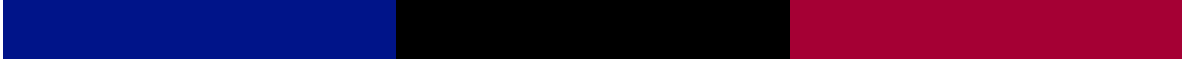




Effects of water ageing on the mechanical properties of flax and glass fibre composites: Degradation and reversibility

G. APOLINARIO TESTONI, P. IENNY, S. CORN, R. LEGER, A. BERGERET, J.M. HAUDIN



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Context of the presentation

- In France:

20.000 boats reach their **end-of-life** in **2015**

95% are manufactured with **Glass-polyester composites**.



Ref.: Le Duigou et al. 2014 / French Nautical Industries Federation.

Context of the presentation

Societal context due to new environmental legislation

Societal promotion to develop bio-based composites to conventional ones



One of the alternatives

Introduction of plant fibres to substitute glass fibres



A scientific challenge

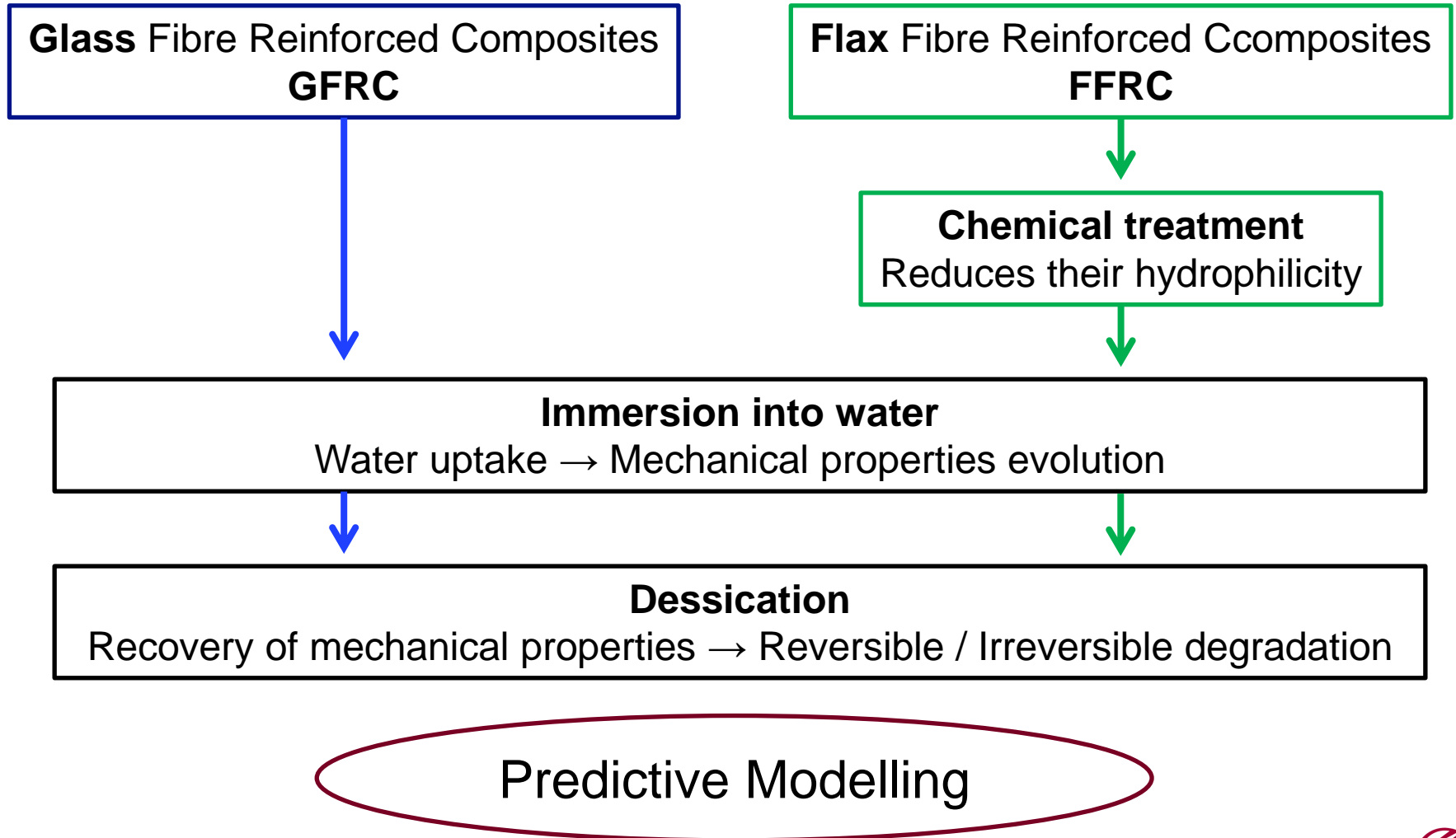
How reducing the water sensitivity of plant based composites ?

Objective of the present study

Understanding the long-term influence of water on diffusivity and mechanical property through modelling

Refs.: Davies et al, 1996 ; Camino et al, 1997 ; Gellert et al, 1999 ; Pillin et al, 2011 ; Darshil et al, 2013 ; Faruk et al, 2012 ; Bledzki et Gassan, 1998 ; Scida et al, 2013 ; Le Duigou et al, 2009; Dhakal, 2007.

Methodology of the study





SUMMARY

Materials & Processing

Methods

Results & Discussion

Conclusions & Perspectives

Materials & Methods

Materials & Processing

Unsaturated polyester resin

Glass & Flax fibres

Chemical treatment

Composites

Methods

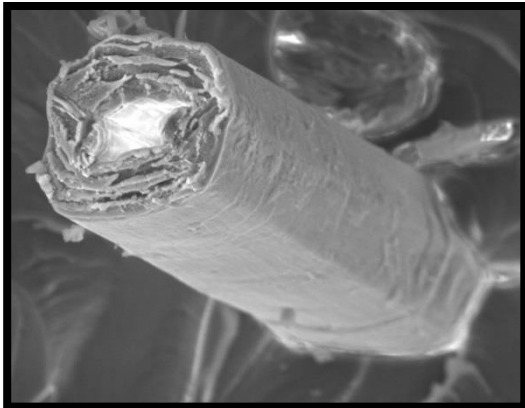
Water ageing

Composites drying

Viscoelastic properties

Uniaxial tensile tests

Differential Scanning calorimetry



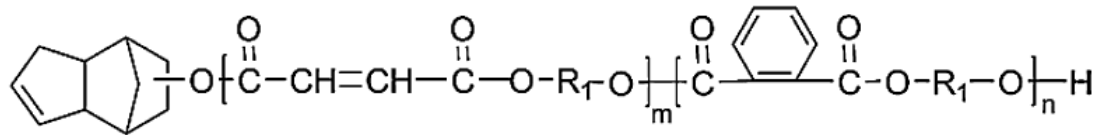
*Flax / Polyester composite
MEB C2MA-Mines Alès (200X).*

Materials

■ Polyester resin

Dicyclopentadiene isophthalic unsaturated polyester resin

Enydyne® N50 1912 Al (Cray Valley)



Catalyzer
1,8% MEKP

Cross-linked resin (supplier datasheet)	
Properties	Values
Density	1,17 g/cm ³
Glass transition temperature	57-60 °C
Degradation temperature	230-250°C
Flexural ISO 178	
Young Modulus	3000 MPa
Maximum strength	70 MPa

■ Fibres

Unidirectionnal fibres



Glass fibres



Flax fibres

Grammage supplier database:

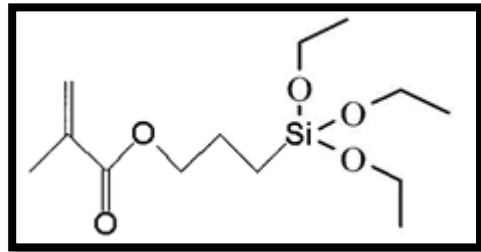
Type	Supplier	Supplier grammage (g/m ²)	Experimantal grammage	Weft		Warp		Thickness	
Fibres orientation				(g/m ²)	(%)	(g/m ²)	(%)	(mm)	
Glass fibre	UD	Chomarat (Fr)	400	416 ± 11	408 ± 17	98%	8 ± 1	2%	0,4
Flax fibre	UD	FRD (Fr)	360	369 ± 14	335 ± 11	91%	34 ± 2	9%	0,4

