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# Characterization of Carbon Fibers Recovered by Pyrolysis of Cured Prepregs and Their Reuse in New Composites

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Additional information is available at the end of the chapter

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## Abstract

The applications of composite materials are rapidly growing. In the aeronautical sector, composites account for up to 50% of the weight of a modern typical commercial aircraft. However, the amount of composites currently recycled is less than 5% of the total amount produced. With environmental concerns becoming an increasingly influential topic, recyclability of composite materials is a key issue. Furthermore, several related European laws have been passed to minimize the environmental impact of composite structures and to make rational use of landfills. In this chapter, the authors analyze recycling techniques for carbon fiber composites with thermoset polymer matrix. The objective is to reuse the fibers in new, lower cost composites with similar properties. Starting from a pyrolysis step, followed by oxidation, an evaluation of the different parameters of the recycling process has been performed. The characterization of the fibers includes tensile tests, scanning electron microscopy, and Raman spectroscopy. The recycled fibers presented a reduction of their initial tensile strength lower than 10%. Then, remanufacturing of laminates using the recycled fibers was achieved by resin film infusion, obtaining laminates with properties similar to the brand-new composites. These results have the potential to be exploited by the automotive, aeronautical, wind energy, construction, and other sectors.

**Keywords:** composites, recycling, pyrolysis, carbon fiber, fracture toughness, resin film infusion

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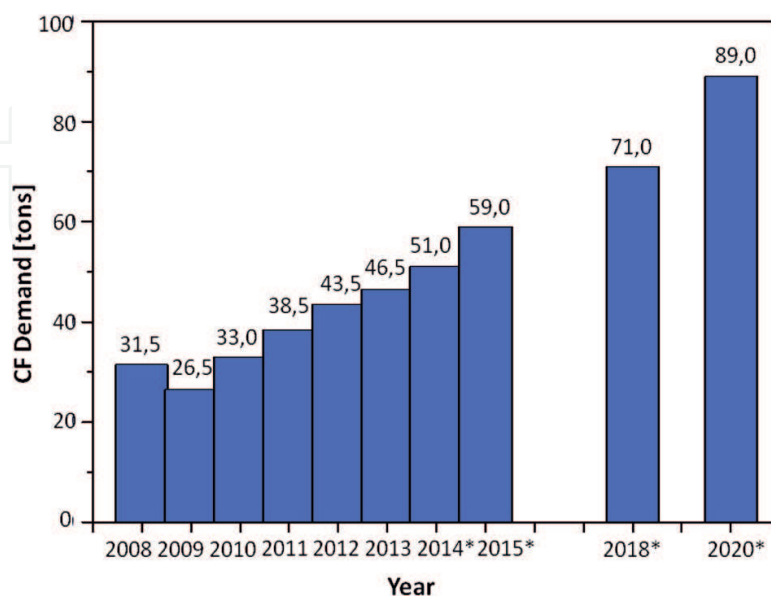
## 1. Introduction

Composites are made from at least two constituents that together produce material properties that are different from the properties of those materials on their own. In practice, most composites consist of a bulk material (plastic matrix), and a reinforcement (typically fibers, i.e. carbon fibers), added primarily to increase the strength and stiffness of the material.

While they offer fantastic durability, high specific stiffness, and strength-to-weight ratio, their properties are essentially controlled by those of their constituents, including fiber/matrix interfaces, their volume fraction, and spatial distribution. The remarkable characteristics of fiber-reinforced plastics (FRPs) led to rapid increase of their use. In the aeronautical sector, the use of composites reaches up to 50% of the total weight of a modern commercial aircraft [1]. But, FRPs are not only used in the aeronautic/aerospace sector. Other industries where weight-efficient performance is a key factor, such as the automotive, naval, and wind energy sectors, are likewise increasing the use of composite materials (annual growth rate of 12–14% **Figure 1**).

Naturally, the increment in demand and use of composites results in more and more waste being generated throughout the life cycle of these materials; in fact, it is estimated that 30–40% of pristine carbon fibers are wasted during the manufacturing process, and significant amounts of off-cuts, rejects, and put-of-date prepregs are generated, causing a significant negative impact on the environment. The excess of carbon fibers that is generated per year equals about 20–25% of the total amount consumed during 2015 [2]. Evidently, the recycling of composite materials is a high priority.

The recycling of carbon fiber-reinforced plastics (CFRPs) not only makes sense from environmental and economic perspectives but also could be a key in increasing the penetration



**Figure 1.** Global demand of carbon fibers over the years [3].

of these lightweight but expensive materials in high-volume markets such as automotive and aeronautical industry.

The principal waste management options that have been adopted for composites are burying, landfilling, or incinerating. Several European Directives and regulations were implemented in order to make better use of landfills (EU 1999/31/EC) [4]; to reduce waste management (EU 2000/53/EC on End-of-Life vehicles) [5]; to prevent or limit the emission levels produced by incineration plants (Directive 2000/76/EC) [6]; as well as to prevent and remedy the environmental damage (2004/35/EC on Environmental Liability) [7]. To reduce the consumption of natural resources and landfill allocations, recycling composite elements for reusing in different applications is postulated as a promising solution. Because of their high initial cost and energy consumption during manufacture, fibers are the most attractive constituent for recycling. In addition to these economic incentives and compared to the production of virgin materials, recycling will also reduce air, water, pollutant emissions (90–95% of CO<sub>2</sub> emissions), as well as energy demand. Therefore, recycling results in a substantial improvement on the environmental impact of composite materials.

The economic costs can be reduced by about 70% (from €30–58/kg to €15–23/kg for carbon fibers) and the energy requirement by nearly 98% (from 55 to 166 kWh/kg to 3–10 kWh/kg), since the majority of energy consumption occurs during production of virgin carbon fibers [8]. Substituting virgin carbon fibers with recycled ones would save enough electricity to power 175,000 homes in a year [9]. However, the amount of composites currently recycled is less than 5% due to their complex composition; the nature of the resin (i.e., thermoset resins have a cross-linked matrix that cannot be simply reprocessed by remelting or remolding); their combination with other materials; and the high variability among waste products [9]. Furthermore, the use of the recycled carbon fibers in industrial applications is currently very limited due to the low quality control of the fibers, i.e., the length, surface quality, and origin of the fibers are difficult to control. In addition, the hierarchical structure of composites is destroyed during recycling; and the resultant laminates composed of recycled fibers present disorientation. Then, these composites do not meet the standards of high-value structural applications.

There are three main general technical approaches to the recovery of the fibers in thermoset-matrix composites: mechanical, thermal, and chemical. The mechanical recycling consists of reducing the size of the scrap composite components by shredding, crushing or milling. Nevertheless, in industry, this technology has not been extensively exploited to treat carbon fiber-reinforced polymers (CFRCs) due to the poor bonding between the recycled fibers and the new resin.

