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## RECOVERY AND REUSE OF CARBON FIBRE AND ACRYLIC RESIN FROM THERMOPLASTIC COMPOSITES USED IN MARINE APPLICATION

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**Abstract:** *This study examines the feasibility of recovering and reusing the reinforcement and matrix of a carbon fibre reinforced thermoplastic composite. A proof of concept based on pyrolysis allowed the depolymerisation of the acrylic matrix (Elium<sup>®</sup>) and the recovery of clean carbon fibres and the matrix monomer. Subsequently, distillation was used to purify the monomer from impurities and to synthesise a recycled Elium<sup>®</sup> resin. The morphological and compositional differences at the fibre scale led to the assumption that the sizing was removed during the depolymerisation process and that only small traces of the polymer are still present on the fibre surface. New composites based on virgin and recycled matrix with recovered carbon fibre were manufactured by resin infusion. Although in-plane mechanical properties remained almost unchanged, the interlaminar shear strength results showed an improved fibre-matrix interface bonding. Dynamic mechanical analysis confirmed the good quality of the recovered carbon fibres and the similar properties of the virgin and repolymerised resin.*

**Keywords:** Carbon fibre; Recycling; Thermoplastic composite; Mechanical properties; Marine application

### 1. Introduction

Fibre reinforced thermosets and thermoplastic resins are increasingly used to replace conventional materials in a number of industrial, transport and sporting applications. One of the biggest challenges posed by fibre-reinforced composites, in particular in marine application, is their recycling (1). Environmental legislation is becoming more and more restrictive and end-of-life solutions for leisure boats waste are limited. The environmental impact of these materials disposed in landfills or drowned in seawater is accelerating the urgency to reach more industrial scale solutions to the recycling of composite. The use of thermoplastic composites allows the recovery of raw materials from end-of-life parts, which could have a substantial environmental and economic benefit. The newly developed reactive methacrylate thermoplastic matrix Elium<sup>®</sup> presents an alternative to thermoset resins currently used in composites for marine structures (2). It can be processed at room temperature with processing techniques typical of thermosets, like resin infusion. This thermoplastic resin reinforced by carbon fibres presents good mechanical and durability properties, compared to a carbon fibre reinforced vinylester composite (3). The recycling of the carbon fibre reinforced thermoplastic resin was investigated by pyrolysis process developed by Arkema. The high temperature associated to a pressurised inert atmosphere allows the recovery and the reuse of both the carbon fibre and the thermoplastic resin by depolymerisation. This method allows the reuse of the recovered fibres

either with virgin resin to form a semi-recycled composite or with recycled resin to form a totally recycled composite. In this study, the efficiency of this method is studied by analysing the residual rate of the polymer into the recovered fibres. The surface quality and diameter change of recycled fibre was investigated using scanning electron microscopy. Further tests consisting in the comparison of the mechanical properties of the initial composite and the totally and semi-recycled composites were carried out.

## **2. Materials and methods**

### **2.1 Materials**

The material considered in this study is a carbon fibre reinforced acrylic matrix laminate composite. The Elium<sup>®</sup> 188-O resin was kindly provided by ARKEMA and the reinforcement was a Cbx600 24 K T620 biaxial stitched carbon fabric from Sicomin. It is a 2 plies ( $\pm 45^\circ$ ) non-Crimp balanced biaxial carbon fibre fabric with an areal weight of approximately 640.5 g/m<sup>2</sup>. Elium<sup>®</sup> 188-O resin is a polymer solution of methyl methacrylate (MMA) monomer (>80 %) and acrylic copolymers, with a viscosity of 100 cPs and activated by a benzoyl peroxide (BPO) initiator from AkzoNobel. The glass transition temperature of the polymerised polymer is approximately 109 °C. The compatibility of the fabric, according to the manufacturer, is for general use as epoxy, polyester and vinylester. Therefore, there is no specific sizing for acrylic resin. Composite laminates of 4 plies ([0/90/0/90]<sub>s</sub>) of CF fabric of 450 × 420 mm<sup>2</sup> were produced by Vacuum Assisted Resin Infusion (VARI) method at room temperature. During curing, an exothermic reaction took place, characterised by a temperature peak. After demoulding, no particular post-curing was performed on the infused plates, which were conditioned at 23 °C and 50% RH. The average thickness of the 4-ply infused laminate is about 2.5 mm. Density measurements on at least three samples of 35 × 12 × 2.5 mm<sup>3</sup> were performed using a Micromeritics gas pycnometer (model AccuPyc 1330) with helium gas in order to calculate the apparent volume fraction of the constituents according to ASTM D317-15. The volume fraction of the voids was deduced from the volume fraction of the fibres and the matrix.