Materials

Chemical treatment

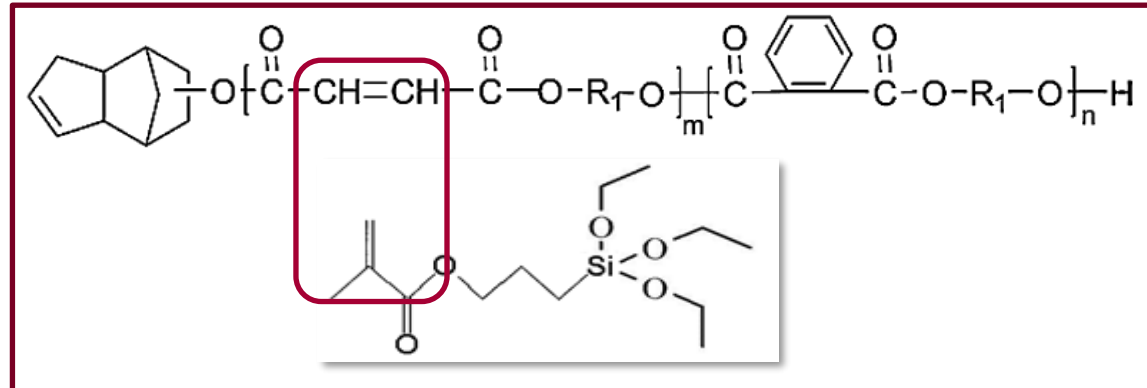
Silane treatment

γ -methacryloxypropyltrimethoxysilane (MPS)



MPS

Methacrylate-function can display **good reactivity** with unsaturated polyester matrix.



Experimental protocol:

- Solvent water/Ethanol (60/40 wt.%)
- 1.0 wt.% compared to flax fibres
- Hydrolyse : 3h
- acid pH 4
- Drying oven 105°C / 2h

Ref. : Xie et al., 2010

Fibre impregnation:
Padding bath with the finishing solution.

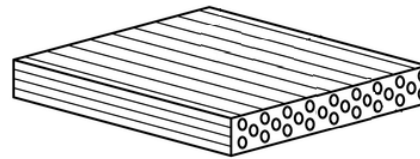
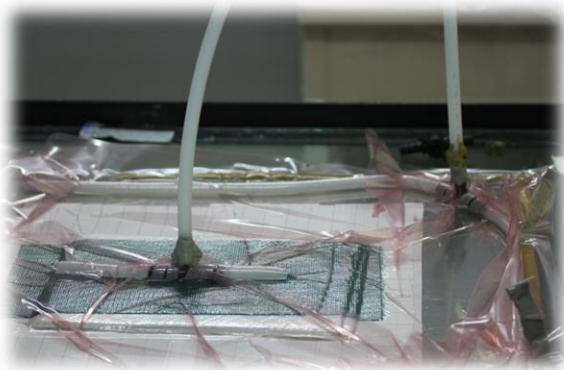
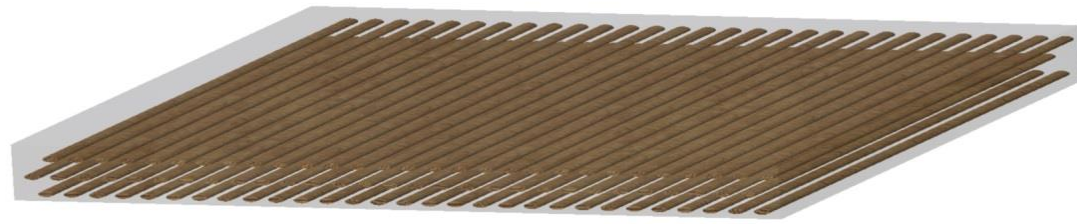


Silane treatment aims to create a **hydrophobic fibre surface**.

Materials

Composites

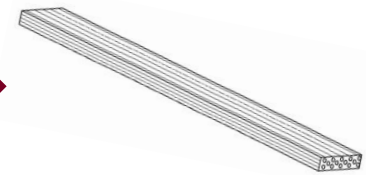
Vacuum infusion processing of composite sheets



Composite sheets



Diamond cutter



Samples
(250 x 25 mm²)

Vacuum pressure: 100 mBar

Conditions : 23°C / 50% h.r.

Post cure:

60°C / 24h

Resin crosslinking rate after postcuring : 88%

Composites	Layers	Thickness	Fibre content
	Units	(mm)	(%)
Glass FRC	6	1.8 – 2.1	52 – 56
Flax FRC	4	2.7 – 3.4	29 – 35

Methods

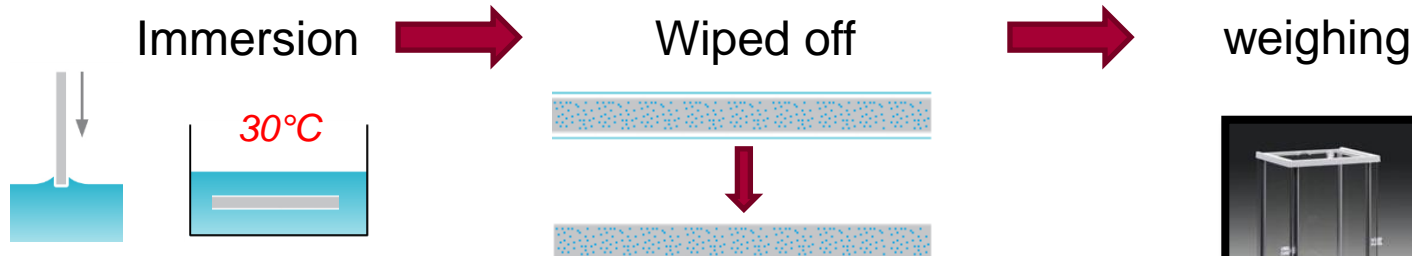
■ Water ageing

- Time, temperature
 - More than 6 months at 30°C

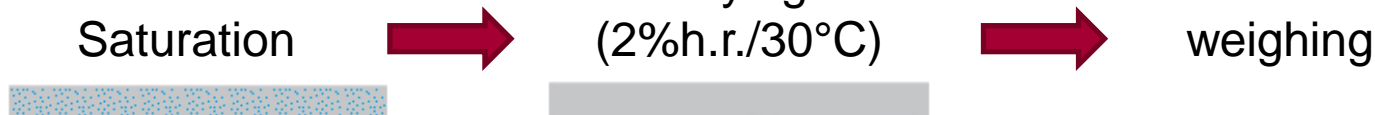
■ Physico chemical characterisation

- Sorption / desorption

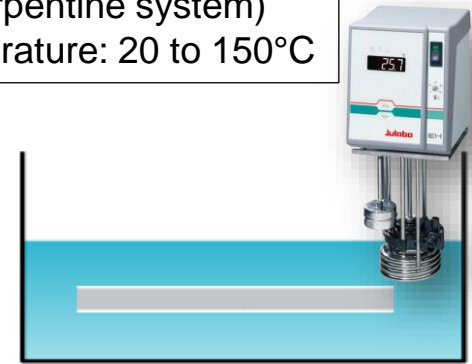
Sorption measurements



Desorption measurements



Julabo Thermostat
(serpentine system)
Temperature: 20 to 150°C



$$W(\%) = ((W_t - W_o) / W_o) \times 100$$

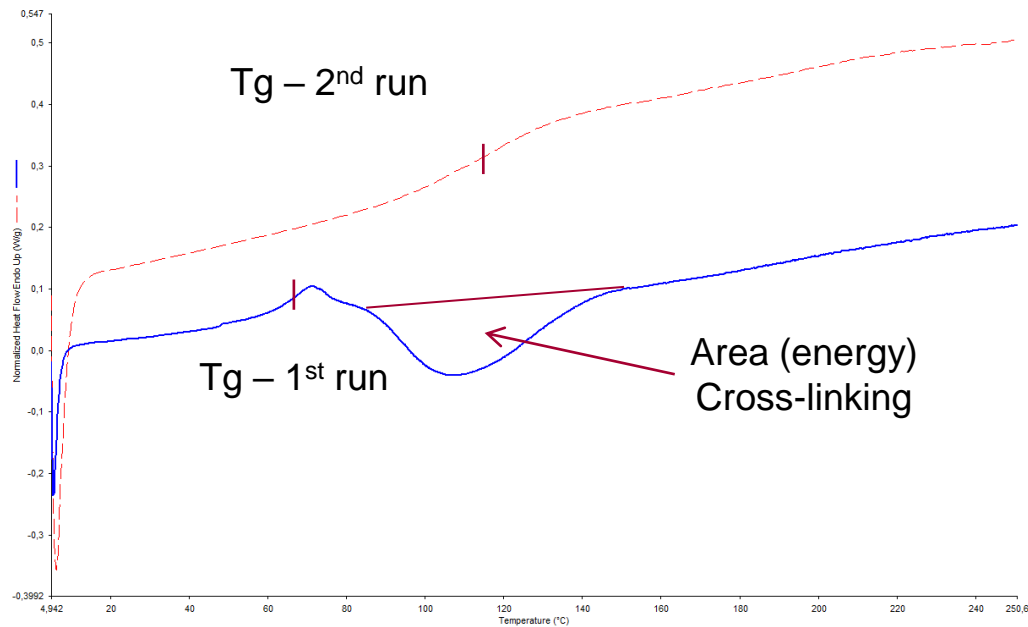


Balance
Mettler-Toledo AT200.
Precision: 0.1 mg

■ Physico-chemical characterization

Differential scanning calorimetry

- Crosslinking rate
- Glass transition temperature (T_g)



