Recycling of CFRP for high value applications: Effect of sizing removal and environmental analysis of the SuperCritical Fluid Solvolysis

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Abstract

The recycling of Carbon Fibers Reinforced Plastics (CFRP) wastes is becoming increasingly important in the aerospace industry. For most of the technologies, the recycled CF (rCF) are discontinuous, misaligned and unsized. Compared to thermal treatments, the orientation, the length and the brittleness of the rCF are better preserved with the SuperCritical Water Solvolysis (SCWS). The effect of the sizing removal on the recycled CFRP behavior is studied by conducting static characterizations. Realigned virgin CF were used to manufacture sample plates which underwent short beam shear tests. An environmental assessment was carried out on the CFRP end-of-life with a focus on SCWS.

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Keywords: Recycling; CFRP; Carbon Fibers; Sizing; Short Beam Shear Test; Interlaminar Shear Strength; Environmental assessment

1. Introduction

Nomenclature

CF: Carbon Fibers
CFRP: Carbon Fibers Reinforced Plastics
EOL: End-of-Life
ILSS: InterLaminar Shear Strength
LCA: Life Cycle Analysis
rCF: Recycled Carbon Fibers
rCFRP: Recycled Carbon Fibers Reinforced Plastic
SC: SuperCritical
SCFS: SuperCritical Fluid Solvolysis
SCWS: SuperCritical Water Solvolysis
SEM: Scanning Electronic Microscopy
Vf: Fiber Content

The use of innovative materials provides a competitive edge for most of the leading manufacturing industries. When new materials are used, it is important to know how to avoid unwanted environmental impact. To do so, the study of recyclability of these new materials has become more and more important. Composites emerged in many applications thanks to their specific mechanical properties and their predispositions for customized design. More specifically, carbon fibers composites are used more and more widely in aerospace components, wind turbine components, automotive components and sports & leisure products.

The growth of CFRP's market is estimated at 18% from 2012 to 2015, and it is predicted to double between 2015 and 2020 to reach overs 200 ktons per year [1]. In terms of sectors, the aerospace field use only 18% of the total quantity of CF but represent more than 40% of the global sales because of the high standards in this field.

1.1. End of life options for CFRP wastes

At the moment, the EOL treatment options for CFRP wastes are incineration and landfill. They are not viable for the long term. CFRP wastes can be separated into two groups:

- New scrap: Wastes from production activities (out-of-date prepreg rolls, offcut, etc.)
- Old scrap: Wastes from dismantling aircrafts (EOL post-consumer products)

According to the project Recycarb [2], the quantity of CF from new scrap in Europe is about 1100 tons/year with a majority of which are prepreg CF (see Table 1). If we consider that the lifespan of an aircraft is about 30 years, the quantity of old scrap CF worldwide from the aerospace sector will be relevant by 2020, with about 3500 tons/year. It will increase to 7000 tons/year after 2030.

Table 1. Proportions of each type of CFRP new scrap at a European level [2]

Woven prepreg	Non-woven prepreg	Dry CF	Selvedge waste	Composites
62,4%	10,9%	14,5%	8,1%	4,1%

The environmental legislation, especially in Europe, is becoming more severe on all manufacturing sectors. For example, for all EOL vehicles in 2015, the re-use and recycling rate shall be increased to a minimum of 85% by weight per vehicles and per year [3]. The current and future wastes management requires all materials to be recyclable to be finally reused. This includes new materials such as CFRP.

1.2. Recycling of CFRP

In CFRP, the CFs are used mainly with thermoset resins thus CFRP cannot be remolded. Recycling composites is challenging because it is composed of different materials. The CFs are high quality materials and require a lot of energy to be manufactured. The average energy needed to fabricate 1 kg of CFRP is about 28MJ; thus it consumes 8 times more energy than ferrous metals do [4]. For this reason, it is worthwhile to study and improve the recycle methods of CFs.