### **2.2. Methods**

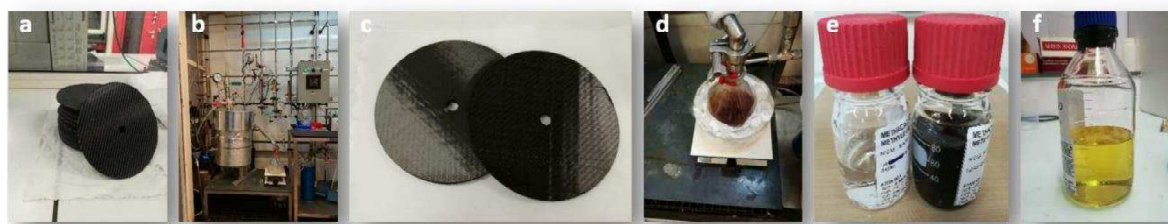
#### **2.2.1. Recycling method**

Around 30 rounded discs having a diameter ranging from 135 mm to 142 mm (Figure 1.a) were machined from composite laminates using a water jet-cutting machine and were stacked into a 4.5L reactor at Arkema CRRRA research center (Figure 1.b). Two sets of around 1500 g of composites were depolymerised under pressurised nitrogen atmosphere and a temperature range from 350 to 450 °C. The condensed vapours were gradually recovered in a liquid receiver flask as the depolymerisation continues. The recovered monomer liquid is then stabilised using hydroquinone as a polymerisation inhibitor. Once the reactor has cooled down to room temperature, the recovered carbon fibre reinforcement was collected from the reactor (Figure 1.c). The experimental results of the two depolymerisations, in terms of recovered fibre weight and raw MMA monomer, are shown in the table below.

*Table 1 : Depolymerisation process results*

Run	Introduced composite weight [g]	Reclaimed carbon fibre weight [g]	Reclaimed crude MMA weight [g]	Solid residue fraction [% vs initial composite weight]	Liquid residue fraction [% vs initial composite weight]	Material balance [%]
1	1577	1137	394	72.1	25.0	97.1
2	1634	1177	428	72.1	26.2	98.2
Total	3211	2314	822	72.1	25.6	97.7

Initial length and orientations of initial fibres were not modified during pyrolysis process. In addition, it was found that the fraction of solid residues in the top of the reactor was slightly higher than in the central region (72.0% versus 70.8%, respectively), which is likely due to the temperature gradient in the reactor due to heat transfer. The reclaimed crude liquid monomer had yellow-orange colour (Figure 1.d). In fact, during the degradation process, a number of small radicals were formed via disproportionation, and they cannot be depolymerised efficiently thus giving rise to the generation of by-products. In order to analyse reclaimed monomer purity and to identify by-products, analysis of the reclaimed crude liquid of present study was performed by gas chromatography with flame ionization detection. Quantification of MMA content in crude MMA using an internal standard was found to be 77% and 72% for respectively for first and second depolymerisation tests. Main identified by-products are methyl isobutyrate, ethyl acrylate, methyl acrylate, methacrylic acid and methanol. Many heavier compounds were detected, but have not been identified (4). Crude monomer solution from both depolymerisation trials were distilled (Figure 1.e). From 703 g of crude MMA at 75% purity, 385 g of MMA with 99.5% GC purity was recovered and formulated by ARKEMA (GRL, France) to finally obtain around 500 g of recycled Elium<sup>®</sup> 188-O resin (Figure 1.f) which will be denoted rElium.



*Figure 1 : a) CFRP discs, b) Pyrolysis reactor, c) recovered CF, d) recovered crude monomer solution, e) distilled MMA monomer (transparent) and by-products (dark), f) repolymerised resin*

