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LABORATOIRE de MÉCANIQUE et GÉNIE CIVIL

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DURABILITY OF AN ACRYLIC THERMOPLASTIC CARBON FIBRE REINFORCED COMPOSITE

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afaq ISO 9001 Qualité AFNOR CERTIFICATION

Context of the study

DURACOMP Project (Bel Haj Frej Thesis) : Durable and recyclable composite laminate for boating sector

Boating sector [1]

- Sector in full economic expansion
- +13000 registrations each year

Recovery

- Only few solutions for end-of-life recovery (high environmental impact)

Marine environment

Harsh conditions (water, UV, T°C,…)

1

2

3

4

5

6

End-of-life boats [2]

- +13000 boats reach the end of their life each year
- Mainly UP/GF or VE/GF (>80%)

Substitution

- Natural fibres
- Bio-based resin
- Properties and durability ?
- Recovery?

Objective

A new composite laminate :

- Easy to process
- Good properties and durability
- Recyclability

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[1] French Ministry of the Sea. The figures for yachting in 2021. https://www.mer.gouv.fr/sites/default/files/2021-12/plaisqqc2021.pdf

[2] ADEME. Preliminary study for the implementation of the collection and treatment of end-of-life recreational or sports vessels under producer responsibility (EPR). 2016

Context of the study

Problematic

UP or VE/GF laminate

- Easy to process
- Cheap with good properties and durability

- COV (styrene)
- Poor environmental footprint

Matrix substitution

Elium/GF laminate

- Easy to process [3][4]
- Resin : good mechanical properties and durability [5][6]

- Expensive
- Matrix recovering ?
- GF Recovering ?

Elium/CF laminate

- Easy to process [3][4]
- Resin : good mechanical properties and durability [5][6]

- Expensive+
- Matrix recovering ?
- Recovering and reuse of CF ?

Comparison

VE/CF laminate

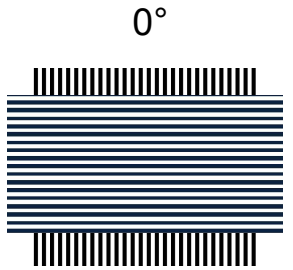
- **Durability ?**

Bel Haj Frej (S12)
6/4/22 at 12:00

[3] Bhudolia SK, Perrotey P, Joshi SC. Proc Inst Mech Eng Part P J Sport Eng Technol 2016;230:64–72.
[4] Becker D, Francois G, Bozsak V, Mitschang P. Kunststoffe Int 2016;106:49–51.
[5] Obande W, Mamalis D, Ray D, Yang L, O'Brádaigh CM. Mater Des 2019;175:107828
[6] Davies P., Le Gac P.Y., Le Gall M. Appl Comp Mat 2017;24:97-111

Fibres

- Carbon fibre NCF (Cbx600 24K T620) from Sicomin
  - Areal mass : 627 g/m²
  - 2 UD plies stitched at 0/90° of 309 g/m² each (fibre type : **T620SC-24k-50C 1850 tex**)
  - Sizing for general use (EP, UP, VE,…)



Matrices

- **Vinylester Atlac E-Nova MA 6215 from DSM**

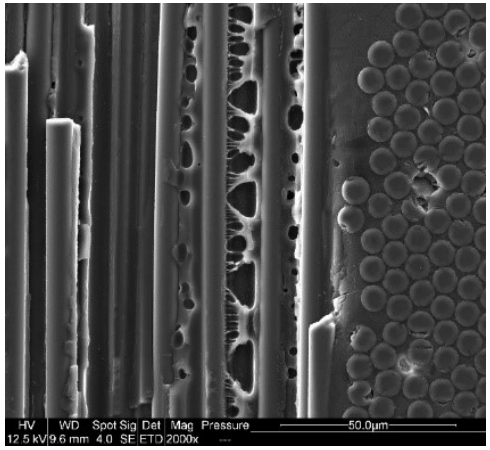
- **Elium 188-O from ARKEMA**
  - For wind and marine application (large structures)
  - Low exothermic reaction

Matrix	VE	Elium 188-O
Density (g/cm^3)	1,17	1,17
Tensile strength (MPa)	70	76
Tensile modulus (GPa)	4	3,3
Ultimate strain	2-3 %	6%
Tg (°C) $_{(DMA)}$	114	104
Viscosity (cP)	90	100

Data from manufacturers

Manufacturing process

- Plates of 4 plies of biaxial carbon NCF : $[0/90/0/90]_S$
- Liquid infusion moulding (p>900 mbar; T=25°C)
- Curing at room temperature / no post-curing

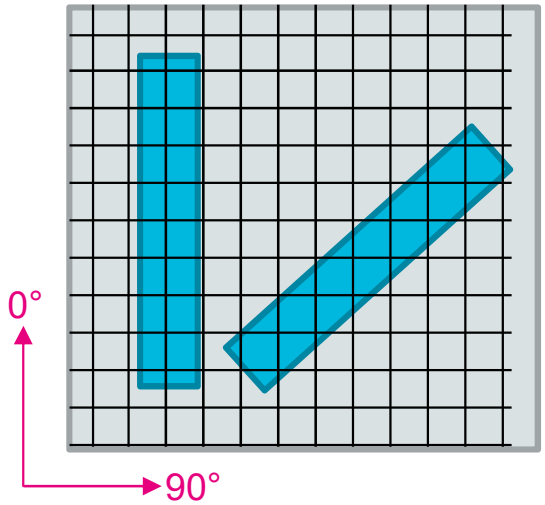


Volume fractions

	V_f (%)	V_r (%)	V_p (%)	T_{mf} (%)
VE/CF	59,74	37,79	2,47	71,03
Elium/CF	61,05	35,11	3,84	71,15