Methods

■ Mechanical characterization

Static tensile testing

E
 σ rupture
 ϵ rupture

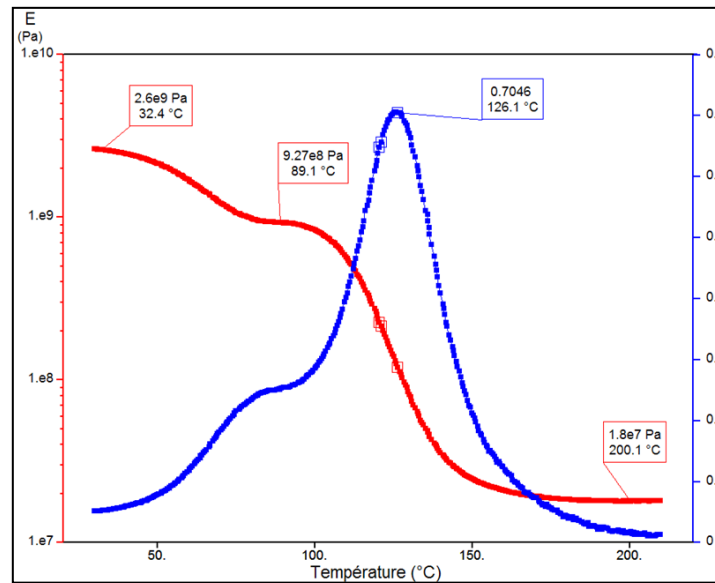


Methods

■ Mechanical characterization

Dynamic tensile testing
(DMA)

$E'(T, \omega)$
 $\eta(T, \omega)$
 $T\alpha$

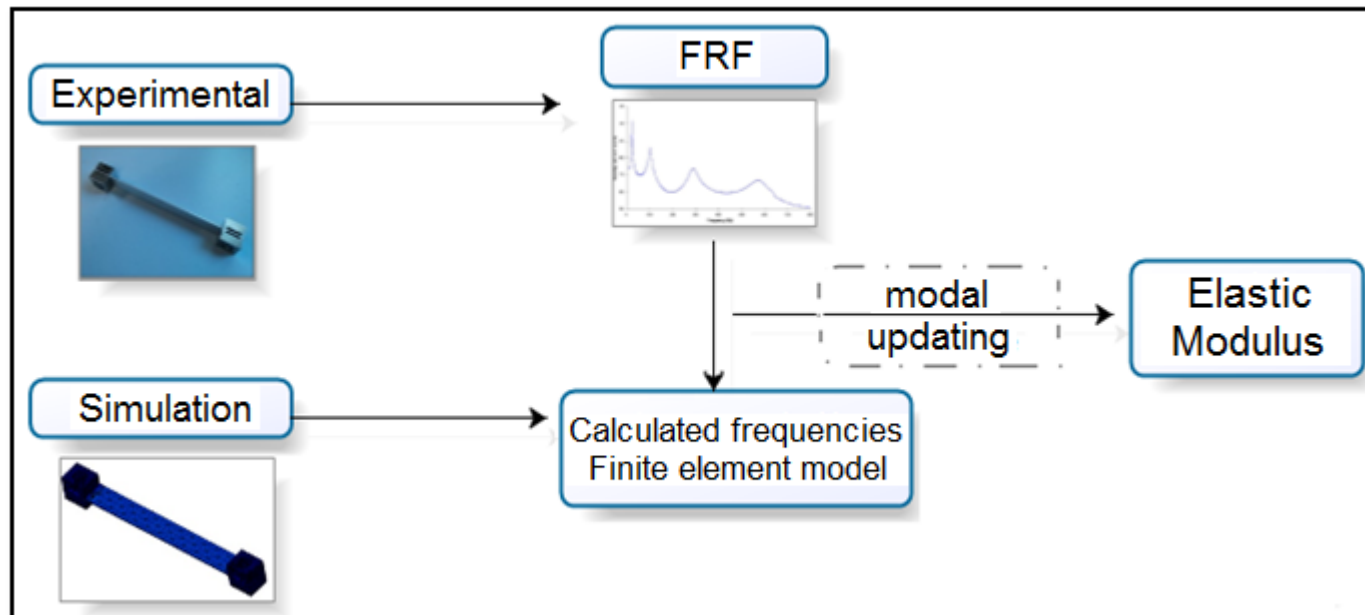


Methods

■ Mechanical characterization

Free vibration analysis
(Non-destructive test)

$E'(\omega_i)$
 $\eta'(\omega_i)$





Results and discussion

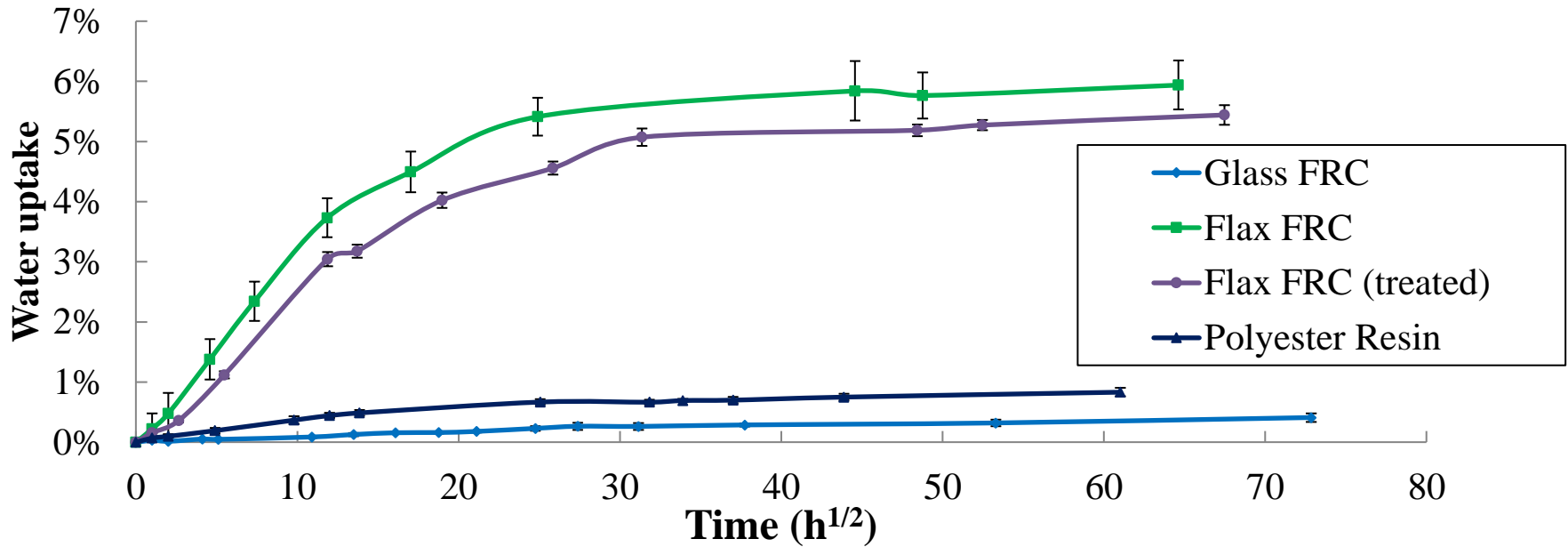
Hydroscopic properties

Mechanical properties

Reversibility

Results and discussion

Hydroscopic properties



Materials	Experimental data	
	Diffusivity (m ² /s)	Saturation (%)
Polyester resin	4.6 x 10 ⁻⁶	0.9
Glass FRC	1.2 x 10 ⁻⁷	0.4
Flax FRC	5.4 x 10 ⁻⁶	5.9
Flax FRC (treated)	4.3 x 10 ⁻⁶	5.3