Thermal recycling of composites involves the separation of the matrix from the fibers by applying heat. There are two main types of thermal recycling methods: pyrolysis and fluidized-bed recycling process. In both, the resin is volatilized into lower weight molecules to produce mainly oil and gases, while fibers are recovered, usually with char on their surfaces. These thermal processes have been widely implemented in industry. Among them, pyrolysis is the most widespread technology. Both glass and carbon fiber-reinforced composites can be recycled through pyrolysis. Because of the much higher market value of carbon fibers,

pyrolysis of carbon fiber-reinforced composites has higher economic attractiveness. The first continuous pyrolysis recycling line, commercially producing recycled carbon fibers, has been introduced by the company Recycled Carbon Fiber Ltd. (RCF) in 2008 [10]. One of the most famous cases of recycling composites is BMW: up to 95% of the BMW, i3 is recyclable [11]. In Spain, the company Thermal Recycling of Composites (TRC, SL) has technology for the thermochemical recycling of composite materials reinforced with both glass and carbon fibers, with a special recycling line for wind turbine blades [12]. ELG Carbon Fiber (ELG-CF), Coseley, UK, develops a pyrolysis process in which they treat around 24,000 tons per year of carbon fiber waste. The process yields a tough and abrasive cotton-wool-like fuzz of carbon fiber, which maintains 90–95% of its original mechanical properties [13].

The recycling of CFRP waste through pyrolysis poses the additional problem of managing the liquids that are produced in the process, as a consequence of the thermochemical degradation of the resins (usually epoxy) [14]. Therefore, other less expensive alternatives are being studied. In this regard, many researchers have investigated the decomposition of resin matrix and CFRP carbon fiber recovery using chemical treatment to break and degrade the resin. The solvent can be water (hydrolysis) or organic (solvolysis). Solvolysis offers a large number of possibilities, thanks to a wide range of solvents, temperatures, pressures, and catalysts. Depending on the amount of solvent and on the temperature, the fluid can be vapor, liquid, biphasic, or supercritical. The latest have gained much attention since 2000 because characteristics between liquid and gas phases can be achieved through combinations of temperature and pressure, allowing the enhancement of the diffusion effect [15]. The results of recent research on the use of supercritical or subcritical fluids including water and alcohol are very promising [16–18].

In this chapter, we propose a two-step carbon-fiber recycling process: pyrolysis followed by oxidation. An optimization of the method in terms of sustainability of the technique and the characteristics of the fibers will be carried by performing surface, microstructure, and mechanical testing of the recovered fibers. With respect to mechanical performance, fiber strength distribution and fracture toughness were the properties analyzed. In addition, the remanufacture of laminates by means resin film infusion using the recycled fibers is proposed. The mechanical performance of the resulting laminates will be evaluated and compared to that of pristine ones.

## 2. Recycling process

A common scrap material from the aeronautic sector was selected for recycling. The recycling steps and process optimization parameters are detailed below.

### 2.1. Scrap material

The composite material used as the basis for the optimization of the experimental parameters was a scrap (HexPly® F593, supplied by AIRBUS OPERATIONS S.L., Getafe, Spain) composed

of a plain woven prepreg made of epoxy resin reinforced with Toray T300/3 k carbon fibers [19] (55–60% carbon fibers [by mass] and 40–45% resin; fiber area weight = 193 g/m<sup>2</sup>) [20]. The carbon fibers were made of PAN. This process is as follows. First, there is a pre-oxidation treatment under 200–300°C; second, a carbonization in high purity inert gas under 1000–1500°C takes place; third, there is a graphitization under 2500–3000°C; and finally, a sizing.

## 2.2. Recycling approach

The process used to recover the fibers was pyrolysis. It is a thermochemical decomposition of the organic part of the composite materials at temperatures between 450°C and 700°C in the nearly absence of oxygen. It is widely performed in the industry due to its easy and cheap implementation.

The recycling process was done in a thermolysis installation (**Figure 2**). It consists of a heating system and a gas condensation device [21]. The muffle furnace (1) contains a 9.6 L steel reactor, sealed by a screw-on lid. The flue gases circulate across four condensers (3–6) connected to each other by six cooling pipes. Each condenser allows the collection of distilled oils as cool gases and has four collection holes for the withdrawal of the distilled liquids and a thermometer to measure their temperature. The noncondensable gases are led to a water-cooling tower (7), where the last fraction of the distilled liquids is collected. These gases pass through a set of three filters (8 and 9) to eliminate pollutant gases and solid particles. The gases can then be mixed with air and burned off or collected for analysis. When the thermolysis is complete (the rotameter (10) inside the tubing no longer detects any distillation gas), the reactors are cooled and the thermolytic solid residues removed, which are mainly composed of pieces of dimensions equal to those of the input material but completely black.

The complete process consists of two steps: a thermolysis or pyrolysis (heat rate of 20°C/min) and a gasification or oxidation (air flow of 5 L/min). In the first one, the separation fiber/resin takes place; on the second stage, there is the removal of the char deposited on the

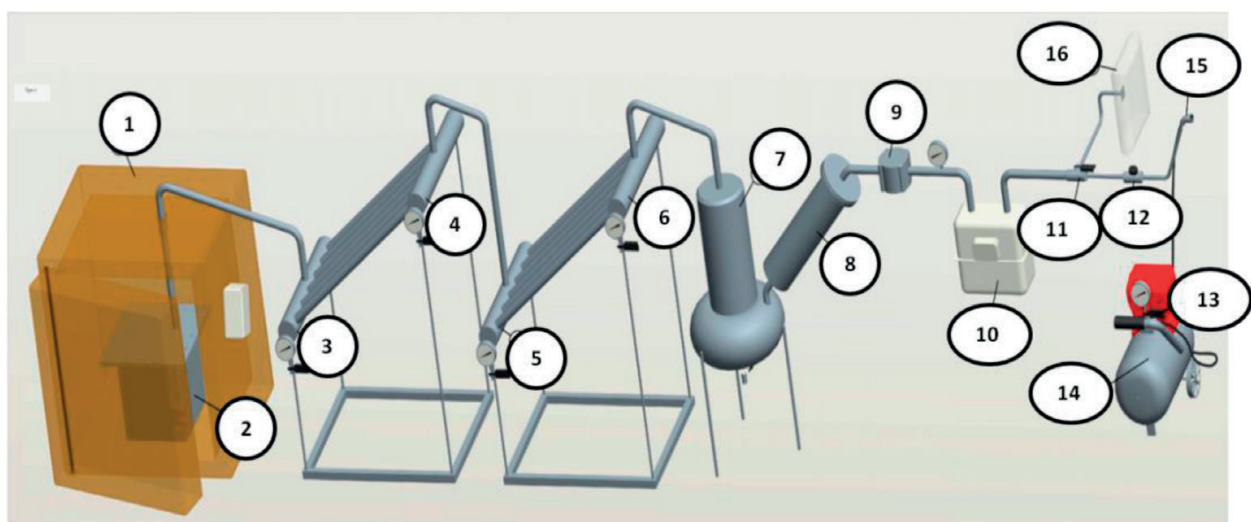


Figure 2. Installation used for the pyrolysis of the carbon fibers [15].

surface of the fibers. However, this second step, if not properly designed, is likely to reduce the mechanical properties of the fibers.