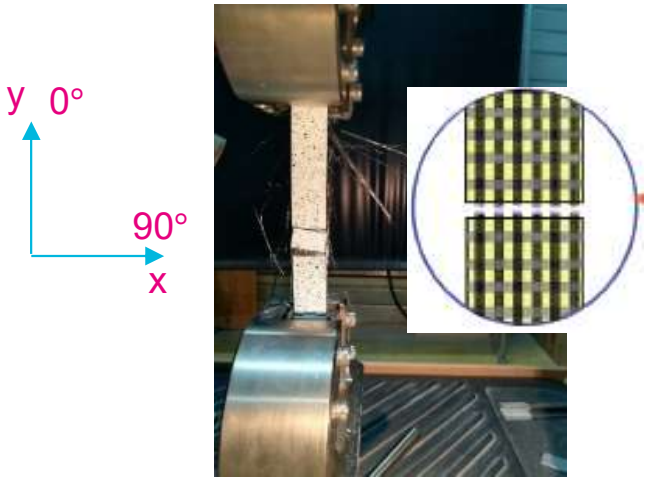
Test specimens

- Tensile tests (250 x 50 x 2,5 mm^3) : 0/90 and -45/+45
- Interlaminar shear tests (30 x 10 x 5 mm^3) : 0/90
- Dynamic mechanical analysis (80 x 10 x 2,5 mm^3) : 0/90

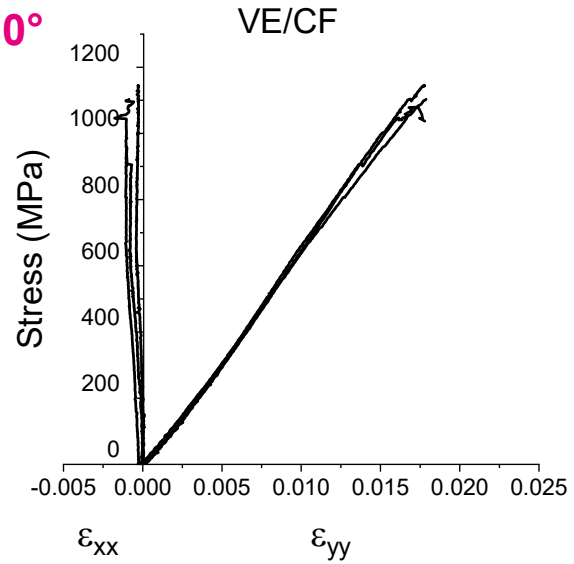


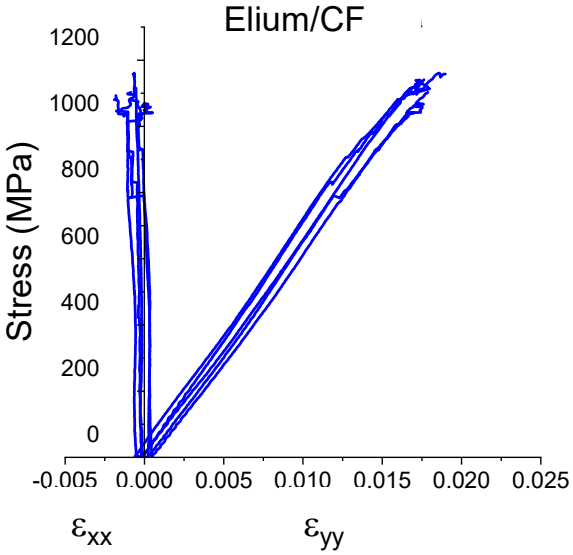
Elastic properties and strength – Tensile tests at 0°

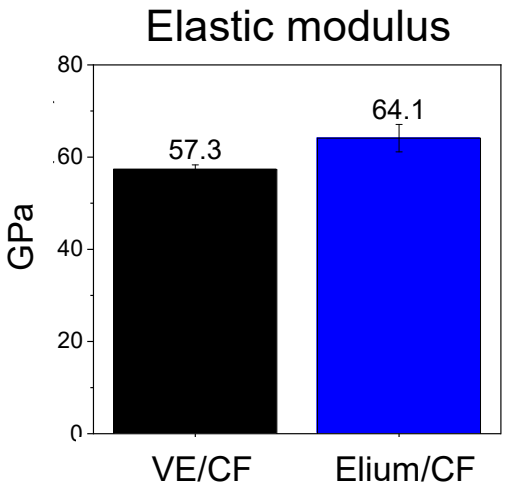
- Displacement : **1 mm/min**

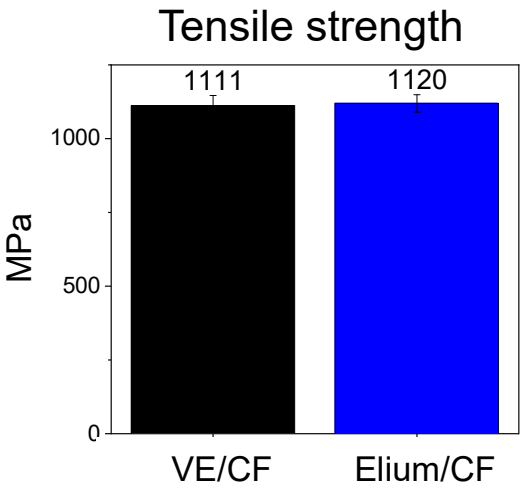


- Mainly driven by the behavior of fibres



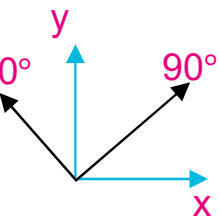


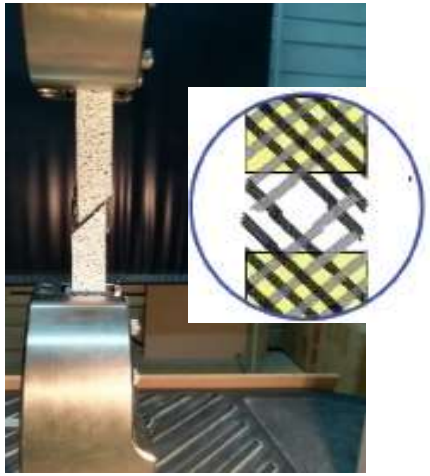




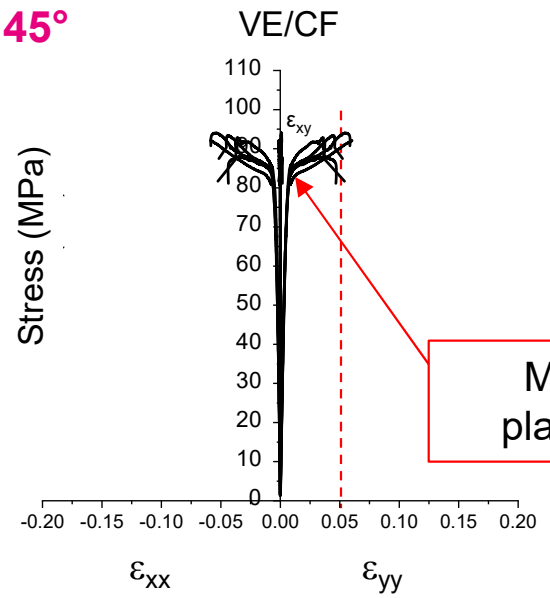
Elastic properties and strength – Tensile tests at 45°

