Environmental Feasibility of the Recycling of Carbon Fibers from CFRPs by Solvolysis Using Supercritical Water

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ABSTRACT: Originally developed for high-tech applications in the aeronautic and aerospace industry, carbon/epoxy composites have been increasingly used in the automotive, leisure, and sports industries for several years. Nevertheless, the carbon reinforcement is an expensive constituent, and it has been recently shown that it is also the most environmentally impacting in a composite part manufacturing. Recycling these materials (even restricted to the reinforcement recovery) could lead to economic and environmental benefits, while satisfying legislative end-of-life requirements. The solvolysis of the matrix by water under supercritical conditions is an efficient solution to recover the carbon fiber reinforcement with mechanical properties closed to the ones of virgin fibers. This paper aims at demonstrating the environmental feasibility of the recycling of carbon fiber/thermoset matrix composites by solvolysis of the matrix in supercritical water. This demonstration is based on life cycle assessment that evaluates benefits and environmental challenges of this recycling loop.

KEYWORDS: Life cycle assessment (LCA), Supercritical water, Solvolysis, Recycling, Composites, CFRP

INTRODUCTION

Carbon fiber-reinforced plastics (CFRPs), or thermoset matrix composites, were originally developed for high-tech applications in the aeronautic and aerospace industry. For several years now, these materials have also been increasingly used in the automotive, leisure, and sports industries. In many applications in these sectors, one may seek aesthetic criterions or a simple feeling of high technology, more than highly technical properties. Thus, constituents’ characteristics, and specifically reinforcements, are considered as a secondary matter and may be overemphasized regarding the function of the product. This is particularly true for nonstructural decorative parts (e.g., with a carbon look finish), for which the reinforcement is the most expensive constituent, and where glass fibers, much more less expensive, cannot be used.1,2

Today, there is no, or a limited, deposit (or very few) of carbon fibers from airplanes at the end of life because airplanes integrating such materials are only currently being built and will become waste later. In the future, the expected amount will grow year after year. Therefore, the question is this: Could carbon fibers recycled from airplanes (or from production waste from aircraft and automotive production) substitute mechanically for the majority of carbon fibers currently used in the automotive, leisure, and sports industries, considering that the recycling can be done in a cost-effective way and that the aeronautic industry will not use recycled fibers? Subsequent questions are these: How can carbon fiber-reinforced plastics be recycled? Is the recycling environmentally more sustainable than the production of virgin carbon fibers?

One of the first uses of the supercritical fluid technology in the field of recycling was applied to polymers. This technique has been developed extensively in Japan since 1995 and has been reviewed many times.3–5 Beyond plastics recycling,6 solvolysis in near- and supercritical fluids of thermosetting resins (phenol and epoxy resins) has attracted a great interest among the scientific community to recover materials like carbon fibers with a high added value in the past few years. To date, few studies have been carried out on the chemical recycling of these waste composites with near- and supercritical solvolysis technology.6–14 Compared to other recycling processes (mechanical recycling processes, pyrolysis, fluidized bed processes, low temperature solvolysis processes), near- and supercritical solvolysis has the huge advantage that clean carbon fibers are recovered with similar mechanical properties to pristine fibers.6 Moreover, these undamaged fibers are obtained at relatively low temperature, without using organic solvents or concentrated acids.

Near- and supercritical water and alcohols were mainly processed as solvolysis media. In fact, near- and supercritical water or alcohols play the role of solvent and reagent for the...
Figure 1. Environmental impacts due to the carbon reinforcement (dark gray), epoxy matrix (light gray), and injection molding process (intermediate gray), while processing a 1 kg carbon/epoxy composite part. The analysis is based on Duflou et al. data.
In our case study, the use phase is not taken into account. Indeed, to the best of our knowledge, the only input data that can be taken into account concern transport operations. Like so, as rather classically, the present simulation shows that this factor did not contribute much to the overall impacts (less than 5%).

Regarding the product’s end-of-life, two scenarios have been modeled: The first one consists of burying the composite part, which is what is currently done, and represents the reality for actual composites at their end-of-life. The second one consists of the recovery of the carbon reinforcement. We focus on the recycling process by solvolysis described in Figure 2). We consider (i) an aqueous solvolysis of the matrix by water under supercritical conditions (temperature around 400 °C and pressure about 25 MPa) and (ii) a hydrothermal oxidation of the effluent to clear matrix components from water at the end of the solvolysis process.

This technology allows the fiber to be recovered. Therefore, it is a real (but partial) recycling and not a simple material valorization. Lastly, the process uses energy, water, and oxygen, and only emits water and carbon dioxide.

Lastly, the research team from the Mechanics Institute of Bordeaux has developed a prototype for packaging these second-generation fibers in an attractive form for users (i.e., designers). Data matching the remanufacturing stage have not been taken into account yet in this very first LCA. However, this energy input is assumed to be very weak compared to those involved in the first-generation reinforcement process. As a consequence, the life cycle only loops after the manufacturing of the first-generation carbon reinforcement, with no specific additional remanufacturing.

Life Cycle Assessment: Software, Database, and Method. The LCA is carried out with the SimaPro software (v.7), Eco Invent database (v.2), and ReCiPe Midpoint (H) method. As previously mentioned, in the recycling stage, the avoided material is the reinforcement. In other words, the production of a new raw material with nonrenewable resources (i.e., first-generation carbon reinforcement) is avoided.