### 2.2.2. Analysis methods

Several techniques were used at both fibre and composite scale in order to investigate the differences between virgin and recovered constituents. Scanning electron microscopy (FEI Quanta 200 FEG) and Thermogravimetric Analysis (Setaram SETSYS Model) were used in order to identify the effect of depolymerisation method at fibre scale. An MTS Criterion C45.105

tensile machine equipped with a 100 kN load cell was used to measure in-plane tensile properties of virgin (vCF/vElium), semi recycled (rCF/vElium) and totally recycled (rCF/rElium) composites. In addition, a Zwick-Roell testing machine (model Z010/TH, 1 mm/minute on load cell of 10 kN and an accuracy of 0.1 N) was used to monitor the quality of fibre/matrix bonding by mean of failure resistance calculations and failure modes identification related to the short-beam test according to ASTM D2344 / D2344 M standard. Finally, Dynamic Mechanical Analysis were conducted in Double Cantilever mode according to ASTM D5418–15 standard on a METRAVIB DMA50 machine (5 Hz frequency, 10  $\mu\text{m}$  dynamic strain amplitude, temperature range from 40 to 160  $^{\circ}\text{C}$ , heating rate of 3  $^{\circ}\text{C}/\text{min}$ ). The storage modulus, loss modulus and loss factor data were directly collected from testing machine and glass transition temperature were reported from tan delta curve peak.

### 3. Results

#### 3.1 Analysis at fibre scale

SEM observations on fibre surface showed a smooth surface of virgin fibres compared to recycled fibres where a residual polymer layer was observed as shown in Figure 2.b. This residual polymer is a local phenomenon as it is not coating the whole fibre surface. Figure 2.c and Figure 2.d present an example of fibre diameter calculations. Measurements performed on around 30 different vCF and rCF showed a similar distribution but a difference in mean diameter of around 600 nm as shown in Table 2.

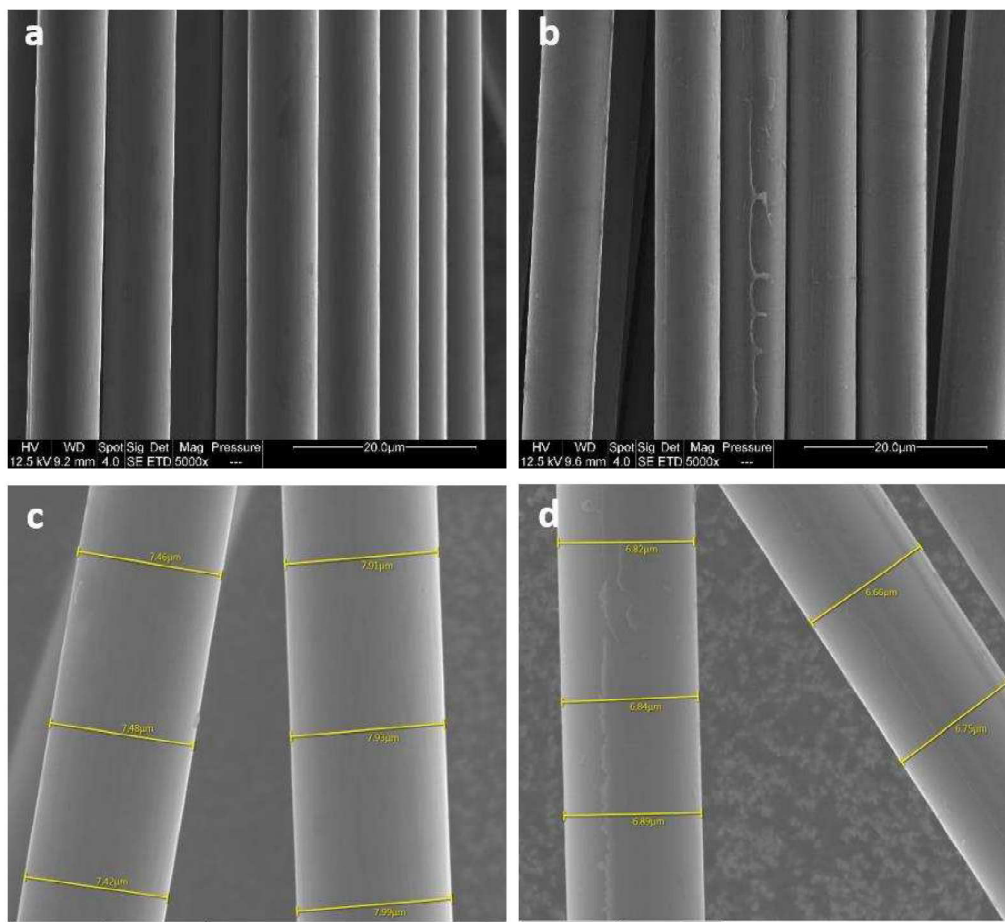


Figure 2: SEM images of virgin (a and c) and recovered (b and d) carbon fibre

Table 2: rCF and vCF diameter measurements

Fibre	vCF	rCF
Diameter [ $\mu\text{m}$ ]	7.48 (0.23)	6.90 (0.29)