For an efficient recycling, different operations are needed:

- The preparation of the wastes: collect, transportation, identification and the separation of undesirable components (e.g. metal inserts)
- The separation of the matrix and the CF ("recycling")
- The remanufacturing of new composite part with the recycled carbon fibers

Three categories of recycling techniques have been identified by researchers: mechanical, thermal and chemical processes [3, 5].

The shredding or grinding, has limited possibilities, and is destined for low value applications [3]. With this process, CFRP wastes are reduced to two fractions: resin powder and a fibrous fraction. It does not fit to the thermosetting composite which represent the majority of the CFRP.

The thermal treatments consist of numerous different methods including pyrolysis [6], fluid bed treatment [7], and microwave pyrolysis [8-9]. The pyrolysis is the only process used on a commercial basis but the rCF are chopped or milled. The fluid bed process produces short rCF in a fluffy form but can treat contaminated wastes with metals. The microwave pyrolysis is still in the prototyping phase but preserved the sizing and had a short dwell time.

The chemical recycling shows the best results for reusing the rCF into high value applications. It can produce semi-long or long rCF by using supercritical fluids [10] or catalyst such as benzyl alcohol [11] which dissolves the resin rapidly during recycling process. On the other hand, it has a low contamination tolerance (e.g. no metals or painting pieces).

The project RECCO, launched in 2009 with EADS, SAFRAN and Airbus as aircraft and aerospace industry partners bet on the supercritical water solvolysis [12]. Carbon fibers recycled through SCWS process can be remanufactured and re-used as secondary primary material [13].

1.3. Remanufacturing of composite with rCF

There are different remanufacturing techniques to reuse rCF [3]: direct molding (injection molding or SMC/BMC), RTM or infusion which are restricted to woven fabric, and compression molding with a preforming phase. The operation of preforming or realignment can be made with a carding machine.

The institute of mechanics of Bordeaux (I2M) participated to RECCO and developed a realignment machine which unwoven woven fabric post SCWS process, realign and pack rCF to produce strands of rCF. It was proven that the strength loss of the rCF is low [10] after SCFS. The three technological key points to reuse the rCF are: the sizing, the length and the orientation (or the form) [14]. The rCF have a specific length, are unsized and misaligned. The mechanical properties of the rCFRP can be improved through the evaluation of the effect of these factors.

The sizing protects the fiber from damage during handling, storage, transportation, manufacturing into composites and to enhance the fiber-matrix adhesion to maximize mechanical performance. The aims of this paper are to evaluate the environmental impact of SCFS recycling in the CFRP EOL and the importance of the sizing in the remanufactured rCFRP product. More specifically, this work focuses on the SCWS recycling and the effect of the removal of the sizing on the mechanical properties such as the inter-laminar shear strength.

2. Experimental procedure

2.1. Materials

A woven fabric of CF (Toray T700) was unwoven then realigned and finally packed by polyamide projection. The packs are 50 mm of width and 200 mm of length (Fig 1C) and was provided by I2M. The area density is about 600 g/m^2.

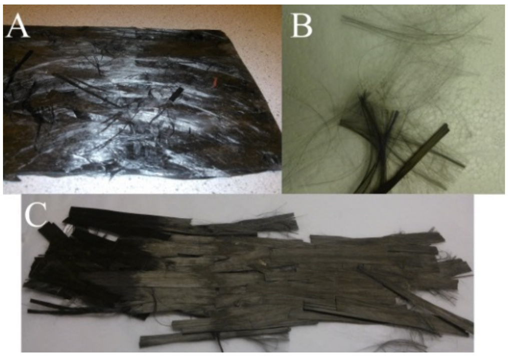


Fig. 1. (A) Composite parts made with CF sized; (B) CF unsized in a filamentous state; (C) Semi-product from I2M.

The removal of the sizing was done by soaking CF packs into a bath of tetrahydrofuran for the total duration of one day. The unsized fibers (Fig 1B) were in a filamentous state and not handy.

2.2. Manufacturing procedure

A mold in steel was pre-coated with Frekote B-15 as sealer and Zyvax EnviroShield as release coating. The Sikadur 300 two part epoxy resin was degassed at 0,1 MPa before use.

