

# HIGH QUALITY CARBON FIBERS FROM END-OF-LIFE FIBER REINFORCED PLASTICS - A NEW RECYCLING TECHNOLOGY

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## Abstract

Carbon Fiber Reinforced Plastics (CFRPs) recycling is very challenging and yet is in high demand, consequence of the increasing use of this material in the automobile and wind energy industries and the high cost of carbon fibers in the market. The existing solutions for CFRPs recycling today often impact on the quality of obtained recycled fibers, thus preventing their use in high-value applications. Aiming to mitigate some of the inconveniences of these processes, we developed a new technology that uses vaporsolvolysis at low temperature (180 °C) and low pressure (11 bars) to degrade the composite resin and recover high quality fibers. In this work, we present the preliminary study and process optimization that led to the final technology as well as the versatility tests proving that the chosen process is compatible with different thermoset and thermoplastic resins. In the experiments, the influence of solvent, catalyst, temperature and autoclave configuration on resin degradation is investigated. The best rate of resin degradation is obtained with the recycling of CFRPs in vapor phase only using acetic acid as solvent and HCl as catalyst at 180 °C under autogenous pressure.

## 1. Introduction

Carbon Fiber Reinforced Plastics (CFRPs) are used whenever high strength-to-weight ratio and rigidity are required. With these features, CFRPs are increasingly replacing metals in a number of new applications like non-structural car parts, sport equipment and boating. But excellence comes at a price. In the automotive industry, for example, replacing steel by CFRPs generates a cost increase of 80 %. The high cost of this material is largely due to the energy intensive processing of carbon fibers, which also impacts its carbon footprint. Regardless, the global demand for CFRP is increasing, and is expected to reach up to 175 000 tons by 2021 [1]. The high demand of CFRP components also impacts the generation of waste, from the production to the end-of-life, that calls for suitable recycling alternatives. Nevertheless, the recycling of CFRPs is complicate. This is due to the large variety of fiber and resin compositions and the presence of different materials and paintings in the pieces. The resin can be thermoplastic or thermoset, and, for the latter, the three-dimensional linking of the matrix is particularly difficult to cleave.

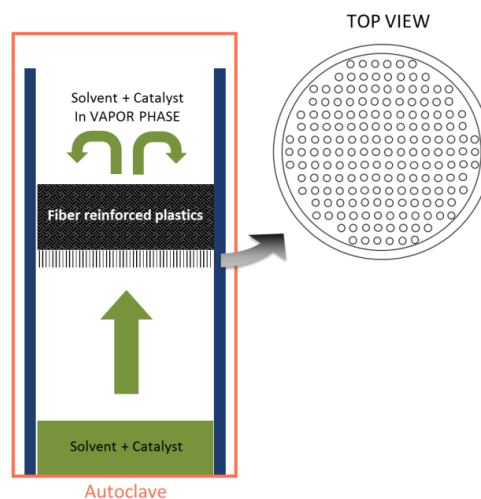
Today, the commonly used methods to recycle CFRPs are pyrolysis and mechanical grinding, but both have its downsides. The first is a very energy intensive process that damages the fibers due the high temperatures used [2]. The latter is mostly adapted to thermoplastic resins and the resulting product can only be used in low value applications. An alternative approach widely studied is wet oxidation in sub or super-critical water [3], [4]. In this process, the main drawback is the high temperature and pressure needed, which are not compatible with industrialization. Another emerging alternative for CFRPs recycling is chemical processing through solvolysis.

Solvolysis has shown to be a promising technology to recycle CFRPs [2]. In this process solvents are used to break up the chemical bonds of the resin, thus releasing the carbon fibers. Solvolysis is especially interesting for the possibility to recover the oligomers as well, providing a full recyclability for CFRPs. When applied at temperatures lower than 200 °C, at ambient or autogenous pressure, the use of catalysts, most often acids and/or oxidation agents, are necessary to degrade the resin. In this case, the use of lower temperature and pressure brings evident positive aspects to the process such as cost savings, lower technical risks and lower environmental impact when the solvents can be re-used. Nevertheless, the strong exposition of the fibers to strong acids such as nitric [5] and sulphuric [6], or strong basis such as NaOH [7] and KOH [8], often impacts the quality of the obtained fibers.

In order to maintain all the positive aspects of solvolysis, but minimizing the exposition of the fibers to the solvent and facilitating the detachment of the resin to the fibers, we developed a new technology for CFRPs recycling based in vaporsolvolytic. The process uses a unique combination of solvent and catalyst that is in vapor phase at temperatures lower than 200 °C, under autogenous pressure, and a modified two-level autoclave that allows to treat the FRPs pieces on vapor phase only. In this work, we present the preliminary studies considering the influence of different solvent and catalysts, the optimization study with a modified autoclave, as well as the results of versatility test of the final solution in different resin and fiber types of FRPs.