### 2.3. Process optimization

With the purpose of designing the experimental procedure toward achieving the best recyclability and keeping the original fiber properties as intact as possible, the pyrolysis and oxidation steps were studied and optimized.

The design of the pyrolysis temperature for the degradation of the resin was performed by conducting tests runs at 500, 600, and 700°C for 6 h. Values below 500°C did not effectively remove all the resin; and values higher than 700°C caused a high degradation of the recovered fibers. The temperature of the pyrolysis (P) stage was then set to 500°C, because for 550°C and above, the preliminary thermogravimetric analysis and surface element concentration tests showed the fibers to be damaged.

The optimum oxidation (O) step was determined by varying the oxidation times between 30 and 90 min. This was done with the following objectives: efficiently removing the char on the fiber surface, while maintaining fiber microstructure intact and retaining fiber mechanical properties as much as possible. Section 3 details the results of this optimization study.

## 3. Recycled fibers

To determine the optimum oxidation time, analyses of fiber surface quality, fiber composition and mechanical properties of the recovered fibers were performed, as described in this section.

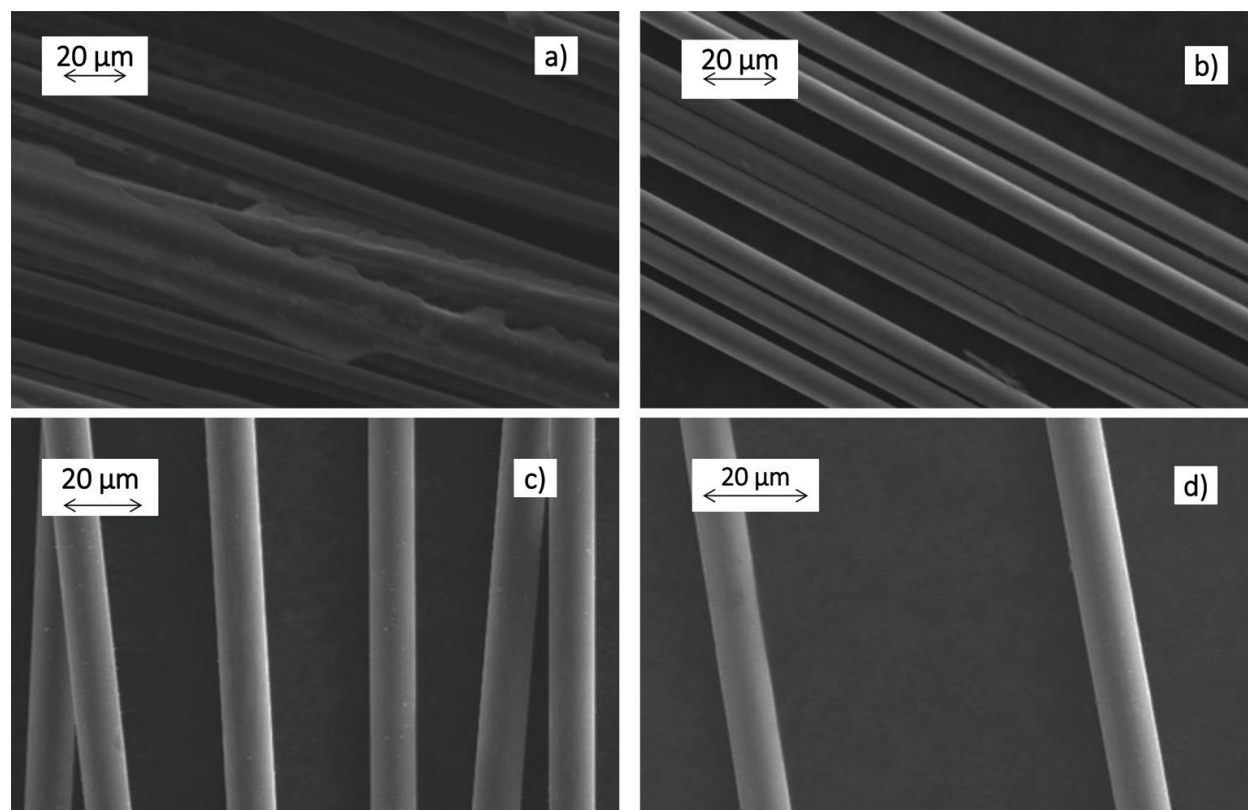
### 3.1. Surface quality

Scanning electron microscope (SEM) was used to evaluate the presence of char on the surface of the recycled fibers and compare with pristine ones. The images of the morphology change of the virgin and the recycled carbon reveal that pristine fibers exhibit a rough and irregular surface, while the recycled fibers are free of resin char, with a much more regular and smooth surface (**Figure 3(a)–(d)**). Only a few traces of micron-sized resin residues can be seen in few regions on the fiber surface. It can be concluded that, independently the oxidation time, the surface of recycled fibers presented a low amount of residual char and was otherwise clean and showed no evidence of fiber damage. This means that the removal of char from the fiber surface was efficient, and that this process requires only short oxidation times, e.g., 30 min.

### 3.2. Composition

#### 3.2.1. Surface chemistry

The surface chemistry of virgin and recycled carbon fibers was examined by X-ray photoelectron spectroscopy by López et al. [20]. As shown in **Table 1**, the surface of all the examined fibers was composed of carbon (C), oxygen (O), and nitrogen (N). While the C content



**Figure 3.** SEM images of the virgin (a) recovered carbon fibers after thermolysis at 500°C and gasification times of 30 min (b), 60 min (c), and 90 min (d).

Fiber sample	C (at.%)	N (at.%)	O (at.%)	Si (at.%)	O/C (at.%)
Virgin	90.1	1.0	8.9	—	0.082
Recycled: P-500°C	89.3	4.5	6.0	0.1	0.067
Recycled: P-500°C/O-30 min	81.2	7.1	10.0	1.7	0.123
Recycled: P-500°C/O-60 min	83.3	4.6	11.7	0.4	0.140

Virgin: virgin TORAY T300/3 k fibers; values provided by manufacturer TORAY JAPAN [22].

**Table 1.** Surface atomic concentration (at.%) of the recovered fibers obtained at the different gasification times, plus concentrations for pristine fibers.

remains practically constant, the O content increases with gasification time and the N content decreases. The increase in the O/C ratio with gasification time is indicative of the degree of fiber oxidation, which can lead to undesirable alterations. The smaller ratio obtained, i.e., the less oxidized recovered fiber (compared to 0.082% of the virgin ones) indicates that the optimum gasification time is 30 min.

