



IMT Mines Alès
École Mines-Télécom



EMMC18

18th European Mechanics of Materials Conference
April 4th-6th, 2022, Oxford

RECOVERY AND REUSE OF CARBON FIBRE AND THERMOPLASTIC RESIN FROM COMPOSITES FOR MARINE APPLICATIONS

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Pierre Gérard and Jean-françois Devaux (ARKEMA)

CONTEXT

DURACOMP Project : Development of a **durable** and **recyclable** monolithic eco-composite for **marine applications**

Pleasure boats

A fast growing economic sector

- +12000 registrations per year [1]
- France: Leader in sailing boats and multihulls



DURACOMP Project : Development of a **durable** and recyclable monolithic eco-composite for **marine applications**

- ▶ Substitution of traditional materials (wood, metals) since 1940 [2]
 - Interesting weight/performance ratio
 - High durability
 - Good fatigue properties

- ▶ Vector for the development of the nautical industry: 95% of pleasure boats are made of composites [3]
 - Design of complex geometries
 - Fast process adapted to large components
 - Increase in production efficiency



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End of Life Boats (ELB)

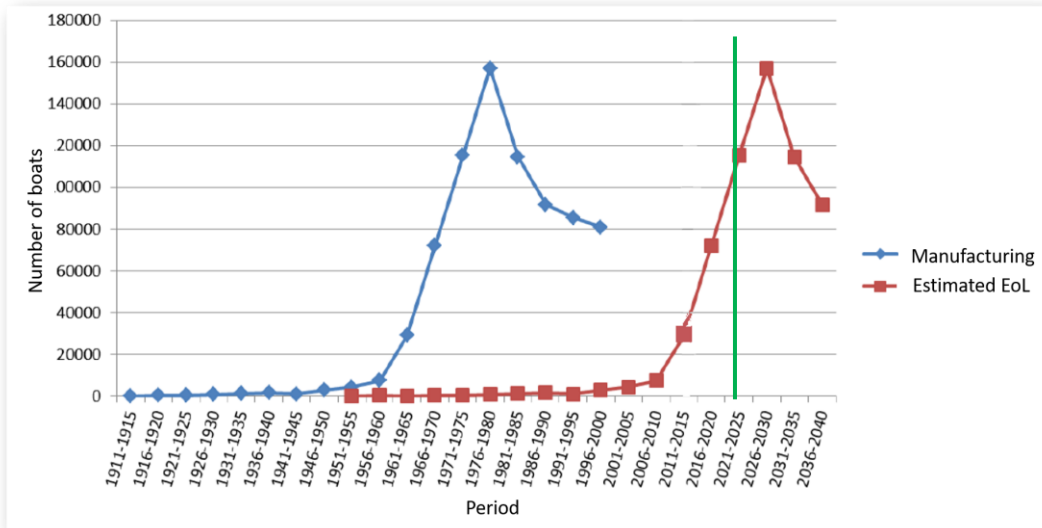
- Glass (carbon) fibre-reinforced organic resins (polyester)
- +13,000 boats reach the end of their life each year [4]

[1] Direction générale des infrastructures des transports et de la mer. La plaisance en chiffres 2017/2018.

[4] ADEME. Étude préalable à la mise en place de la filière de collecte et de traitement des navires de plaisance ou de sport hors d'usage sous la responsabilité des producteurs (REP). 2016

DURACOMP Project : Development of a **durable** and **recyclable** monolithic eco-composite for **marine applications**

- ▶ Estimated lifetime: 30 ~ 45 years
- ▶ 2015: ~ 40% of the park is over 30 years old [5]
- ▶ End of life following the production trend



End of life scenarios:



Abandoned



Sunk / Burned



Landfilled



Deconstructed

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Valorisation

Restrictive legislation

- High production costs
- Low environmental impact
- Lack of sustainable solutions for end-of-life recovery

1

3

2

4

End of Life Boats (ELB)

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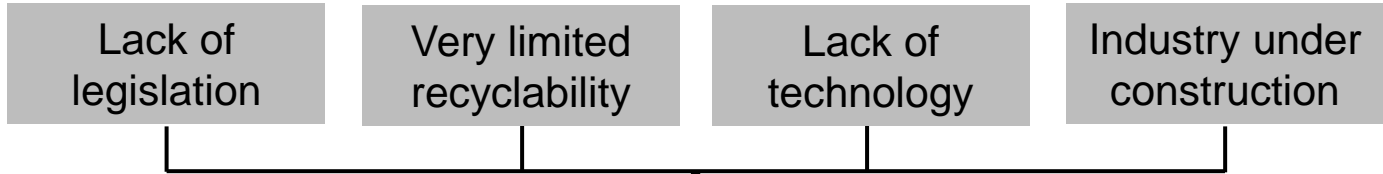
Ecologisation of the field

Substitution tentative by:

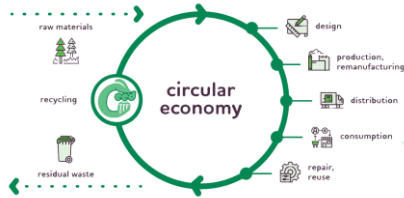
- Natural fibres: Mechanical and functional limitations
- Biosourced resins : Operational and mechanical limitations



DURACOMP Project : Development of a **durable** and **recyclable** monolithic eco-composite for **marine applications**



End-of-life boats (ELB)



Upstream

Downstream

Eco-design

Valorisation



Raw material with minimal environmental impact

Valorisation favouring recycling

Design driven by the end of life

Re-use

Material recycling

Energy Recovery

Ban landfilling

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Valorisation

Restrictive legislation

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Marine environment

Combined stresses

- Mechanical (alternating tensile, fatigue, impact)
- Biological
- Thermochemical
- UV

5



6

2

End of Life Boats (ELB)

- Glass (carbon) fibre-reinforced organic resins (polyester)
- +13,000 boats reach the end of their life each year[4]

Ecologisation of the field

Substitution tentative by:

- Natural fibres: Mechanical and functional limitations
- Biosourced resins : Operational and mechanical limitations

Objectives

- Substitute thermosetting resin by thermoplastic resin
- Investigate the *durability* and ***recyclability potential*** of the substitute composite



[1] Direction générale des infrastructures des transports et de la mer. La plaisance en chiffres 2017/2018.

[4] ADEME. Étude préalable à la mise en place de la filière de collecte et de traitement des navires de plaisance ou de sport hors d'usage sous la responsabilité des producteurs (REP). 2016

Aim of the work

Reference material

CF/Vinylester composite

- Widely used in the advanced marine industry
- Processed at room temperature
- High ultimate mechanical properties
- Corrosion resistant
- Processabilité et VOCs (styrene)
- Requires post-curing
- Low environmental impact



Substitution material



CF/Elium 188-O composite

- Liquid thermoplastic resin Low viscosity: Vacuum infusion [9]
- Radical polymerisation [10]
- Corrosion resistance: Suitable for marine environment
- Mechanical properties similar to epoxy [11]
- Durability
- Recyclability

R. Léger (S8) 05/04/2022 5pm

[9] Bhudolia SK, Perrotey P, Joshi SC. Experimental investigation on suitability of carbon fibre thin plies for racquets. Proc Inst Mech Eng Part P J Sport Eng Technol 2016;230:64–72.