Identification: Fick's Law 1D

Fibres	Saturation (%)
Glass fibres	- 0,21
Flax fibres	+ 16,4

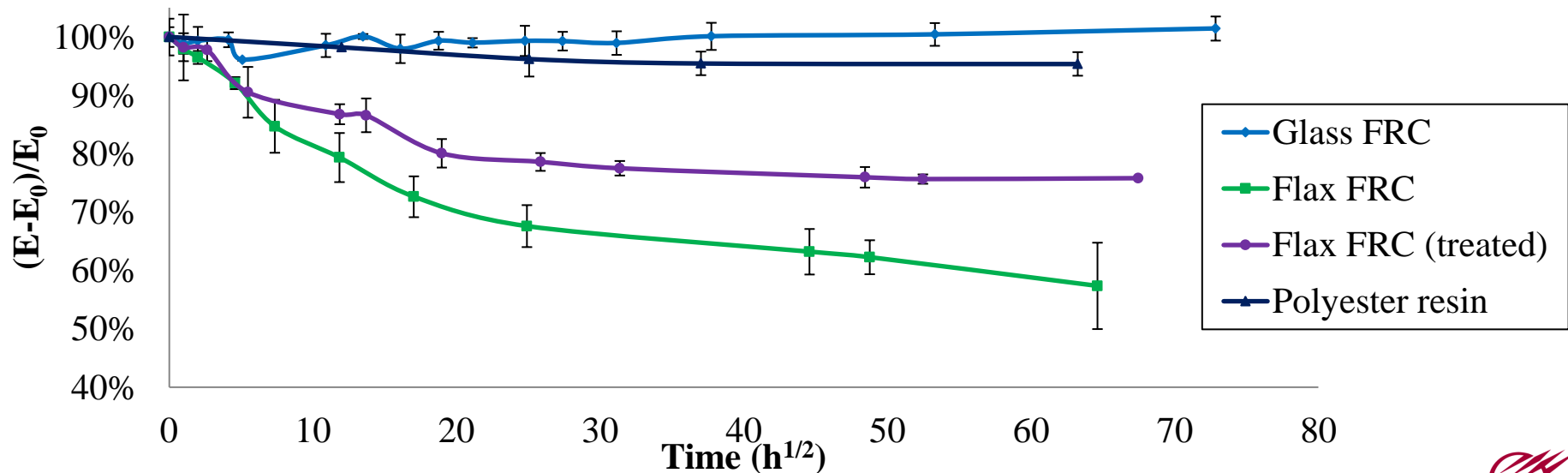
Rule of mixtures (inversed method)

Results and discussion

Mechanical properties

- Relative modulus evolution (vibration analysis)

Materials	Initial E_0 (GPa)	Modulus evolution E_{sat}/E_0
Polyester resin	3.25 ± 0.64	-5%
GFRC	34.88 ± 1.16	0%
FFRC	20.26 ± 1.16	-37%
FFRC (treated)	20.44 ± 0.74	-22%

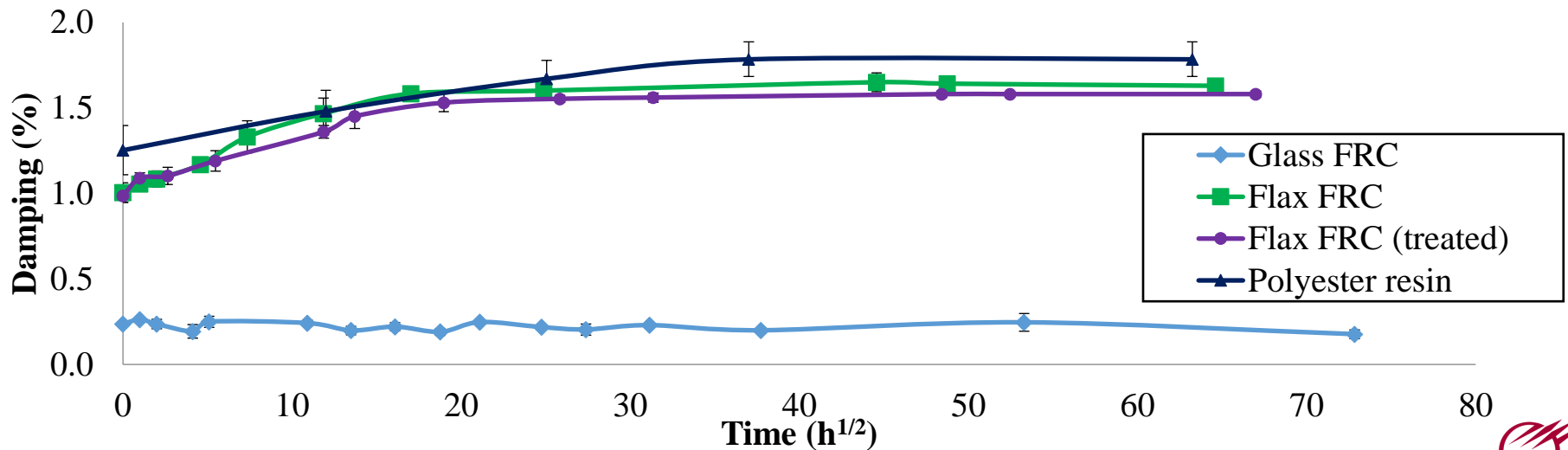
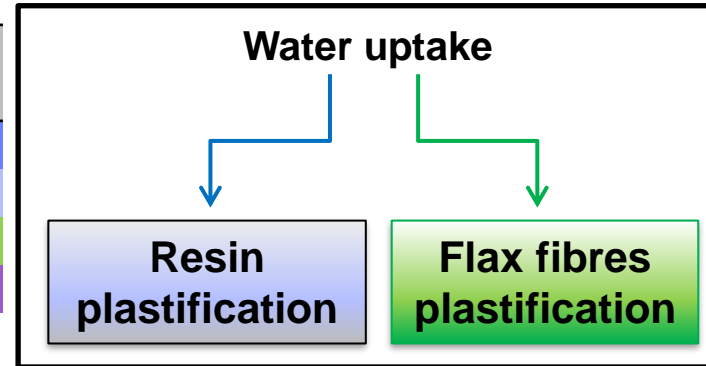


Results and discussion

Mechanical properties

- Damping evolution (vibration analysis)

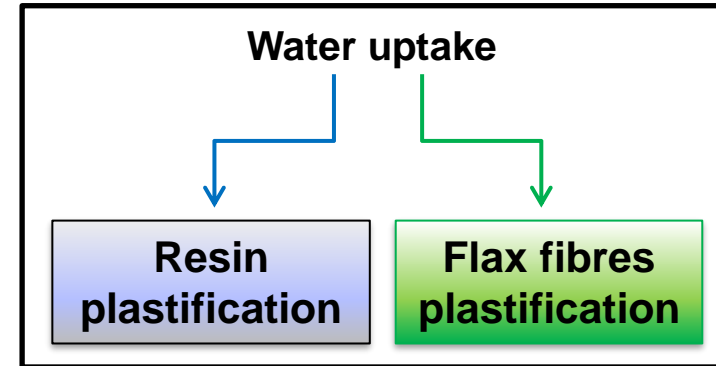
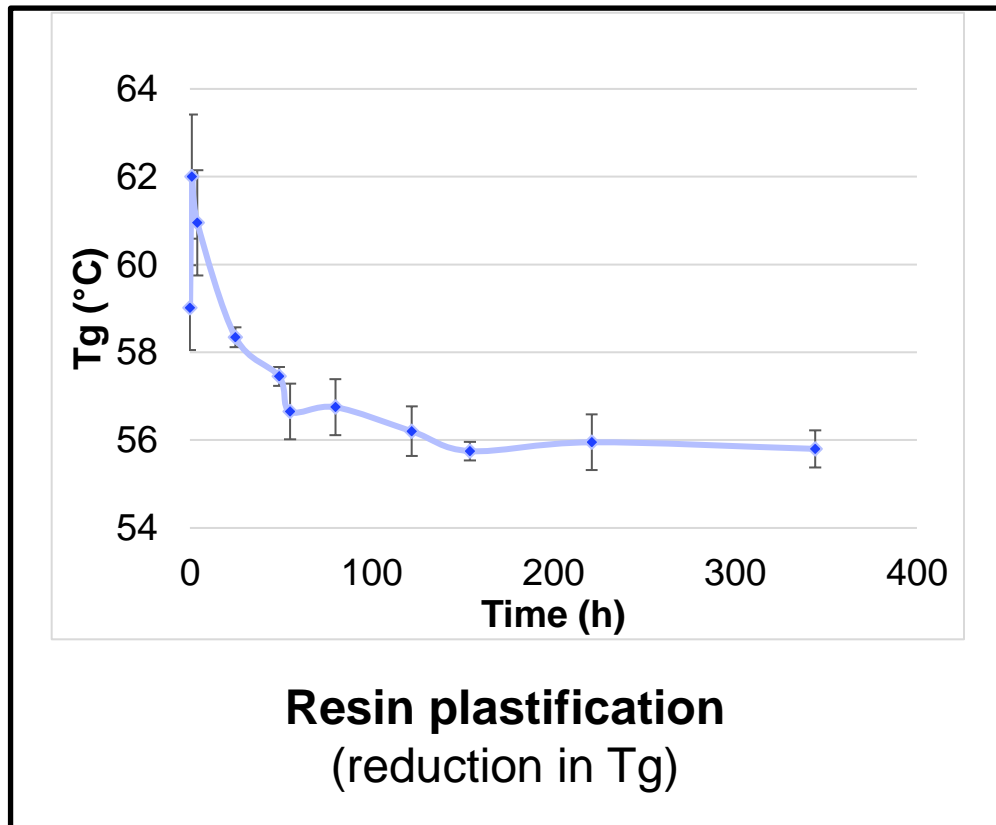
Materials	Initial a_0 (%)	Damping evolution a_{sat}/a_0
Polyester resin	1.25 ± 0.18	+42%
GFRC	0.24 ± 0.01	-8%
FFRC	1.00 ± 0.06	+62%
FFRC (treated)	0.99 ± 0.04	+57%