Moreover, according to the thermolytically derived solid residue, 500°C is the condition in which the best atomic surface composition was obtained, due to the smallest quantity of C=O and COOH groups, which suggests the formation of oxygenated compounds on the surface of the solid residue, potentially caused by secondary repolymerization reactions in the gaseous phase.



### 3.2.2. Crystallite structure

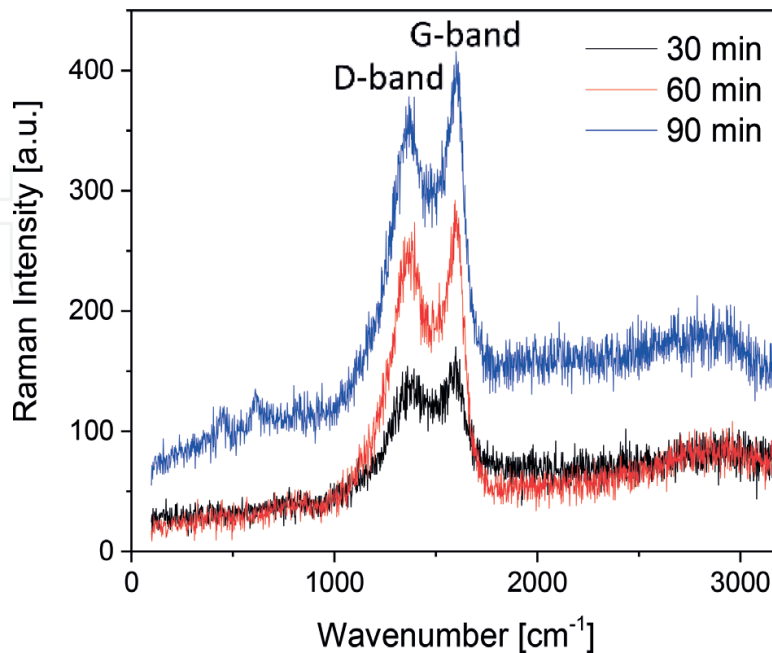
Raman spectra of the surface and transversal section of the carbon fibers (**Figure 4**) were obtained at room temperature to detect the changes in crystallite structure of the recycled carbon fibers at a penetration depth of the order of 60 nm. Independently of the zone evaluated, all first-order Raman spectra for the recycled carbon fibers exhibited two broad peaks at about 1350 and 1580  $\text{cm}^{-1}$  corresponding to the D and G bands, respectively.

The G band is associated with a single crystal of graphite, whereas the D peak is from the structural imperfections created by the attachment of hydroxyl and epoxide groups on the carbon basal plane. The ratio of the intensity of the D and G bands ( $I_D/I_G$ ) indicates the measurement of the graphitic plane size, so the lateral crystallite size ( $L_a$ ) of the recycled fibers had become smaller [23]. The recycling process generated surface defects caused by the reduced  $L_a$  values through the oxidation effect, as is indicated in **Table 2**. The general expression that gives the crystallite size from the integrated intensity ratio is given by Ref [24].

$$L_a \text{ (nm)} = (2.4 \cdot 10^{-10}) \cdot (\lambda_1)^4 \cdot \left(\frac{I_D}{I_G}\right)^{-1} \quad (1)$$

where  $\lambda_1$  is the laser line wavelength in nanometer units.

The variation of  $L_a$  is generally indicative of a change in material strength. It can be inferred that the larger the reduction in  $L_a$ , the lower the tensile strength of the recycled fibers. Therefore, these results indicate that the lowest reduction in fiber tensile strength is likely to be achieved for an oxidation step of 30 min.



**Figure 4.** Raman spectra for the recycled carbon fibers.

Fiber sample	D band position (cm <sup>-1</sup> )	G band position (cm <sup>-1</sup> )	I <sub>D</sub> /I <sub>G</sub>	L <sub>a</sub> (nm)
P-500°C/O-30 min	1357	1588	0.93	21
P-500°C/O-60 min	1364	1582	0.98	20
P-500°C/O-90 min	1364	1580	0.98	20

**Table 2.** Microstructure parameters of the recycled T300 carbon fibers at different gasification times using Raman spectrometer.

### 3.3. Mechanical properties

To achieve an objective determination of the optimum oxidation time based on mechanical properties, evaluations of the tensile strength and of the fracture toughness of the recovered fibers were performed.

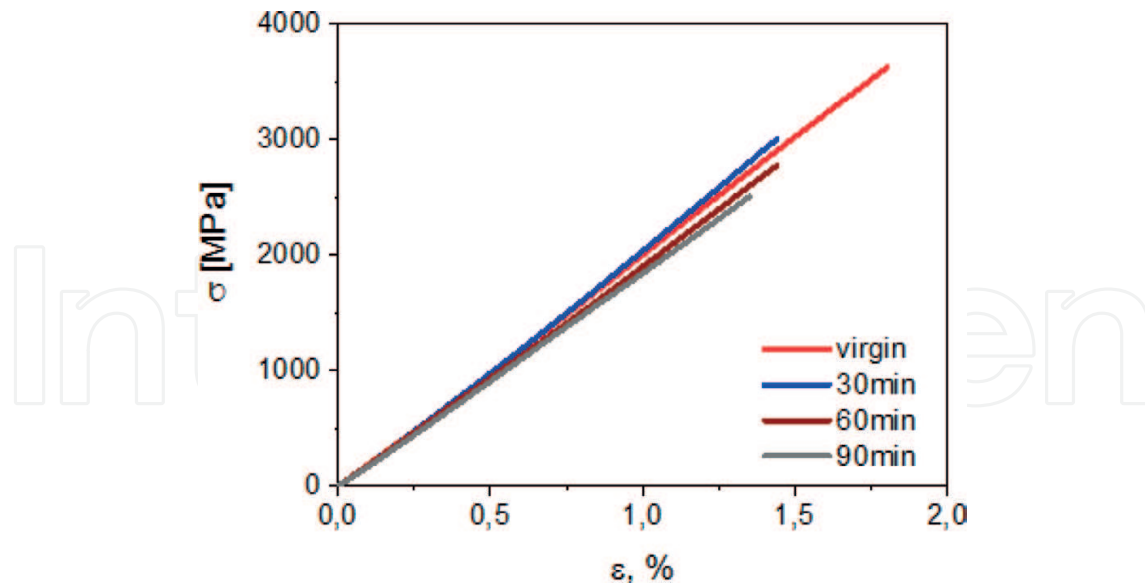
#### 3.3.1. Fiber tensile strength

The tensile properties of the carbon fibers were determined through tensile tests at a gage length of 20 mm in the fiber tensile tester at room temperature. Each single fiber was directly connected to the mechanical grips and then submitted to uniaxial straining up to failure under stroke control at 1 mm min<sup>-1</sup>. Then, the natural frequencies were extracted to determine the linear density (using the frequency method according to the ASTM D1577 standard [25]), and subsequently, the cross-section area was calculated with the known fiber density, in order to finally determine the average fiber diameter at 20 mm gage length [26].