[10] Becker D, Francois G, Bozsak V, Mitschang P. Combining the best of two polymer worlds. Kunststoffe Int 2016;106:49–51.

[11] Obande W, Mamilis D, Ray D, Yang L, Ó Brádaigh CM. Mechanical and thermomechanical characterisation of vacuum-infused thermoplastic- and thermoset-based composites. Mater Des 2019;175:107828

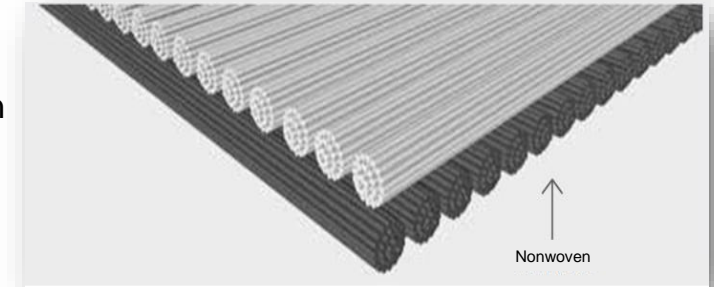
SUMMARY

1. MATERIALS AND METHODS
2. RECYCLABILITY
3. CONCLUSIONS & PERSPECTIVES

MATERIALS AND METHODS

Reinforcement

- ▶ Equilibrated nonwoven CF fabric (Cbx600 24K T620) from Sicomin
 - Density: $1,77 \text{ g/cm}^3$ / Areal density: 629 g/m^2
 - 2 UD at $\pm 45^\circ$ of 309 g/m^2 (**T620SC-24k-50C 1850 tex**)

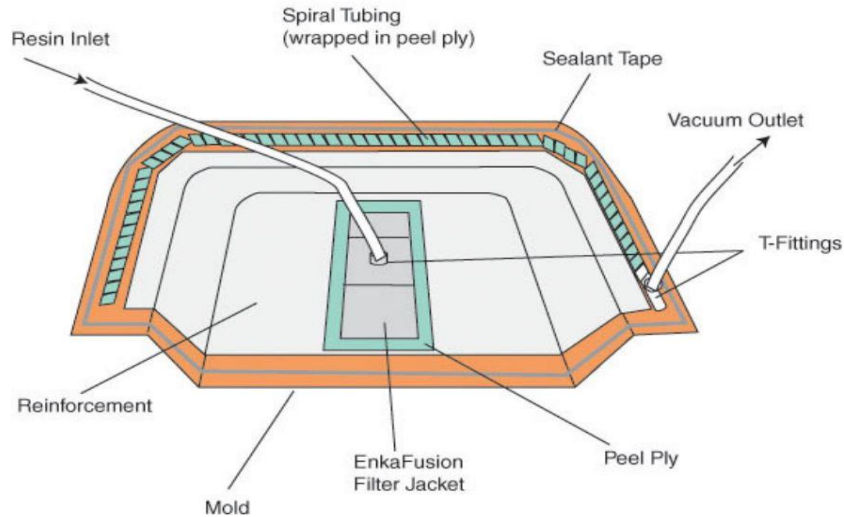


Matrix

- ▶ **Elium 188-O resin**
 - Methyl methacrylate ($\approx 80 \%$) + acrylic copolymers
 - Viscosity $\approx 100 \text{ cPs}$
 - Radical polymerisation initiated by peroxides (Perkadox[®] CH50X) (1,5 ~ 3% in weight)

Résine	Vinylester	Elium 188-O
Density [g/cm^3]	1,17	1,17
Ultimate tensile strength [Mpa]	70	76
Tensile modulus[GPa]	4	3,3
Elongation at break	2-3 %	6%
T_g ($^\circ\text{C}$) _(DMA)	114	104

Vacuum assisted resin infusion (VARI)

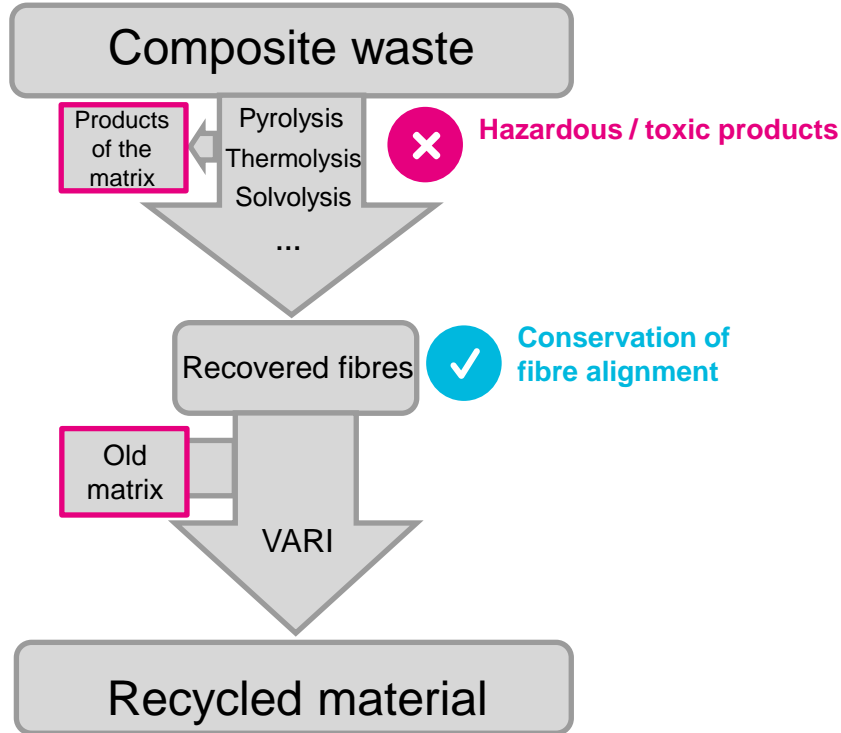


- ▶ $P_{\text{Infusion}} > 900 \text{ mbar}$ and $T^{\circ}_{\text{Infusion}} \approx 25 \text{ }^{\circ}\text{C}$
- ▶ 4 plies plates: $[0/90]_4$ et $[+45/-45]_4$ (thickness $\approx 2,5 \text{ mm}$)
- ▶ Curing at room temperature - No post-curing