Thermogravimetric analysis on virgin and recovered fibres showed a major difference in the 220~400 °C temperature range as virgin fibres have lost around 1% of their initial weight as shown in Figure 3.a. This weight change may be related to the fact that, when depolymerised, carbon fibres have lost the polymer-based sizing layer already present on fibre surface. The derivative TG curves (Figure 3.b) showed a pic of depolymerisation at around 345 °C. In addition, an acceleration of weight loss rate can be observed starting from around 620 °C indicating the damage of fibres.

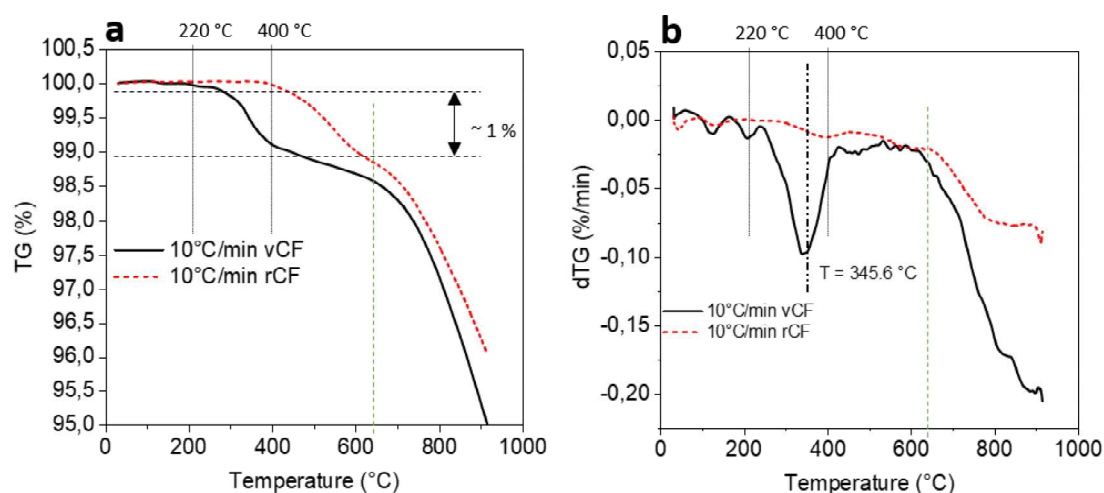


Figure 3 : Thermogravimetric analysis (TG) and derivative thermogravimetric analysis (dTG) of vCF and rCF at 10°C/min under nitrogen atmosphere

### 3.2. Analysis at composite scale

To assess the mechanical properties of semi- and fully recycled composites in comparison to virgin material, composite plates were manufactured by VARI method like reference material using rCF and rElium resin.

Table 3: Calculated constituent volume fractions of virgin, semi- and fully recycled composite laminates.

Properties	Fibre volume fraction $v_f$ [%]	Matrix volume fraction $v_m$ [%]	Void volume fraction $v_v$ [%]	Fibre weight fraction [%]	Fibre areal weight [ $\text{g}/\text{m}^2$ ]	Density [ $\text{g}/\text{cm}^3$ ]
vCF/vElium	61.9 (0.53)	36.6 (0.51)	1.5 (0.02)	70.9 (0.39)	640.5 (2.66)	1.53
rCF/vElium	54.8 (1.1)	43.6 (1.27)	1.6 (0.16)	66.4 (1.14)	631.4 (4.89)	1.49
rCF/rElium	55.4 (1.12)	42.9 (1.9)	1.7 (0.77)	67.1 (0.38)	628.2 (1.08)	1.50



After optimisation of the infusion method for round shaped fabric, the fibre volume fraction of semi-and fully recycled composites was measured and compared to virgin composites. Results are presented in Table 3 and standard deviations are given between parentheses. It can be noted that laminates with rCF presents higher matrix volume fractions compared to reference material. Subsequently, the difference can be observed on fibre volume fraction, which decreased from around 62% to 55%. This difference is mainly related to the total degradation of PET stitching fibre after depolymerisation, which led to more free volume between carbon fibre tows.

