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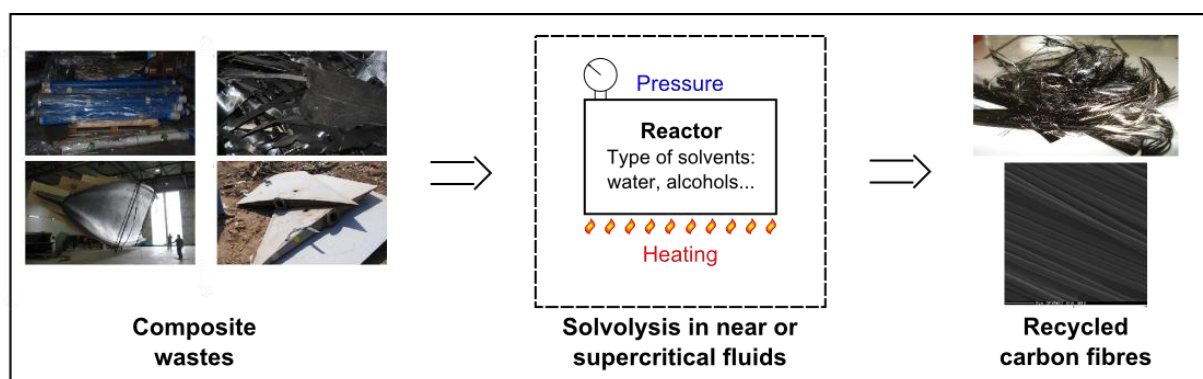
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Near Sub- and Supercritical solvolysis of Carbon Fibre Reinforced Polymers (CFRPs) for Recycling Carbon Fibres as a Valuable Resource: State of the Art

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Highlights

- * Main recycling technologies for carbon fibre reinforced plastics (CFRPs)
- * Advantages and disadvantages for each technology
- * Focus on the chemical recycling of CFRPs using a solvolysis process in near of supercritical fluids
- * REcycling Carbon fibre reinforced Composites (RECCO) project

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Near Sub- and Supercritical solvolysis of Carbon Fibre Reinforced Polymers (CFRPs) for Recycling Carbon Fibres as a Valuable Resource: State of the Art

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Abstract

This paper presents the main technologies for recycling carbon fibre reinforced plastics, focusing on the chemical recycling using the supercritical fluids technology. The conventional technologies of carbon fibres recycling are described with their advantages and drawbacks. After a brief introduction on the specific properties of supercritical fluids and some of the green associated technologies, the development of the chemical recycling of carbon fibre reinforced plastics by solvolysis in near- and supercritical fluids is reviewed. Research efforts on the technology have shown great results at the lab-scale and should then contribute to the development of this process at the industrial scale in a near future.

Key words: carbon fibres, carbon fibre reinforced plastics, recycling, solvolysis, supercritical fluids.

1 - Introduction

1
2 Over the past decades, engineering of more complex and efficient composite materials has
3
4 boosted many industrial fields such as aeronautics, automobile and sports. Nowadays studies
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6 focus on finding new composite materials and developing better, optimized fabrication
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8 process to lower the fabrication costs and improve the materials properties. One additional
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10 key aspect is to develop efficient ways to recycle those materials. Indeed, the extensive use of
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12 composite materials due to its outstanding properties results in an increase of the amount of
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14 wastes produced. As composite materials are very difficult to fractionate into elemental
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16 components, composite wastes are principally disposed in landfills or incinerated without any
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18 recycling approaches. These techniques are not sustainable in the long term and have become
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20 strictly regulated by the European commission. Even though composite waste is relatively
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22 inert compared to other waste – they produce no leachate and methane gas- new alternatives
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24 should be taken in order to reduce the amount of waste disposed and therefore reduce the
25
26 impact on the environment. This motivates new researches and developments to improve the
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28 recyclability of these materials. In order to facilitate the continued use of the composite
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30 material in some applications, it is important to transform composite waste into a valuable
31
32 resource and to close the loop in the composite life-cycle (Figure 1). Both environmental and
33
34 economic aspects are today the driving force for the development of recycling routes. A good
35
36 knowledge of composite materials is first required to work on their recycling.

37
38 Composites materials are combination of two or more individual materials referred to, in this
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40 paper, as polymer matrices, carbon fibres and filler(s). In 2008, 35,000 tonnes of carbon fibres
41
42 have been used world-wide and this number is expected to double by 2014. [1] As Carbon
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44 Fibre Reinforced Polymers (CFRPs) present interesting properties, their demand has increased
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46 in many applications such as aeronautics and aerospace, automobile industries and in sporting
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48 goods.
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Thermosetting (e.g epoxy or phenol resins) and thermoplastic (for the next generation of CFRPs) polymers are generally used for the matrix. In the case of carbon fibres, their processing specifies their final properties. They are produced by the same process steps which are fibre formation, stabilization and carbonization of carbon-rich organic precursors such as rayon, polyacrylonitrile (PAN) and pitch either isotropic or mesophase. Carbonaceous precursor is first converted into fibre form, then crosslinked in order to make it resistant to very high temperatures. Precursor fibre is then carbonized at temperatures ranging from 1000 to 3000°C in an inert atmosphere. This step allows nearly all the non-carbon elements to drive off and convert the precursor fibre to a carbon fibre. Details of the processes of fabrication of carbon fibres from the three different carbonaceous precursors are reviewed by Manocha *et al.* [2]

PAN-based carbon fibre is the most widely used reinforcement for high strength composites. Indeed, polymer form fibres have a non graphitic and fibril structure which explains the fact that they tend to develop higher tensile strength than pitch-based carbon fibres. They are generally characterized by low moduli, but as this property depends on the temperature in the last stage of the process, it is still possible to produce PAN-based carbon fibres with high moduli. By contrast, liquid crystalline materials ie pitch-based carbon fibres have a high degree of molecular orientation. Thus it exhibits high moduli and thermal conductivities. However, they have a low tensile strength. Rayon-based carbon fibres were the first to be commercialized. As they present lower mechanical properties than PAN or pitch-based carbon fibres, they are not so much in use by industries anymore.

Carbon fibres are then impregnated by dipping or hot melt processing with a polymer (usually thermosets) matrix to produce pre-pregs. These fibres preforms are then shaped by the techniques detailed by Plummer *et al.*: press molding, vacuum and autoclave molding, resin infusion or resin transfer molding (RTM), pultrusion or filament winding. [3] For most

1 applications, the type and proportion of resin and reinforcement and the shaping techniques
2 used are tailored to the particular end product.
3

4 Carbon fibre reinforced plastics present promising properties such as low thermal expansion,
5 high fatigue resistance and good resistance to corrosion in addition to the mechanical
6 properties specified above. This explains their application in high technology sector such as
7 aerospace and nuclear engineering, industrial and sports. However, each sector does not
8 present the same interest in using carbon fibres. For instance, in aerospace and aircraft,
9 choices of materials are driven by the materials performance and fuel efficiency. This makes
10 the high stiffness and relatively low weight of carbon fibres a very attractive alternative. On
11 the contrary, in general engineering and surface transportation, the use of carbon fibres is
12 determined by cost constraints, high production rate requirements and generally less critical
13 performance needs. [4]
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29 In Europe, the management of composite wastes is regulated by the European Union (EU)'s
30 Waste Framework. This organization aims at reducing the amount of waste disposed and
31 incinerated and promoting the reuse, recycling and recovery of the composite wastes. The
32 European directives related to the composite wastes are listed below.
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38 The Council Directive 1999/31/EC of 26 April 1999 regulates the amount of waste disposed
39 in landfills. It intends to prevent or reduce the negative effects of the landfill of waste on the
40 environment and human health during the whole life cycle of a landfill. It defines the different
41 categories of waste (municipal waste, hazardous waste, non-hazardous waste, inert waste) and
42 applies to all landfills. According to Law No 92-646 of 13 July 1992 (Journal Officiel de la
43 République Française of 14 July 1992) by the end of 2010, only final wastes can be disposed
44 in landfill sites.
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55 Directives 2000/76/EC of the European Parliament and of the Council of 4 December 2000 on
56 the incineration of waste promote the incineration of waste with material and energy recovery.
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It intends to prevent or limit the negative effects of the incineration and co-incineration of waste on the environment and human health by the regulation of the operating conditions and technical requirements of incineration plants.