During the test, the force-strain curve was recorded. These curves indicate linear and elastic behavior up to failure (**Figure 5**). The maximum load attained was used to calculate the strength of each individual fiber, and the elastic modulus in the fiber direction was determined from the slope of the stress-strain curve.

The large reductions in tensile strength with increases of the gasification time are attributed to the large number of micropits on the fiber surfaces generated due to the severity of the oxidation. The higher void content also contributes to strength degradation. Overall, the oxidative effect results in a higher amount of surface defects, which leads to a reduction in the tensile strength and lateral crystallite size, as demonstrated above.

The average fiber diameter (D), elastic moduli (E), and tensile strength ( $\sigma_u$ ) of fibers recycled with different gasification times are given in **Table 3**. It is shown that the decrease in strength is more significant compared to that of the modulus. This is caused by the presence of large number of defects on the thermally oxidized surface of fibers. At 30 min of oxidation time, the modulus seems to be slightly higher than the one of the virgin fibers (+2%). This can be due the presence of a layer of residual matrix or char on the surface of some recycled fibers. The modulus for the recovered fibers drops by about 10% with respect to virgin fibers after 90 min of gasification. With longer oxidation times, the modulus further reduces, which can be attributed to the removal of the amorphous carbon layer resulting from the oxidizing thermal treatment (corroborated with the decrease of the fiber diameter). This is consistent with



**Figure 5.** Strain vs. strain relationship for a pristine and recovered carbon fiber at different oxidation times.

Fiber sample	Diameter $D$ ( $\mu\text{m}$ )	Elastic modulus $E$ (GPa)	Tensile strength $\sigma_u$ (GPa)
Virgin	$7.5 \pm 0.2$	$197 \pm 18$	$3.4 \pm 0.4$
Recycled: P-500°C/O-30 min	$7.2 \pm 0.1$ (-4%)	$200 \pm 4$ (+2%)	$3.0 \pm 0.3$ (-10%)
Recycled: P-500°C/O-60 min	$7.1 \pm 0.2$ (-5%)	$189 \pm 9$ (-4%)	$2.7 \pm 0.3$ (-20%)
Recycled: P-500°C/O-90 min	$6.6 \pm 0.6$ (-12%)	$178 \pm 5$ (-10%)	$2.4 \pm 0.4$ (-30%)

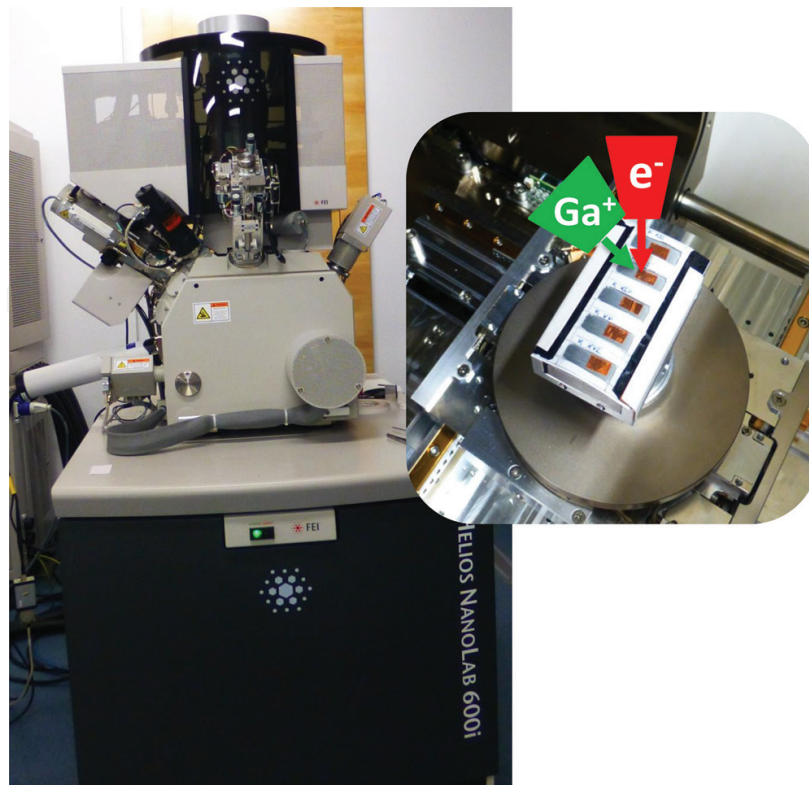
**Table 3.** Average diameter and mechanical properties of the fibers analyzed as function of the oxidation time.

the finding that heat treatment affects the diameter of the fibers. Consequently, gasification times of 60 min already lead to severe reductions in elastic modulus and tensile strength.

### 3.3.2. Fiber fracture toughness

In spite of the remarkable specific properties mentioned above, fracture of fiber-reinforced composite materials tends to occur in a brittle way due to their low capacity for plastic deformation and relatively low fracture toughness. In combination with the fiber/matrix interface, fiber fracture plays a role on the ultimate failure stress and energy dissipation mechanisms in brittle unidirectional composites. However, this property is less widely reported owing to the experimental difficulties associated with evaluation fracture in small-diameter fibers.

The methodology used consists on the introduction of artificial notches in the fibers by removing material using a focused ion beam (FIB) (**Figure 6**) [26–28]. A fine tungsten pin covered with liquid gallium (Ga) is used as an ion source from which Ga atoms are extracted and ionized via high voltage. This methodology allows precise monitoring of the notch geometry in terms of length, depth, and tip radius.



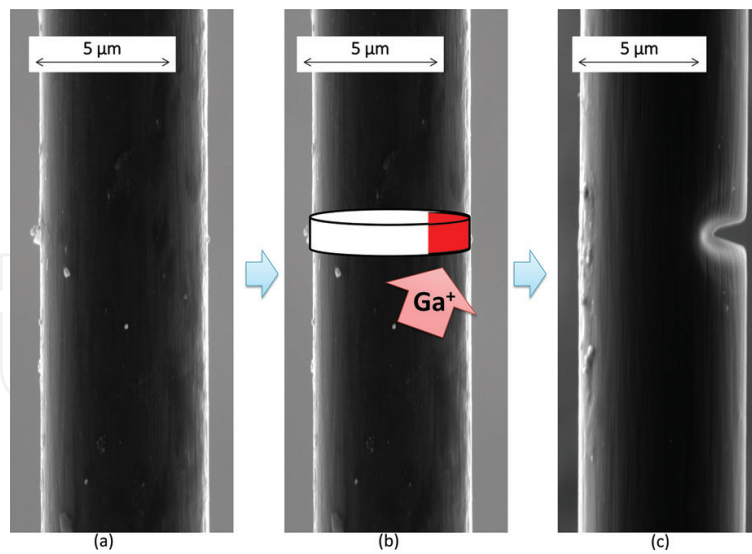
**Figure 6.** Fiber-milling system by focused ion beam (FIB).