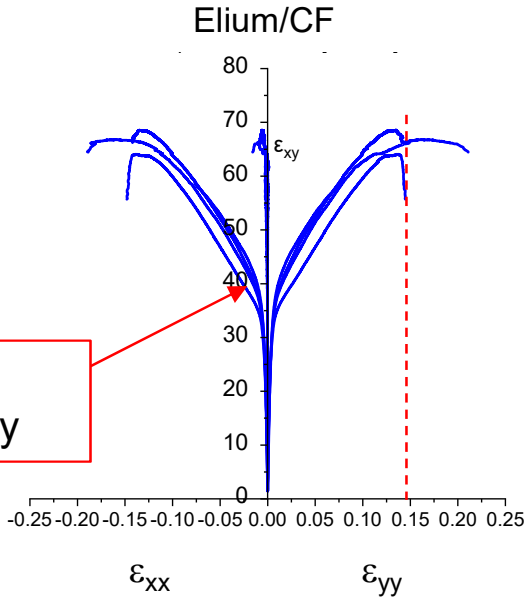
- Displacement : **1 mm/min**

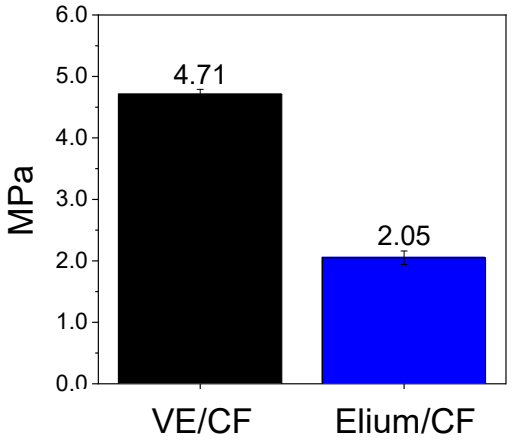


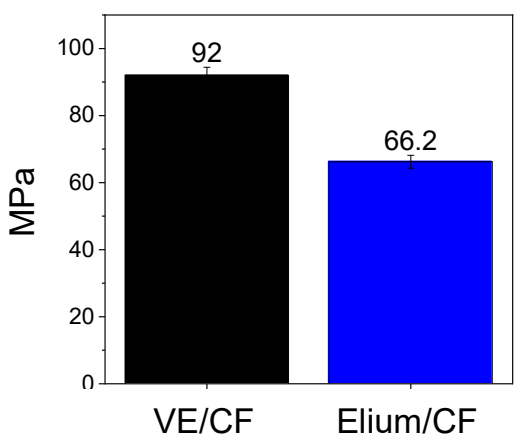


- In-plane shear behavior mainly driven by the matrix
  - Thermoplastic vs thermoset
  - Interface (Sizing)



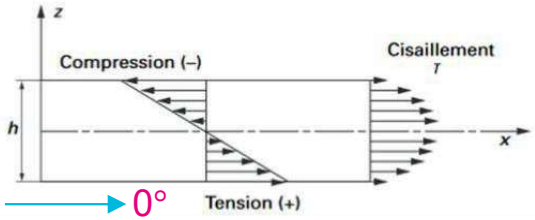


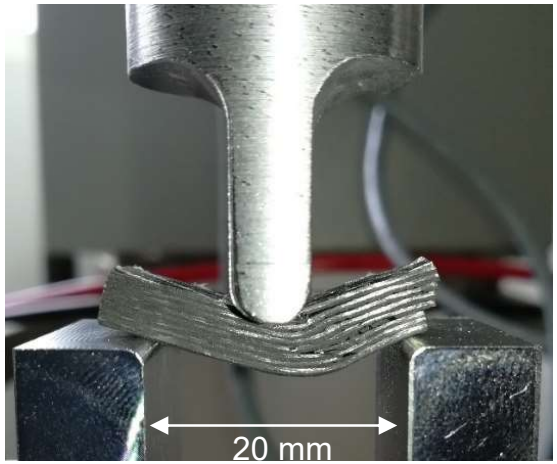


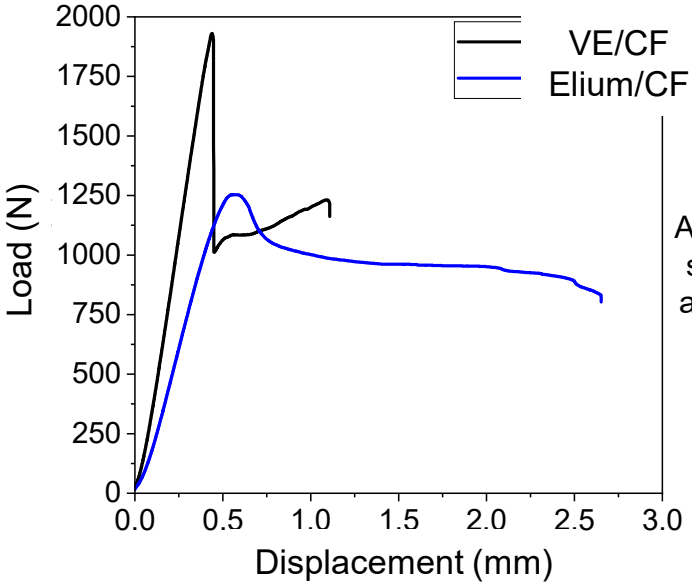


Elastic properties and strength – ILSS Tests

- Displacement : **5 mm/min**
- Reduced span < **5xh**

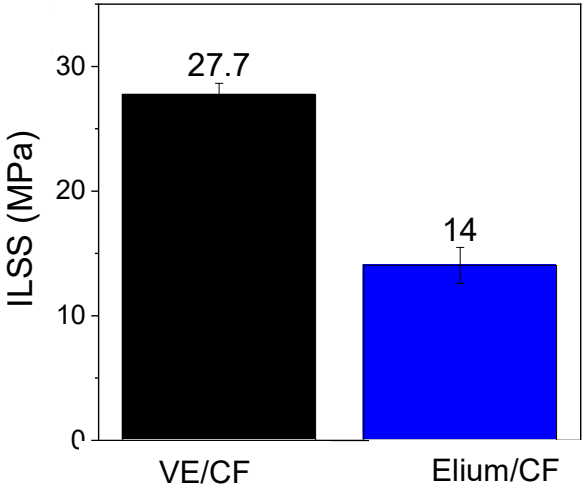






At max load, tensile stress is **230 MPa** and **150 MPa** resp.