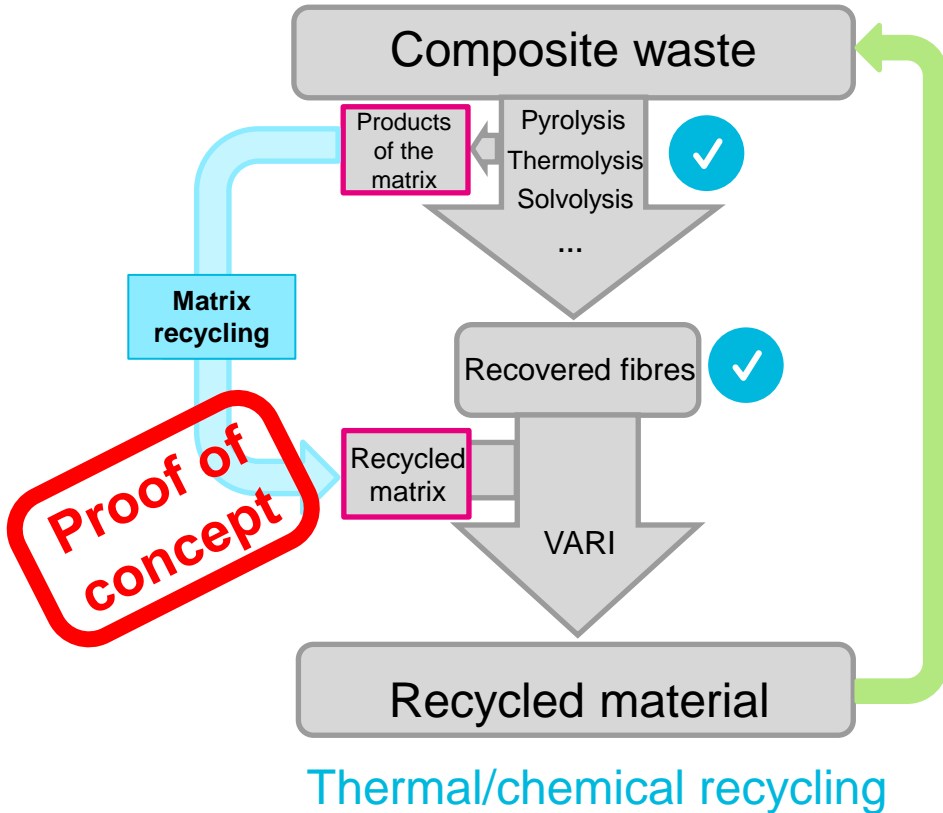
RECYCLABILITY

Recycling scheme

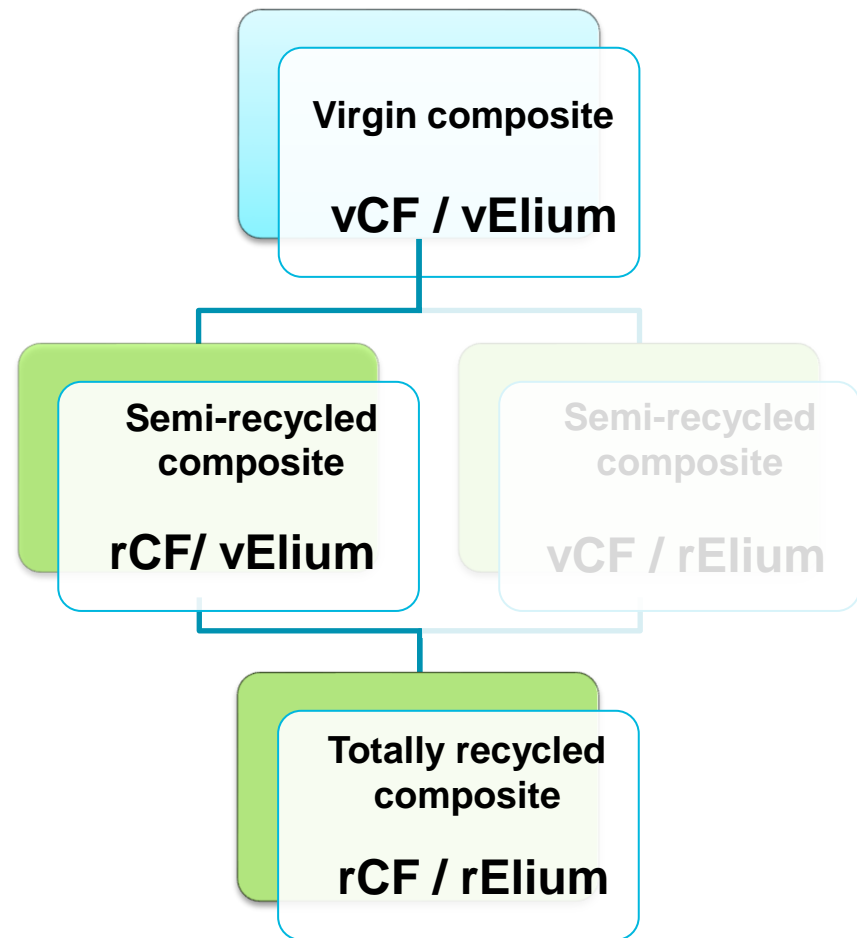
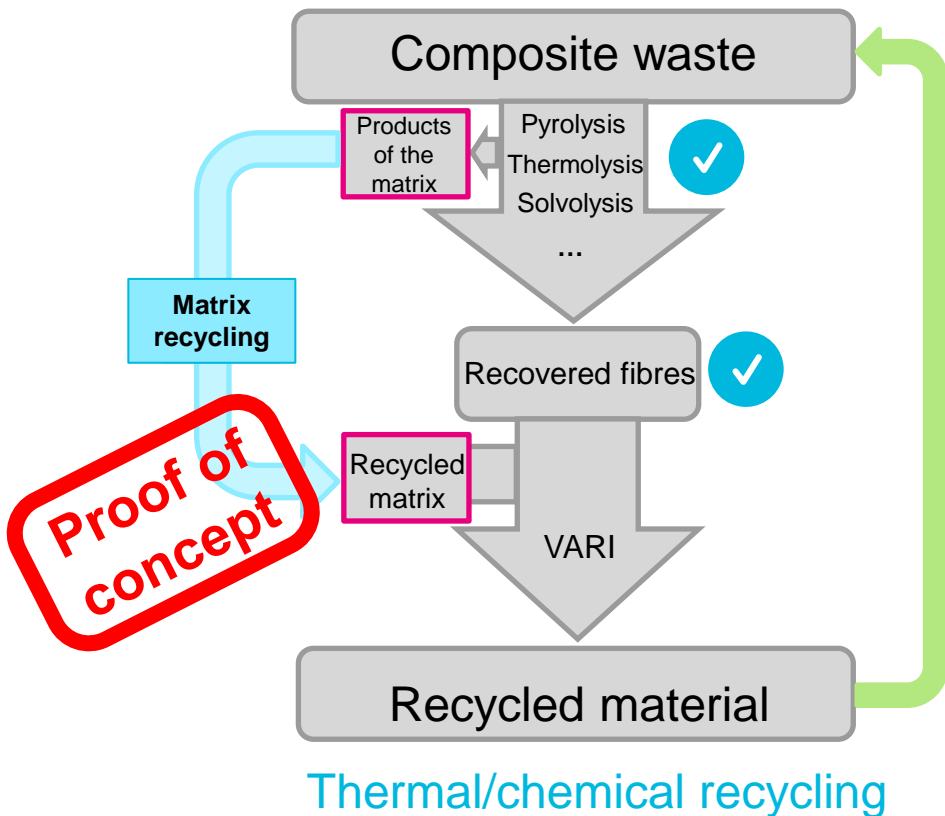