The End-of-Life of Vehicles Directive (Directive 2000/53/EC) also known as ELV directives set new objectives to reuse, recycle and recover components, materials and energy from end-of-life vehicles. By 2015, new vehicles must be 85% reusable or recyclable (by mass) and 95% recoverable. Moreover, a type-approval is needed before vehicles can be manufactured, imported or registered in Europe. [5] A directive on waste electrical and electronic equipments (Directive 2002/96/EC) has also been issued, promoting the reduction of disposal waste by encouraging resource efficiency. [6]

As future legislations are likely to restrain the use of landfill and incineration to dispose of composite wastes it is necessary to develop alternative solutions such as recycling. The different recycling technologies for CFRPs are reviewed in this paper. The advantages and disadvantages will be given for each technology. A focus on the chemical recycling of fibre reinforced plastics using a solvolysis process in near or supercritical fluids is investigated as these new reaction media have proven to be more manageable and efficient to recover clean fibres with good mechanical properties.

2 - Main recycling technologies for CFRPs

The potential recycling technologies for CFRPs are summarized in Figure 2. Four categories of recycling techniques can be applied to composite wastes: primary, secondary, tertiary and quaternary methods. [7]

Primary and secondary recycling technologies [8-11] involve mixing of some waste material with virgin raw material, which is then processed to form a new one. The difference between the two approaches is based on whether the final properties of the new material are equivalent

1 (primary recycling) or inferior (secondary recycling) to those of the original one. These
2 recycling techniques are also known as material recovery or mechanical recycling. A wide
3 range of waste composites can be recycled through these techniques. However, in the case of
4 carbon fibre reinforced composite waste, carbon fibres are recovered as powder or short fibres
5 and hence, can only be reused as fillers in the production of new composites.
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11 Tertiary recycling of composite wastes refers to chemical decomposition of the polymer into
12 useful chemical substances and/or fuel. Depending on the type of chemical process used,
13 carbon fibres can be recovered with good surface and mechanical properties and be reused for
14 the production of new materials as raw materials or in combination with virgin fibres. The
15 main processes concerned are: solvolysis at low temperature, [12-15] pyrolysis [16-19]
16 fluidized bed processing [20, 21] and solvolysis at near sub- or supercritical fluids. [22-29]
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19 Recycling of composites via pyrolysis is widely used by industrials around the world. For
20 example, Recycled Carbon Fibre Ltd. recycling plant in West Midlands, UK and Materials
21 Innovation Technologies RDF (MIT-RCF) in the USA are using pyrolysis for recycling CFRP
22 scraps; recovered carbon fibres can be re-manufactured for the production of new composites.
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25 [30] Other recycling plants using a pyrolysis process exist in Germany (CFK Valley Stade
26 Recycling GmbH & Co. KG and HADEG Recycling Ltd) and in Italy (Karborek S.p.a.). [1]
27
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29 Nowadays, chemical recycling using sub- or supercritical fluids is a great alternative to
30 chemical methods for recycling carbon fibres from CRFPs as they can be inexpensive media,
31 recyclable, non-toxic and relatively easy to handle. [25] Other processes such as gasification
32 and pyrolysis/ gasification [8] have been developed for the recycling of carbon fibre
33 composites. In this paper, we will outline the advantages and drawbacks of the different
34 recycling techniques.
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37 Quaternary recycling is considered as a recycling process only if the energy released by the
38 combustion is recovered. Incineration is not a long term solution for recycling composites as
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it results in the production of a large amount of FRP dust with remaining waste such as ash or slag. Moreover, only the resin matrix is burnt by the process leaving the fibres and the fillers as a residue after incineration. Co-incineration in cement kilns can be considered as a viable solution for the treatment of FRP waste as it combines material and energy recovery with no impact on the environment. [31]

2.1 - Primary and secondary recycling or mechanical recycling

Recycling of glass and carbon fibre composites through mechanical recycling techniques has been under study. However, most research focused on the recovery of glass fibre reinforced composites as these products present low-value applications. [1] To facilitate the mechanical recycling process, it is important to identify the type of polymer matrix composite to be recycled. Indeed, compared to thermoplastic polymers which can be remoulded an infinite number of times eg. polyethylene, polypropylene, etc...; thermosetting polymers are cross linked and cannot be remelted and remoulded as easily. Even though recycling of these composites is considered to be difficult, it is still possible to grind them up and reuse them in new composite structures as filler or reinforcements [8] or in construction industry. [9]

Initially, large waste composites must be reduced in size. They are generally cut into small pieces in the order of 50-100 mm in size and fed into a shredder after removal of all metal inserts and fasteners. These pieces are then ground into finer products ranging from 10 mm down to 50 μ m in size; the decrease in the size of the materials results in an increase of the energy consumption of the process. The different fractions of the composite are finally separated by size (coarse or fine particles). The coarse particles or fibrous fractions contain the largest portion of reinforcement agents (fibres). They are reused for reinforcing purposes, for example in Bulk Molding Compound (BMC) composites. The fine particles or referred to as fine powder fractions are composed of bigger parts of the polymeric matrix. They can be

1 reuse as active fillers in either BMC or Sheet Molding Compound (SMC) composites. [8,10]
2 Recovered fibrous fractions can be reused in thermoset composites without mechanical
3 properties degradation when combined with virgin fibres (50 wt.%). When reused at 100%,
4 mechanical properties of the new thermoset composites are affected. They can also be directly
5 reused as reinforcements in new thermoplastic composites without affecting the mechanical
6 performance of the new composite. [11] Carbon fibres from carbon fibre reinforced
7 thermoplastic composites can be recovered as a high quality reinforcing material in injection
8 moulds, or as press moulding compounds. [10]

9 Mechanical recycling presents few advantages as it recovers both fibres and resins [8] without
10 any use or production of hazardous materials. However, the mechanical properties of the
11 recovered fibres are significantly degraded; [8] their architectures are unstructured, coarse and
12 non-consistent [32] and hence, the possibilities for their re-manufacturing are limited.

31 **2.2 - Tertiary recycling**

32 **2.2.1 - Pyrolysis**

33 Recycling of glass and carbon fibre reinforced plastics using a pyrolysis process consists of
34 the thermal degradation (between 450°C and 700°C) of the organic part of the composite
35 materials in the nearly absence of oxygen. Gaseous, oily and solid fractions are produced
36 during the process. The gaseous fraction is mainly constituted by hydrogen, methane and
37 other hydrocarbons. The oily and solid fractions are constituted by lower molecular weight
38 organic substances and recovered glass or carbon fibres respectively. [33] The operating
39 temperatures have a significant influence on the fibres properties (mechanical, electrical and
40 surface properties) [17] and thus, need to be adapted to the type of composites to be treated. A
41 diagram of a typical pyrolysis process to recycle glass or carbon fibres from scrap composites
42 with energy recovery is shown in Figure 3a. [8]