## 2. Experimental method

The experiments were carried out using two methods: i) with CFRPs pieces completely immersed in the solvent and catalyst mixture, and ii) at vapor phase only, thanks to a modification in the autoclave in two levels that avoid the direct contact of the fibers with the solvent, catalyst and residual resin that is not in vapor phase. In the first series of experiments, the resin degradation reactions were carried out in Teflon-lined autoclave with internal volume of 50 ml. In the second series of experiments and for the versatility tests, a modified two-level Teflon-lined autoclave with internal volume of 250 ml was used (Figure 1). In the latter, a Teflon-lined pierced piece is introduced in the autoclave and separates it in two levels. The solvent and catalyst are introduced in the lower part (1<sup>st</sup> level) and the CFRPs pieces are placed in the upper part (2<sup>nd</sup> level).



**Figure 1.** Scheme of the modified autoclave used for vaporsolvolytic to recycle fiber reinforced plastics.

The samples used in the optimization tests were cut from a CFRP piece of end-of-life aircraft sent by Veolia. The samples used for the versatility tests were new carbon or glass FRP pieces made with different resin types. For the study, formic acid (90 % w/w), acetic acid (90 % w/w) and distilled water were tested as solvent. Gallium trichloride, antimony pentachloride, aluminum chloride and

hydrochloric acid were tested as catalyst. The reaction took place in temperatures from 120 to 180 °C depending on the experiment, for 6 hours. After cooling, the fibers were cleaned with direct water jets, and then dried at 60 °C for 12 hours.

The recycled fibers were characterized using a Field-Emission Gun Scanning Electron Microscope (FEG-SEM) to observe their morphology and possible traces of residual resin.

### 3. Results and discussion

#### 3.1. Preliminary study

In the preliminary study the influence of different solvents and catalysts were investigated. Table 1 lists the conditions used in each experiment.

**Table 1.** Chemicals and conditions used in each experiment of the preliminary study.

Solvent	Catalyst	Reaction temp. (°C)	Reaction time (h)	Weight loss (%)	Comments
Acetic acid	AlCl <sub>3</sub>	180	6	19.6	Good resin degradation but presence of solid by-products
Acetic acid + water (1:1)	AlCl <sub>3</sub>	180	6	7.4	Partial resin degradation
Formic acid	AlCl <sub>3</sub>	180	6	6.7	Partial resin degradation
Acetic acid	SbCl <sub>5</sub>	180	6	-	Poor resin degradation
Acetic acid	GaCl <sub>3</sub>	180	6	17.9	Good resin degradation
Acetic acid	HCl	180	6	22.1	Good resin degradation
Acetic acid	-	180	6	-	No sign of resin degradation

Considering the solvent, acetic acid has shown to be the best to allow resin degradation. From the experiment with acetic acid only, the CFRPs was considerable swollen, as was also previously observed in other studies [9], [10]. The degradation mechanism is likely explained by the swelling action of acetic acid that enables the catalyst to penetrate the matrix and cleave the resin's polar bonds. Therefore, without catalyst, the resin can not be degraded.

From these experiments, AlCl<sub>3</sub>, GaCl<sub>3</sub> and HCl have shown to be the best catalysts with a high rate of resin degradation. In all three experiments the fibers could be easily separated from the resin after cleaning with continuous water jets. However, small yellowish grains were present within the recycled fibers in the experiment using AlCl<sub>3</sub>, probably a product from the reaction between the catalyst and the resin.

#### 3.2. Process optimization: two level autoclave

In the previous experiments, clean recycled fibers were obtained only after a long cleaning process to wash away all the degraded resin that was still mixed with the fibers. Aiming to optimize the cleaning process as well as the reaction efficiency, we separated the autoclave into two levels so the CFRPs could be recycled using vaporsolvolyis. To do so, a pierced piece was designed to retain the FRPs pieces in the upper part of the autoclave. With the increase of temperature, the solvent and catalyst get into vapor phase and react with the sample. In this case, the CFRPs is in contact only with pure solvent and catalyst, as the resin solubilizes from the fibers into solvent droplets and is washed away to the 1<sup>st</sup> level of the autoclave.

Based on the results of the preliminary tests,  $\text{AlCl}_3$ ,  $\text{GaCl}_3$  and  $\text{HCl}$  were selected to be tested as catalysts in this new autoclave configuration. The influence of the temperature in the reaction efficiency was also investigated. The experiments of the process optimization part are detailed in Table 2.

**Table 2.** Chemicals and conditions used in each experiment of the process optimization.

Solvent	Catalyst	Reaction temp. ( $^{\circ}\text{C}$ )	Reaction time (h)	Weight loss (%)	Comments
Acetic acid	$\text{AlCl}_3$	180	6	20.8	Good resin degradation but presence of solid by-products
Acetic acid	$\text{GaCl}_3$	180	6	14.9	Partial resin degradation
Acetic acid	$\text{HCl}$	180	6	36.8	Good resin degradation
Acetic acid	$\text{HCl}$	150	6	7.6	Partial resin degradation
Acetic acid	$\text{HCl}$	120	6	5.6	Partial resin degradation

Figure 2 shows the recycled carbon fibers obtained with  $\text{GaCl}_3$ ,  $\text{HCl}$  and  $\text{AlCl}_3$  as catalyst using vaporsolvvolysis.