Mechanical tensile tests performed on 125×12.5×2.5 mm<sup>3</sup> samples from virgin, semi-recycled and fully recycled composites in longitudinal direction (at 0/90°) showed a similar elastic and brittle behaviour. In addition, regarding tensile modulus and ultimate stress and strain, the decrease is statistically slight and within the standard deviation range (Figure 4). As load direction and fibre direction are superimposed, the results are known to be fibre-dependant. Therefore, an evidence can be obtained about the good quality of rCF by pyrolysis method.

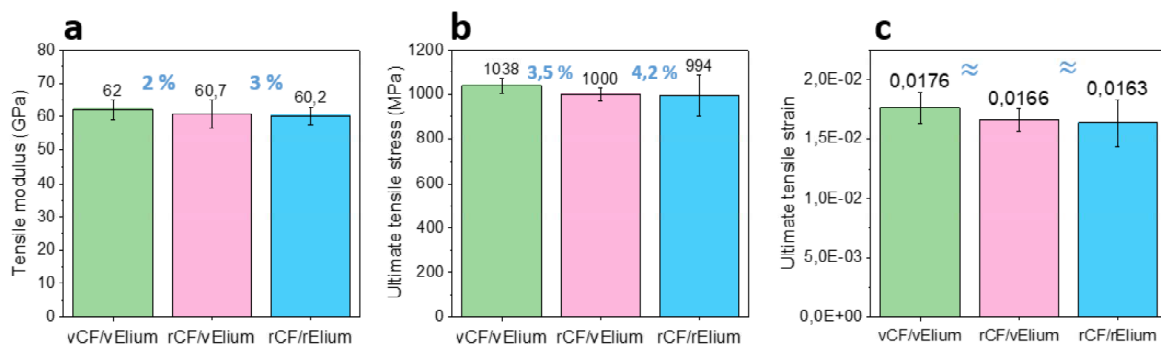


Figure 4 : Tensile elastic modulus (a), ultimate tensile stress (b) and strain (c) obtained by longitudinal tensile tests on virgin, semi-recycled and fully recycled composites

Furthermore, short beam bending tests performed on 5 mm thick samples showed significant differences in interlaminar shear strength between virgin and recycled composites as can be seen in Figure 5.

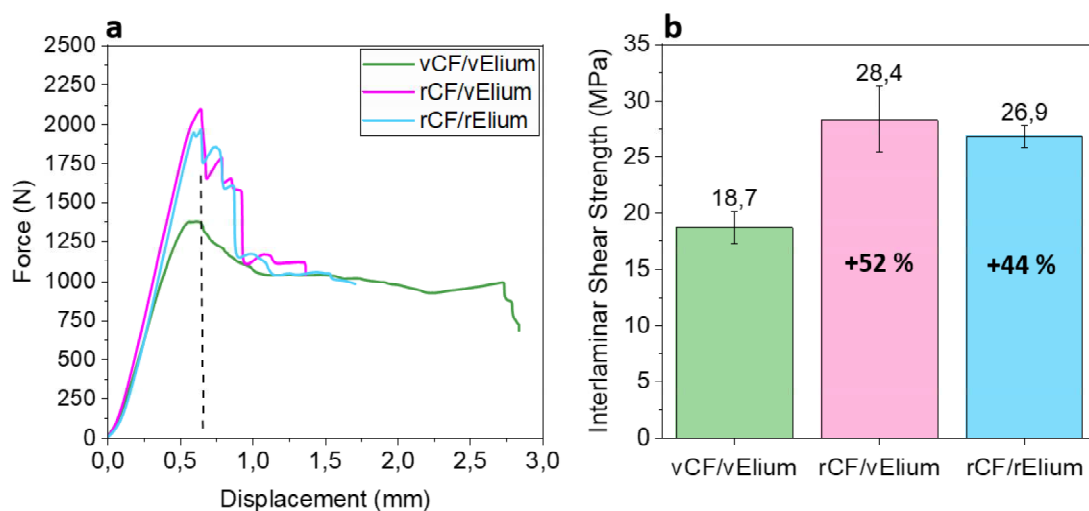


Figure 5: a) Load-displacement curves and b) Interlaminar shear strength of virgin, semi-recycled and fully recycled composites

However, load displacement curves of virgin fibres reinforced composites show a continuous drop after reaching the maximum force that may be related to a plastic deformation and an initially limited fibre/matrix bonding. On the other hand, semi- and fully recycled composites have undergone an interlaminar failure with sharp and instantaneous drop in force-displacement curve. These differences are directly reflected in the calculation of the interlaminar shear strength as they present values 50% higher than virgin material (Figure 5.b)

