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Catalytic Hydrothermal Treatment for the Recycling of Composite Materials from the Aeronautics Industry

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Abstract: Epoxy resin composite matrices reinforced with carbon fibers are highly demanded by certain industries such as the aeronautics industry because of their exceptional mechanical properties. Unfortunately, the use of reinforcing carbon fibers makes these composite materials hard to recycle by conventional methods. Therefore, in this study, specific hydrothermal treatments have been employed to recover carbon fibers from the offcuts of composite parts from the aeronautics industry. The resin decomposition rates (DRs) achieved by different settings of the operating parameters, such as the use of alkaline catalysts (KOH, NaOH, or K₂CO₃), the application of mechanical stirring, the use of different reaction times, the solvent volume/composite mass ratio, the specific surface area (surface area/mass) of the composite pieces, and the operating temperature and pressure (subcritical or supercritical conditions), have been examined and assessed. Under the conditions that have been evaluated, resin decomposition rates nearly as high as 98% have been achieved, while the recycled fibers retained over 95% of their original tensile strength (TS).

Keywords: carbon fiber; epoxy resin; recycling; catalyst; hydrothermal processes



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1. Introduction

In recent years, the use of carbon fiber-reinforced polymers (CFRPs) has increased in a variety of sectors, and particularly in the aeronautics industry, because of their exceptional mechanical strength, stiffness, fatigue resistance, lightweight composition, and ability to withstand high temperatures and the action of chemicals. Global market demand for CFRPs has grown from 68 kilotonnes in 2010 to 170 kilotonnes in 2020, and it is estimated that it will exceed 190 kilotonnes by 2050 [1,2].

We are currently facing a series of challenges in relation to the management of the CFRP wastes generated, which can be divided into two categories: those generated during the manufacturing process (offcuts, which account for 40% of the CFRP used in the industry) and those that result after the end of the useful life of the manufactured components. In any case, the recycling of CFRPs is a major problem still to be solved, since a large part of the generated waste is currently either disposed of in landfills or incinerated. Such solutions are unsatisfactory, from both the environmental and the economic point of view, and fail to meet both legal and social demands. Global CFRP waste generation is estimated to reach 20 kilotons per year by 2025 [3,4].

Composite materials are the result of combining two or more constituents with a strong interface between them [5] so that they can exhibit superior properties than those corresponding to each individual constituent on its own. Composite materials normally consist of a matrix, that binds and shapes the composite material, and a reinforcement

element that provides stiffness and strength. Depending on the material used for the matrix, they can be metallic, ceramic, or polymeric. Depending on the reinforcing element, they can be fiber-reinforced, particle-reinforced, or fabric-reinforced composites [5–7].

Epoxy resins are thermosetting polymers. This means that after their cross-linked molecular structures have been formed as a result of their curing process, they cannot be recycled using standard methods, nor can their structure be reshaped. These structures are actually the ones that confer the polymer with its thermal and dimensional stability as well as its high mechanical strength. Epoxy resins exhibit average density values of 1.1–1.4 g/cm³, Young's modulus of 3–6 GPa, tensile strength (TS) of 35–100 MPa, and a deformation at failure of 1–6% [5,6].

These resins that are used today should be recycled when they reach the end of their useful life, which is why it is necessary to develop an optimal recycling process [8].

Carbon fibers (CFs) offer high fatigue strength levels, low coefficients of linear thermal expansion, and low corrosion susceptibility. Their main average mechanical properties are their density of 1.5 g/cm³, Young's modulus of 151 GPa, and tensile strength (TS) of 2500 MPa [5,6]. On the other hand, they have a low impact resistance and a high electrical conductivity.

Thermosetting composites are difficult to recycle because of their cross-linked molecular structures. In particular, thermosetting resins such as epoxy cannot be easily depolymerized to their initial monomers, and therefore, conventional techniques such as those described below cannot be successfully applied to the recycling of this type of polymer [3].

Given that the manufacturing of virgin carbon fibers is a costly and energy-intensive process, which may also produce dangerous gases that are harmful to both health and the environment, the development of new recycling methods for the recovery of carbon fibers is of particular interest [1,9].

The different techniques that are currently used for the recycling of CFRPs can be mainly classified as mechanical, thermal, or chemical.

The mechanical recycling techniques involve the size reduction of the composite material by crushing or fracturing. Quick processing speed and a straightforward scalability of their operating conditions are among their key advantages. On the other hand, they present certain downsides, such as a considerable reduction in size of the recovered fibers and in their mechanical properties, both of which result in a low market value that affects their economic viability [4,9,10].

Thermal recycling techniques use high temperatures to break down the matrices and to recover the fibers. Pyrolysis is one of the most prominent of these techniques, whose main advantage lies in the fact that it is currently at an advanced development stage and is already suitable for application at an industrial level. In addition, pyrolysis allows the recovery of lengthy carbon fibers and does not require the use of solvents or chemical compounds. On the other hand, it presents some drawbacks, such as its high temperature requirements (400–1000 °C) or the carbon deposits that may appear on the fiber surfaces. The removal of these deposits may require additional processes that pose a considerable risk of altering the mechanical properties of the recovered fibers, which could represent a drastic reduction in their actual value [1,4,9]. Wu T. et al. [11] managed to mitigate some of the drawbacks of pyrolysis by using a catalytic pyrolysis process where the composite material was submerged into molten ZnCl₂ that was capable of completely degrading the resin matrix at 360 °C in 80 min. They succeeded in recovering CFs that retained 95% of their tensile strength (TS), as the molten ZnCl₂ contributed to preventing the oxidation of the fiber surfaces. On the other hand, this process required the immersion of the CFRP pieces into a pure chemical compound, which not only makes the process more hazardous and less environmentally friendly, but also increases its economic cost and hinders its scalability for larger CFRP parts.

Chemical recycling techniques use reagents and/or solvents to break down or dissolve the resin matrix and recover the carbon fibers. These techniques include acid/base digestion, electrochemical methods, and solvolysis.

Acid/base digestion uses acidic or basic reagents at high concentrations. As a major advantage, they operate at low temperatures ($<150\text{ }^{\circ}\text{C}$); on the other hand, these reagents can be highly corrosive or hazardous and may damage the fibers when very high concentrations are used [4]. Liu Y. et al. [12] succeeded in completely breaking down epoxy resin matrices to recover their CFs with minimal damage (1.1% TS loss). On the other hand, they required the use of an 8 M nitric acid solution at $90\text{ }^{\circ}\text{C}$ for 720 min.