Straight and sharp notches perpendicular to the fiber axis were introduced, as shown in **Figure 7**. The fiber diameter and the notch length of each test specimen were measured with a SEM associated to the FIB apparatus. Once the notch was milled into the fiber, the fibers were submitted to uniaxial loading up to failure in similar form as for the plain tensile strength tests described previously.

The fracture process started from the crack tip induced by FIB milling, and the response was also linear and elastic up to failure. The residual strength of the notched fiber was determined from the failure load and the corresponding area of the cross section of the fiber. The mode-I apparent fracture toughness,  $K_{IC}$ , was evaluated from the residual strength based on Linear Elastic Fracture Mechanics (LEFM) postulates. It is assumed that neither the small crack tip radius ( $\approx 50$  nm) nor the possible material modification induced during the milling will excessively affect the fracture behavior of the fiber, and thus, the result can be considered a good approximation of the real material property. Hence, the failure of the fiber is dictated by

$$K_{IC} = \left( \frac{a}{D}, a, \sigma \right) = Y \left( \frac{a}{D} \right) \cdot \sigma_c \cdot \sqrt{\pi a} \quad (2)$$

where  $K_I$  depends on the specimen geometry, the crack depth, and the far-field stress applied. The parameter  $Y$  is a dimensionless stress intensity factor calculated according to the literature that assumes the geometric effects and the elastic anisotropy of the material [29].



**Figure 7.** SEM micrographs the milling procedure; (a) original fiber; (b) gallium ions focusing and (c) notched fiber.

The critical energy release rate, or fracture energy,  $G_{Ic}$  is computed through Irwin's equation, assuming the validity of LEFM, as

$$G_{Ic} = \frac{K_{Ic}^2}{E^*} \quad (3)$$

where  $E^*$  is the effective modulus which is taken as  $E^* = E$ , assuming plane strain conditions. The calculation of the plastic region length ahead of the crack tip,  $l_p$ , is based on

$$l_p = \frac{1}{2\pi} \cdot \left( \frac{K_{Ic}}{\sigma_0} \right)^2 \quad (4)$$

where  $\sigma_0$  is the average tensile strength of the Weibull statistics given by

$$F = 1 - \exp\left(-\frac{L}{L_0} \left(\frac{\sigma}{\sigma_0}\right)^m\right) \quad (5)$$

The function  $F$  above is the cumulative fracture probability function, wherein  $L$  is the fiber length,  $L_0$  is an arbitrary reference length, and  $\sigma_0$  and  $m$  are the characteristic strength and the Weibull modulus of the fiber [26].

The average fracture toughness and fracture energies obtained for virgin and recycled fibers, at different oxidation times, are given in **Table 4**. The small value of the plastic radius compared to the fiber diameter demonstrates the validity and applicability of LEFM postulates. Very large reductions in fracture toughness and fracture energy (in the order of 50% for  $K_{Ic}$  and 70% for  $G_{Ic}$ ) result of the recycling process, independently of the oxidation time, and they are presumably affected mostly during the thermolysis step. The operated material modifications that lead to these property reductions are also unclear. Hence, these aspects are under

Fiber sample	$a_0/D$	Apparent fracture toughness $K_{Ic}$ (MPa m <sup>1/2</sup> )	Apparent fracture energy $G_{Ic}$ (J m <sup>-2</sup> )	Irwin plastic radius $l_p$ (μm)
Virgin	0.15 ± 0.01	2.4 ± 0.5	24 ± 8	0.19 ± 0.01
Recycled: P-500°C/O-30 min	0.10 ± 0.03	1.2 ± 0.2	8 ± 3	0.15 ± 0.06
Recycled: P-500°C/O-60 min	0.15 ± 0.02	1.2 ± 0.3	7 ± 4	0.20 ± 0.03
Recycled: P-500°C/O-90 min	0.12 ± 0.02	0.9 ± 0.1	4 ± 1	0.15 ± 0.03

**Table 4.** Geometry and mechanical properties of the pristine and the recovered fibers for different gasification times.

investigation. However, it should be noted that the reduction in fiber fracture toughness is bound to have a limited influence on the fracture of the fiber-reinforced composite ply, as this property ( $G_{Ic}^{ply} \approx 100$  kJ/m<sup>2</sup>) is mostly determined by the fiber/matrix interface behavior.

Given the results achieved in terms of tensile strength and fracture toughness, it can be concluded that the optimal recycling process conditions consist on a thermolysis step at 500°C, for 6 h followed by gasification step for another 30 min. These conditions result in retentions of 100% of fiber elastic modulus and 90% of fiber tensile strength, although the brittleness of the fibers is seriously increased.

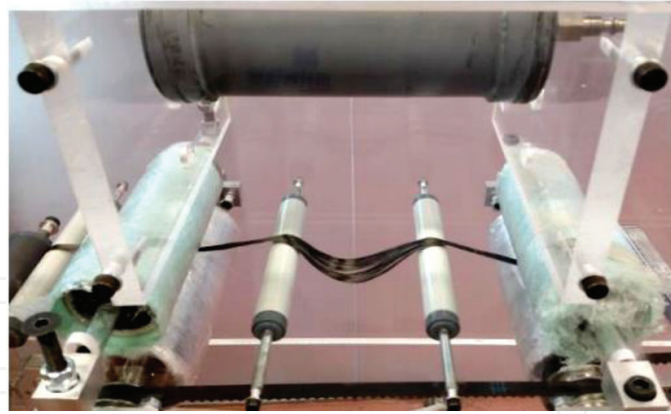
## 4. Remanufacturing of composites

Remanufacturing of unidirectional composites was pursued with the optimal fibers resulting from the optimization of the recycling process (thermolysis at 500°C for 6 h and oxidation at 500°C for 30 min). This section describes the adopted fabrication route and the preliminary evaluation of the mechanical performance of the resulting laminates.