Thermal/chemical recycling

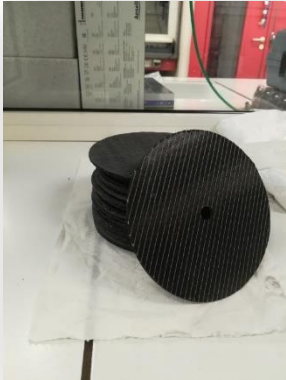
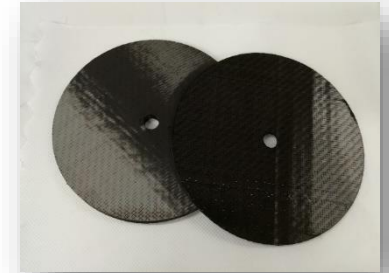
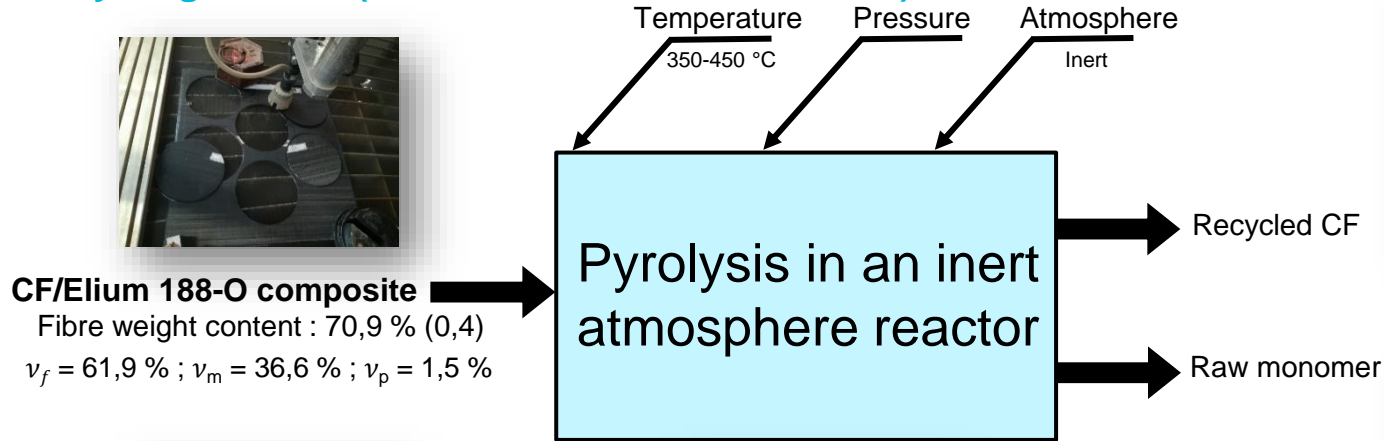
Recycling scheme



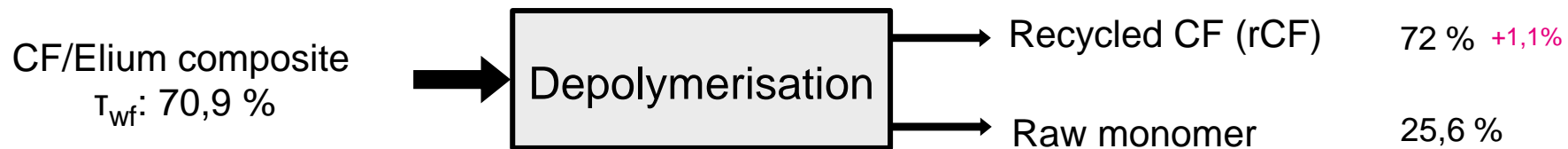
Recycling scheme



Recycling method (in collaboration with ARKEMA)



Quantitative analyses of the method's efficiency



Materials balance 97,6 %



Temperature Pressure



Raw monomer

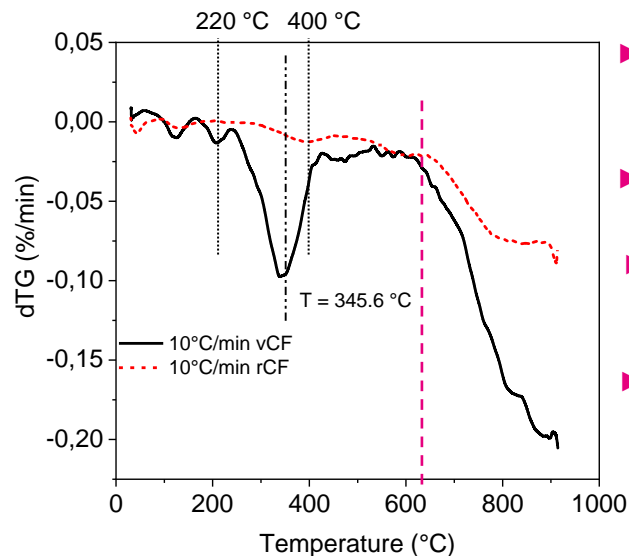
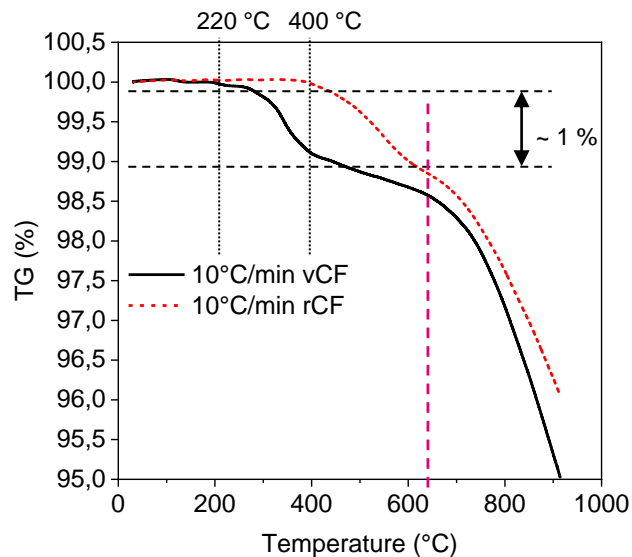
Distillation

MMA (purity > 99,5%)

Impurities : Methanol
Methacrylic acid
...New
Elium

Thermogravimetric analysis under N₂: Mechanisms of fibre degradation

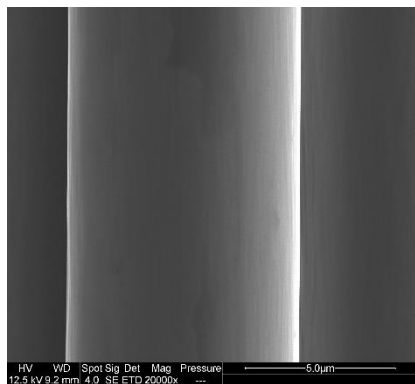
Comparison of virgin carbon fibre (vCF) and recycled carbon fibre (rCF)