Electrochemical methods lie in the application of electricity to break down the resin, thus recovering long, clean carbon fibers. Unfortunately, they are not cost-effective in a commercial context because of their high energy demand [1].

Solvolysis is a thermochemical recycling method that combines the use of solvents (mainly alcohols and water) with heat to degrade CFRP matrices, providing a more economical and environmentally friendly way to recover high-quality carbon fibers. It can be categorized into low-temperature ($<200\text{ }^{\circ}\text{C}$) and high-temperature ($200\text{--}440\text{ }^{\circ}\text{C}$) processes. Low-temperature solvolysis occurs under mild pressure and temperature conditions, reducing energy consumption and preserving the mechanical properties of the fibers, but typically requires longer reaction times and the use of hazardous solvents (e.g., benzyl alcohol, acetone), catalysts, and pretreatments for effective resin decomposition [13]. For instance, Li J. et al. [8] achieved over 90% resin decomposition and retained more than 90% of fiber tensile strength using a mix of H_2O_2 and acetone, although pretreatment with nitric acid was necessary. High-temperature solvolysis, on the other hand, operates at higher pressures (80–300 bar) and temperatures, achieving better reaction rates and resin degradation efficiency, often using non-hazardous solvents like water, which, under supercritical conditions, enhances reactivity and may eliminate the need for catalysts [4,10,13]. This method yields clean carbon fibers with minimal loss in mechanical properties and also recovers depolymerized resins and monomers [9].

The main solvent used is water, which is non-toxic, easy to handle, and environmentally friendly. Okajima I. et al. [14] succeeded in degrading resins with water at $380\text{ }^{\circ}\text{C}$ and 250 bar with a DR of 90%. Morales Ibarra et al. [15] broke down 89.1% of the resin using supercritical water ($400\text{ }^{\circ}\text{C}$, 372 bar) in 60 min, although they required the use of benzyl alcohol ($400\text{ }^{\circ}\text{C}$, 27 bar, 60 min) to bring up the DR to 93.7%. Kim et al. [16] used supercritical water ($405 \pm 2\text{ }^{\circ}\text{C}$, 280 ± 10 bar) to reach a DR of 90–99% in 10–120 min, but the TS of the recovered fibers went down by 18–36%.

Other solvents or co-solvents, such as alcohols and organic solvents, can also be used. In addition, a series of catalysts can be added to increase resin degradation rates so that the process can be conducted at lower temperatures or using shorter reaction times [4,9,10]. Thus, Keith M.J. et al. [17] used an acetone/water mixture (80:20 *v/v*) at near-critical conditions ($297\text{ }^{\circ}\text{C}$, 120 bar) in combination with different weak Lewis acids to act as a catalyst (ZnCl_2 and MgCl_2 0.05 M, or AlCl_3 0.005 M) and degrade a carbon fiber-reinforced RTM6 epoxy resin matrix. Regardless of the catalysts used, they reported DRs $\approx 95\%$ for either $290\text{ }^{\circ}\text{C}$ and 90 min or $300\text{ }^{\circ}\text{C}$ and 45 min as the operating conditions. Liu Y. et al. [18] used a KOH/phenol/water mixture at an optimum ratio of 1/10/100 g/g/mL, since they had corroborated that the combination of KOH and phenol exhibited a synergistic effect on the degradation of the studied resin (DGEBA with DDM as curing agent). This allowed them to reach a DR of 95% at $315\text{ }^{\circ}\text{C}$ and 30 min. In their study, they removed the sizing from the raw and recovered fibers before performing the tensile tests and confirmed that there were no significant TS differences between the raw and recovered fibers. Liu W. et al. [19] used supercritical n-butanol ($330\text{ }^{\circ}\text{C}$, 65 bar) together with 0.05 M KOH for 60 min to recycle CFRPs (DGEBA matrix and DICY as the curing agent) and achieved a DR of around 98%. By means of scanning electron microscopy (SEM), they could observe that the sizing of the recycled carbon fibers (rCFs) had been removed. Piñero-Hernanz et al. (2008) [20] achieved 95.4% resin degradation using supercritical water ($400\text{ }^{\circ}\text{C}$, 281 bar) and 0.5 M KOH for 15 min. The CFs recovered using this method had suffered a loss in their original tensile strength (TS) of 2–10%. Knight C. C. et al. [21] achieved a DR $\approx 97\text{--}99\%$ of a CFRP (TGDDM matrix with DDS as curing agent) by employing supercritical water ($395\text{ }^{\circ}\text{C}$, 281 bar) and

0.05 M KOH for 15–60 min in a stirred reactor, and employed the resulting rCFs to fabricate new composites.

Our research group has already investigated the recycling of CFRP offcuts from the aeronautics industry. We have tested the effect of using acetone and isopropanol (IPA) either as pure solvents or as aqueous solutions at different concentrations [22,23]. The use of IPA is particularly interesting from a circular economy viewpoint, as this lays the groundwork for a potential utilization of IPA-rich byproducts from the semiconductor industry [24]. Furthermore, it has been observed that when only water is used as a solvent, part of the byproducts resulting from the resin degradation remain adhered to the reactor's inner walls, while the addition of just a small amount of IPA (water–IPA 5 wt.% solutions) is enough to successfully dilute these byproducts and keep the reactor surfaces clean, which would facilitate a potential scaling up of the process. Therefore, in the present study, we have opted for the use of water–IPA 5 wt.% solutions as the main solvent in the process.

The objective of the present work is to find a suitable combination of moderate operating conditions for the effective application of a hydrothermal treatment for the recycling of composite waste from the aeronautics industry. This is an exploratory work, where the influence of a selected number of operating variables on the resin decomposition rate (DR) is evaluated in order to determine the least demanding and most viable conditions to recover clean carbon fibers that retain their mechanical strength properties.

Thus, the effect of the principal variables, such as temperature and pressure (which determine whether the assay is carried out either under supercritical or subcritical conditions), the reaction time, and the catalyst used (KOH, NaOH, or K_2CO_3), have been analyzed. Moreover, other parameters that have been less studied, such as the use of mechanical stirring, solvent volume/composite mass ratio, or the specific surface area (surface area/mass) of the composite samples, have also been examined.

2. Materials and Methods

2.1. Materials and Reactants

Composite offcuts from the aeronautics industry supplied by Titania S.L. (Cádiz, Spain), composed of unidirectionally oriented TORAY T800S carbon fibers (5 μm fiber diameter, 0.447 ± 0.027 μm sizing thickness) and epoxy resin matrix cured at 180 $^\circ\text{C}$, corresponding to 34 ± 2 wt.%, were used. Pieces of 20 mm \times 10 mm and 20 mm \times 5 mm, all of them with a thickness of 2 mm, were used.