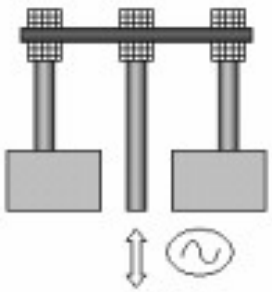
- Interlaminar shear behavior driven by the matrix
  - Thermoplastic vs thermoset (plastic vs brittle failure)
  - Interface (Sizing)



Viscoelastic properties – DMA

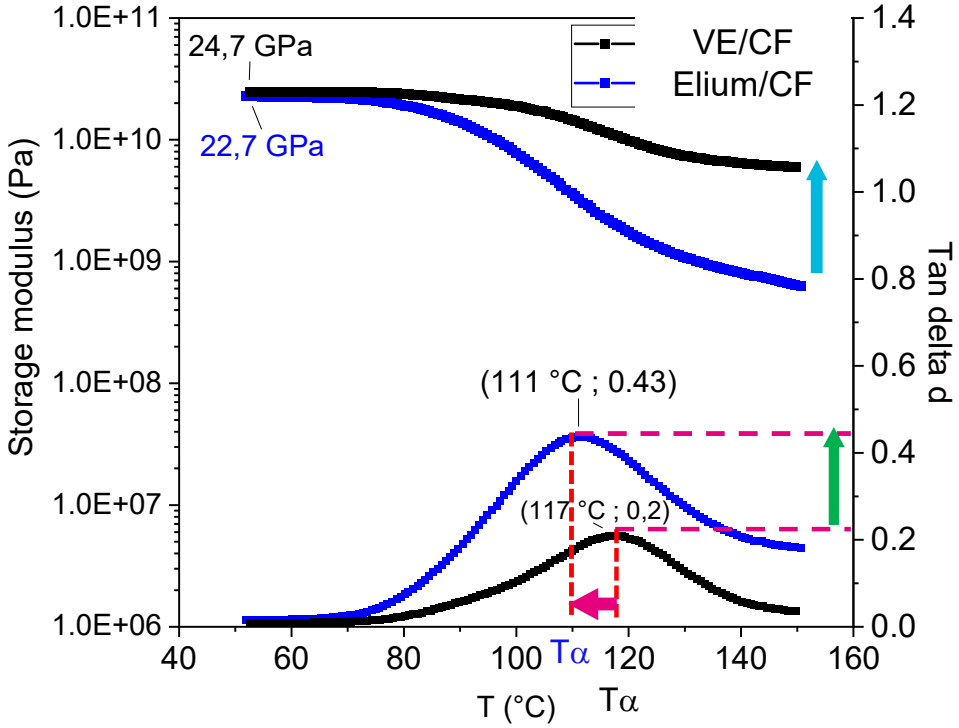
- Amplitude : **10µm** ; Frequency : **5 Hz** ; Heat rate : **3°C/min**