The packs of CF were disposed on the mold by hand and impregnated by the resin with a syringe and spread on CF with a brush. The dimensions of the plates were 2x100x200 mm. Two plates (Fig 1A) with 4 plies and sized as well as unsized CF were made by compression molding at 2.5 MPa with a manual press and heating at 50 °C for 12 hours.

The aimed fiber content is 60%, however the average of Vf varied a lot. A dissolution method helps to measure the true Vf. Different samples were tested for the possible variation in the realigned fibers tape density. The average Vf is 68% for plate with sized fibers and 64.75% for the other plate. The high deviation of both of the CFRP panels can be attributed to the hand manipulations of the CF, especially for the unsized CF which were more difficult to impregnate.

Table 2. Fiber content with different samples from the two plates

	Minimum	Maximum	Average	Deviation
Samples with sizing	63%	73%	68%	5,77%
Samples without sizing	55%	72%	64,75%	8,18%

2.3. Short beam shear test

The inter-laminar shear strength was determined under a 3-point bending test. The tests were performed and analyzed according to the conditions specified in the ASTM D 2344 standard [15]. All of the samples were subjected to a test at 1 mm/min by a MTS Insight 5 machine with a 5 kN load cell. A spread-sheet of load / extension data was obtained for each test.

7 samples at the size of 24x11x2,4 mm were cut with a diamond saw from the plate with unsized fibers and 11 samples at the size of 21x10,8x2,2 mm from the other plate. The inter-laminar shear stress and deflection curves of these samples are shown in Fig. 2. The shear strength data is summarized in Table 3. Due to the short thickness, the length and the width were defined according to the ISO 14130:1997 standard [16]. The results of the inter-laminar shear strength tests are discussed in Section 3.1.

2.4. Analysis by SEM

A Hitachi SU3500 Variable Pressure scanning electron microscope with Oxford SDD EDS and EBSD was used to observe the samples after the short beam shear tests and to verify the surface state of the sized and unsized fibers.

3. Result of the tests

3.1. Interlaminar shear strength (ILSS)

The ILSS in MPa was calculated with the equation (1).

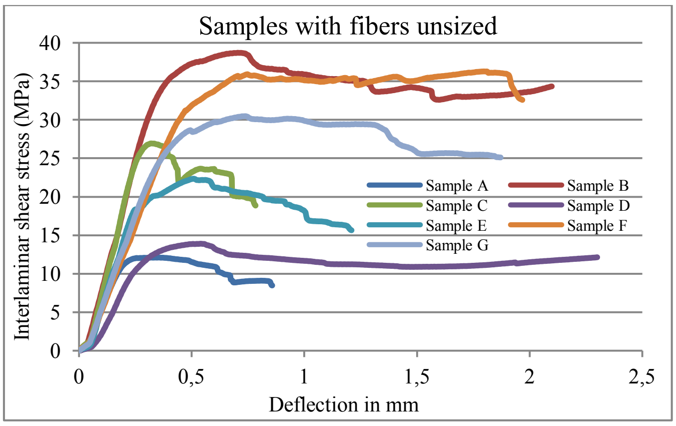
$$\tau_M = \left(\frac{3}{4}\right) \times \left(\frac{F_M}{bh}\right) \qquad (1)$$

- τ_M the interlaminar shear strength in MPa,
- F_M the maximum load in N before it plastifies,
- h the thickness in mm of the samples,
- b the width in mm of the samples

Table 3. Interlaminar shear strength of the different samples

ILSS in MPa	Minimum	Maximum	Average	Deviation
Samples with sizing	24,5	41,9	30,8	6,4
Samples without sizing	12,1	38,7	25,8	10,3

The ILSS of the sized CFRP is 5 MPa and is higher than the unsized CFRP. The lost can be explained by the absence of sizing or by the difference in the Vf. The standard deviation is high for both of the specimens, and even more for the unsized CFRP. It can be linked to the deviation of Vf or to the presence of void content.