The Milli-Q quality deionized water (conductivity 0.0 $\mu\text{S}/\text{cm}$) was produced onsite. The isopropanol (100% purity) was supplied by Brenntag. The potassium hydroxide (KOH) at 90% purity was supplied by Sigma-Aldrich. The sodium hydroxide (NaOH) at 98% purity was supplied by Panreac, and the potassium carbonate (K_2CO_3) at 98% purity was supplied by Honeywell (Charlotte, NC, USA). Finally, the pure nitrogen was supplied by Carburros Metálicos (200 bar bottle).

2.2. Equipment and Experimental Procedures

An AUTOCLAVE ENGINEERS (Erie, PA, USA) stirred tank batch reactor (Figure 1a), made of 316 stainless steel and with a capacity of 284 mL, was used for the hydrothermal treatment of the CFRPs under subcritical conditions. The reactor was equipped with a model TC21 PID ICP controller (3) with the capacity to maintain a constant temperature at ± 2 $^\circ\text{C}$ accuracy, connected to a type K thermocouple (1) installed within the reactor, which operated a 1.2 kW cylindrical electric heater (4). The system was fitted with an inlet and outlet purging valve system that allowed the implementation of an initial N_2 pressure and the collection of the samples (5). A pressure gauge allowed us to monitor the pressure inside the reactor for a range of 0–550 bar (2). The mechanical stirrer, “0.7502 Magnedrive”, featured a belt-driven head and a magnetically driven propeller (6).

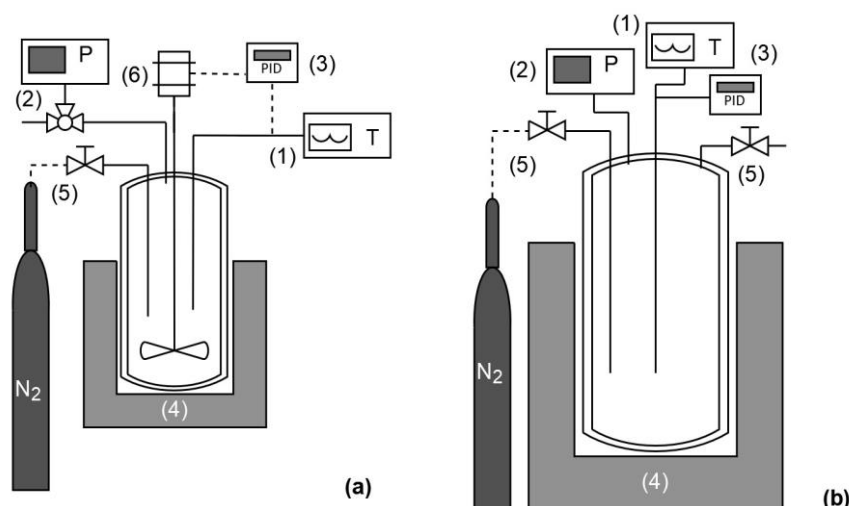


Figure 1. Diagram of a stirred AUTOCLAVE ENGINEERS subcritical reactor (a) and a PARR 4570 supercritical reactor (b). Temperature sensor (1). Pressure sensor (2). PID temperature controller (3). Heater (4). Valve system (5). Stirrer (6).

The hydrothermal treatment of the CFRPs under supercritical conditions was conducted using a PARR 4570 Series non-stirred tank batch reactor (Figure 1b), which is made of 316 stainless steel, has a capacity of 1084 mL, and can operate at 570 °C and 277 bar maximum temperature and pressure. The reactor was equipped with temperature (1) and pressure (2) sensors linked to the ParrCom application to allow real-time data logging and temperature adjustments by means of a PID controller (3) that operated a 2.3 kW cylinder electric heater (4). The reactor was also equipped with a purge and gaseous sampling valve system (5).

The experimental procedure described below was applied to both reactors. First of all, the composite sample was placed on a coiled tubing support made of 316 stainless steel. This supporting accessory ensured that the entire surface of the composite samples remained in direct contact with the solvent but not with the reactor walls. The solvent, consisting of either pure water or an aqueous solution of IPA 5 wt.%, was added together with the corresponding catalyst at 0.1 M concentration.

As a first step, the reactor was closed and purged with N₂ for 15 min in order to remove the oxygen from inside the reactor. For the tests under subcritical conditions, the AUTOCLAVE ENGINEERS reactor was pressurized with N₂ up to 35–40 bar to ensure that the solvent remained liquid at the setpoint temperature. Also, the stirring of the reactor was set at 60 rpm.

Then, a 30 min heating phase was started until 300 °C was reached in the AUTOCLAVE ENGINEERS reactor. In the PARR 4570 reactor, the heating phase took 100–105 min and 400 °C was reached. A reaction time (rt) was then allowed, and then the oven was turned off and allowed to cool down to room temperature. The gas was sampled and the reactor was opened to extract the coiled tubing support that held the recycled fibers and to collect the liquid effluent containing the degraded resin. Triplicate tests were carried out to confirm the repeatability of the experimental procedure, and deviations lower than 2% in DR were registered.

2.3. Analytical Methods

The resin decomposition rate (DR, %) [15,25] indicates the effectiveness of the hydrothermal treatment applied to the composite samples, as it represents the amount of degraded epoxy resin with respect to its initial content in the untreated samples.

DR is calculated according to Equation (1), through the gravimetric analysis of the samples, before ($m_{i,s}$) and after the hydrothermal treatment ($m_{f,s}$), with respect to the initial resin mass contained in the composite sample ($m_{i,r}$). The initial resin mass is calculated, as

shown in Equation (2), by considering the initial resin content in the composite samples, which in this case represents 34% of the initial mass of the composite sample.

$$DR(\%) = \frac{m_{i,s}(g) - m_{f,s}(g)}{m_{i,r}(g)} \cdot 100, \quad (1)$$

$$m_{i,r}(g) = 0.34 \cdot m_{i,s}(g), \quad (2)$$

To ensure a moisture-free mass measurement, the standard method for dry total solids (2540B) is applied [26]. Both the original and the recycled samples were dried for 24 h in an oven at 105 °C before being weighed.