1 Studies on the recycling of carbon fibre/ epoxy and phenolic resin composites using this
2 process have been undergone by Ushikoshi *et al.* [16] and Meyer *et al.* [17] The first
3
4 continuous pyrolysis recycling line producing commercial carbon fibre recyclate has been
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6 introduced by the company Recycled Carbon Fibre Ltd (RCF) of West Midlands, UK in 2008.
7
8 Ushikoshi *et al.* experiments were carried out in temperatures of 400, 500 and 600°C for
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10 extended periods of several hours in an inert atmosphere. They have demonstrated that for
11
12 high temperatures up to 600°C, the degree of oxidation of carbon fibres was severe resulting
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14 in a significant loss in the tensile strength (about 30%) of the recycled carbon fibres. [16]
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17 Meyer *et al.* aimed at providing an optimization of the pyrolysis process in order to recover
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19 carbon fibres with mechanical properties close to those of new fibres. The influence of
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21 different process parameters other than the operating temperatures, such as isothermal dwell
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23 time and oven atmosphere, was investigated by thermogravimetric analysis (TGA).
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25 Experiments were carried out in nitrogen and synthetic air atmospheres. Results from
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27 Scanning Electron Microscopy (SEM) and Raman spectroscopy analysis showed that the
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29 decomposition of epoxy resin in an inert atmosphere was temperature dependent and not very
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31 much time dependent. Carbon fibres were recovered with very little pyrolytic carbon residues
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33 at 700°C. In air atmosphere, the pyrolysis temperature and the reaction time have a strong
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35 influence on the degradation of the polymer matrix and also on the properties of the recycled
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37 carbon fibres. Indeed, a very high operating temperature up to 600°C combined with a long
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39 reaction time resulted in a damage of the fibres properties. From these results, pyrolysis tests
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41 on a semi-industrial-scale were undertaken. The process combined a first pyrolysis step at
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43 550°C for 2h in an inert atmosphere and a second step around 550°C in air atmosphere. Clean
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45 recycled carbon fibres on level of new fibres were obtained. [17]
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55 Williams *et al.* have studied the recycling of fibre reinforced polymeric composite waste by
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57 pyrolysis in a bench-scale, static bed reactor. Experiments were undertaken at temperatures
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1 from 350 to 800°C. Samples of polyester, phenolic and epoxy resins, as well as polypropylene
2 combined with glass and carbon fibre reinforcement and calcium carbonate filler have been
3 investigated. For a sample of carbon fibre reinforced epoxy resin composite, it was found that
4 the decomposition of the composites produced solid residues of 65.3-81.7 wt%, gas yields of
5 0.2–3 wt% and oil and wax yields of 18–31.7 wt%. They have also demonstrated that the
6 product mass balance and gas composition depended on the polymer matrix and the operating
7 temperature. [19]
8

9 RCF can process over 2,000 tonnes per year of carbon-composite waste. [34] CFRP scraps
10 have to be assessed and separated from metals inserts before processing at operating
11 temperatures ranging from 500 to 900°C. Recovered carbon fibres are clean with only 10%
12 loss in tensile strength compared to virgin fibres. [30]
13

14 Carbon fibres of CFRPs can also be recovered by the action of catalytic, vacuum and
15 microwave pyrolysis processes. [8, 35] Adherent Technologies Inc (ATI) [8] in Albuquerque,
16 New Mexico, USA has worked on the recycling of carbon fibre composites based on epoxy
17 resin using either a catalytic pyrolysis process also known as catalytic conversion or a vacuum
18 pyrolysis process or a combination of both processes. The catalytic conversion consists of a
19 pyrolysis of the composites at a low temperature (around 200°C) in the presence of a
20 catalyst. The polymer is completely decomposed into low molecular weight hydrocarbon
21 liquid and gas products. The carbon fibres can be recovered with good surface and mechanical
22 properties and be reused in new composites. Vacuum pyrolysis is used at an operating
23 temperature of around 500°C to recover resins and carbon fibres. Compared to the catalytic
24 pyrolysis process, recycled carbon fibres are not as clean as there is a char residue on the
25 fibres surface. ATI have then combined both processes to obtain a maximum quality of the
26 recyclate. They have implanted a pilot scale reactor with a capacity for recycling CFRPs
27 scraps of 23 kg per hour. The first part of their process consists of removing the bulk of the
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1 resin and some contaminants. The remaining resin is then eliminated by thermal post-
2 treatment to produce 99% fibre purity with a loss of only 5% in strength. [30, 36] Microwave
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4 treatment consists of heating the composite from the inside out; the polymer content is
5
6 evaporated leaving the carbon fibres clean for potential reuse in high-grade applications. A
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8 study has been carried out by Lester *et al.* on the recycling of carbon fibres from polymer
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10 composites using a multimode microwave cavity powered at 3 kW for 8 s. They have
11
12 demonstrated that it was feasible to obtain clean, although with a different surface topology
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14 carbon fibres with good mechanical properties by using this technique. However, more
15
16 research will be needed in order to establish whether or not this process is viable. [35] In
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18 2007, a pilot-scale installation has been built by Firebird Advanced Materials Inc in Raleigh,
19
20 North Carolina, USA, to investigate the process. [30]

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Researches on the recycling of glass fibre composites using a pyrolysis process have also
been undertaken by the school of engineering in Bilbao, Spain [18] and by Williams *et al.*
[19]

The advantages of the pyrolysis process are that there is no use of chemical solvents and that
all the products can be recovered and reused in one form or another. [37] The gases are
generally reused to provide the energy required for the process. Recovered glass fibres can be
reused as reinforcements in the same way as the fibrous fractions produced from the
mechanical recycling processes. [8] Recovered carbon fibres have mechanical properties close
to virgin fibres (from 4 to 20 % of loss in tensile strength) and can be re-manufactured. [1]
However, the properties of recycled fibres are very sensitive to processing parameters. [17]

2.2.2 - Fluidized bed processing

The University of Nottingham has developed recently an alternative process to recover glass
or carbon fibres from scrap glass or carbon fibre reinforced composites. [20, 21] During this

1 so-called “Fluidized bed processing”, scrap composites, reduced to about 25 mm in size are
2 first fed into a bed of silica sand. The sand is then fluidized with a hot stream of air at
3
4 temperatures ranging from 450 to 550°C, creating a fluidized bed. In the fluidized bed, the
5
6 polymer matrix of the composites is vaporized therefore releasing the fibres and fillers which
7
8 are then carried out in the gas stream. The fibres and fillers are finally separated from the gas
9
10 stream in a cyclone. As this process operates at low temperature, the fibres are not entirely
11
12 released from the organic constituents. Thus, a secondary combustion chamber operating at a
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14 higher temperature (around 1000°C) is necessary to recover clean fibres. A schematic
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16 diagram of the process is shown in Figure 3b.
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21 Similar recycling of carbon fibres from scrap composites has been investigated by Yip *et al.*
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23 [21] Experiments were carried out at a temperature of 450°C and a fluidized velocity of 1.0
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25 m/s. Recovered carbon fibres were characterized by using image analysis, strength
26
27 measurements, SEM and XPS analysis. Results showed that clean carbon fibres were
28
29 recovered with a mean length of 5.9-9.5 mm. A loss of 25% of the tensile strength of the
30
31 fibres was obtained, while their stiffness remained unchanged and their surface chemistry
32
33 suffered from little change. [38] Overall, the properties of the recycled carbon fibres were
34
35 closer enough to the virgin fibres to be reused in moulding compounds for reinforcements and
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37 electrical screening, [39] tissue or veil products. [8]
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43 Pickering *et al.* [20] had recovered glass fibres from scrap composites such as sheet moulding
44
45 compound (SMC), filament wound pipe and E-glass/ polyester panel by using a fluidized bed
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47 process at the same conditions of the previous studies. Recovered glass fibres from SMC feed
48
49 were characterized by a mean fibre length by weight of 5.6 mm. It was demonstrated that the
50
51 reduction in strength was temperature dependent. Indeed, the tensile strength of the recycled
52
53 glass fibres was reduced by 50% compared to virgin fibres at a temperature of 450°C and this
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55 value decreased by up to 90% at a temperature of 650°C. No significant effect of temperature
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1 on the stiffness of recycled glass fibres was observed. Recovered glass fibres could be reused
2 as partial or full replacement of virgin fibres in dough moulding compounds (DMC), [20, 40]
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4 and for up to 50% of virgin fibres in veil products. [20]
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7 A few advantages of this process are that it can tolerate mixed and contaminated materials
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9 such as end of life vehicle components; clean fuel gases are produced and hence, energy can
10
11 be recovered. [8] Clean recycled carbon fibres can be recovered. [38] However, their
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13 architectures are unstructured (“fluffy”) and their length and strength are damaged by the
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15 process. [1]
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21 ***2.2.3 - Solvolysis at low temperature***