### 4.1. Resin film infusion of recycled fibers

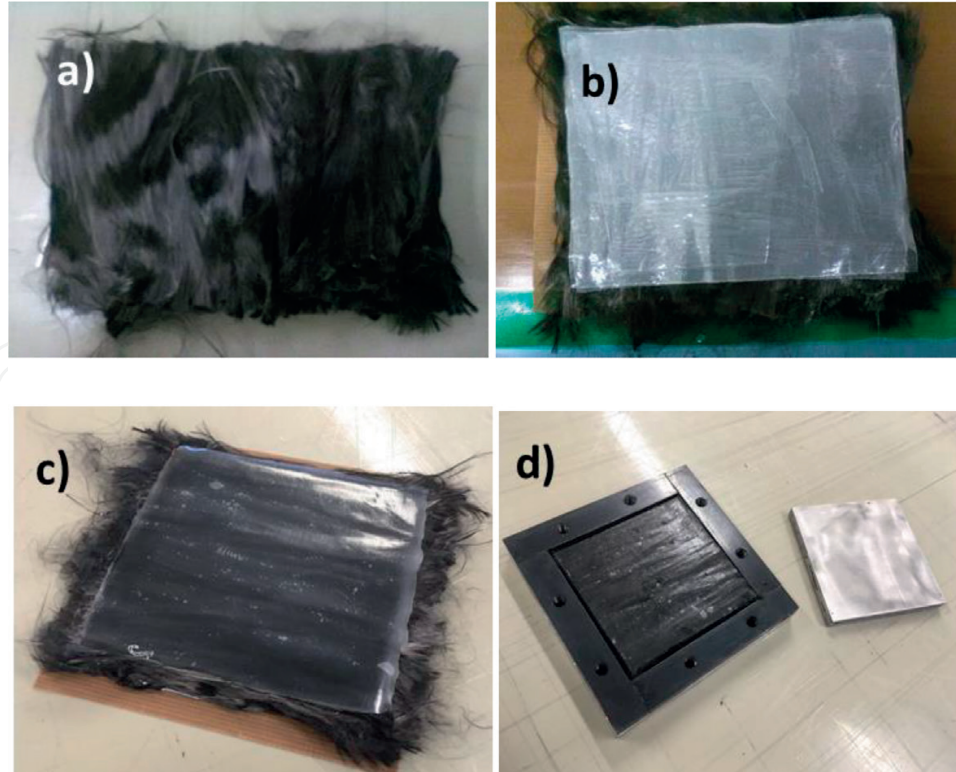
A tow-spreading technique was used to compact the nearly unidirectional fiber tows in order to obtain a high fiber volume fraction in plies of thin thickness. The fibers passed through a spreading machine, which is equipped with an air duct and rolls (**Figure 8**). The air pressure can be regulated and flows between two guide rolls, making the tows sag downward toward the air direction. This creates a momentary free tension stage that allows the tow to be spread.

Afterward, the resin film infusion technique (RFI) was used for manufacturing new laminates. In this way, the recycled fiber tows were laid down next to each other to complete a thin fiber bed layer. The fiber layers were interleaved with layers of semi-solid epoxy resin film Letoxit® LFX 060 [30] for subsequent consolidation. The fibers/resin consolidation is characterized by



**Figure 8.** Tow-spreading equipment.

three major steps: intimate contact, adhesion, and fiber impregnation. The configurations carried out were [2x rCF layer/2x LFX 060 film/ ...], with three LFX 060 film epoxy sheets placed on the top and bottom layer (the number of repetitions depends on the desired thickness). The final kit was introduced in a close-mold and cured in a hot-plate press, applying pressure (0.7 MPa) and heat (125°C for 25 min) simultaneously. The steps followed to make a laminate are depicted in **Figure 9**. It was then confirmed that the degree of resin curing was optimal by means of Differential Scanning Calorimeter (DSC) tests.



**Figure 9.** Staking sequence: (a) recycled carbon fiber layer; (b) LFX 060 film; (c) laminate after 2 h in the thermal plate; and (d) laminate in the close-molding.

## 4.2. Quality and properties of remanufactured composites

The quality of the composites recycled according to the methodology described above was evaluated by means of ultrasonic C-scan laminates. It was confirmed that the laminates were free of major porous, voids, or delaminations.

Thermogravimetric analyses (TGA) were carried to evaluate the composition of the laminates. It was determined that the nominal fiber volume fraction,  $V_f$ , was approximately 50%, a value not far from the typical  $V_f \approx 60\text{--}65\%$  of high-performance unidirectional composites.

As means of rapidly assessing the mechanical performance of the remanufactured laminates, their interlaminar shear strength (ILSS) was evaluated by means of Short Beam Shear tests. This consists on flexural testing method using a very short beam relative to its thickness in order to promote interlaminar shear failure [31]. According to the test standard ASTM D2344 [32], all specimens ( $27 \times 9 \times 4.5 \text{ mm}^3$ ) were loaded in a three-point bending configuration. The interlaminar shear strength was calculated using the equation:

$$F^{sbs} = \frac{3}{4} \cdot \frac{P}{b \cdot h} \quad (6)$$

where  $P$  is the maximum applied load,  $b$  is the measured specimen width, and  $h$  is the measured specimen thickness. The measured average ILSS of the remanufactured laminate was  $64.3 \pm 1.8 \text{ MPa}$ , a value close to the lower bound of typical carbon fiber composite laminates (60–120 MPa). This might be a result of the lower  $V_f$  and flexural stiffness but also of the degradation of fiber/matrix interface properties. In fact, this aspect was previously reported in other researcher works [33] and will be investigated by the authors in the future. The interlaminar shear mode of failure confirms that this test is valid in terms of fracture mechanism.

## 5. Conclusion

This chapter dealt with the study of recycling technologies, of properties of the recovered fibers, and of the composites formed from these fibers. Regarding the recycling methodology, a thermolysis process at  $500^\circ\text{C}$ , for 6 h, followed by an oxidation/gasification step in air atmosphere at the same temperature, for 30 min, has been found to constitute the optimum recycling process. The combination of pyrolysis and gasification provides high process reliability, repeatability, product quality, and cost reduction. Moreover, remanufacture of composites was successfully achieved. As a whole, this constitutes a complete process of recycling carbon fibers that significantly reduces the environmental footprint and improves the life cycle of lightweight CFRP structures.

Regarding the properties of the recovered fibers, an oxidation time of 30 min leads to a full retention of elastic modulus and a 90% retention of tensile strength, relatively to pristine fibers. Longer gasification times lead to more significant decreases in these properties and undesirable alterations in the atomic composition of the surface of the fiber (increase of the O/C ratio). Moreover, the fracture toughness of the recycled fibers was found to decrease



significantly, independently of the oxidation time. These results still have to be investigated but are judged not to impact the properties of the remanufacture composites.

With respect to the composites remanufacturing process, tow-spreading of the unidirectionally aligned recycled fibers followed by means of resin film infusion is postulated to be an appropriate method in terms of resulting ply thickness, disposition of the fiber, fiber/resin ratio, and porosity control. It provides a potential solution to prepreg production scraps with enhanced quality assurance, resulting in the reduction of toxic emissions. The resulted laminates presented similar fiber content and interlaminar shear properties as compared to the brand new composites.