A scanning electron microscope (FEI Nova NanoSEM 450) located at the Scientific and Technological Research Central Services (SC-ICYT; University of Cádiz, Cádiz, Spain) was used to capture high-resolution images of the fibers' surfaces. This allowed us to examine their state and appearance and to determine whether they had suffered any damage as well as to measure their diameter.

The tensile strength and elastic modulus of a selection of recycled carbon fibers were evaluated using single-fiber tensile tests performed by Titania S.L. in accordance with the ISO 11566 standard [27].

3. Results and Discussion

In the present work, different experiments were carried out to determine how different operating conditions affect the recovery of carbon fibers. The tests were carried out under both subcritical (temperature of 300 °C and pressures around 105–130 bar) and supercritical conditions (temperature of 400 °C and pressures around 240 bar).

A temperature of 400 °C was chosen for the supercritical conditions to ensure a temperature above the critical point of water (374 °C), but away from instabilities around the critical point, and to avoid too high temperatures. Similarly, 300 °C was selected, as it is sufficiently lower than the critical point of water, but sufficiently high to achieve a reasonable DR but without reaching 100%, so that it would also allow us to study the effect or improvement that the use of catalysts can have.

Other variables that were considered were the use of stirring, the specific surface (S.S.) of the composite samples (ratio between the surface of the samples and their masses), the reaction time (rt), the solvent/mass ratio of the composite, and the specific catalyst used in each case. The efficiency of the hydrothermal treatments applied was primarily determined as a function of the resulting resin degradation rate, DR (%).

The primary goal of the process is the recovery of carbon fibers, as outlined in the introductory section. This is necessary from an environmental standpoint as well as from the perspective of the high economic and energetic value of virgin carbon fibers. Furthermore, it has been demonstrated that carbon fibers can be recovered while maintaining their mechanical properties. However, upon hydrolysis of the resins, they break down into numerous fragments, probably rendering them unsuitable for reuse in resins. Indeed, a complex mixture of products is generated in the aqueous phase, making the recovery of any particular compound in large quantities a challenging endeavor.

The effects of most of the variables were studied by means of the AUTOCLAVE ENGINEERS subcritical reactor (≈ 300 °C and 132 bar). The tests under supercritical conditions were performed in the PARR 4570 reactor (≈ 400 °C and 243 bar). Table 1 shows the tests' operating conditions and results.

Table 1. Test operating conditions and results.

Test	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	P11	P12
Stirring (rpm)	0	60	60	60	60	60	60	60	60	60	-	-
T (°C)	300	300	300	300	300	300	300	300	300	300	400	400
P (bar)	125	132	104	132	134	132	132	132	129	136	242	244
t (min)	35	35	120	80	80	80	80	80	80	80	35	35
Solv. (wt.%)	5% IPA	5% IPA	5% IPA	5% IPA	5% IPA	5% IPA	5% IPA	5% IPA	5% IPA	5% IPA	Water	5% IPA
Cat. (0.1 M)	KOH	KOH	KOH	KOH	KOH	KOH	NaOH	K ₂ CO ₃	-	KOH	-	KOH
Ratio (ml _{solv} /g _{comp})	303	300	299	301	448	223	301	301	302	222	311	302
S.S. (mm ² /g)	924	927	925	973	950	850	972	932	973	716	849	826
DR (%)	49	51	97	95	94	90	90	95	27	84	94	98

3.1. Effect of Using Alkaline Catalysts

Different catalysts were used to evaluate their effect on the resulting DRs. According to reports by other studies, alkaline catalysts at concentrations around 0.1 M [19,21,28] can achieve a significant improvement in the depolymerization reaction kinetics. In this way, higher concentrations have been discarded in order to use the minimum amounts of additives that have demonstrated good efficiencies in the process. Alkaline catalysts considerably accelerate hydrothermal solvolysis processes due to the following mechanisms: increasing the concentration of hydroxyl ions (OH[−]) that attack the electrophilic carbon atoms of the target compound; enhancing the electrostatic interaction between these negative hydroxyl ions and the positively charged hydrogen atoms so that the bonds between the atoms of the target compound are weakened, making them sensitive to breakage; and promoting the ionization of water molecules that generate hydronium ions (H₃O⁺) that promote the hydrolysis reaction [29].

For this purpose, a number of experiments were performed, as follows: catalyst-free (P9), 0.1 M KOH (ac) (P4), 0.1 M NaOH (ac) (P7), and 0.1 M K₂CO₃ (ac) (P8). All the tests were performed at 300 °C, 130 bar, 60 rpm, 80 min reaction time, 300 ml_{solv}/g_{comp} solvent/sample ratio, and 5 wt.% IPA solution as co-solvent. Figure 2 shows the DR values (%) obtained from the different experiments, where no relevant differences could be observed between the results that could be attributed to the catalyst used.

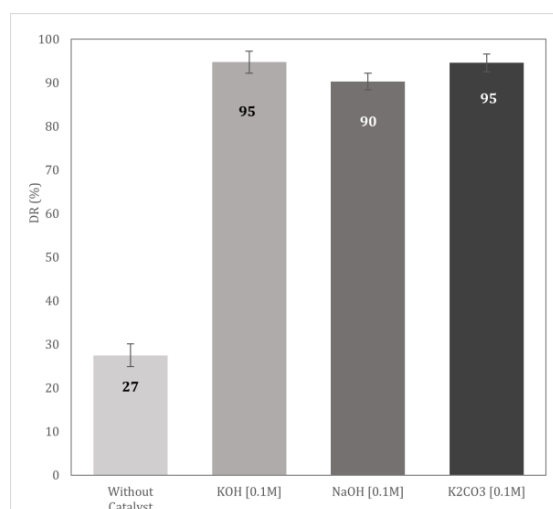


Figure 2. DRs obtained using different catalysts or no catalyst at 300 °C, 130 bar, 60 rpm, 80 min, 300 ml_{solv}/g_{comp}, IPA 5 wt.%.

The tests that used 0.1 M KOH and K₂CO₃ presented the highest DR values, at 95% and 95%, respectively. The test where NaOH was used showed a slightly poorer removal performance, with a 90% DR. Finally, the experiment that was performed without any catalysts showed a significantly lower DR (27%) than those in which a catalyst had been used.

The comparison of these results allows us to confirm that the decomposition of the resin was substantially improved when a catalyst was added to the hydrothermal treatment under subcritical conditions, as in the tests where a catalyst was used, the decomposition rates were three times higher than when no catalyst was used.