Results and discussion

■ Mechanical properties

- Damping evolution (vibration analysis)

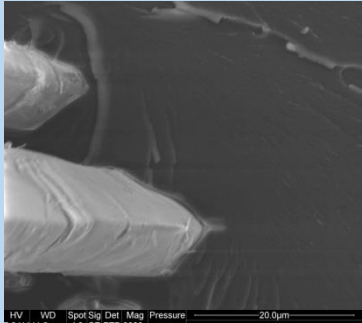


Results and discussion

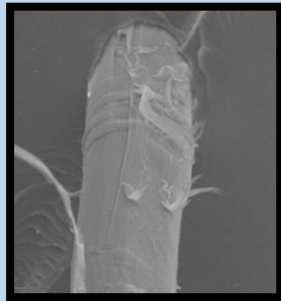
■ Mechanical properties

- Fracture surface analysis of Flax FRC (ESEM)

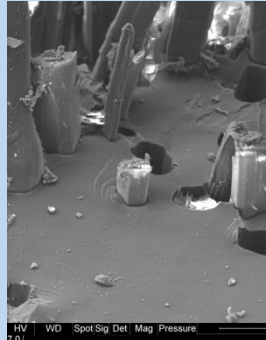
Before immersion



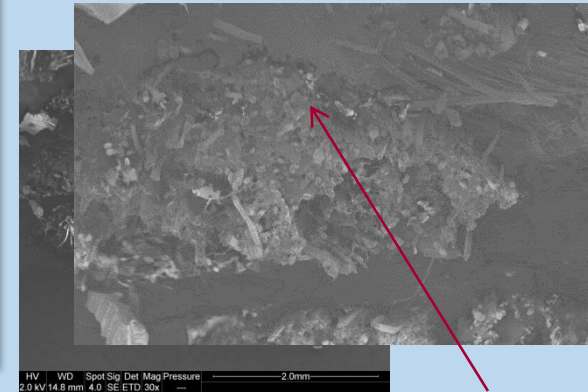
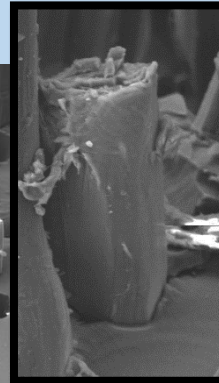
Interfacial cohesion



Fibres
« Peeling »