**Figure 2.** Recycled carbon fibers obtained by vaporsolvvolysis using as catalyst a)  $\text{GaCl}_3$ , b)  $\text{HCl}$ , and c)  $\text{AlCl}_3$ .

The sample recycled with  $\text{AlCl}_3$  presented small yellowish grains which were also detected during the preliminary study. These grains rest attached to the fibers, making it very difficult to completely separate them from the recycled fibers. The recycled sample using  $\text{GaCl}_3$  still had resin attached to the main fiber filets. The efficiency of this catalyst was lower than in the preliminary studies, and this is probably due to the high boiling point of this material ( $201^{\circ}\text{C}$ ). Yet, this material could still be considered if the process temperature is increased to up to  $201^{\circ}\text{C}$ . The rate of resin degradation using  $\text{HCl}$  in this new configuration is even higher than in the observed preliminary studies. From the three catalysts testes,  $\text{HCl}$  showed the best result, with excellent resin degradation and without the generation of solid-by-products.

### 3.3. Versatility tests

The optimal solution choose to recycle CFRPs is the use of acetic acid as solvent and  $\text{HCl}$  as catalyst in a modified autoclave that enables the reaction in vapor phase only. The degradation process takes 6 hours at  $180^{\circ}\text{C}$ . In one of the experiments, a manometer was used to measure the autogenous pressure inside the autoclave at  $180^{\circ}\text{C}$ , which is 11 bar. The use of acetic acid and  $\text{HCl}$  as reagents are convenient as these chemicals can be re-used after a simple distillation process. Both, the low

autogenous pressure and the chemical recycling, bring evident advantages for the process industrialization.

The robustness of the process was verified in six different samples as detailed in Table 3.

**Table 3.** Samples material and result obtained during the versatility tests.

Fiber type	Matrix composition	Weight loss* (%)
Carbon	Epoxy	31.6
Carbon	Epoxy HTG 40	33.3
Carbon	PEEK	30.8
Carbon	Cyanate ester	34.9
Carbon	Polyamide 6	40.5
Glass	Epoxy	59.6

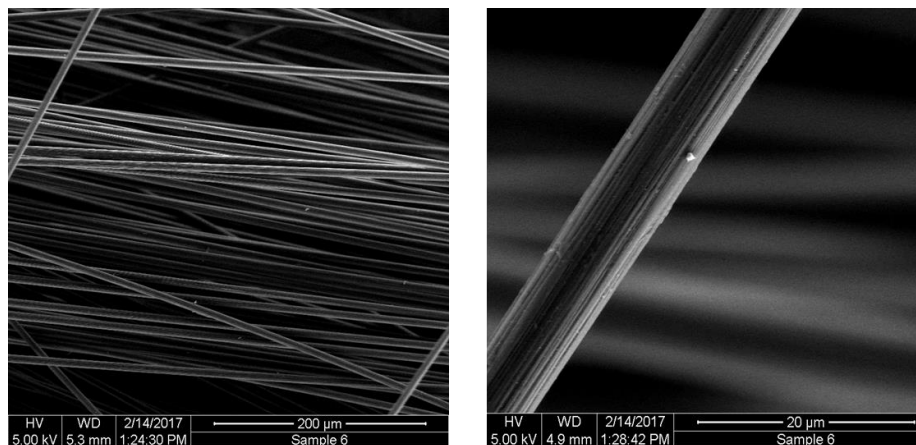
\*Please note that these samples were collected from different pieces from different manufacturers, thus the fiber/resin weight proportion is not the same between samples.

Figure 3 shows two examples of glass and carbon fibers recycled using the method applied in the versatility tests. The recycled fibers obtained after the process had between 2 and 5 cm of length, were non-woven, and still shiny.



**Figure 3.** Examples of glass and carbon fiber recycled during the versatility tests.

A FEG-SEM was used to analyze the recycled fibers morphology and look for traces of residual resin. Figure 4 shows a representative sample of the analysis. From the images, we can observe that the fibers do not present any signals of surface damage, and only very few spots of residual resin can be observed within the fibers.



**Figure 4.** FEG-SEM images of recycled carbon fibers obtained during the versatility tests.

The experimental protocol used proved to be efficient in degrading the resin of all samples tested.

### 3. Conclusions

This work investigated the influence of solvent, catalyst, temperature and autoclave configuration on resin degradation of CFRPs using solvolysis at temperatures lower than 200 °C. The preliminary study showed that the resin has a higher degradation rate using acetic acid as solvent in the presence of AlCl<sub>3</sub>, GaCl<sub>3</sub> or HCl as catalyst. The optimization study concluded that the reaction is optimized using vaporsolvolysis, which was tested through a modification in the autoclave into two levels. In this configuration, HCl proved to be the best catalyst. However, the autoclave temperature should be of 180 °C or higher in order to completely degrade the resin in 6 hours. In this recycling process, the solvent is probably responsible for the swelling of the composite matrix whereas the catalyst is cleaving the resin's polar bonds. This promising technology has many industrial-friendly aspects such as compatibility with a large range of composite resins, easy chemical recycling, low work temperature and pressure and the possibility of total recyclability of the fibers as well as the oligomers from the degraded resin.

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