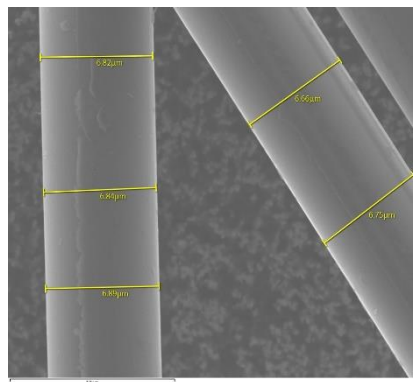
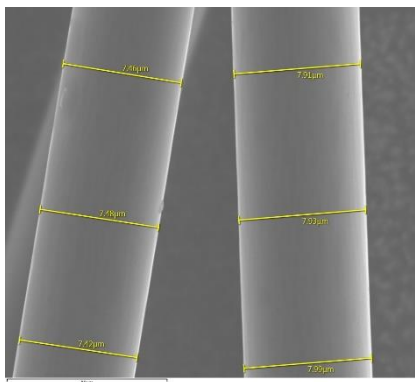
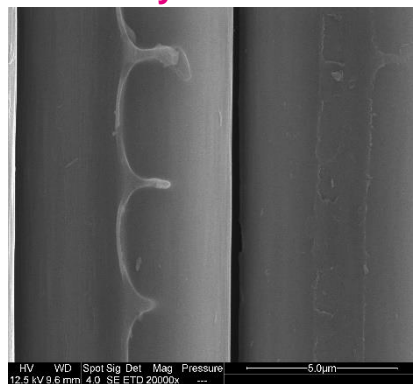
- ▶ 1% loss by weight between 220 °C and 400 °C
- ▶ Loss due to degradation of the sizing
- ▶ Acceleration of fibre degradation at around 660°C
- ▶ **Depolymerisation at 350 - 450°C does not degrade carbon fibres**

Scanning Electron Microscopy : Morphological analysis

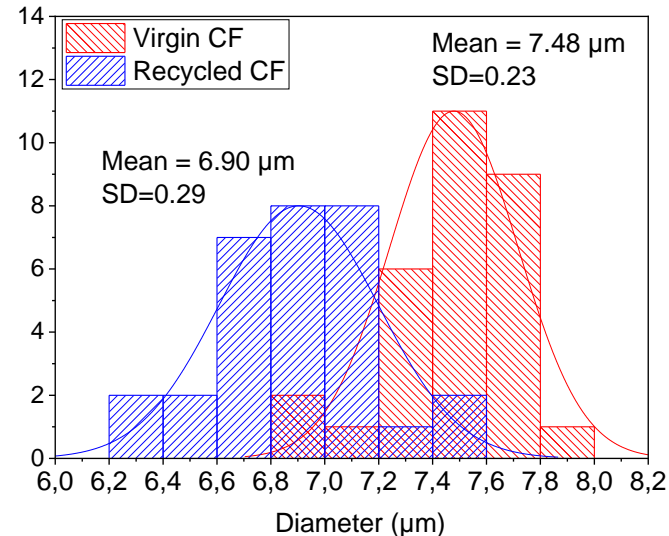
Virgin fibre



Recycled fibre



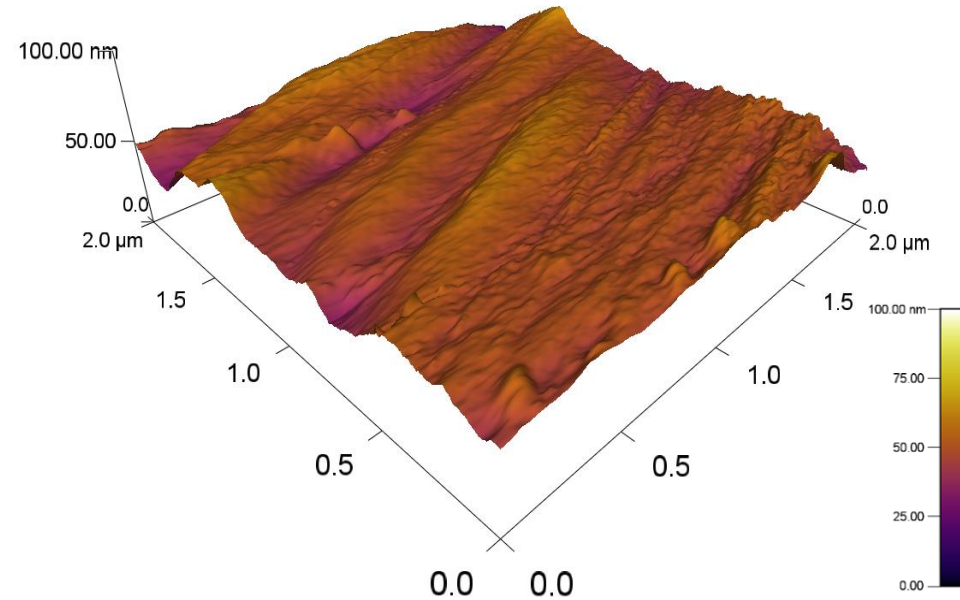
- ▶ Virgin fibres: smooth and homogeneous surfaces
- ▶ Recycled fibres: irregular, discontinuous and localised residue



- ▶ Increased dispersion: Irregularity
- ▶ 600 nm variation: decomposition of the sizing layer (~300 nm thick)
- ▶ Measures confirm TGA results

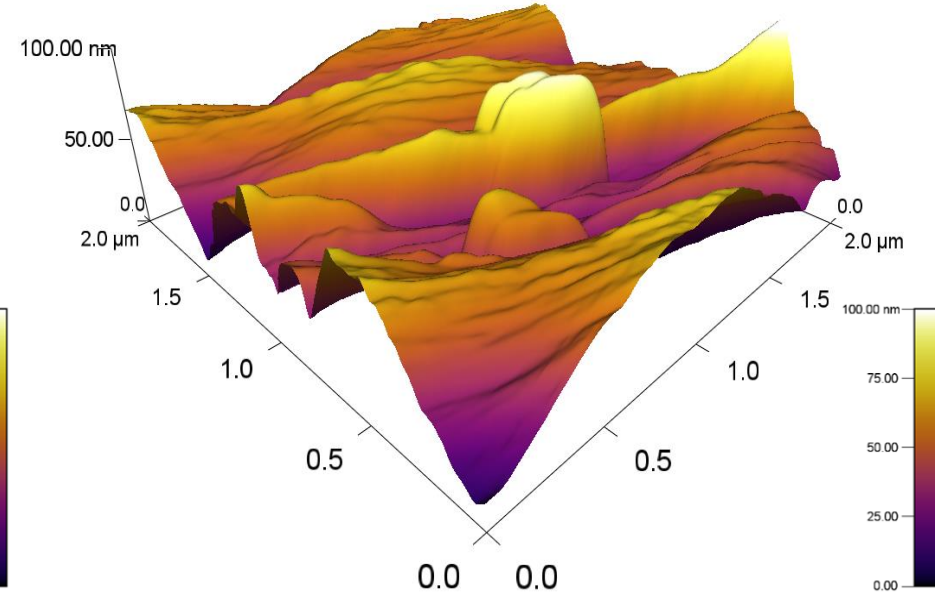
Morphological analysis : Atomic Force Microscope in topography mode

Virgin fibre



► vCF: Rough but not deep valleys

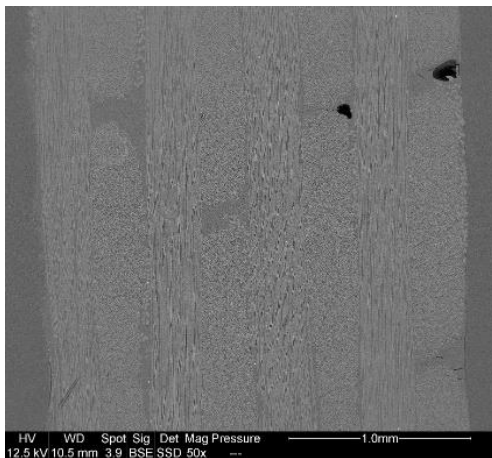
Recycled fibre



► FCr: Smooth and deeper valleys

Plates reprocessing by VARI: Virgin Elium resin (vElium) vs recycled Elium resin (rElium)