RESULTS

Recycled Carbon Fibers Obtained by Hydrolysis in Supercritical Water. The hydrolysis of the epoxy resin matrix in supercritical water (\(p_c = 22.1\) MPa, \(T_c = 374\) °C) has been published many times as well as the alcoholysis in supercritical water and carbon dioxide. Lastly, the process uses energy, water, and oxygen, and only emits water and carbon dioxide.

Morin et al. have also performed the recycling of carbon fibers from carbon fiber-reinforced composites in a semi-continuous flow reactor. Experiments were carried out at a temperature around the critical temperature of water for a reaction time of about 30 min. The process has been optimized in order to improve the solvolysis rate of the resin without the degradation of the mechanical properties of the fibers. Water or alcohols can be used as the solvolysis medium. They are different in terms of energy consumption because the critical coordinates of alcohols are generally lower than those of water. Therefore, recycling of CFRPs using an alcoholysis process could require less energy, but the hydrolysis process is safer and greener. In this study, water was used as solvent for the recycling of carbon fibers from CFRPs. The epoxy resin was completely decomposed into lower molecular weight organic compounds. Recovered carbon fibers were characterized using thermogravimetric analysis (TGA) to determine the amount of resin removed by the process, scanning electron microscopy to observe the fibers, and single fiber tensile tests to evaluate the mechanical properties of the recycled fibers. Recycled carbon fibers from CFRPs are clean (Figure 3). All the resin was removed according to the TGA results. Furthermore, the recycled carbon fibers present good mechanical properties; a tensile loss close to the one of virgin fibers is obtained. The final liquid phase is also analyzed by gas chromatography. The monomers of the initial resins have been identified.

Environmental Evaluation. The LCA of a 1 kg composite part that takes into account the recycling of the reinforcement clearly shows the interest of this end-of-life option. Actually, it almost offsets the whole environmental impacts of the composite manufacturing (Figure 4).

By recycling a product mainly sourced with carbon fossil fuel (Figure 1), impacts on climate change or fossil depletion can be almost completely avoided (Figure 4). For marine eutrophization, recycling allowed for a larger avoidance than the impacts of manufacturing. This is due to the use of European electricity.
257 for the injection molding of the matrix, while we use a French
258 mix for recycling process (it impacts systematically onto this
259 indicator).
260 When comparing the environmental impacts of a 1 kg
261 composite part during its life cycle, depending on the end-of-
262 life scenario (landfill or recycling of carbon fibers), and despite
263 electricity consumption in the recycling process, emission of
264 greenhouse gases may be divided by 10 (Figure 5). The
265 environmental gain is on average about 80%, according to the
266 ReCiPe Midpoint (H) method. For the climate change
267 indicator, it is about 100%. This is because of the use of a
268 French electricity country mix, which is mainly sourced by
269 nuclear energy, which is energy that has no impacts on climate
270 change (it does impact principally on the ionizing radiation
271 category).
272 Negative impacts (for eutrophication and natural land
273 transformation indicators) do not mean that they are “good"
274 for the environment. This only means that it is an avoided
275 impact; to recycle, allows for avoiding some impacts due to the
276 manufacture stage.
277 Economic Validation. We recently made a market study
278 showing that there will always be relevant uses for recycled
279 reinforcements or for semi-products based on second-
280 generation fiber, whatever their mechanical characteristics are
281 and as long as the price remains reasonable.” The integration
282 of recycled carbon fiber is only interesting if the mechanical
283 performance/price ratio is higher than that of glass fiber. Therefore, in light of excellent second-generation reinforce-
284 ment mechanical properties,27 this ratio should be much higher
285 than for new carbon fibers. Thus, the feasibility of recycling will
286 be provided if the second-generation semi-products price does
287 not exceed 70–80% of the new ones.
288
289 DISCUSSION
290 In the present context, the use of carbon/epoxy composite is
291 ever increasing. As indicted, these composites can be recycled
292 by solvolysis,6 keeping good mechanical properties.27 Anticipat-
293 ing that they may soon be subjected to regulation, it is essential
294 to show it is feasible that a composite recycling network can be
295 set up that is both economically and environmentally favorable.
296 The recovery of the carbon reinforcement (which is the most
297 environmentally impacting constituent in the composite
298 manufacturing) by an aqueous solvolysis of the composite’s299 matrix leads to an average gain of about 80% for all eco-
300 indicators compared to the landfill end-of-life option.
301 Lastly, the remanufacturing process developed allows for
302 obtaining a semi-product easily usable. Consequently, from an
303 economic point of view, the mechanical performance/price
304 ratio of the second-generation carbon fiber should be higher
305 than that for the virgin carbon fibers or the glass reinforcement.
306

Figure 4. Life-cycle impact assessment of the landfill of a 1 kg carbon/epoxy composite part (dark gray) compared with the reinforcement’s recycling (light gray). The analysis is based on the ReCiPe Midpoint (H) method.

Figure 5. Comparison of the environmental impacts of a 1 kg composite part during its life cycle, depending on the end-of-life scenario of carbon fibers (landfill in dark gray; recycling in light gray).
The next step in the maturation of this technology is the development of a pilot scale facility for the recycling of carbon fibers from CFRPs using the supercritical fluid technology.

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**Notes**

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