Similar results have been reported in the literature. For example, Liu J. et al. [30] used methanol as a solvent and KOH as a catalyst under subcritical conditions to recycle CFRPs. In their study, they examined the contribution of the catalyst to the resin degradation reaction and concluded that, in the absence of KOH, the process needed to reach a temperature of 275 °C to achieve complete decomposition of the resin, while in the presence of 0.036 M KOH, it could do it at 210 °C, which demonstrates that a small amount of KOH can drastically reduce temperature requirements. Piñero-Hernanz et al. [20] demonstrated the major impact of catalysts when recovering CFs from CFRPs, by achieving a DR of 95% using 0.5 M KOH in an aqueous solution, while a DR of only 79% was reached when no catalyst was used under the same operating conditions (400 °C, 281 bar, 15 min).

Given that KOH was one of the most often used catalysts [20,29,31] and that it did not affect fiber recovery rates nor the mechanical properties of the recovered fibers, our research team used KOH at 0.1 M used for the rest of the study.

3.2. Effect of the Specific Surface Area

The influence of the specific surface area (S.S.) on the outcome of hydrothermal treatments was studied in order to delve into the results obtained from the tests where samples of exactly the same size could not be used. This should allow us to determine the effect of this variable on a prospective scaling and provide us with a more realistic approach to the recycling of actual aeronautical components.

For comparison purposes, two tests on composite samples of different sizes were used, which caused them to have different S.S.s, being 850 mm²/g for the sample used in the P6 test and 716 mm²/g for the one in the P10 test. The rest of the variables were set to the following values: 300 °C, 130 bar, 60 rpm, 80 min reaction time, 222 ml_{solv}/g_{comp} solvent/sample ratio, 5 wt.% IPA solution, as solvent and 0.1 M KOH as catalyst. The specific surface area (S.S.) was calculated by dividing the external surface area of the samples by their mass.

Figure 3 shows the DR values obtained from the tests on different specific surface area samples. Based on these results, it can be observed that the test where the samples had a higher specific surface area (850 mm²/g) achieved a higher DR (90%) than the test where the sample had a lower S.S. (716 mm²/g), 84%. This allowed us to conclude that the higher the S.S., the higher the DR achieved, which is of special interest for the comparison of results between samples that are not strictly identical.

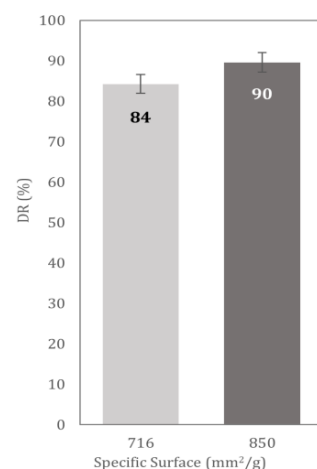


Figure 3. DR values reached when processing pieces with different specific surface areas at 300 °C, 130 bar, 60 rpm, 80 min, 300 ml_{solv}/g_{comp}, IPA 5 wt.%, KOH 0.1 M.

3.3. Effect of Stirring

Given that the AUTOCLAVE ENGINEERS reactor is equipped with a stirring system, the effect of stirring on the DRs reached by the hydrothermal treatment under subcritical conditions was evaluated. For this purpose, two tests were conducted, one without stirring (P1) and another with a gentle stirring of 60 rpm (P2). The rest of the operating conditions remained unchanged at 300 °C, 130 bar, 35 min reaction time, 300 ml_{solv}/g_{comp} solvent/sample ratio, 5 wt.% IPA dilution as solvent, and 0.1 M KOH as catalyst.

Figure 4 shows a comparison between the resin decomposition rates (DRs) achieved with and without stirring. A slightly higher DR (51%) could be observed when stirring was used with respect to the DR reached (49%) without the stirring of the reaction medium, even if it was not a significant difference.

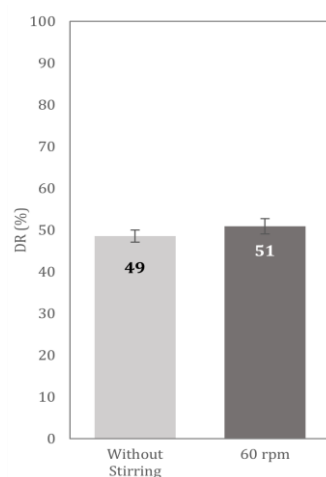


Figure 4. Decomposition rates obtained with and without stirring at 300 °C, 130 bar, 35 min, 300 ml_{solv}/g_{comp}, IPA 5 wt.%, KOH 0.1 M.

Similar results have been obtained by other authors. In their study, Piñero-Hernanz et al. (2008) [29] claim that, although the use of mechanical stirring would improve the matter transfer and therefore the performance of the hydrothermal treatment itself, the agitators might also affect the mechanical properties of the recovered fibers. In order to improve matter transfer while allowing a reduction in the reaction temperature, they proposed to operate under continuous flow conditions, using 5 mL/min of 1-propanol with 0.02 M KOH. Under these conditions, they registered DRs of 93% at 300 °C and 98% at 350 °C.

Therefore, the small increment in the removal of resin that has been observed when mechanical stirring is used can hardly justify the additional complexity involved in the employment of reactors operating at high pressure and temperature while equipped with a stirring system (a growing complexity when the process is scaled up). Furthermore, the negative effect that stirring may have on the mechanical properties of the fibers should also be borne in mind.

3.4. Effect of the Reaction Time

In order to evaluate the correlation between the reaction time and the DRs achieved by the hydrothermal process under study, a number of tests were carried out using different reaction times, as follows: 35 min (P2), 80 min (P4), and 120 min (P3). The rest of the variables remained unchanged: 300 °C, 100–130 bar, 60 rpm, 300 ml_{solv}/g_{comp} solvent/sample ratio, 5 wt.% IPA solution as solvent, and 0.1 M KOH as catalyst. The resulting DRs (%) can be seen in Figure 5.

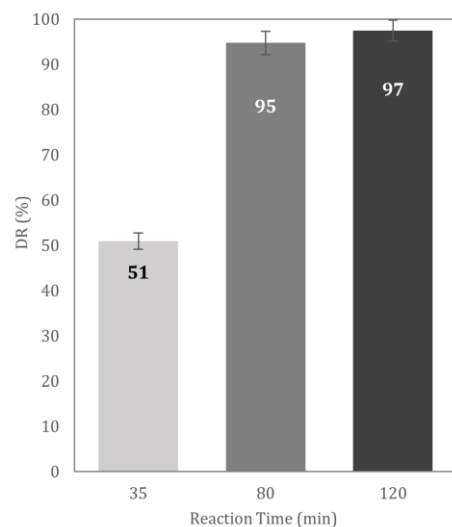


Figure 5. Decomposition rates achieved when using different reaction times at 300 °C, 100–130 bar, 60 rpm, 300 ml_{solv}/g_{comp}, IPA 5 wt.%, KOH 0.1 M.