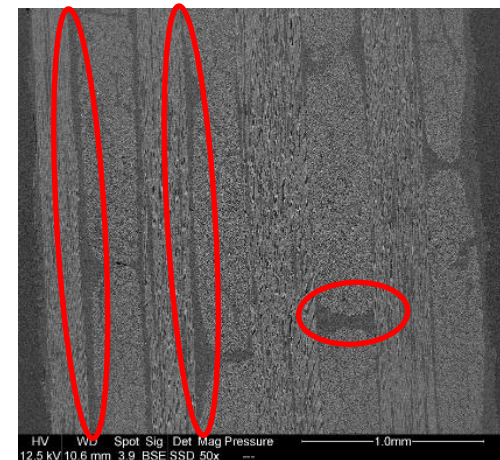
vCF/vElium



rCF/vElium



rCF/rElium



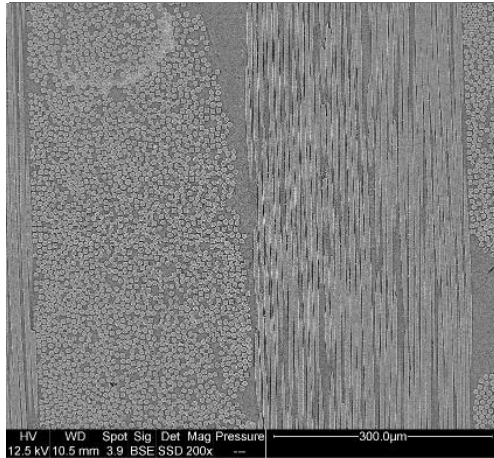
Resin-rich inter-ply areas
(stitching yarn degradation: $A_w \sim 9 \text{ g/m}^2$)

Material	V_f (%)	V_r (%)	V_v (%)	T_{wf} (%)	Areal weight [g/m^2]
vCF/vElium	61 (1,8)	35,1 (1,2)	3,8 (1,27)	70,9 (0,41)	640,5 (2,66)
rCF/vElium	54,8 (1,1)	43,6 (1,27)	1,6 (0,16)	66,4 (1,14)	631,4 (4,89)
rCF/rElium	55,4 (1,12)	42,9 (1,9)	1,7 (0,77)	67,1 (0,38)	628,2 (1,08)

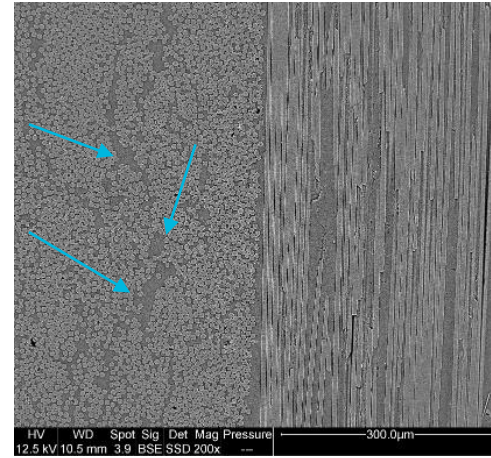


Plates reprocessing by VARI: Virgin Elium resin (vElium) vs recycled Elium resin (rElium)

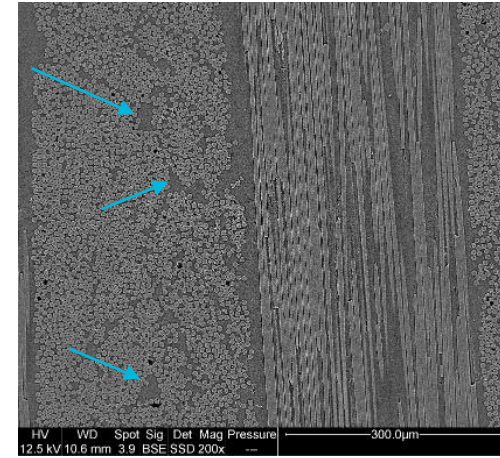
vCF/vElium



rCF/vElium



rCF/rElium



Resin-rich intra-ply areas

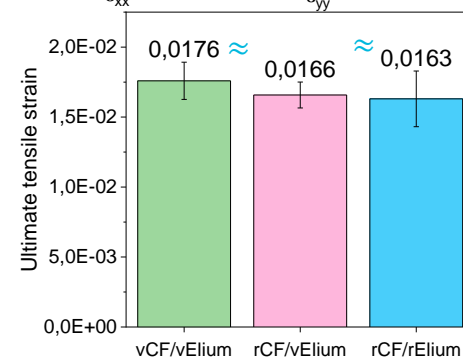
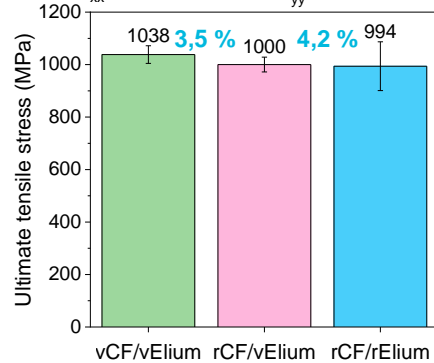
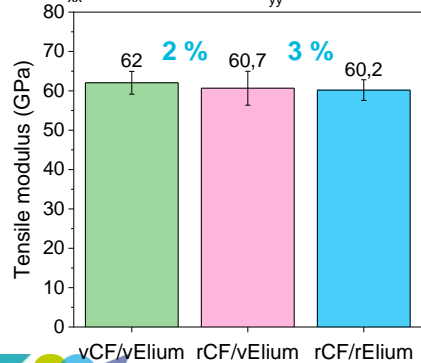
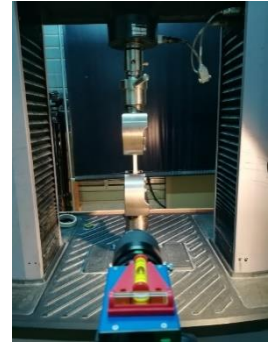
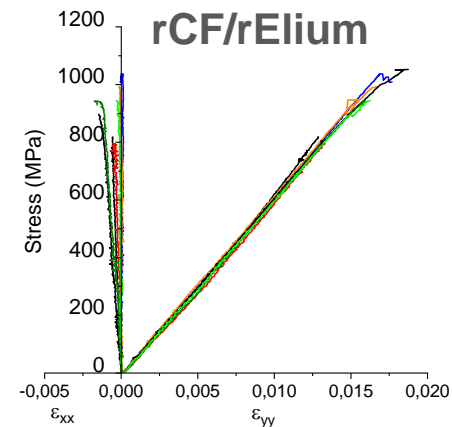
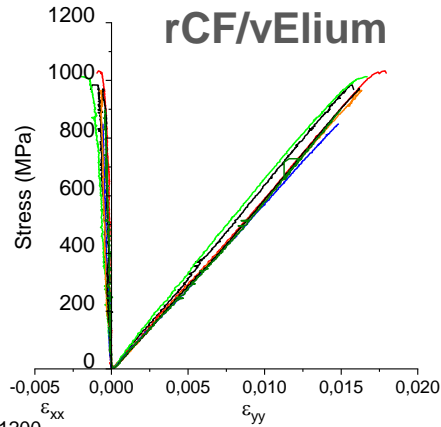
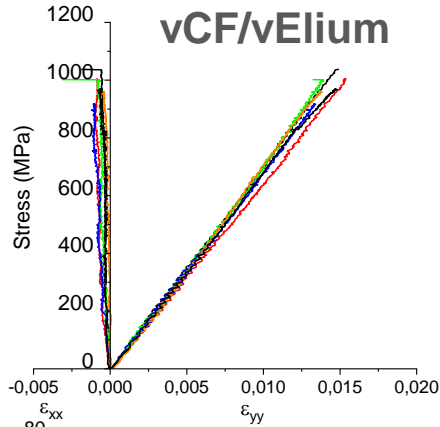
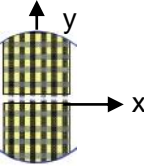
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Tensile tests