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23 Solvolysis uses reactive solvents such as water, alcohol, ammonia and glycol to break down
24
25 the chemical bonds of the polymer matrix (epoxy or phenolic resins) within fibre reinforced
26
27 composites. The end products of the process are valuable matter such as the solids consisting
28
29 of fibres and other inorganic parts and an organic liquid consisting of a mixture of monomers
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31 and excess reactive solvent. [41] A schematic diagram of the process is shown in Figure 3c.
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35 The decomposition of carbon fibre reinforced epoxy composites using a solvolysis process at
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37 low temperature was investigated by Liu *et al.*, [12] Chang-Sik *et al.*, [14] and Hitachi
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39 Chemical Co., Ltd. [15]
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43 Liu *et al.* have conducted the experiments in a glass vessel (with a diameter of 100 mm and a
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45 length of 300 mm) at a temperature of 90°C, with a nitric acid solution concentration of 8 M
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47 and a ratio of the sample weight to the nitric acid solution of 60 g: 1 L. At these operating
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49 conditions, the epoxy resin was decomposed into low-molecular-weight compounds and the
50
51 undamaged carbon fibres were recovered with tension strength loss of 1.1 %. [12]
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55 A new chemical recycling system was recently proposed by Chang-Sik *et al.* Experiments
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57 were carried out in a circulating flow reactor system. The optimum conditions for the
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1 decomposition of the epoxy matrix were found to be: a concentration of nitric acid aqueous
2 solution of 12 M, a temperature of 90°C, a flow rate of circulating solution of 1.0 cm/sec and
3
4 a decomposition time of 6 hours. At these conditions, the surface of recycled carbon fibres
5
6 was clean with very little contamination and a tensile loss of 2.92% was obtained. [14]
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8
9 Hitachi Chemical Co., Ltd has developed a solvolysis process at 180°C under ordinary
10 pressure to recycle FRPs. CFRP sporting equipments were processed using tripotassium
11 phosphate as a catalyst and benzyl alcohol as a solvent and it took from 5 to 20 hours to
12 recover the carbon fibres. Recycled CF was reused to produce a new CFRP. However, it has
13
14 been demonstrated that the tensile strength of the recycled CFRP decreased dramatically with
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16 the fibre length and then that short recycled carbon fibres cannot be reused as a reinforcement.
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24 [15]
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26 The recycling of glass fibres using a solvolysis process at low temperature was investigated
27 by Dang *et al.* [13] Initially, they have studied the chemical recycling of epoxy resin using a
28 nitric acid solution. [42] The epoxy resin was completely decomposed with a solution of nitric
29 acid of 4 M under a temperature of 80°C. They have then applied the same conditions to
30
31 recycle glass fibres from glass fibre reinforced epoxy resin. The epoxy resin was degraded
32
33 and glass fibres (E-glass and T-glass fibre types) were recovered. No tensile strength and
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35 stiffness measurements were undertaken on the glass fibres. However, it has been
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37 demonstrated that E-glass fibres possessed less corrosion resistance to nitric acid solution than
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39 T-glass fibres; therefore it was more suitable to recycle T-glass fibres reinforced epoxy resin
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41 using this process. [13, 42]
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50 Compared to the pyrolysis and fluidized bed methods, the low temperature solvolysis process
51 is more efficient as it recovers useful chemicals from the polymer matrix and carbon fibres
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53 with very high mechanical properties and fibre length. [1] However, some solvents can be
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55 aggressive and sometimes toxic to the environment. Therefore, a new reaction medium is
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1 needed in order to reduce the impact of the process on the environment. In this way,
2 supercritical fluids are considered to be good reaction media for the recycling of composite
3 materials by solvolysis. [43-45] They are manageable and effective to recycle fibres with
4 surface and mechanical properties close to virgin fibres. In the next part, a review on the
5 chemical recycling of CFRPs using supercritical fluids is presented and we will also present
6 our results in this field.
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17 **3 - Solvolysis of CFRPs in near- and supercritical fluids**

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19 Supercritical fluids have recently been used in technological areas for the development of
20 green processes. Three main applications of emerging technologies for the environment with
21 supercritical fluid technology are identified in waste treatment, biomass gasification and
22 composite / plastics recycling. [43, 44, 46]
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28 First, the specific properties of supercritical water have been exploited in SuperCritical Water
29 Oxidation (SCWO). SCWO consists of the oxidation of organic pollutants with an oxidizing
30 agent in a homogeneous supercritical medium. It implies pressures and temperatures varying
31 between 22.1 and 35 MPa, and 400 and 650°C, respectively. The advantages of this process
32 are that the oxidation presents very short residence times (<1 min); there are no toxic products
33 released into the environment and all the elements that emerge (minerals, metals, energy, and
34 CO₂) can be recovered. This process is especially effective in treating hazardous industrial
35 waste such as oils, solvents, and pesticides, and also complex, corrosive, and resistant waste.
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50 SuperCritical Water Biomass Gasification (SCBG) is also a green technology which takes
51 advantage of the specific properties of the water in supercritical conditions. Loppinet-Serani
52 *et al.* has reviewed the potential of SCBG processes to transform biomass into gas and liquid
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1 energy sources and highlights the developments that are still necessary to push this
2 technology onto the market. [48]
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4 The solvolysis process (Figure 3d) for CFRPs recycling using supercritical fluids will be
5 reviewed in the following sections. First, the specific thermophysical properties of
6 supercritical fluids are presented and then a review on the solvolysis reaction in supercritical
7 conditions for the treatment of FRPs and recovery of the fibres is outlined. This will
8 demonstrate the benefits of using this type of solvent in regards to its efficiency and reactivity
9 for the decomposition of the polymer matrix and the recovery of the fibres with proper surface
10 and mechanical properties.
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24 **3.1 - Specific thermophysical properties of supercritical fluids**

25 Supercritical fluids are green solvents which are used at temperatures and pressures above
26 their critical point. For instance, the phase diagram for pure water is represented in Figure 4.
27 The main solvents used in the recycling process of CFRPs using solvolysis in supercritical
28 conditions are water, alcohols (methanol, ethanol and isopropanol) and acetone. Their critical
29 coordinates are given in Table 1.
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38 Supercritical fluids exhibits unique properties such as densities, viscosities and other
39 properties intermediate between those of gases and liquids. They are characterized by low
40 densities from one-tenth to half as large as a common liquid and several hundred times as
41 large as a gas; by low viscosities like a gas and a diffusion coefficient intermediate between a
42 liquid and a gas. [49]
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50 In addition to the general properties of supercritical fluids listed above, supercritical water has
51 specific properties like a very low dielectric constant. This is explained by the reduced
52 number of hydrogen bonds which results in a high solubility of organic compounds and gases
53 and a low solubility in salts. [50] Supercritical water can support very fast reactions as the
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1 diffusion coefficient is high due to a low viscosity at high temperatures. In supercritical
2 conditions, water has a lower ionic product than at ambient temperature. Under these
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4 conditions, water becomes a poor medium for ionic reactions as the concentration of H^+ and
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6 OH^- ions are low. The variation of the ionic product of water with the temperature is given in
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9 Figure 5.

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11 These specific properties of supercritical fluids have been exploited in the last 15 years in the
12
13 chemical recycling of plastics extended today to the recycling of CFRPs.

14 15 16 17 18 19 **3.2 - Chemical recycling of plastics and waste composites by solvolysis in near- and** 20 21 **supercritical fluids**

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24 Chemical recycling of plastics using supercritical fluids has been developed extensively in
25
26 Japan since 1995 and reviewed by Goto in 2009. [51] Supercritical fluids are great reaction
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28 media for the depolymerization or decomposition of polymers as the reaction is rapid and
29
30 selective. Condensation polymerization plastics such as polyethylene terephthalate (PET),
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32 nylon, and polyurethane can be depolymerized into high yield monomer components.
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34 Addition polymerization plastics such as phenol resin, epoxy resin and polyethylene can also
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36 be decomposed into monomer components. Composite plastics such as glass and carbon fibre
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38 reinforced plastics can be decomposed into smaller molecular components and fibre materials.
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41 Although not necessary, the presence of catalysts can improve significantly the decomposition
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46 reaction. [25, 52]