According to the DRs obtained, it could be confirmed that the test with the longest reaction time (120 min) achieved the highest decomposition rate (98%), while the tests that used 80 and 35 min as reaction times registered DRs of 95% and 51%, respectively.

A clear connection can be inferred from these results with respect to the subcritical conditions under which these tests were carried out (300 °C): namely, the longer the reaction time, the higher the resin decomposition rate. Nevertheless, the comparison between the DRs obtained from the 80 and the 120 min tests revealed that the actual increases in DR were not so significant. This led us to conclude that, from 80 min onwards, longer reaction times would result in gradually smaller increases of the DRs.

Yuyan L. et al. (2009) [32] studied the influence of the reaction time on the DRs by using water at 260 °C to treat the CFRPs for times ranging between 45 and 105 min. The resulting DRs were between 0% and 100%. This corroborates the results obtained from the experiments conducted under subcritical conditions in the present study, where it was observed that a minimum time is required to start degrading the epoxy resin, and emphasizes the relevance of this variable with regard to the potential degradation rates that can be achieved.

3.5. Effect of Solvent Volume/Composite Mass Ratio

In order to determine the effect of the solvent volume/composite mass ratio on the DRs obtained, a number of experiments were carried out using the following ratios: 223 ml_{solv}/g_{comp} (P6), 301 ml_{solv}/g_{comp} (P4), and 448 ml_{solv}/g_{comp} (P5). The other operating variables remained unchanged: 300 °C, 130 bar, 60 rpm, 80 min, 5 wt.% IPA solution as solvent, and 0.1 M KOH as catalyst.

Given that the specific surface area (S.S.) could not be kept constant for these tests, with a surface area of 850 mm²/g in the 223 ml_{solv}/g_{comp} test, 973 mm²/g in the 300 ml_{solv}/g_{comp} test, and 950 mm²/g in the 448 ml_{solv}/g_{comp} test, the conclusions reached in Section 3.2 should be taken into account. According to those conclusions, a certain increase in the DR is to be expected when the specific surface area of the sample also increases.

According to the DR values (%) that are shown in Figure 6, the test with the lowest solvent/mass ratio (223 ml_{solv}/g_{comp}) presents a slightly lower resin removal rate than the tests with greater ratios of 301 and 448 ml_{solv}/g_{comp}, namely, 90% versus 95% and 94%, respectively.

A slight DR increment can therefore be observed as the solvent ratio increases. However, as the experiments seem to have been performed using a substantial excess of solvent,

we can conclude that, in this case, the solvent/mass ratio should not have a great impact on the resin decomposition rates to be expected.

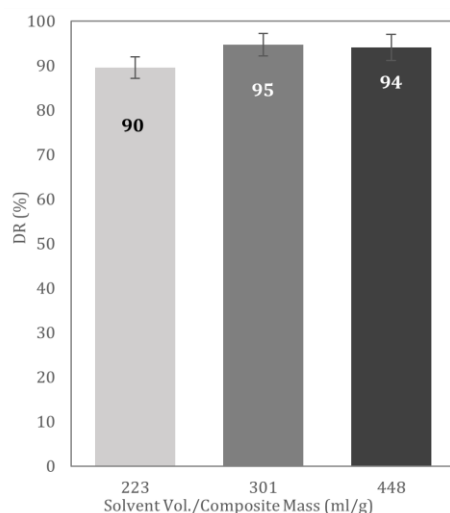


Figure 6. Decomposition rates obtained when varying the solvent volume/composite mass ratio at 300 °C, 130 bar, 60 rpm, 80 min, IPA 5 wt.%, KOH 0.1 M.

Moreover, the fact that the S.S. of the composite samples could not be kept constant for these tests may have had some influence on the results. It is a fact that the experiment run at 223 ml_{solv}/g_{comp}, which had the lowest S.S., also produced the lowest DR, while the experiment run at 301 ml_{solv}/g_{comp}, which was the highest S.S., resulted in the highest DR.

Sokoli H.U. et al. (2017) [33] studied the recycling of a composite material with hybrid reinforcement (glass fibers and carbon fibers) for which water was used at conditions close to its critical point. As part of the tests performed, the effect of the ratio (solvent volume/composite mass) was evaluated, and it was observed that for ratios between 0.8 and 1.96 ml_{solv}/g_{comp}, the registered DRs consistently maintained levels in proximity to 95%, which indicates that, under these conditions, the solvent/mass ratio is not a variable with a substantial impact on DR, as similar resin degradation rates can be achieved by using much lower amounts of solvent.

3.6. Effect of Operating Under Supercritical Conditions

The industrial application of processes involving pressures and temperatures above the critical point of water (374 °C, 221 bar) presents major difficulties from a technical and economic point of view due to the severe conditions that the process must comply with and because of a number of problems related to the insolubility of the salts and the occurrence of corrosion, among others [34]. However, in this section, our aim is to ascertain whether obtaining high DR values using shorter reaction times can justify the use of hydrothermal treatments under supercritical conditions.

For this purpose, two tests were carried out at 400 °C temperature (P11 and P12) and at a pressure of about 240 bar. Both experiments were carried out without stirring and using a reaction time of 35 min. For the P11 test, pure deionized water (Milli-Q) was used as solvent, while in the P12 test, an aqueous solution of 5 wt.% IPA with 0.1 M KOH as catalyst was used.

The DRs obtained from these tests are shown in Figure 7. The graph displays the DRs according to each experimental temperature and reaction time, and a clear difference can be seen between the experiments where a catalyst was used (solid columns) and those where no catalyst was used (striped columns). Thus, the DR values achieved in P11 and P12 were 94% and 98%, respectively. The graph also shows the results that correspond to the tests that were carried out under subcritical conditions (300 °C, 100–130 bar) so that they can be compared against those obtained under supercritical conditions.