Dual Cantilever



$$E^* = E' + i\,E''$$

$$tan(\delta) = \frac{E''}{E'}$$

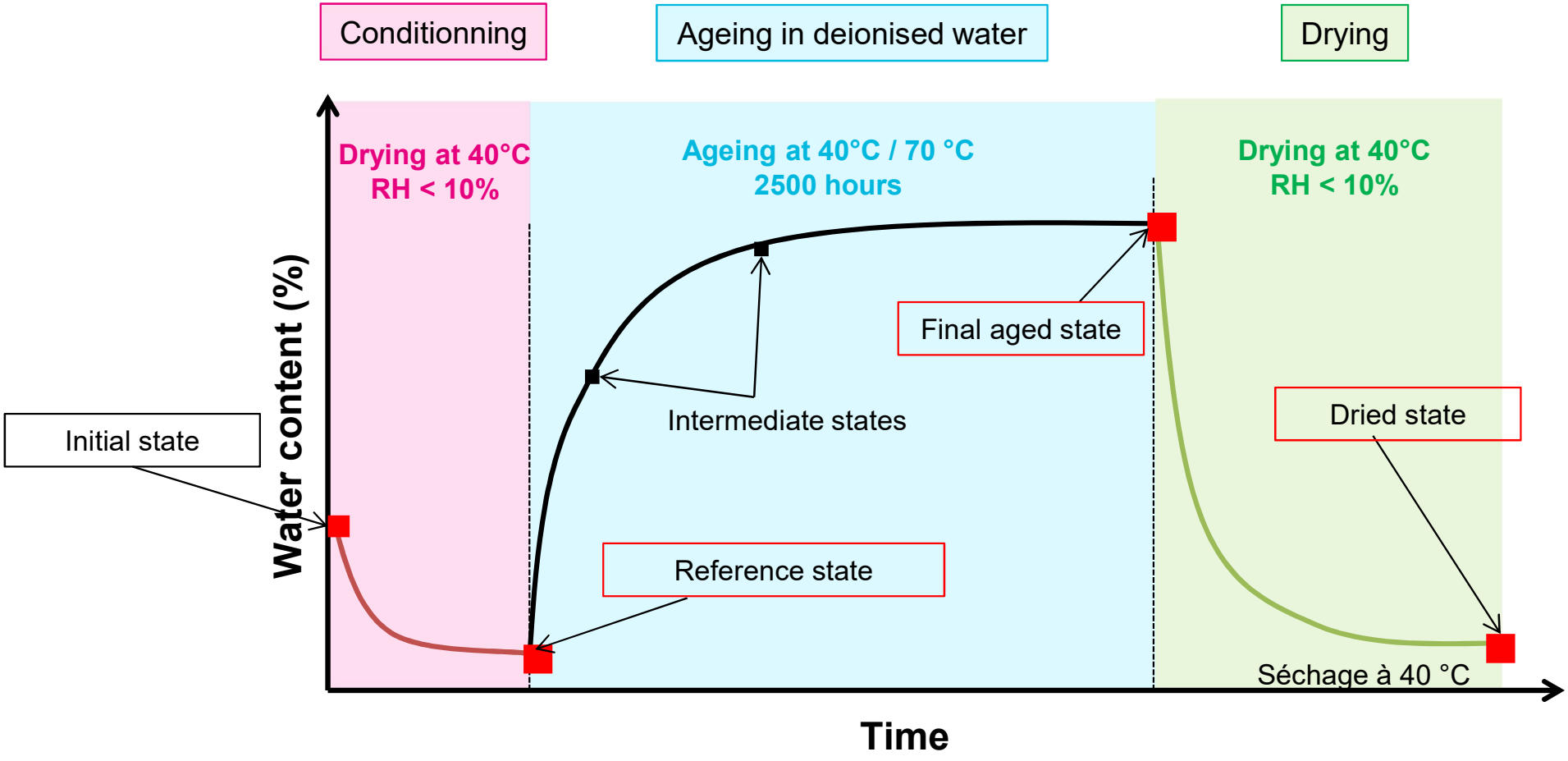


Tα (Tg) ↘ & Damping tan (δ) ↗

Storage modulus E' is more sensitive to T°C

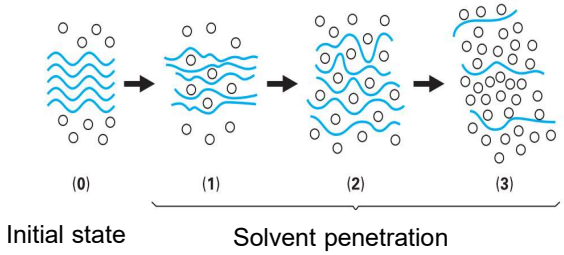
- Viscoelastic behavior driven by the matrix
  - Thermoplastic vs thermoset

Ageing Protocol



Impact of water on mechanical properties : what to expect ?

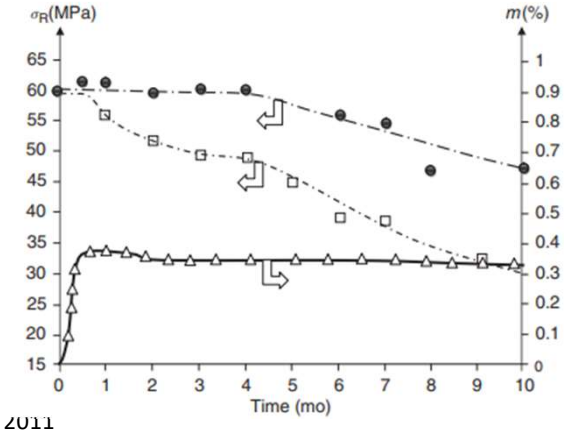
- **Plasticization** (increase of chains mobility) [7]
  - Decrease of modulus, strength and Tg, increase of deformability after ageing
  - Reversible



- **Post-curing** (polymer chains are more mobile which facilitates further incomplete cross-linking/polymerisation reaction) [8]
  - Increase of modulus and strength after ageing
  - Irreversible

Network	T_g (dry) (°C)	T_g (wet)(°C)[a]	ΔT_g (°C) (=T_g(dry)–T_g(wet))	T_g (des)[b]
Epoxy-aliphatic system [8]	63	52	11 (3.4)	71

- **Damage** (chemical reaction between water and polymer that cause multiple phenomena such as chain breaks, new chemical bonds, porosity formation, leaching of elements,...) [9, 10]
  - Increase (leaching of plasticizers) or decrease (hydrolysis, osmosis,…) of modulus and strength.
  - Irreversible

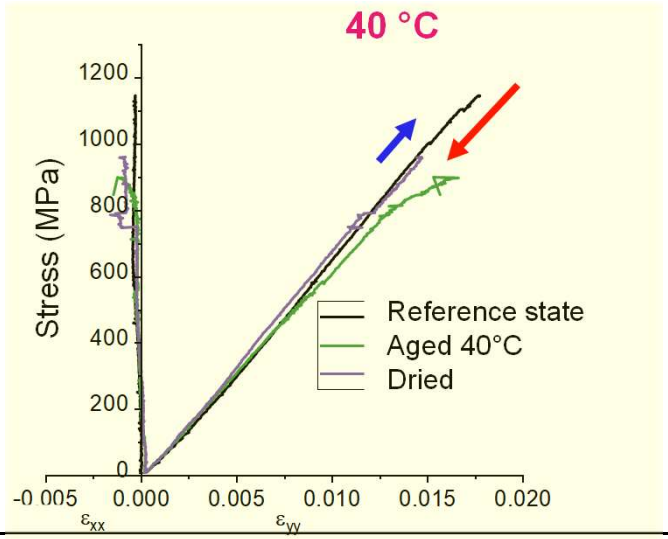


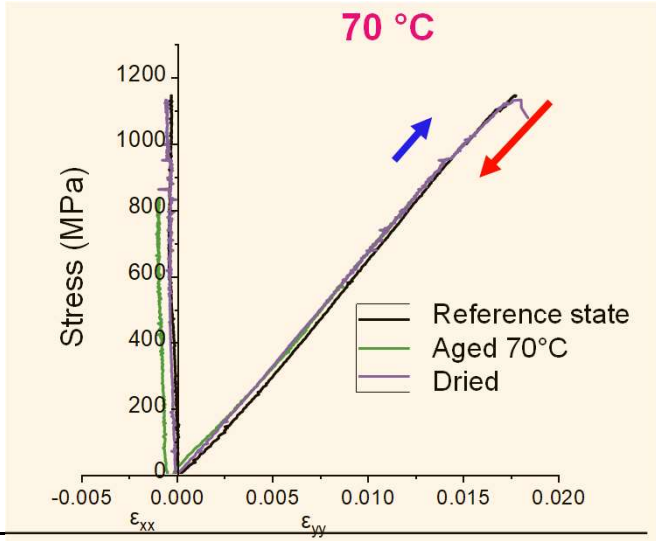
Hydrolysis of E-Glass/Polyester comp. [10]

[7] Fayolle B, Verdu J. Techniques de l'Ingénieur 2005; COR108V1
[8] Perrin FX, Nguyen MH, Vernet JL. Eur Polym J 2009;45:1524–34.
[9] Colin X, Verdu J. In: Deborah B. Song, editor. Res Prop. Prod. Appl., 2011 Nova Science Publishers, Inc; 2011
[10] Jacquemet R. [PhD thesis]. University of Nancy, France. 2008. June.