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48 To date, in comparison with what was performed on polymers, few studies have been carried
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50 out on the chemical recycling of waste composites with the solvolysis ecotechnology using
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52 supercritical fluids. Research and development on this technique are reviewed in the
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54 following paragraph. First, studies on the chemical recycling of glass fibre reinforced plastics
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1 are reviewed and then, a focus on the chemical recycling of carbon fibre reinforced plastics is
2 proposed.
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4 Glass fibre reinforced plastics (GFRPs) are composed of unsaturated polymer (UP) resin with
5 glass fibres and filler. In order to achieve practical chemical recycling of GFRPs, every
6 component should be separated and ready for recycle use. Water or organic solvent near
7 supercritical conditions were used as reaction media to recover glass fibres from GFRPs,
8 studies were investigated by Sugeta *et al.* [22] and Goto *et al.* [52]
9

10 Sugeta *et al.* have studied the decomposition of GFRPs using supercritical water. The
11 unsaturated polymer (UP) matrix was decomposed in supercritical water in carbon dioxide
12 and carbon monoxide in gas phase and styrene derivatives and phthalic acid in liquid phase.
13 The glass fibres were recovered after decomposition of the polymeric matrix with good
14 surface properties. [22] The decomposition of unsaturated polymer (UP) resin in FRP
15 subcritical fluids was undertaken by Goto *et al.* Experiments were carried out in
16 diethyleneglycol monomethylether (DGMM) and benzyl alcohol (BZA) with or without
17 potassium phosphate (K_3PO_4) as catalyst at temperatures ranging from 190 to 350°C for 1 to
18 8h in a batch reactor. The influence of the quantity of solvent, the amount of catalyst, the
19 reaction temperature and reaction time on the depolymerization of the GFRPs was
20 investigated. BZA was the most effective solvent for the reaction of degradation of UP. It was
21 demonstrated that the decomposition rate increased with the catalyst/solvent and
22 solvent/GFRPs ratio and the reaction temperature. The addition of K_3PO_4 enhanced the
23 degradation process. The recovered glass fibres were not damaged during the reaction, and
24 hence reusable for the production of a new GFRPs. [52]
25

26 Kamimura *et al.* have treated waste glass fibre reinforced plastics using supercritical alcohol
27 in the presence of catalytic amounts of N,N-dimethylaminopyridine (DMAP). The GFRPs
28 were completely decomposed at a temperature of 275°C, with a pressure of 10 MPa and a
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1 reaction time of 5h. The final mixture was then separated into organic monomeric
2 compounds, polymeric materials and inorganic additives. All of these materials were ready
3 for recycle use. It has been demonstrated that the catalyst had an influence on the degradation
4 kinetics of GFRPs. Recovered glass fibres had sufficient mechanical and surface properties to
5 be reused with virgin fibres in the manufacturing of new glass fibre reinforced plastics
6 materials. [23]
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14 Panasonic Electric Works Co., Ltd has been working on FRP recycling using hydrolysis in
15 subcritical water since 2002. Thermosetting resin in FRP is dissolved into unsaturated
16 polymer (UP) components (glycols and fumaric acid) and styrene-fumaric acid copolymer
17 (SFC). Recovered UP components and SFC were used respectively to produce recycled UP
18 resin and low-profile additive (LPA) for FRP forming. The inorganic materials were also
19 recovered although no details were given on the reuse of these materials. In 2008, they have
20 implanted a successful pilot plant for the treatment of 400 kg of FRP per operation and they
21 aim at treating 200 tonnes of FRP manufacturing waste by 2012. [53-54]
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34 Carbon fibre reinforced plastics (CFRPs) are mainly composed of carbon fibres and epoxy
35 resin for the polymer matrix. The solvolysis of the epoxy resin matrix in supercritical water
36 conditions has been undertaken by Okajima *et al.*, [24] Pinero-Hernanz *et al.*, [25] Liu *et al.*,
37 [28] and Wang *et al.* [29] Supercritical alcohols were also referenced as reaction media to
38 recover carbon fibres from CFRPs, studies being performed by Pickering *et al.*, [26] Pinero-
39 Hernanz *et al.* [27] Overall, carbon fibres are recovered with mechanical and surface
40 properties close to those of virgin fibres.
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51 Okajima *et al.* have studied the decomposition of epoxy resin and the recycling of CFRPs in
52 sub- and supercritical water in the temperature range between 300 and 450°C. Clean carbon
53 fibres are recovered after a treatment at 380°C and 25 MPa. [24] Pinero-Hernanz *et al.*
54 experiments were undertaken in a batch reactor type without stirring at temperatures ranging
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1 from 250 to 400°C, pressures from 4 to 27-28 MPa and reaction time up to 30 min. The
2 purpose of these experiments was to determine the optimum operating conditions at which the
3 carbon fibres can be recovered. Temperature and alkali catalyst (e.g potassium hydroxide
4 KOH) were found to be the most important variables in the solvolysis process of the epoxy
5 resin. At a temperature of 400°C and a pressure of 28 MPa, the removal efficiency of epoxy
6 resin was 79.3 wt.% and carbon fibres were recovered with good mechanical properties. The
7 tensile strength of the fibres was approximately 2% lower than the virgin fibres. The use of
8 potassium hydroxide as a catalyst has improved the removal efficiency up to 95.4 wt.%.
9 However, this increase has resulted in a bigger loss in tensile strength (up to 10%) of the
10 recovered carbon fibres. SEM pictures showed that the surface of the carbon fibres after
11 treatment still contained resin impurities when the alkali catalyst was not used. [25] Liu *et al.*
12 have studied the influence of reaction conditions on the decomposition rate of carbon
13 fibre/epoxy resin composites. Temperature, reaction time, catalyst, feedstock ratio and
14 pressure were selected as controlled variables. Results showed that carbon fibres were
15 successfully recycled at 260°C for 105 min with 1:5 g/mL feedstock ratio and at 290°C for 75
16 min with 1:5 g/mL feedstock ratio. Several measurements such as SEM, Atomic Force
17 Microscopy (AFM) and tensile measurements, were undertaken to characterize the properties
18 of the recycled fibres. Overall, they demonstrate that this chemical recycling method was
19 effective and was producing recycled fibres with good mechanical properties for reuse (tensile
20 reduction of 1.8% compared with precursors). [28] Wang *et al.* have suggested a promising
21 way of recycling carbon fibres from carbon fibre reinforced epoxy composites by the use of
22 oxygen in supercritical water. The experiment was carried out at 30 MPa and 440 °C for 30
23 min. The mass ratio of the composite to water was below 10%. Tensile strength
24 measurements and microstructure analysis such as SEM and AFM showed that the recycled
25 carbon fibres had great surface and mechanical properties when the decomposition rate was