The glass transition temperature of virgin and recycled Elium<sup>®</sup> resin was measured from the loss factor ( $\tan \delta$ ) peak and results are presented in Figure 6.a. A slight difference of around 3.5 °C can be noticed between virgin and recycled neat Elium<sup>®</sup> resins. These findings lead to admit the hypothesis of the good properties of recovered Elium<sup>®</sup> resin as no significant difference was recorded compared to virgin resin. Concerning the composites, a significant difference of around 10 °C is found between virgin and rCF based composites as illustrated in Figure 6.b. Furthermore, it was observed that the virgin material showed a higher damping peak and a 10 °C shift in the onset of the  $\tan \delta$  peak. As the loss factor is defined by the ratio of the loss modulus to the storage modulus, a higher peak corresponds to greater molecular mobility through temperature effect. As the same virgin Elium<sup>®</sup> resin was used for both the reference and the semi-recycled composite (rCF/vElium), the difference may therefore be due to different polymerisation conditions in the absence of sizing of the polymer to the fibre surface resulting in a better fibre/matrix bond. These differences in loss factor curves confirm previous results on the drop of ILSS of virgin composites. In fact, in the absence of a good fibre/matrix bonding, the matrix exhibits a plastic deformation that explains the continuous drop in force-displacement curves related to ILSS tests.

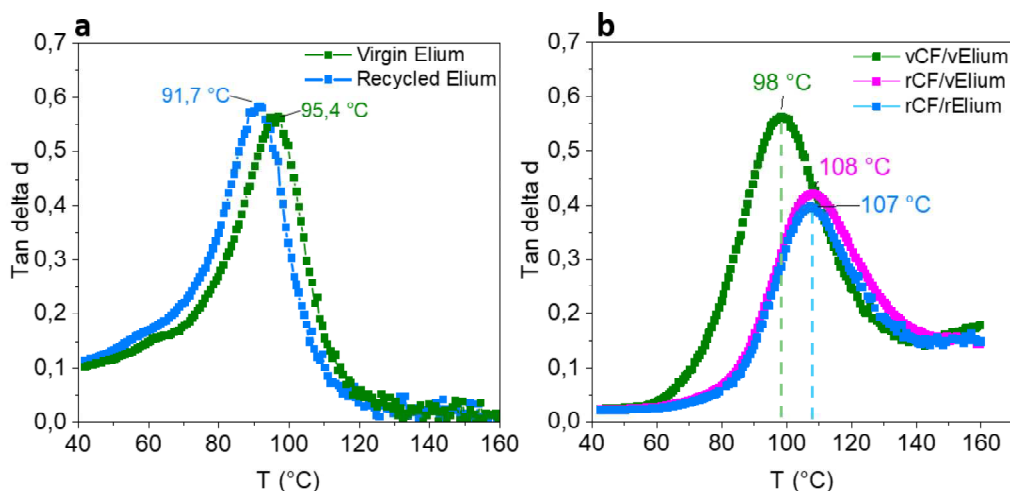


Figure 6 : DMA  $\tan \delta$  curves as a function of temperature of a) virgin vs recycled Elium<sup>®</sup> resin and b) virgin vs semi- and fully recycled composites

#### 4. Conclusions

This study was carried out with the aim of developing an initial proof-of-concept of the recyclability of a carbon fibre reinforced Elium<sup>®</sup> composite using the pyrolysis method. The resin-infused composite was depolymerized at a temperature range of 350-450 °C. The solid residue from the pyrolysis method containing carbon fibres was about 72%, while the condensed gas fraction was about 26%, from which a purified monomer solution was used to



formulate the recycled Elium<sup>®</sup> matrix. TGA on the recycled fibres showed degradation of the sizing, which was approximately 300 nm thick. The recovered carbon fibres with the recycled matrix were used to remanufacture good quality semi- and fully recycled composites by resin infusion with a fibre volume fraction of about 55%. The mechanical tensile properties were sufficiently conserved compared to the reference material. The same trend was found by dynamic mechanical analysis, with clear similarities between the virgin and recycled Elium<sup>®</sup> resin. Interlaminar shear analysis showed significantly higher interfacial strength than the reference material. This is the first time that this approach is proposed for a complete valorisation of good quality recovered carbon fibre and Elium<sup>®</sup> monomer from a reference material used in marine environment.

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