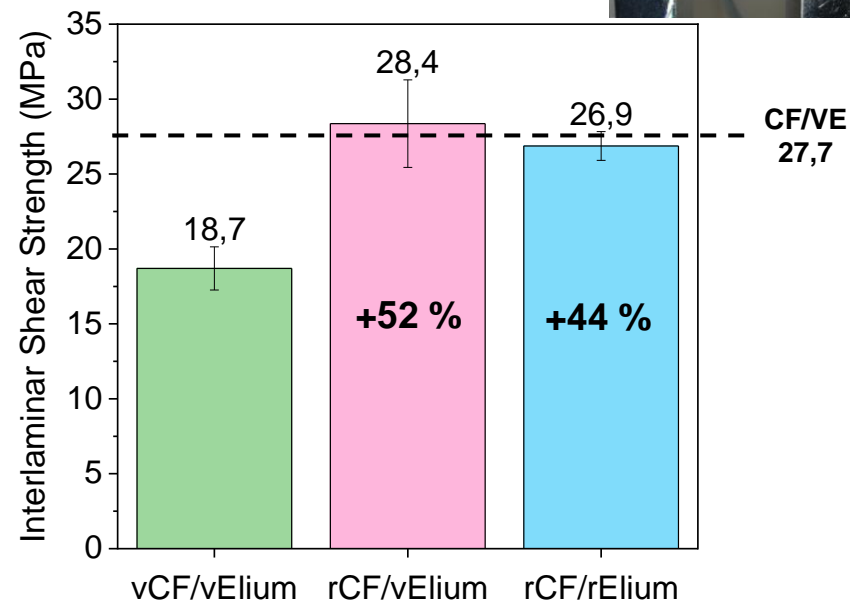
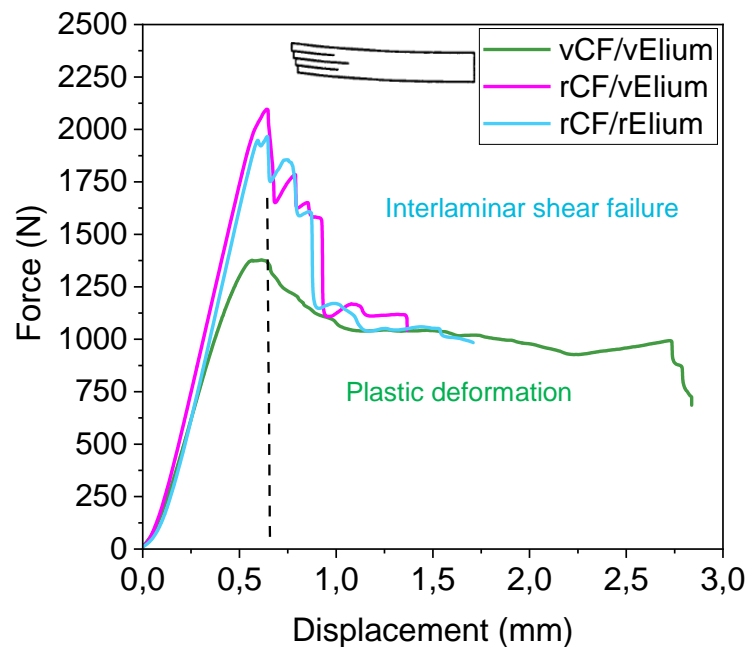
- Recycled CF: circular geometry and limited dimensions

- ISO 572-4: Specimen size: 125x12.5xth



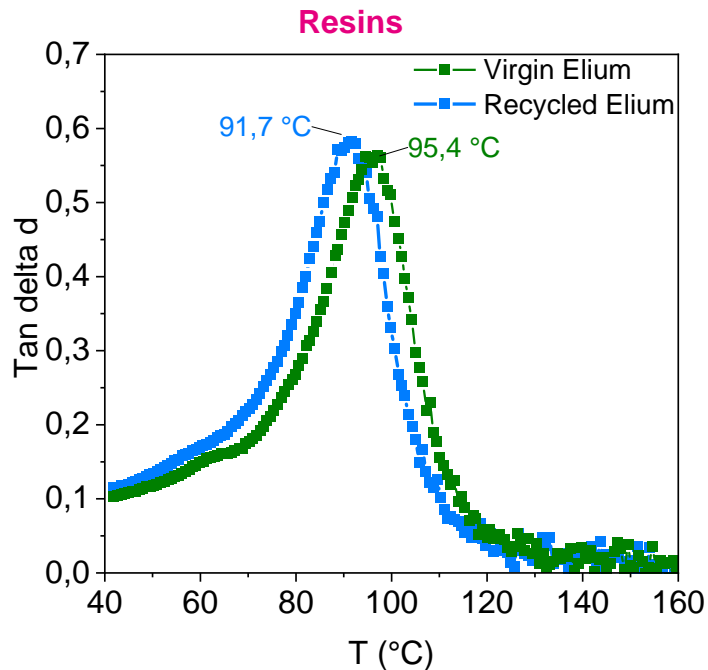
Interlaminar shear strength - ILSS

- ▶ Short bending test: ASTM D2344 (1 mm/min);
- ▶ Spacing between supports = 21 mm (4 × thickness)
- ▶ Specimen size: 30 × 10 × ~5.25 mm³

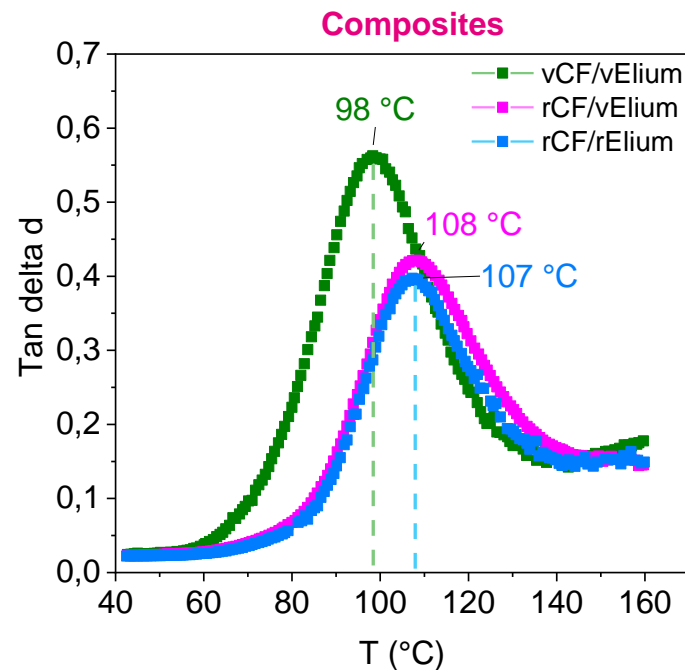


Improved bonding in the absence of the sizing: Better rCF / Elium compatibility?