1 between 94 and 97 wt.%. The decomposition ability of the supercritical water is increased
2 with the presence of oxygen during the reaction. However, an excessive oxidation has resulted
3
4 in the damage of the recycled carbon fibres and hence, in a decrease of its mechanical
5
6 properties. [29]
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9 Pickering *et al.* have reported a chemical recycling process for the recycling of carbon fibre
10 epoxy resin composites in supercritical alcohol using a semi-continuous flow reactor. The
11
12 experiments were investigated at a temperature of 310 °C, a pressure of 5.2 MPa and a
13
14 reaction time of 20 min. The carbon fibres have been recovered with good mechanical and
15
16 surface properties. [26] Pinero-Hernanz *et al.* experiments were conducted in batch and semi-
17
18 continuous type reactors with methanol, ethanol, 1-propanol and acetone as solvent reagent at
19
20 temperatures ranging from 200 to 450°C. It has been demonstrated that the degradation of the
21
22 epoxy resin was improved by using a semi-continuous flow system and an alkali catalyst.
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24 Compared to batch reactors without stirring, semi-continuous flow systems enhanced the
25
26 mass transfer and with the use of alkali catalysts reduced temperature requirements. At a
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28 temperature of 350°C and a solvent flow rate of 1.1 kg-alcohol/kg-fibre/min, 98 wt.% of
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30 epoxy resin was eliminated. With the same solvent flow rate, a temperature of 275°C and 0.02
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32 mol/L of KOH, elimination of resin was up to 96.5 wt.%. Clean carbon fibres were recovered
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34 and a tensile loss of only 1 to 15% was obtained. [27]
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43 A summary of the different studies undertaken on the recycling of CFRPs using solvolysis in
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45 near- or supercritical conditions is given in Table 2.
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48 Overall, solvolysis using supercritical fluids has been proven to be a great alternative for
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50 recycling of carbon and glass fibres in polymer composites. First studies in these conditions
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52 have been investigated on the recycling of plastic waste and glass fibre composites. In Japan,
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54 a pilot plant has been implanted to recycle GFRPs wastes using subcritical water and has a
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56 capacity of 400 kg of GFRPs wastes per operation. To date, this plant is the only one using
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1 this technique to recycle composite wastes. [54] Further researches have been undertaken for
2 the recycling of carbon fibre reinforced composites as this material has been used more and
3 more often in new applications. This review has shown that there are a few parameters to take
4 into consideration in order to recover carbon fibres with properties at the same level as virgin
5 fibres properties. The type of reactor used, the type of fluids, the reaction time, temperature
6 and pressure, the presence or not of a catalyst and the type of atmosphere are very important
7 factors in this process.
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17 As an illustration of this paragraph, the Institute of Condensed Matter Chemistry of Bordeaux
18 (ICMCB) is involved in the RECCO project (REcycling Carbon fibre reinforced COmposites)
19 research project aiming at the development of a pilot scale plant operating with supercritical
20 fluids for the recycling of carbon fibre reinforced composites. This project, leaded by the
21 French company Innoveox [47] is in collaboration with other industry partners such as
22 Snecma Propulsion Solide of Safran group (European leader in the field of propulsion, and a
23 technical and industrial centre of excellence for thermostructural composites), Astrium ST (a
24 wholly owned subsidiary of EADS, the global leader in aerospace and defense) and the
25 aircraft manufacturers Airbus from the EADS company. [55] The RECCO project is also
26 supported by the ADEME organization.
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41 The recycling of carbon fibres from carbon fibre reinforced composites is conducted in a
42 semi-continuous flow reactor as shown in Figure 6. Carbon fibre/ composites were provided
43 by our industry partners. Experiments were carried out at a temperature around the critical
44 temperature of water for a reaction time of about 30 min. The process has been optimized in
45 order to improve the solvolysis rate of the resin without the degradation of the mechanical
46 properties of the fibres.
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55 Water was used as solvent for the recycling of carbon fibres from CFRPs. The epoxy resin
56 was completely decomposed into lower molecular weight organic compounds. When the
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1 system was cooled down, the carbon fibres were collected from the reactor. Recovered carbon
2 fibres were characterized using single fibre tensile tests, SEM and XPS analysis. Recycled
3 carbon fibres from CFRPs are clean (Figure 7) and presents good mechanical properties; a
4 tensile loss close to the one of virgin fibres is obtained.
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9 Today all the parameters necessary for the scale up of this technology have been determined
10 at the laboratory scale. These parameters are used for the development of a pilot scale facility
11 which should be built in the next few months.
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19 **4 - Conclusion**

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21 The carbon fibre reinforced composites industry is under strong pressure to provide
22 viable recycling scenarios for their materials as the European commission has restrained
23 landfill and incineration to dispose of these materials.
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28 A review on the existing type of recycling technologies of CFRPs was presented in this paper.
29 Each recycling processes present specific advantages and drawbacks. Chemical recycling
30 offers the recovery of long fibres with good mechanical properties compared to mechanical
31 recycling. Therefore recycled fibres resulting from this recycling technique can be reuse in the
32 re-manufacturing of new composites and the loop in the CFRC life-cycle can then be closed
33 properly.
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43 However, chemical processes may use solvents which can have negative effects on the
44 environment and the human health. Thus in order to reduce these impacts, supercritical fluids
45 have been used as a green reaction media for the solvolysis of CFRPs. Researches and
46 developments on emerging green technologies using supercritical fluids are expected to
47 increase in the near future. The recycling of CFRPs using solvolysis in supercritical
48 conditions has been highlighted in this review. Compared to pyrolysis, fluidized bed and low
49 temperature solvolysis processes, solvolysis near sub- or supercritical fluids is a great
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1 alternative to recover fibres as it provides a high retention of mechanical properties and fibre
2 length and a high potential for material recovery from resin. Although this process has
3
4 presented great results for the recycling of CFRC at the lab scale, further studies need to be
5
6 undertaken in order to design a cost effective pilot plant to be used at industrial scale.
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10 11 **5 - Acknowledgement**

12 The financial support for the RECCO project provided by Snecma Propulsion solide, Astrium
13
14 ST, Airbus and the ADEME organization is gratefully acknowledged. The involvement of the
15
16 start up company Innoveox is also acknowledged for bringing RECCO as the industrial
17
18 success story.
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22 The authors gratefully acknowledge C. Magro for his time and efforts in the RECCO
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24 consortium.
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Figure captions

Figure 1: Composite Life-cycle

Figure 2: Recycling technologies for composite wastes

Figure 3: Thermophysical processes for the recycling of CFRPs

Figure 4: Phase diagram of pure water and its thermophysical properties

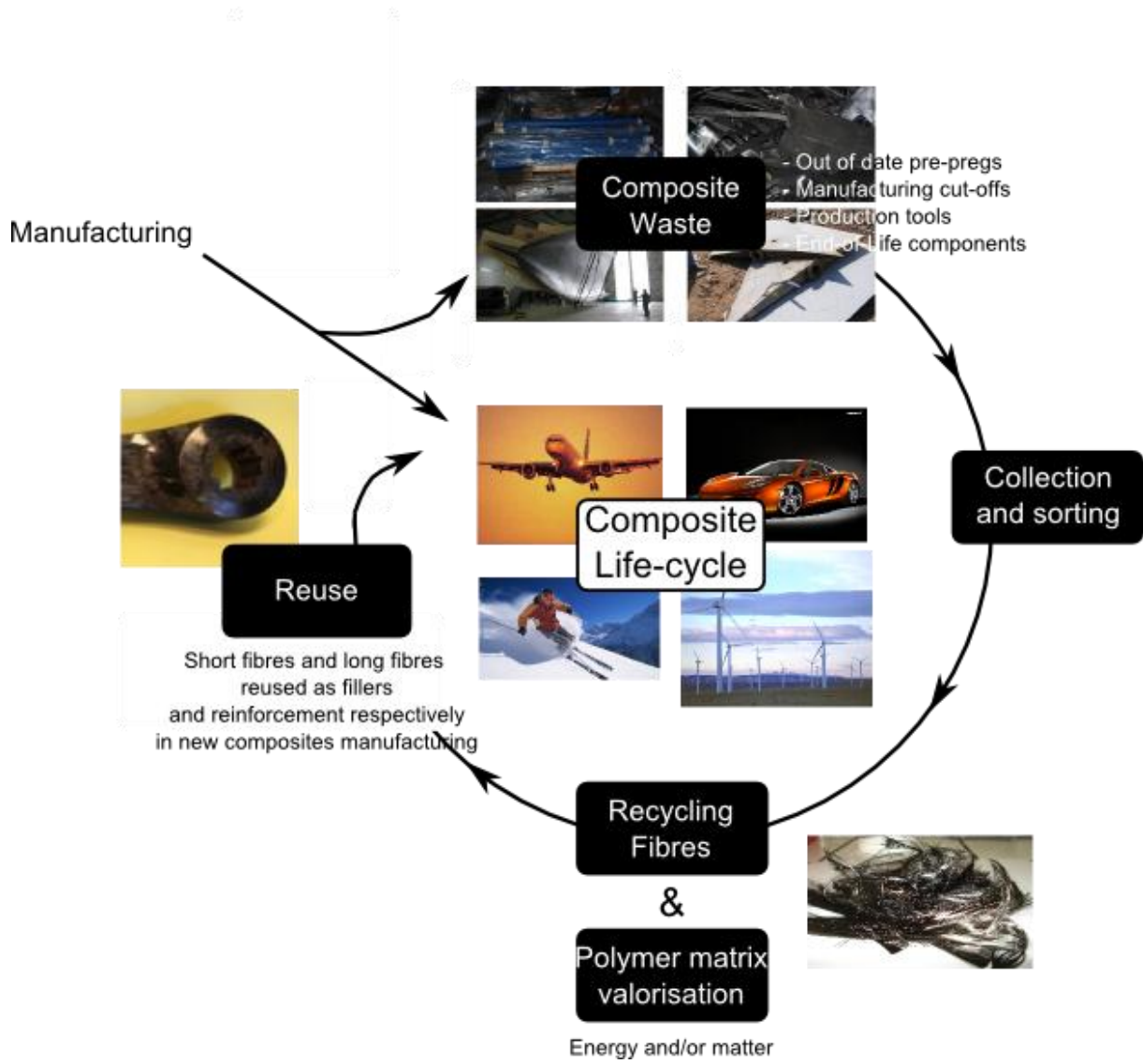
Figure 5: Variation of the density and ionic product of water with temperature (reprinted from [56] with permission)