Fibres sharp break



Revelling length

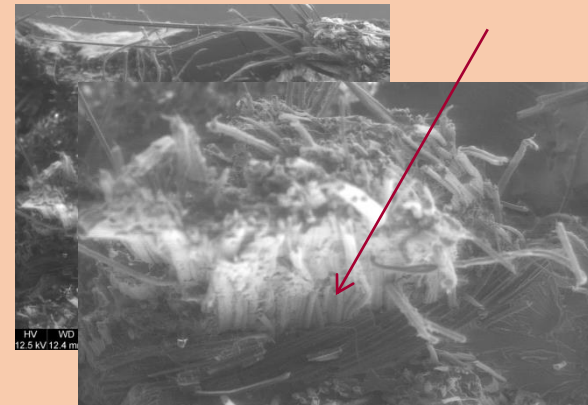
After immersion



Surface debonding



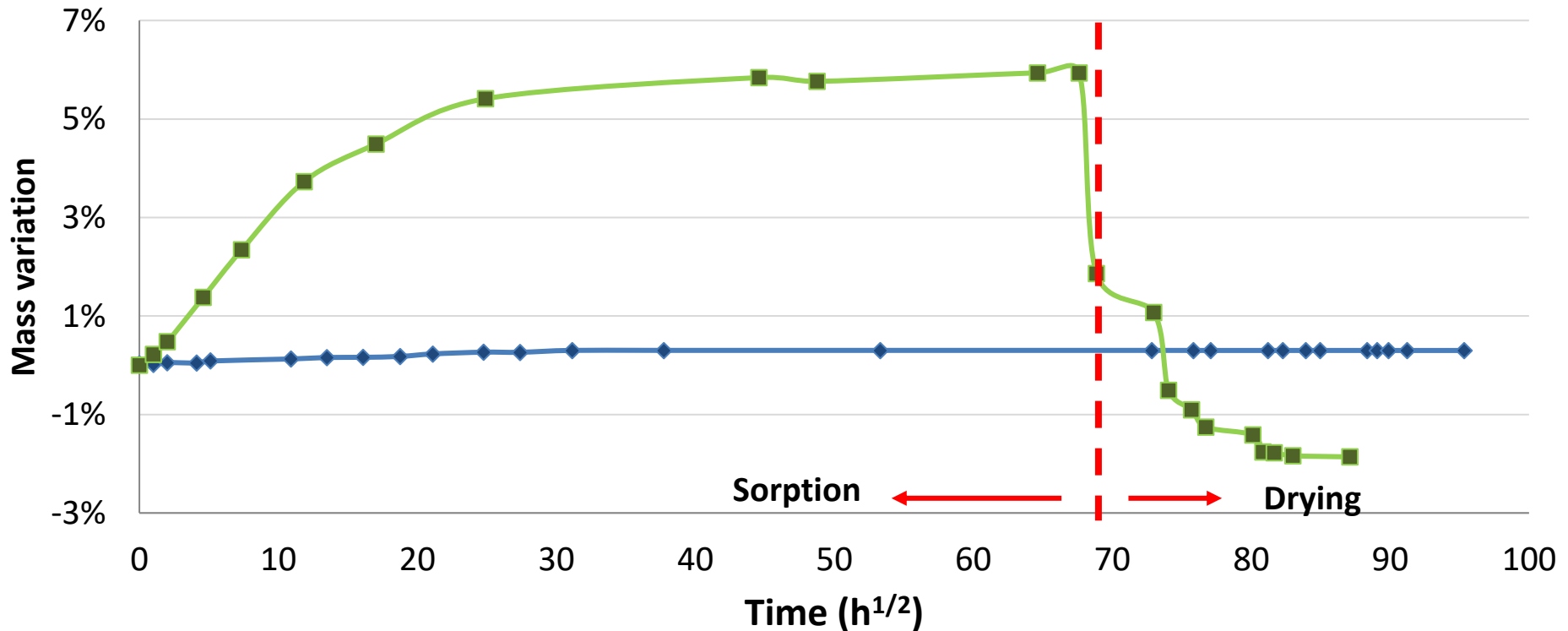
Fibre plasticization



Results and discussion

■ Reversibility

Sorption : Immersion at 30°C
Drying: 2%h.r. / 30°C



Results and discussion

Reversibility

Sorption : Immersion at 30°C
Drying: 2%h.r. / 30°C

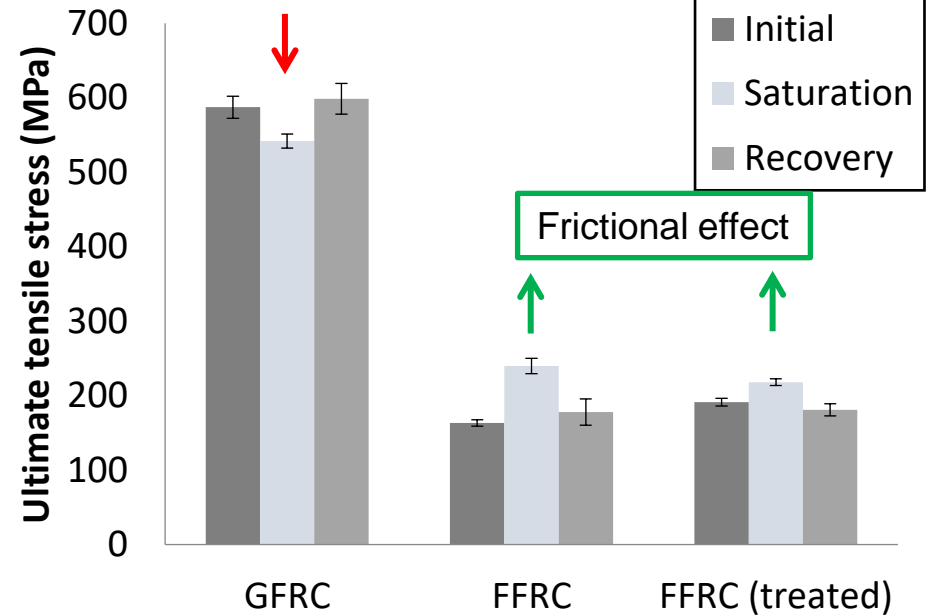
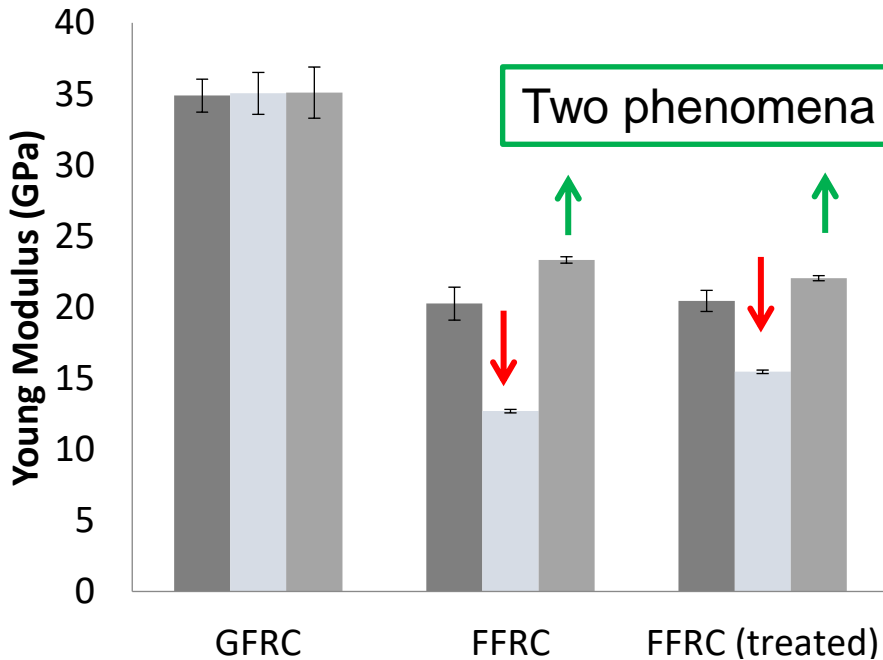
GFRC are not affected

Two phenomena

Interfacial debonding


Frictional effect

Initial
Saturation
Recovery



Results and discussion

■ Reversibility

Materials	Initial E (GPa)	Reversibility E (GPa)
CRFV	34.88 ± 1.16	35.09 ± 1.79
CRFL	20.26 ± 1.16	23.32 ± 0.22  13%

Rule of mixtures

$$E_c = V_f E_f + V_m E_m \quad \Rightarrow \quad E_c \uparrow \underline{13\%}$$

$\Rightarrow E_m \uparrow \underline{21\%}$ -Crosslinking

Hypotheses

Evolution of the matrix crosslinking rate throughout water ageing period.

Results and discussion

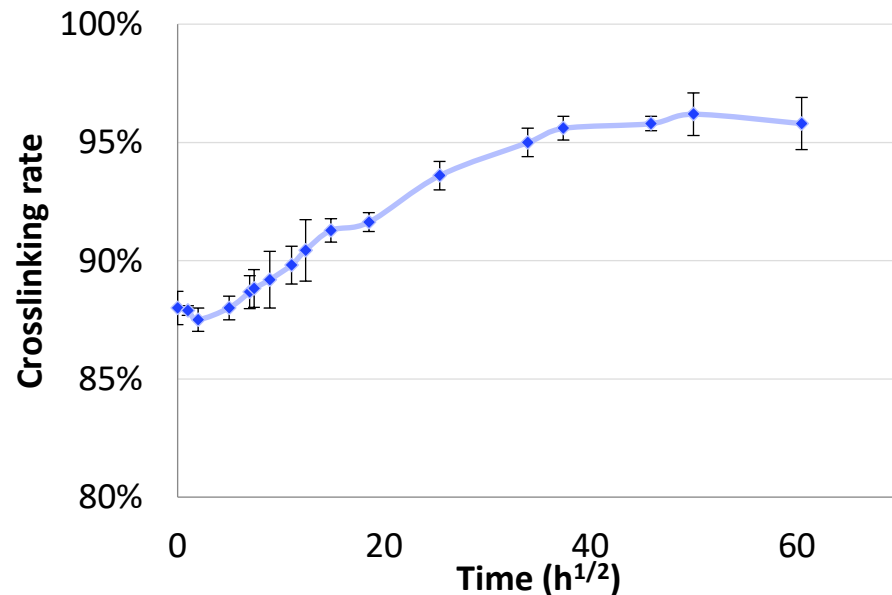
■ Reversibility

DSC characterization:

Cross-linking conditions:
Cure - 24h at room temperature
Post-cure - 16h at 40°C

Hypotheses


Evolution of the matrix crosslinking rate throughout water ageing period.



Polyester resin	E - 30°C(MPa)	Tan delta (30°C)
Before immersion	2827 ± 165	0,044 ± 0,005
After drying	3434 ± 71	0,026 ± 0,002

Results and discussion

■ Reversibility

Materials	Initial E (GPa)	Reversibility E (GPa)
CRFV	34.88 ± 1.16	35.09 ± 1.79
CRFL	20.26 ± 1.16	23.32 ± 0.22  13%

Rule of mixtures

$$E_c = V_f E_f + V_m E_m \quad \Rightarrow \quad E_c \uparrow \quad \underline{13\%}$$