Viscoelastic properties: Dynamic mechanical analysis



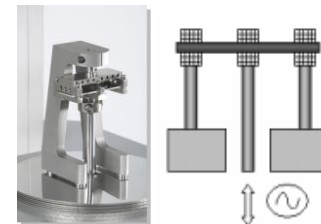
- Depolymerisation **does not affect** the viscoelastic properties of the resin



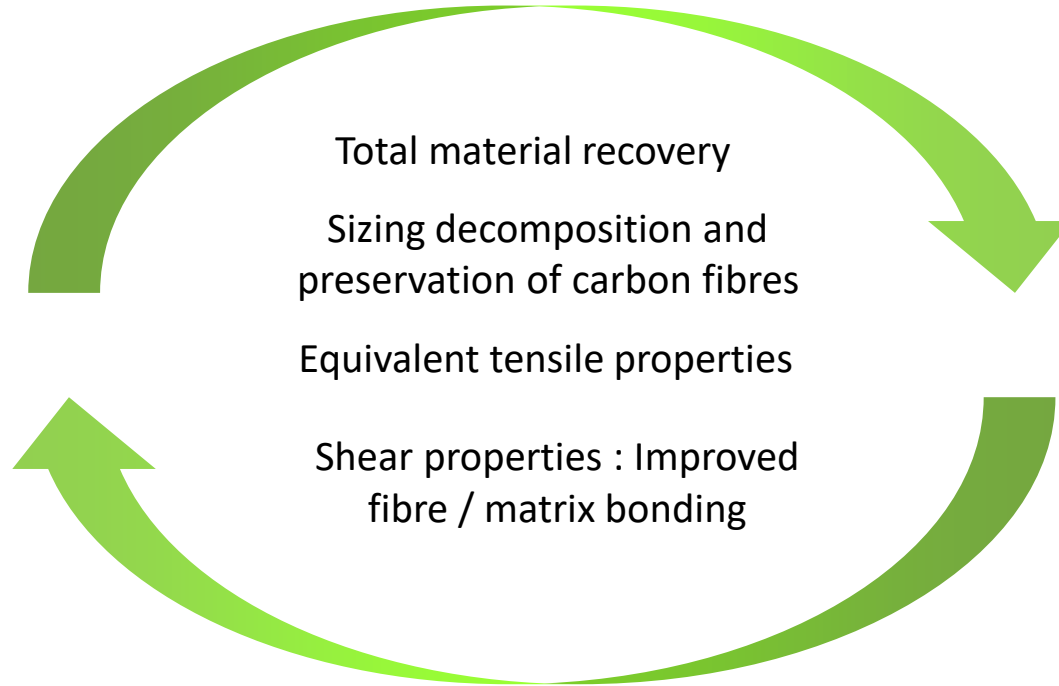
Higher Tan (δ)

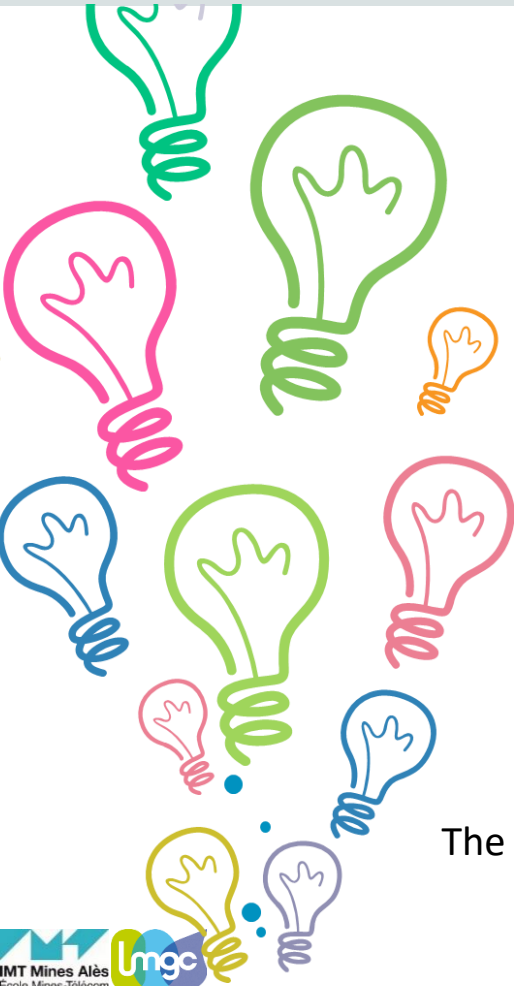
- Better bonding between **rCF** and virgin/recycled resin
- Dissolution of the sizing in the polymer during processing and before polymerisation [13]

Dual Cantilever Beam



CONCLUSIONS & PERSPECTIVES





The impact of the recycling process on the physical and mechanical properties of carbon fibres:

- Surface tension
- Interfacial shear strength (IFSS)

Environmental and financial sustainability of the depolymerisation process : the application of a life cycle analysis

The durability of recycled composites compared to reference material

Resources, Conservation & Recycling 173 (2021) 105705



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Contents lists available at ScienceDirect

Resources, Conservation & Recycling

journal homepage: www.elsevier.com/locate/resconrec

Full length article

Recovery and reuse of carbon fibre and acrylic resin from thermoplastic composites used in marine application

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ARTICLE INFO

Keywords:

Recycling
Carbon fibre
Thermoplastic composite
Mechanical properties
Formulated plastics
Marine application

ABSTRACT

The development of new sustainable routes towards better environmental footprint of composites for marine boatbuilding is motivated by the absence of eco-friendly and economically viable recycling techniques to deal with growing end-of-life thermoset boats waste and increasing restrictive legislation. Thermoplastic composites may offer the possibility to recover raw materials from retired parts, which could have a substantial environmental and economic benefit. This study investigates the feasibility of recovery and reuse of both reinforcement and matrix from a carbon fibre reinforced thermoplastic Elium composite. An original pyrolysis process allowed the depolymerisation of the acrylic matrix and recovery of clean carbon fibres and matrix monomer. Distillation was used to purify the monomer from impurities and a recycled Elium resin was synthesized and reused as matrix with long and aligned recycled carbon fibre reinforcement. The study of the morphological and composition differences at fibre scale resulted in concluding that sizing has been decomposed during depolymerisation process and only small traces of polymer were left on fibre surface. Virgin and recycled resin reinforced with carbon fibre laminates were produced by resin infusion. While tensile modulus, strength and strain at break were nearly unchanged, interlaminar shear strength results showed enhanced fibre-matrix interphase bonding. Dynamic mechanical analysis confirmed the good quality of recovered carbon fibres as well as similar virgin and repolymerised resin properties. The new composite made from both recycled fibre and matrix could be used in the same application field.