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## References

- [1] Marsh G. Airbus A350 XWB update. *Materials Today*. 2010. Available from: <https://www.materialstoday.com/composite-applications/features/airbus-a350-xwb-update/>
- [2] ELG Carbon Fibre [Internet]. [cited 2016 Oct 24]. Available from: <http://www.elgcf.com/>
- [3] Boeing [Internet]. 2017 [cited 2017 Jun 12]. Available from: [Boeing.com/commercial/aeromagazine%0A](http://Boeing.com/commercial/aeromagazine%0A)
- [4] Council Directive. Council directive 1999/31/EC on the landfill. *Official Journal of the European Communities*. 1999;**10**:L182/1-L18219

- [5] European Parliament, Council of the European Union. Directive 2000/53/EC of the European Parliament and of the Council of 18 September 2000 on end-of life vehicles—Commission Statements. *Official Journal of the European Union*. 2000;**269**(September 2000):34
- [6] Council Directive. Council directive 2000/76/EC on the Incineration of Waste. *Official Journal of the European Communities*. 2000;L **332**(February 1997):91-111
- [7] European TEP& TC of. Directive 2004/35/CE of the European Parliament and of the Council of 21 April 2004 on environmental liability with regard to the prevention and remedying of environmental damage. *Regulation*. 2004;**2003**(807):56-75
- [8] Oliveux G, Dandy LO, Leeke GA. Current status of recycling of fibre reinforced polymers: Review of technologies, reuse and resulting properties. *Progress in Materials Science [Internet]*. 2015;**72**:61-99. Available from: <http://linkinghub.elsevier.com/retrieve/pii/S0079642515000316>
- [9] Roberts T. Rapid growth forecast for carbon fibre market. *Reinforced Plastics*. 2007; **51**(2):10-13
- [10] ELG CARbon Fibre Ltd. [Internet]. 2017 [cited 2018 Jan 3]. Available from: <http://www.elgcf.com/home>
- [11] BMW i3 [Internet]. [cited 2018 Jan 3]. Available from: <https://secure.bmw.com/com/en/newvehicles/i/i3/2016/showroom/sustainability.html>
- [12] Thermal Recycling of Composites. Available from: <http://www.trcsl.com>
- [13] Recycling carbon fibres. *Engineering Materials*. Available from: <http://www.materialsforengineering.co.uk/engineering-materials-features/recycling-carbon-fibre/160324/>
- [14] Yang YX, Boom R, van Heerden I, Kuiper PH, de Wit PH. Recycling of composite materials. *Chemical Engineering and Processing*. 2012;**51**:53-68
- [15] Hyde JR, Lester E, Kingman S, Pickering S, Wong KH. Supercritical propanol, a possible route to composite carbon fibre recovery: A viability study. *Composites. Part A, Applied Science and Manufacturing*. 2006;**37**(11):2171-2175
- [16] Okajima I, Sako T. Recycling of carbon fiber-reinforced plastic using supercritical and subcritical fluids. *Journal of Material Cycles and Waste Management*. 2017;**19**:15-20
- [17] Oliveux G, Bailleul JL, Le Gal La Salle E. Chemical recycling of glass fibre reinforced composites using subcritical water. *Composites: Part A*. 2012;**43**:1809-1818
- [18] Morin C, Loppinet-Serani A, Cansell F, Aymonier C. Near- and supercritical solvolysis of carbon fibre reinforced polymers (CFRPs) for recycling carbon fibers as a valuable resource: State of the art. *Journal of Supercritical Fluids*. 2012;**66**:232-240
- [19] Torayca. T300 Data Sheet. No CFA-001 [Internet]. 2002;6-7. Available from: [www.toray-cfa.com/pdfs/T300DataSheet.pdf](http://www.toray-cfa.com/pdfs/T300DataSheet.pdf)
- [20] López FA, Rodríguez O, Alguacil FJ, García-Díaz I, Centeno TA, García-Fierro JL, et al. Recovery of carbon fibres by the thermolysis and gasification of waste prepreg. *Journal of Analytical and Applied Pyrolysis*. 2013;**104**:675-683

- [21] López FA, Martín MI, Alguacil FJ, Rincón JM, Centeno TA, Romero M. Thermolysis of fibreglass polyester composite and reutilisation of the glass fibre residue to obtain a glass-ceramic material. *Journal of Analytical and Applied Pyrolysis* [Internet]. 2012;**93**:104-112 Available from: <http://dx.doi.org/10.1016/j.jaap.2011.10.003>
- [22] TORAY – Innovation by Chemistry [Internet]. [cited 2018 Jan 12]. Available from: <http://www.toray.com/>
- [23] Tanaka F, Okabe T, Okuda H, Ise M, Kinloch IA, Mori T, et al. The effect of nanostructure upon the deformation micromechanics of carbon fibres. *Carbon* [Internet]. 2013;**52**:372-378. Available from: <http://dx.doi.org/10.1016/j.carbon.2012.09.047>
- [24] Cañado LG, Takai K, Enoki T, Endo M, Kim YA, Mizusaki H, et al. General equation for the determination of the crystallite size  $l_a$  of nanographite by Raman spectroscopy. *Applied Physics Letters*. 2006;**88**(16):2-5
- [25] Test Method for Linear Density of Textile Fibers, ASTM Standard D 1577-79
- [26] Herráez M, Fernández A, Lopes CS, González C, Materials I, Kandel CE. Strength and toughness of structural fibres for composite material reinforcement. *Philosophical Transactions. Series A, Mathematical, Physical, and Engineering Sciences*. 2016;**374**:20150274. Available from: <http://dx.doi.org/10.1098/rsta.2015.0274>
- [27] Kant M, Penumadu D. Fracture behavior of individual carbon fibers in tension using nano-fabricated notches. *Composites Science and Technology* [Internet]. 2013;**89**:83-88. Available from: <http://dx.doi.org/10.1016/j.compscitech.2013.09.020>
- [28] Tanaka F, Okabe T, Okuda H, Kinloch IA, Young RJ. Factors controlling the strength of carbon fibres in tension. *Composites Part A: Applied Science and Manufacturing* [Internet]. 2014;**57**:88-94. Available from: <http://dx.doi.org/10.1016/j.compositesa.2013.11.007>
- [29] Ogihara S, Imafuku Y, Yamamoto R, Kogo Y. Application of FIB technique to introduction of a notch into a carbon fiber for direct measurement of fracture toughness. *Journal of Physics Conference Series*. 2009;**191**:12009
- [30] Technical data sheet Letoxit LFX 060. 2011;1-5. Available from: [www.5M.cz](http://www.5M.cz)
- [31] Shah DU, Schubel PJ. On recycled carbon fibre composites manufactured through a liquid composite moulding process. *Journal of Reinforced Plastics and Composites*. 2015;**35**(7):533-540
- [32] Standard Test Method for Short-Beam Strength of Polymer Matrix Composite Materials and Their Laminates-ASTM D2344
- [33] Pimenta S, Pinho ST. Recycling carbon fibre reinforced polymers for structural applications: Technology review and market outlook. *Waste Management* [Internet]. 2011; **31**(2):378-392. Available from: <http://dx.doi.org/10.1016/j.wasman.2010.09.019>