Figure 6: A schematic flow diagram for the recycling process

Figure 7: SEM pictures of the recycled carbon fibres after sc-water treatment in a semi-continuous reactor at 400°C, 25 MPa and a reaction time of 30 min

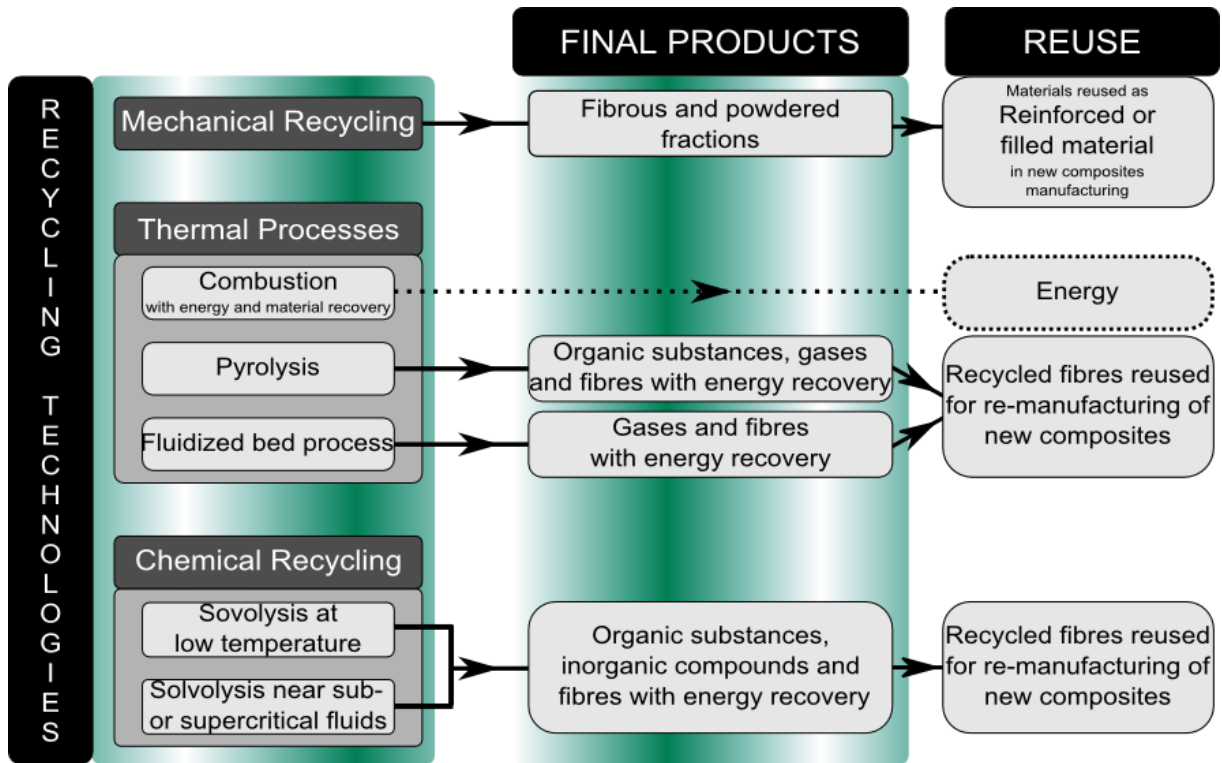
Figures

Figure 1



Figures

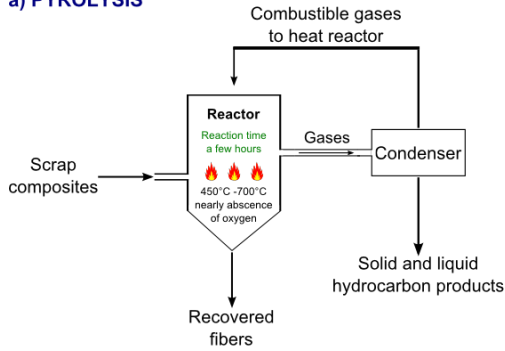
Figure 2



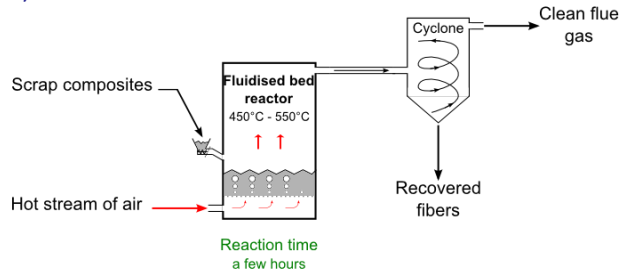
Figures

Figure 3

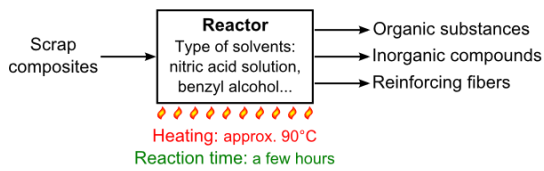
a) PYROLYSIS



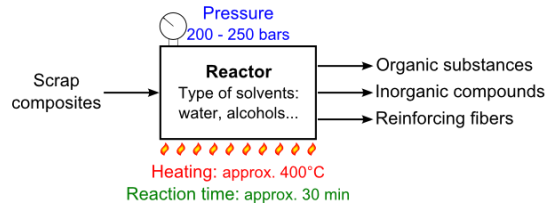
b) FLUIDISED BED PROCESS



c) SOLVOLYSIS AT LOW TEMPERATURE

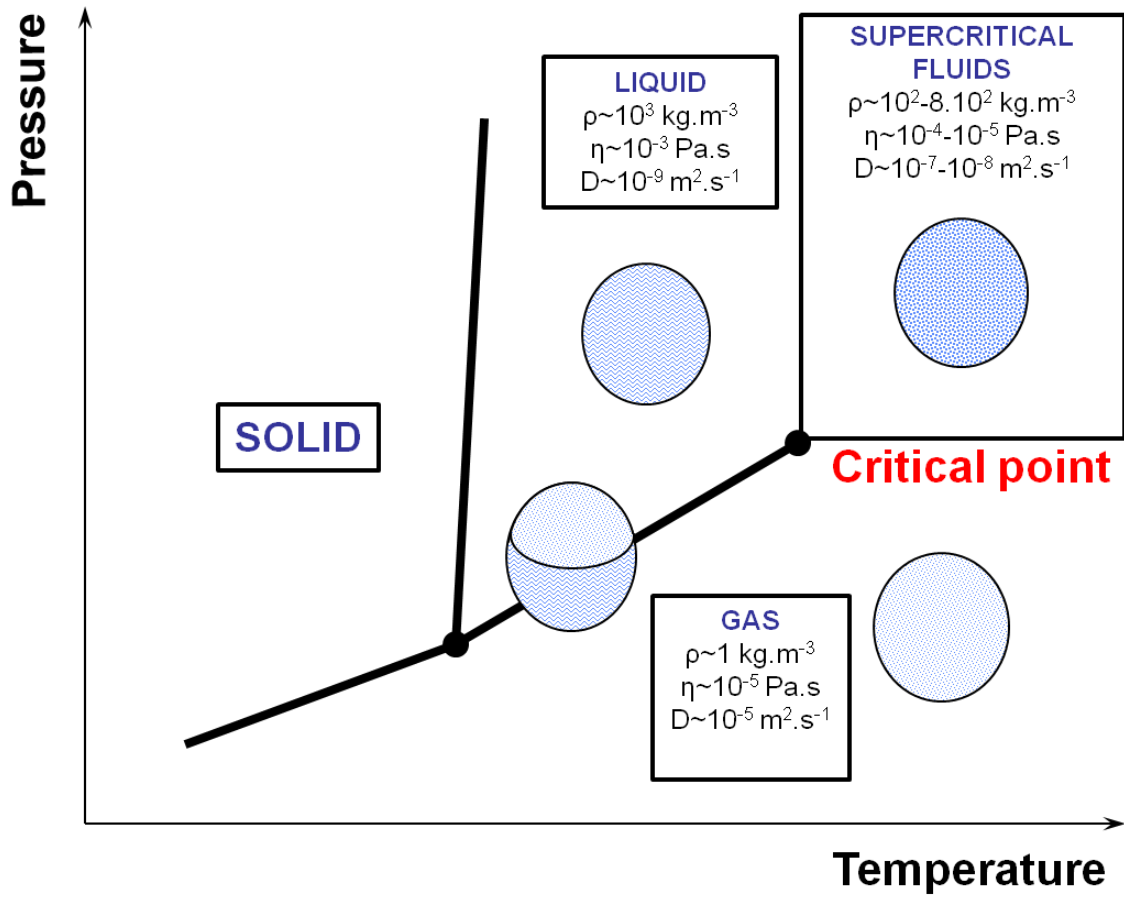


d) SOLVOLYSIS IN SUPERCRITICAL CONDITIONS



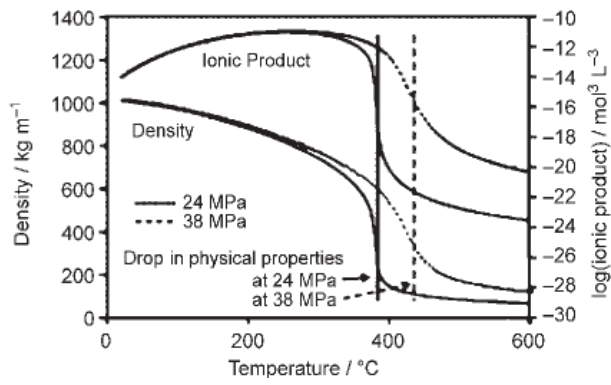
Figures

Figure 4



Figures

Figure 5



Figures

Figure 6.

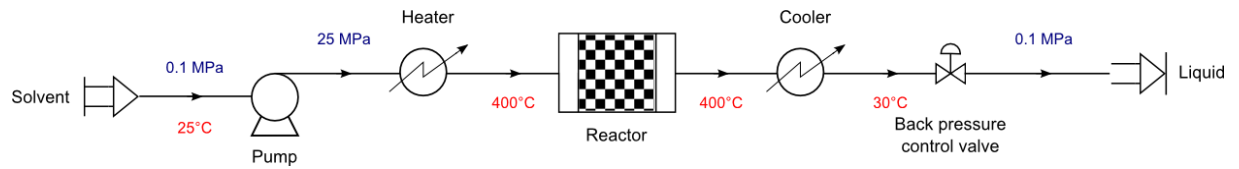
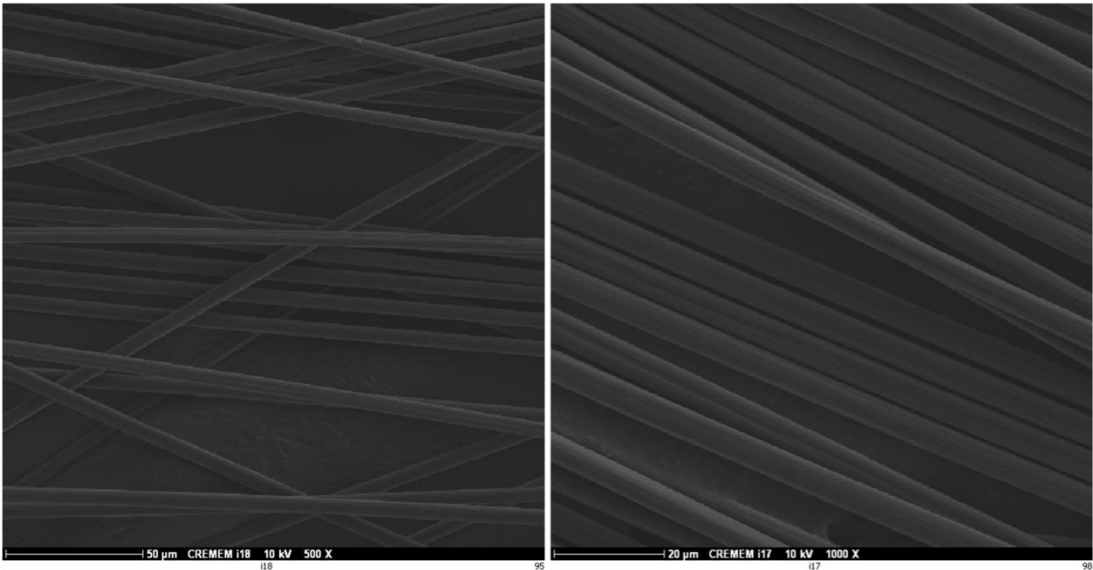


Figure 7



Tables

Table 1: Critical coordinates of usual pure fluids in supercritical fluid processes. T_c and P_c are the critical temperature and pressure respectively (adapted from [49])

Table 2: Summary of the different studies on the chemical recycling of CFRPs using solvolysis in near- or supercritical fluids

Tables

Table 1

Fluid	T_c (°C)	P_c (MPa)
Methanol	240.0	7.95
Ethanol	243.1	6.39
Isopropanol	235.6	5.37
Acetone	235.0	4.76
Water	374.1	22.1

Tables

Table 2

	Operating conditions	Results
Okajima <i>et al.</i> [24]	<ul style="list-style-type: none"> • Reactor type : unknown • Solvent : water • T = 380°C • P = 25 MPa 	– Recovery of clean carbon fibres