$$\Rightarrow \quad E_m \uparrow \quad \underline{21\%}$$

$$\Rightarrow \quad E_f \uparrow \quad \underline{17\%}$$

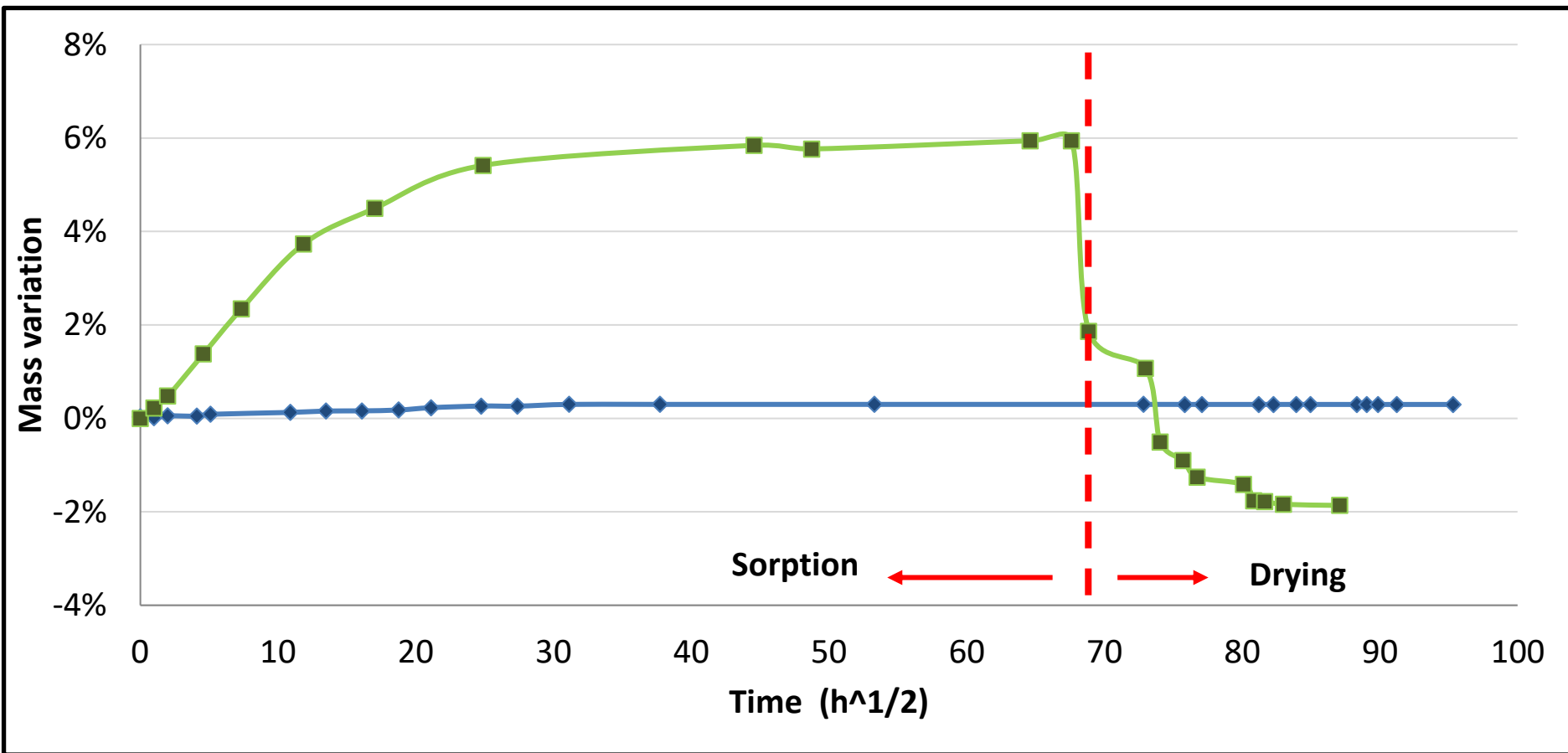
Hypotheses

- Crosslinking

- Fibres drying

Results and discussion

■ Reversibility



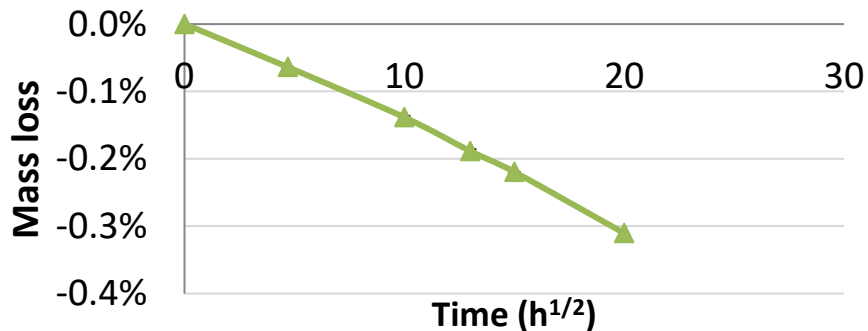
Results and discussion

■ Reversibility

Flax FRC reach a dried mass 2% lower than initial state before immersion:

The weight loss after desiccation could be explained by two factors:

- The **fibres get drier** than at the initial state;

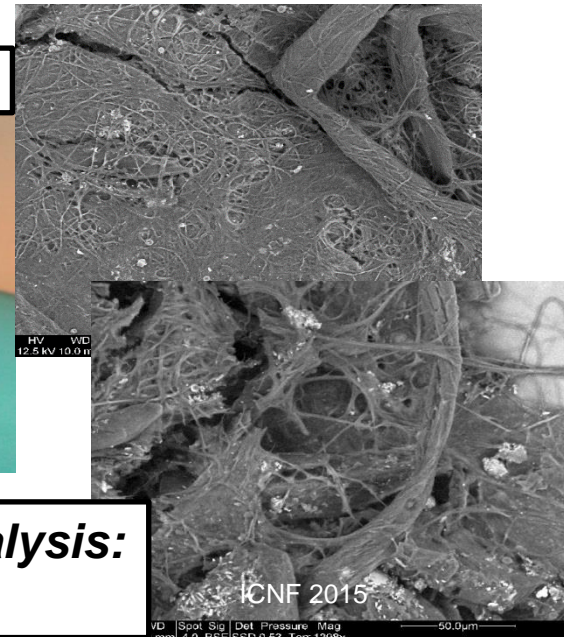
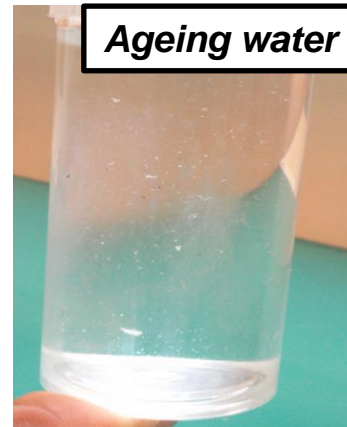


0,3% of total loss weight



Initial fibre humidity content.

- The **extractibles** (small cell-walls components) **were removed** during immersion

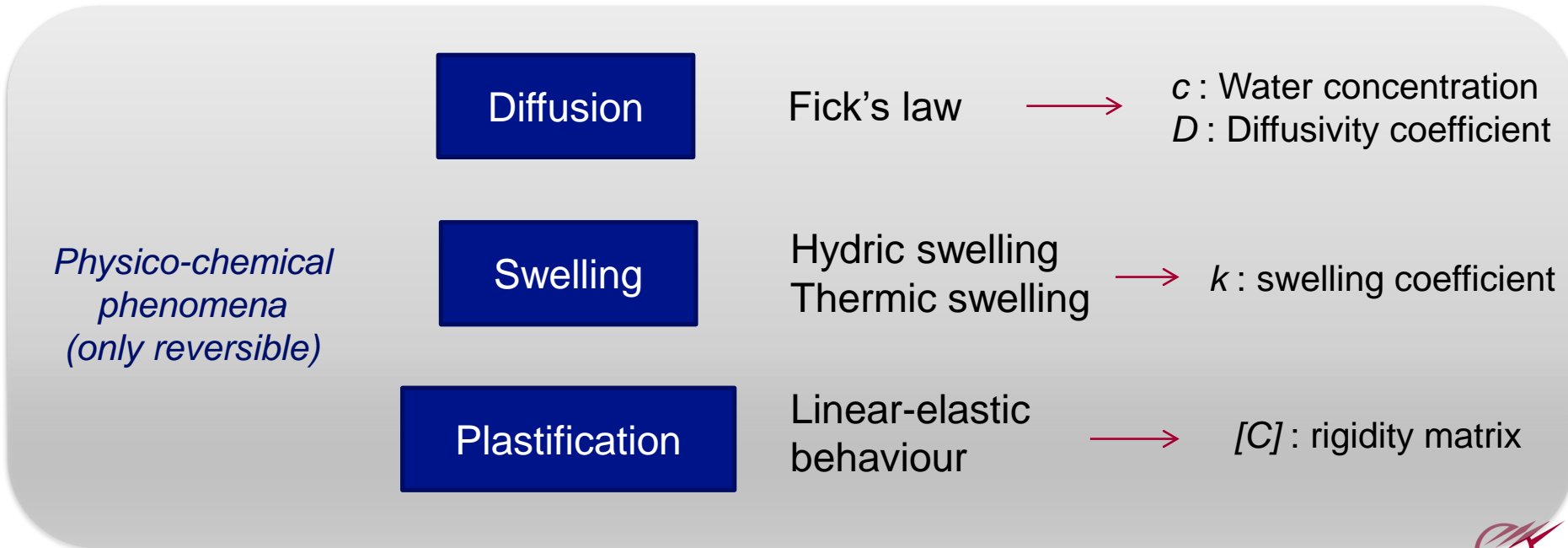
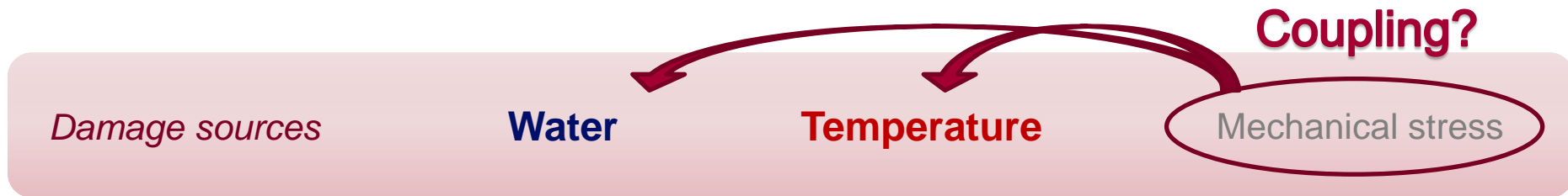