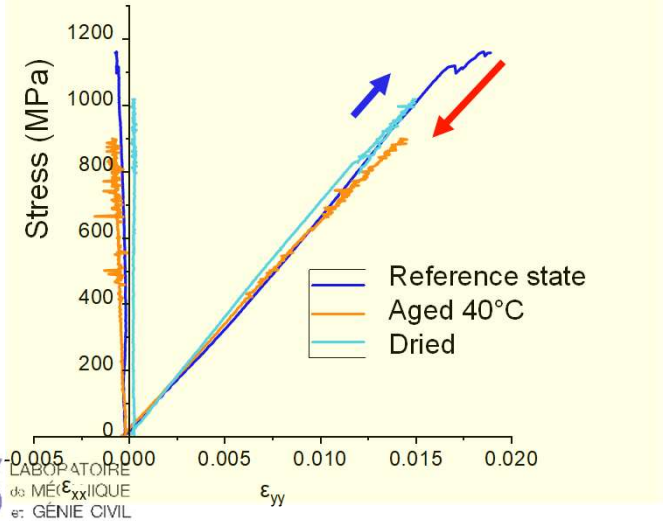
Impact of ageing on mech.prop. Tensile test 0/90°

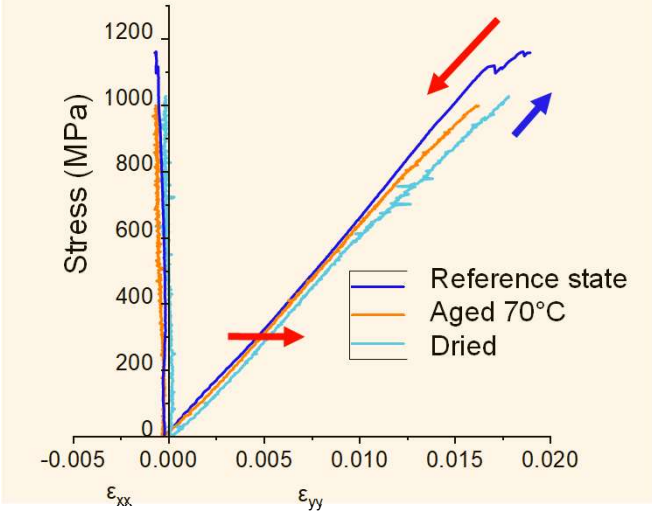
VE / CF





Elium / CF

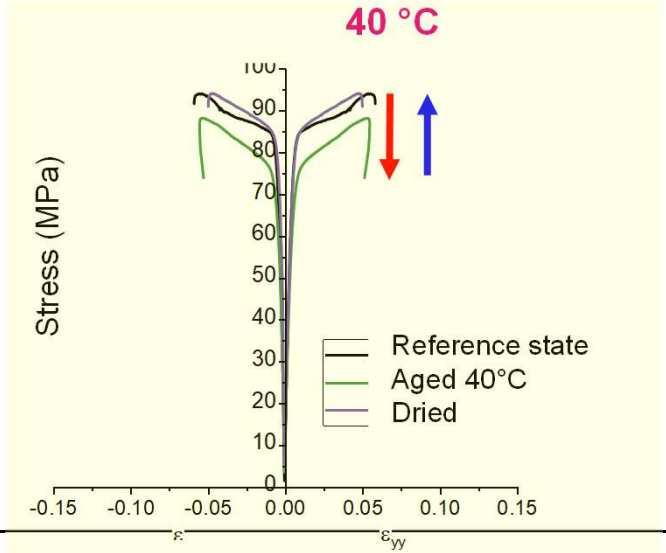


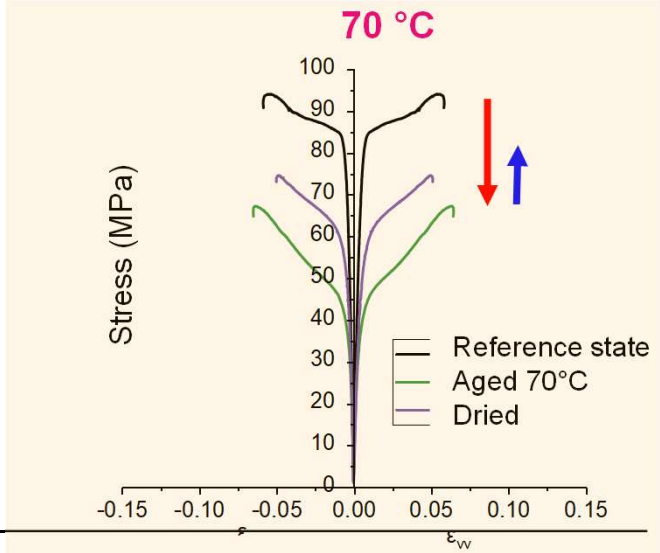


- Tensile modulus is not impacted for both mat. Expect for Elium/CF at 70°C (-10%)
- Tensile strengthes decrease after ageing and partially recovery for all mat.