Pinero Hernanz <i>et al.</i> [25]	<ul style="list-style-type: none"> • Reactor type : batch without stirring • Solvent : water • T = 400°C • P = 29 MPa • Reaction time: 30 min 	– <u>Without an alkali catalyst:</u> Decomposition rate of the epoxy resin: 79.3% and recovered carbon fibres with good mechanical properties (loss of 2% in tensile strength) – <u>With an alkali catalyst (KOH):</u> Decomposition rate of the epoxy resin: 95.4% and recovered carbon fibres with a loss in tensile strength of 10%
Liu <i>et al.</i> [28]	<ul style="list-style-type: none"> • Reactor type : batch autoclave without stirring • Solvent : water • T = 260°C for a reaction time = 105 min • T = 290°C for a reaction time = 75 min • P = unknown • Feedstock ratio: 1:5 g/mL 	– Recovered carbon fibres with good mechanical properties (loss of 1.8% in tensile strength)
Wang <i>et al.</i> [29]	<ul style="list-style-type: none"> • Reactor type : unknown • Solvent : water • Excess of oxygen • T = 440°C • P = 30 MPa • Reaction time: 30 min 	– Decomposition rate of the epoxy resin: 94-97 % – Recycled carbon fibres with great surface and mechanical properties
Pickering <i>et al.</i> [26]	<ul style="list-style-type: none"> • Reactor : Semi continuous flow reactor • Solvent : n-propanol • T = 310°C • P = 5.2 MPa • Reaction time: 20 min • Solvent flowrate: 2 mL/min 	– Recycled carbon fibres with great surface and mechanical properties

Pinero Hernanz *et al.* [27]

- Reactor : Semi continuous flow reactor
 - Solvent : alcohols
 - P = 15 MPa
 - Reaction time: 70 min
 - Solvent flow rate: 5 mL/min
- Without an alkali catalyst at T = 350°C: Decomposition rate of the epoxy resin: 96.5%
 - With an alkali catalyst (KOH, concentration of 0.02 mol/L) at T = 275°C: Decomposition rate of the epoxy resin: 98%
 - Clean recovered carbon fibres with a loss in tensile strength of 1 to 15%
-