Future work

Three different approaches tested

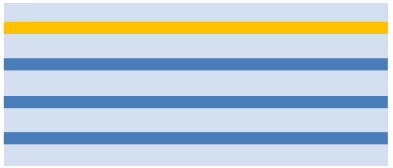
First approach: *Partial modification of the resin with FR on the exposed surface*



Second approach: *Partial modification of the resin + fibres with FR on the exposed surface*



Third approach: *Partial modification fibres with Si-N or Si-P on the exposed surface*



- Good flame retardancy performances obtained with both entirely and partially modified composites
- Protection of the fibres thanks to MAP
- Interaction of the fibres and the MAP during the degradation (phosphoric acid reacts with cellulosic part of the fibres to lead to char and water)

Same approach with thermoset resins

- Pre-treatment + treatment with R'-SiO-R realized on comingled fabrics
- Deposit / grafting on the Flax fibres but erosion of the PLA fibres with condensation of the silane
- Improvement of the fire behavior

Test the behavior in cone calorimeter/ other silane or combinations

FLAME RETARDANCY OF BIO-BASED FLAX COMPOSITES : SOL-GEL AND REACTIVE APPROACHES

Fabienne SAMYN, Oscar GALVIS, Sophie DUQUESNE, Séverine BELLAYER

Unité Matériaux Et Transformations, UMR CNRS 8207, Ecole Nationale Supérieure de Chimie de Lille, Villeneuve d'Ascq, France

sophie.duquesne@ensc-lille.fr