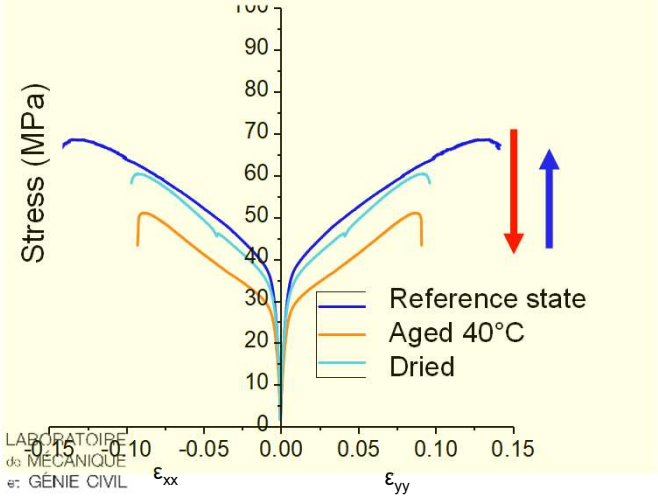
Impact of ageing on mech.prop. Tensile test +45/-45°

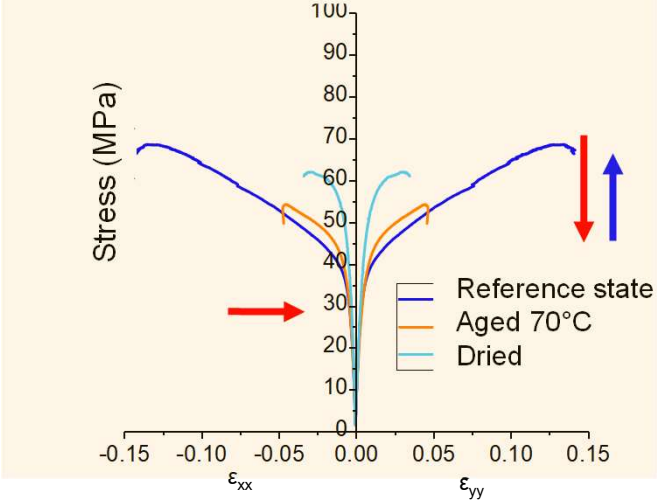
VE / CF





Elium / CF

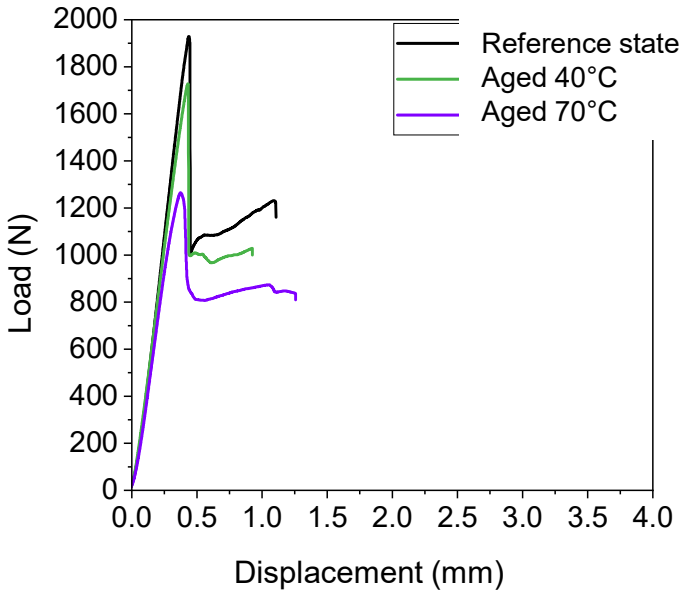




- At 40°C, decrease of shear modulus and strength after ageing and almost complete recover for both mat.
- At 70°C, important decrease of shear modulus and strength after ageing and partial recover for both mat.
  - Elium/CF gets more brittle (post polymerisation)

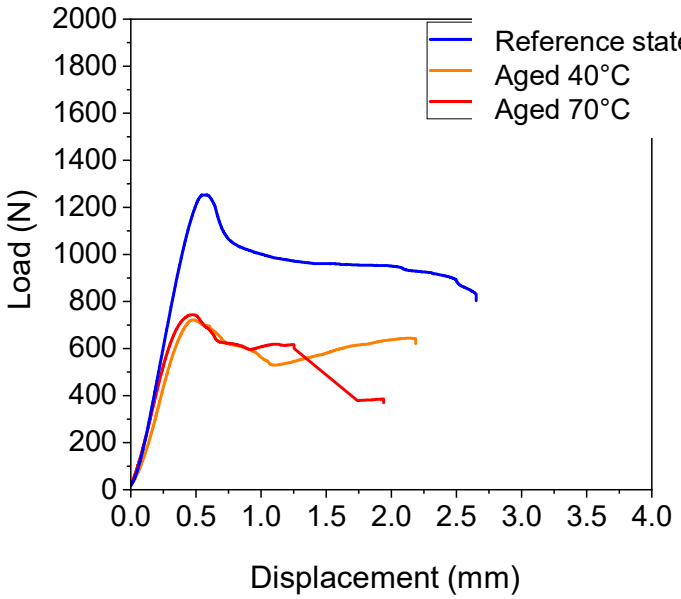
Impact of ageing on mech.prop. Interlaminar shear strength

VE / CF



ILSS : **28 MPa** → **25 MPa** → **17 MPa**

Elium / CF

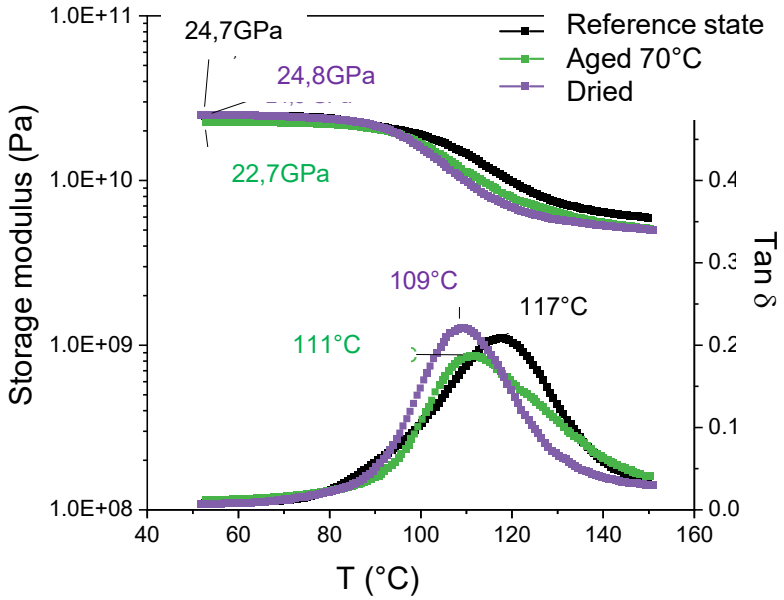


ILSS : **14 MPa** → **8 MPa** → **8 MPa**

- VE / CF : ILSS mostly impacted at 70°C but brittle (sudden) failure.
- Elium / CF : Plastic failure strongly impacted by ageing at 40 and 70°C (interface problem?)