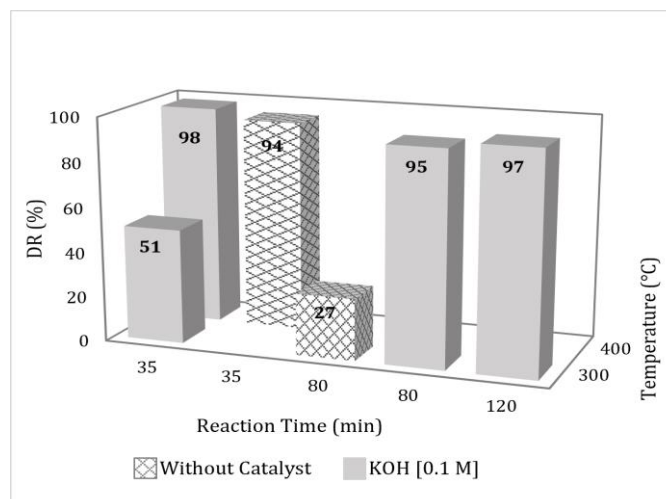


Figure 7. Comparison between the DRs achieved when operating at supercritical (400 °C; 243 bar) or subcritical (300 °C; 100–130 bar) conditions using an approximately 300 ml_{solv}/g_{comp} ratio and IPA 5 wt.% (except for P11, where pure water was used).

Table 2 presents the severity factor (SF) as determined according to Equation (3) for the different temperature levels and reaction times that were studied. Generally, a lower SF means lower temperature and reaction time, that is, lower technical and economical requirements to carry out a thermochemical process. It can be observed that the tests under supercritical conditions (400 °C) present a higher SF (10.38) than the subcritical tests (SF between 7.43 and 7.97 at 300 °C) despite the significant differences between reaction times [35,36]. A value of SF = 7.97 is better than a value of 10.38, because a lower value of SF indicates a better combination of temperature and reaction time; that is, it means that the conditions are milder. At 300 °C, the best reaction time is clearly 120 min, because it provides a considerable increase in DR, while the SF at 300 °C and different reaction times shows a very small increase. The two tests conducted under supercritical conditions achieved high DR values, the highest (98%) being reached by the tests that were performed at 400 °C using KOH 0.1 M as catalyst and IPA 5 wt.% as solvent. This particular test required just 35 min reaction time to reach a DR comparable to those obtained under subcritical conditions (300 °C) using reaction times nearly four times longer (120 min). Nonetheless, despite the longer time required, because of the lower demands with regard to their pressure and temperature conditions (lower SF), the subcritical hydrothermal processes were deemed more appropriate for a potential scaling up.

$$SF = \log \left[t \cdot \exp \left(\frac{T - 100}{14.75} \right) \right], \quad (3)$$

Table 2. Severity factor (SF).

t (min)	T (°C)	SF	DR (%)
35	300	7.43	51
80	300	7.79	95
120	300	7.97	98
35	400	10.38	98

3.7. Scanning Electron Microscopy (SEM) Analysis of the Recovered Fibers

Scanning electron microscopy (SEM) was used to examine the appearance/state of the fibers and their possible damage and also to determine their diameters. Thus, the diameters of the rCFs measured using SEM allowed us to determine whether the fibers

retained their sizing layer or whether, on the contrary, their sizing had been degraded by the hydrothermal process.

Sizing is a thin, homogeneous coating that is applied to the surface of fibers during the manufacturing process to protect them during their handling and processing. In addition, sizing improves the chemical, mechanical, and thermal properties of the fibers and also improves the bond between the fibers and the resin matrix [37].

Figure 8a shows a raw composite sample before being subjected to a hydrothermal treatment. It can be seen in the SEM image of this part in Figure 8d that the fibers of the raw composite piece are embedded in the epoxy resin. Figure 8b shows the fibers recovered through the P3 test (300 °C; 100 bar; 120 min; IPA 5 wt.%; KOH 0.1 M) and its SEM image; Figure 8e shows that these fibers have a fairly clean surface with hardly any traces of epoxy resin, which is in agreement with the 98% DR registered for this test. On the other hand, Figure 8c,f show the fibers recovered through the P12 test (400 °C; 240 bar; 120 min; IPA 5 wt.%; KOH 0.1 M), which was run under supercritical conditions. Their corresponding SEM image, Figure 8f, shows a rougher and more irregular surface that also presents adhered residues of a larger size. This may be related to the fact that P12 also uses a catalyst under supercritical conditions.

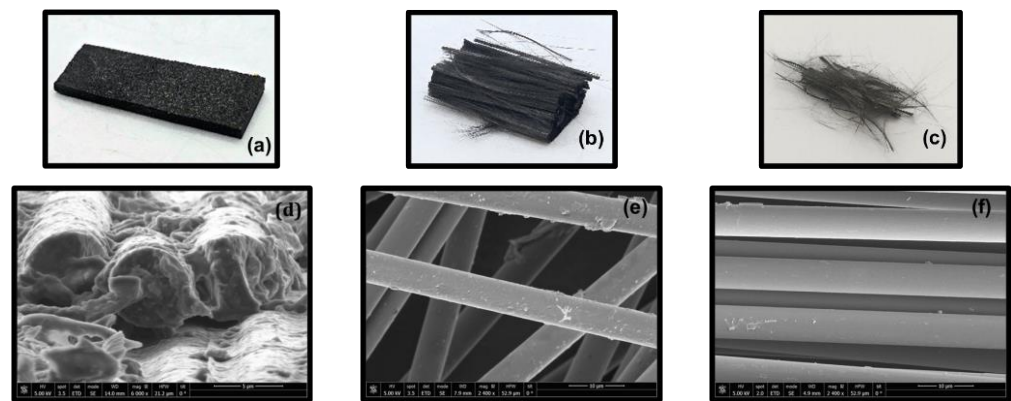


Figure 8. Appearance of a piece of composite material before and after the hydrothermal treatment. Photography of the raw sample (a) and of the fibers recovered through the P3 (b) and P12 (c) tests. SEM images of the raw sample (d) and of the fibers recovered through the P3 (e) and P12 (f) tests.

The diameter of the carbon fibers in the original composite sample (Figure 8d) as well as the diameter of the recovered carbon fibers were measured by SEM. The difference between the measured diameter of the CFs in the original composite material and the diameter specified by the manufacturer (5 µm) is considered to represent the average thickness of the sizing that covers the CFs. Table 3 includes the measured average diameters and the estimated average sizing thickness for each of the tests.

Table 3. Carbon fiber measured diameters and estimated sizing thickness.