EDX/MEB analysis:
Mainly C, O

Modelling

■ Hydro-thermal ageing modelling

- A Realistic predictive model take into account :



Modelling

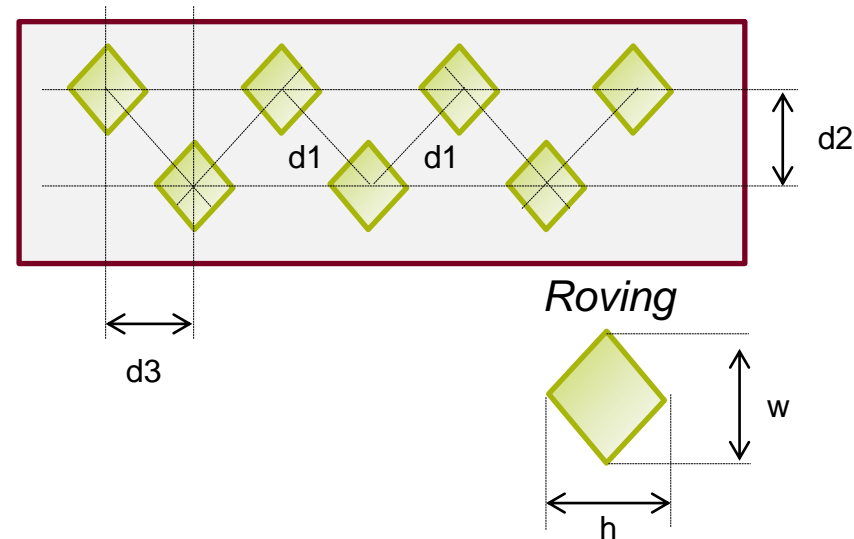
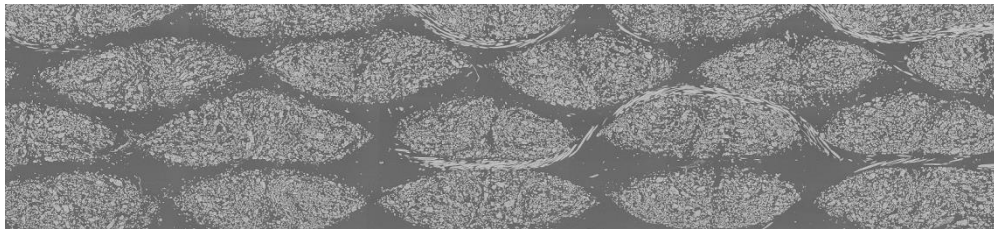
■ Multiphysics modelling

To obtain a realistic predictive model:

Complex multiscale composite morphology:

Statistics of roving parameters (size and distribution measurements);

Statistics of fibres / bundles (surface area, form factor, inter-particle distance).



Modelling

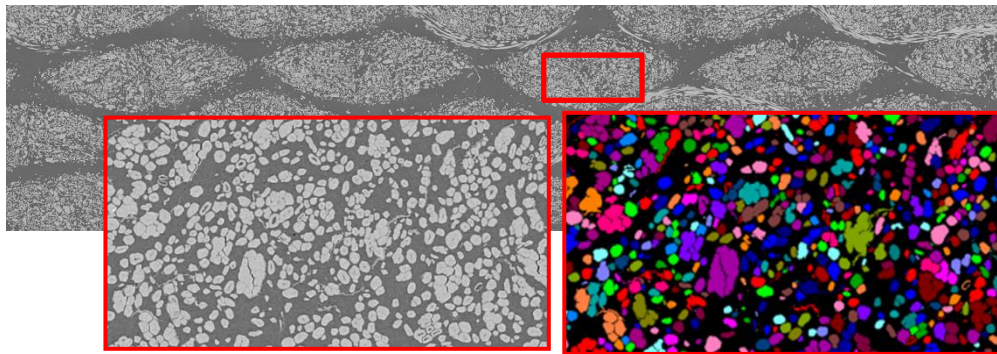
■ Multiphysics modelling

To obtain a realistic predictive model:

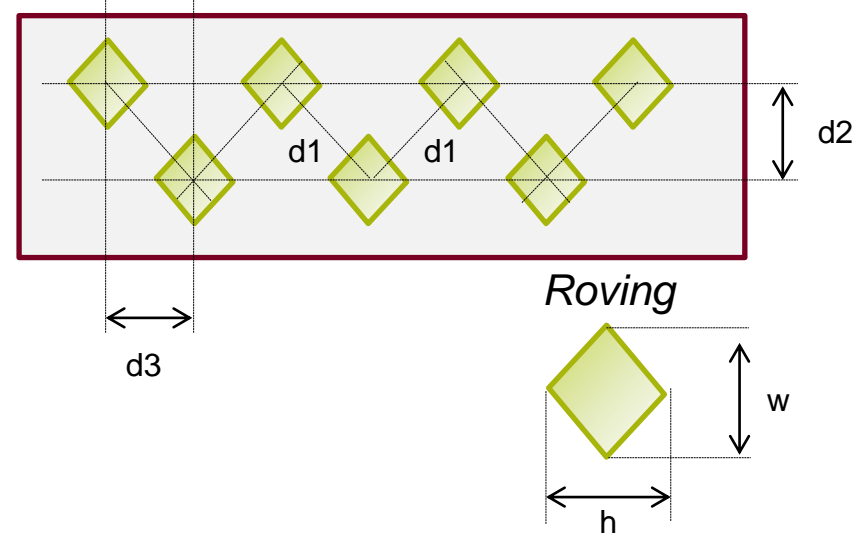
Complex multiscale composite morphology:

Statistics of roving parameters (size and distribution measurements);

Statistics of fibres / bundles (surface area, form factor, inter-particle distance).



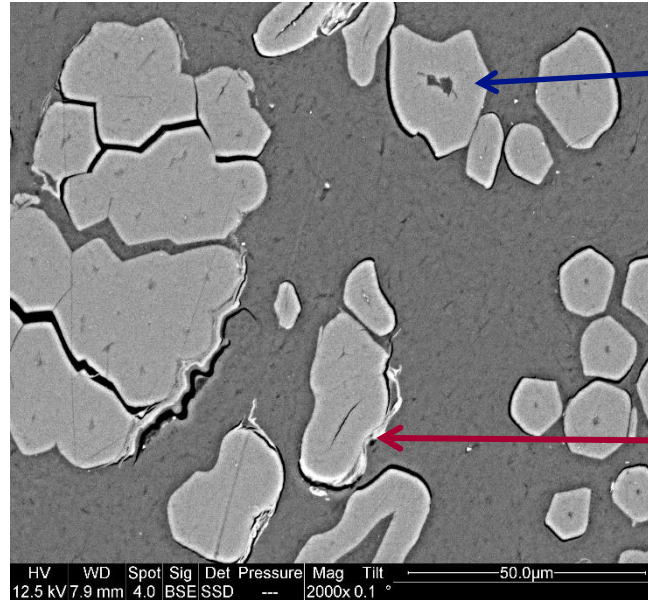
Bundles / fibres



Modelling

■ Multiphysics modelling

Influence of processing conditions on composite morphology:



Matrix inside the lumen

Lumen flattened during vacuum infusion

The evolution of fibre and matrix behaviour (irreversible):

Matrix hardening

Fibres extractibles removing

Conclusions

■ The composites water uptake is mainly controlled by natural fibres.

- Composites rigidity decreases while damping increases;
- Ultimate properties increases at saturation.

Fibres
plastification

Frictional effect caused
by fibres swelling

■ Reversible ageing occurs during immersion at 30°C but:

- Further crosslinking is observed;
- Dried composites mass 2% lower than initial state before immersion

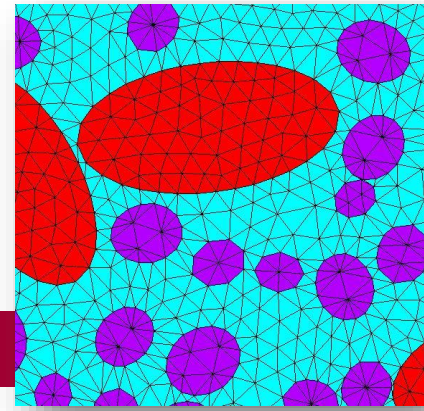
The loss weight is explained by drying the fibres initial humidity and by the removing of small cell-walls components removed during immersion.

■ Define fibres distribution in composites after processing

Modeling

Perspectives

- Modeling should take into account both **fibres swelling** and the **influence of processing** conditions on composite morphology;
- To mimic real in-service conditions, **thermo-hydro-mechanical ageing** tests will be investigated on studied materials.





Thank you