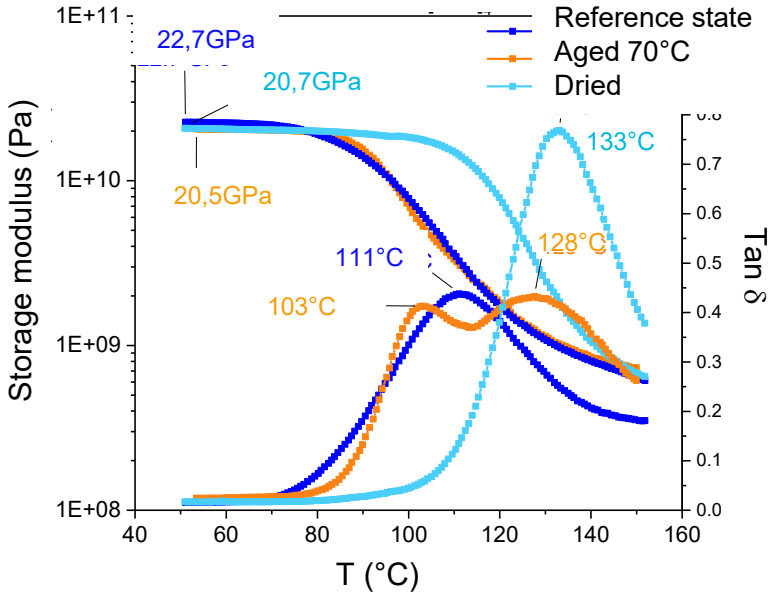
Impact of ageing on mech.prop. Viscoelastic properties / Tg

VE/CF

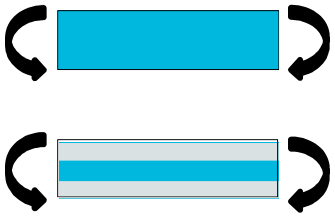


- Storage modulus E' not much impacted
- Tg decreases after ageing (-6°C)
- After drying, Tg lower than ref. state

Elium/CF



- Storage modulus E' not much impacted
- After ageing :
  - 1st peak : aged mat.
  - 2nd peak : dry mat.
- After drying, Tg and damping increase



Initial properties

- Properties in the fibre direction are equivalent
- Off-fibre direction properties and ILSS are lower for Elium composites
- Elium composite is more sensitive to temperature

After aging

- Decrease of most properties due to plasticization for both mat. (VE / CF more impacted off-axis)
- Elium / CF interface strongly impacted (ILSS)
- Tg not much impacted for both mat.

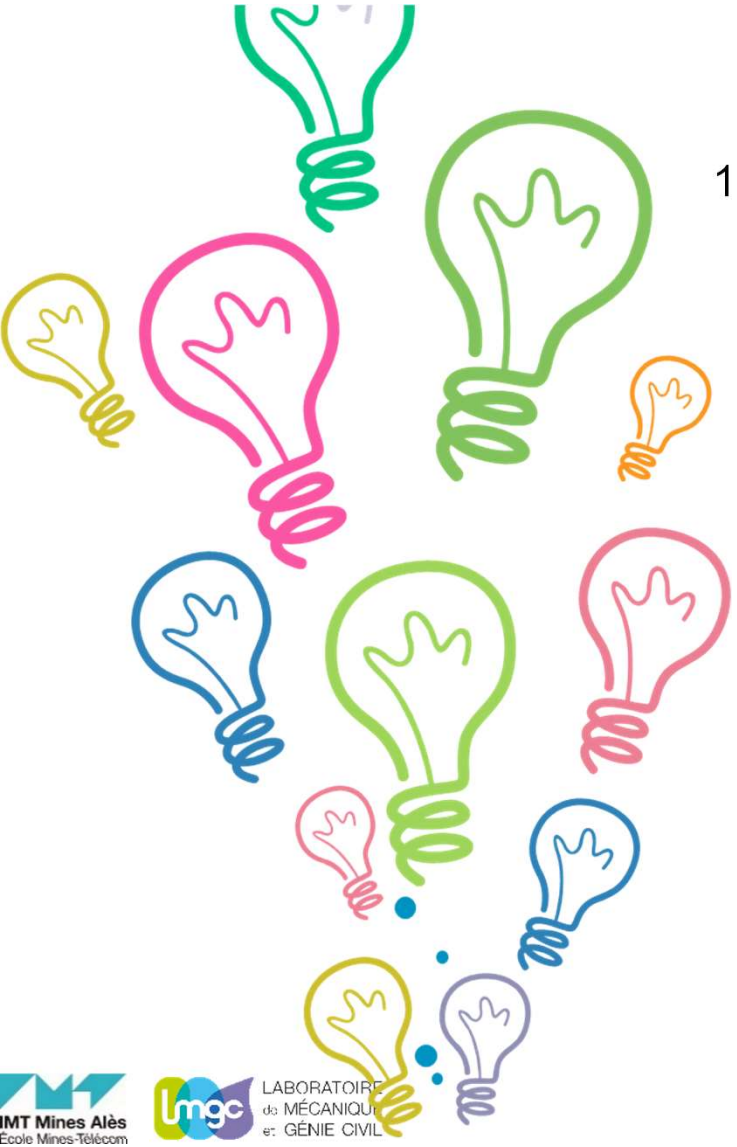
After drying

-No full recovery for both mat.
-VE / CF : chemical degradation (hydrolysis)
-Elium / CF more stable

Recycling

H. Bel Haj Frej (S12)
6/4/22 at 12:00

With a dedicated sizing (improve the shear behavior)
a substitution is possible



1) Impact of ageing on the recyclability of Elium / CF

2) Obtain NCFs from recovered fibres : discontinuous (10^{-2}m) and not aligned after recycling.

3) Investigating the environmental and financial sustainability of depolymerisation through the development of life cycle assessment models

- Bel Haj Frej, H., Léger, R., Perrin, D. et al. Appl Compos Mater 28, 899–922 (2021)
- Bel Haj Frej H, Léger R, Perrin D, Ienny P. Journal of Composite Materials. 2021;55(19):2673-2691.
- Bel Haj Frej H, Léger R, Perrin D, Ienny P., Gérard P., Devaux J.F. Resources, Conservation and Recycling, Volume 173, 2021, 105705.

Thank you for your attention

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