Test	Original	P2	P3	P7	P8	P9	P12
Average diameter (µm)	5.89 ± 0.04	5.85 ± 0.04	5.96 ± 0.11	5.90 ± 0.08	5.83 ± 0.08	5.83 ± 0.06	5.82 ± 0.03
Average sizing thickness (µm)	0.446 ± 0.02	0.426 ± 0.07	0.479 ± 0.03	0.450 ± 0.04	0.413 ± 0.04	0.416 ± 0.03	0.412 ± 0.01

Based on the results presented in Table 3, it can be concluded that the hydrothermal treatment corresponding to the P3 test (300 °C; 100 bar; 120 min; IPA 5 wt.%; KOH 0.1 M) and P7 tests (300 °C; 130 bar; 80 min; IPA 5 wt.%; NaOH 0.1 M) did not damage either the fibers or their sizing, as they exhibited thicker sizing than the original fibers. The rest of the tests resulted in fibers with a marginally lower thickness than that corresponding to the fibers in the raw sample. This might suggest that their sizing had not been damaged at all or that only minimal sizing damage had occurred.

3.8. Tensile Strength Assays

Tensile strength assays on individual recovered carbon fibers from the most severe test conditions, such as P11 (400 °C; 35 min; water) and P12 (400 °C; 35 min; IPA 5 wt.%; KOH 0.1 M), were carried out. These tests would allow us to evaluate the tensile strength (TS) and elastic modulus (E) of the recovered fibers. The results from these tests are presented in Table 4 together with the reference values corresponding to the raw T800S fibers.

Table 4. Tensile strength (TS) and elastic modulus (E) of the recycled carbon fibers.

Sample	TS (MPa)	TS Loss (%)	E (GPa)	E Loss (%)
T800S CF	5880	-	294	-
P11 (400 °C//242 bar//35 min//Water)	5769 ± 650	1.88 ± 11.1	228 ± 29	22.4 ± 10
P12 (400 °C//242 bar//35 min//5%IPA)	5735 ± 544	2.47 ± 9.3	280 ± 77	4.8 ± 26

As can be seen, the fibers' TS loss is notably small for both tests (≈ 1.9 – 2.5%), similarly to their loss of elastic modulus in the case of the fibers recovered through the P12 test ($\approx 5\%$). However, a noticeable drop in the elastic modulus of the fibers recovered through the P11 test does occur.

Since this test is the one that was conducted under the most severe conditions considered in this study, it could plausibly be assumed that any losses in mechanical properties experienced by the fibers obtained from the rest of the tests, performed under subcritical conditions, will be either similar or lower. These results suggest that the employment of hydrothermal processes for the recovery of CFRPs should result in fibers that would be hardly damaged and, therefore, would retain most of their mechanical properties.

3.9. Potential Economic and Environmental Impacts

The hydrothermal CFRP recycling method studied is very interesting, especially for the aeronautics sector. CFRPs are essential for reducing the weight of aircraft, which improves fuel efficiency and reduces emissions. However, their disposal poses problems due to their durability and the fact that they are not biodegradable. Dong et al. (2018) [38] conducted an economic analysis of CFRP waste management, showing that recovery processes, including hydrothermal techniques, can be economically viable, especially when targeting the recovery of high-quality fibers for aerospace applications. In this regard, Krauklis et al. (2021) [39] emphasized how hydrothermal hydrolysis offers a sustainable recycling route, especially from high-volume industries such as aerospace.

From an economic point of view, this process enables the following:

- Reducing dependence on expensive virgin fibers, making recycled fibers a more cost-effective alternative, especially for industries such as automotive and sports equipment.
- Encouraging the development of industries related to the production and application of recycled fibers, thus promoting a circular economy.
- Saving on the cost of disposing of waste that is currently sent to landfill, especially as waste legislation is becoming more and more restrictive.
- Providing a new source of revenue for waste-management companies, as they can sell the recovered carbon fibers.

In terms of environmental impact, this recycling process allows the following:

- Reducing the consumption of raw materials and natural resources that would be used to produce new fibers.
- Reducing greenhouse gas emissions and meeting sustainability targets, as CF recycling uses less energy than virgin fiber production.
- Reducing waste to landfills by recovering or recycling waste from industries such as aviation.

- Promoting a circular economy that contributes to more sustainable industries.

The main challenges for the implementation of this recycling technology are the high initial investment required for equipment and infrastructure, the optimization of the process to minimize its environmental footprint, the market acceptance of the recycled fibers, and the compliance with the regulations that will be developed to guarantee the quality of the recycled materials.

4. Conclusions

The results that have been obtained from the tests conducted in the present study allow us to draw several conclusions regarding the use of hydrothermal processes for the recycling of CFRPs.

Specifically, with respect to the addition of alkaline catalysts to the solvent, it was observed that they represent a clear improvement when subcritical conditions are used (300 °C; 100–130 bar), since they allow reaching DRs of around 90%, compared with the 30% reached under the same conditions when no catalyst is used. Although this enhancing effect was observed for all three catalysts studied, KOH stands out over NaOH and K₂CO₃, as it achieved DRs of around 95%.

It was observed that the use of catalysts under subcritical conditions (300 °C) resulted in DR values similar to those obtained under supercritical conditions (400 °C). Nonetheless, considerably longer reaction times were required when operating under subcritical conditions (120 min vs. 35 min under supercritical conditions). Even so, the use of a catalyst can still be considered a major advantage, as it allows the CFRPs to be recycled under less severe conditions in terms of pressure and temperature.

The solvent volume/composite mass ratio did not significantly improve the efficiency of the recovery treatments according to the DRs achieved. This could be attributed to the fact that, in all of the tests that were carried out, an excess of solvent was employed.

In our study, we investigated the influence of a variable specific surface area of the treated samples, as the samples used could not always be of the same size. Even though it was observed that a higher specific surface area (S.S.) of the fibers would result in moderately greater DRs, we must not forget that, from an operational point of view, larger composite pieces are normally more desirable.

The SEM images allowed us to corroborate that the sizing of the fibers was either fully or virtually fully preserved, regardless of the specific processing conditions tested. Similarly, the results from the tensile tests revealed that, even under the most severe conditions tested, 400 °C and 243 bar, the recovered fibers had lost just between 1.9% and 2.5% of their tensile strength with respect to that of the raw fibers.

Based on the results from the present study, the use of catalytic hydrothermal treatments for the recycling of CFRP appears as a promising solution to cope with the increasing generation of this type of waste. This makes us think that it would be worthwhile to pursue further research in this area.

The industrial scale-up of hydrothermal solvolysis for recycling aeronautical waste may offer significant economic and environmental benefits, from reducing raw material costs to lowering emissions. While challenges exist, overcoming them can lead to a more sustainable and circular approach to managing CFRP waste in the aeronautics industry.

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