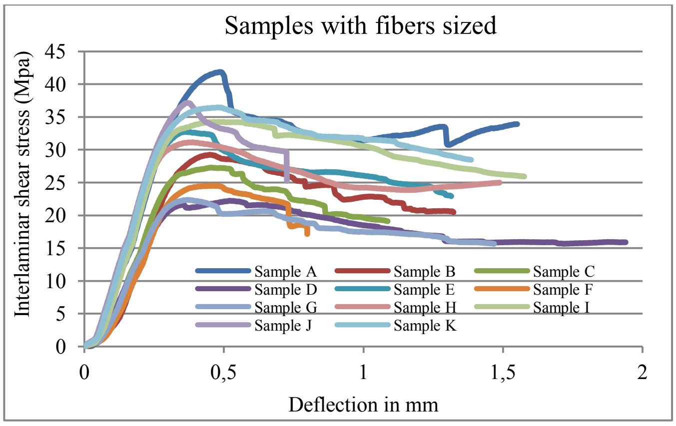


Fig. 2. Interlaminar shear stress / deflection curves from the tests

3.2. Delamination of the plates

During the mechanical tests, the delamination occurred for most of the samples from both plates (Fig 3). The failure is due to the shear stress applied which leads to the separation of the layers of reinforcement.

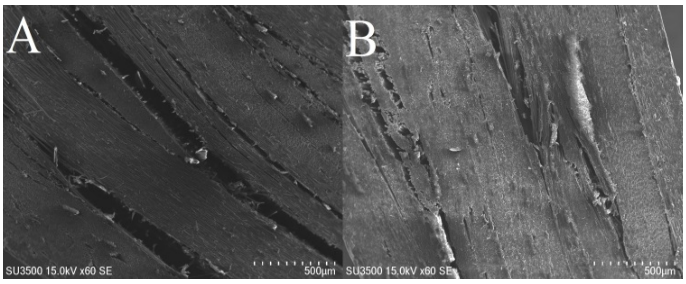


Fig. 3. SEM images from samples with (A) sized CF; (B) and unsized CF

3.3. Removal of the sizing

The observation of the fibers by SEM (Fig 4) showed that the sizing was removed. The diameter of unsized CF is about 6,5 µm against 7 µm for the diameter of sized CF. The coating can be seen on the Figure 4F at the left side of the fiber.

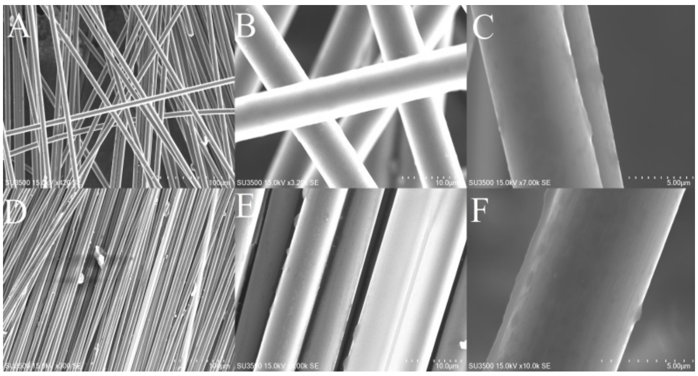


Fig. 4. SEM images of (A-C) unsized CF; (D-F) and sized CF

4. Recycling by SuperCritical Fluid Solvolysis (SCFS)

Before the SCFS, the chemical recycling was limited to low temperature solvolysis with aggressive chemicals such as nitric acid. The solvents were toxic for environment and hazardous for human. Thus, the process needed a better reaction medium to reduce its impact on environment [10]. It motivated researchers to use supercritical fluids [17-23].

The SCFS is not the most environmental friendly recycling process [24] compared to the mechanical recycling or the pyrolysis. However, the process can produce high quality rCF in only 15 to 120 min and it can lead to a possible reuse of the matrix (e.g. manufacturing of epoxy [17, 21]).

Table 4. Data considered for the SCWS [17]

Electricity	Natural gas	Deionized water	Tap water for cooling
1042 kWh	559 m^3	700 kg	28 828 kg

The water is widely used as supercritical fluid [17-20] since it is harmless and inexpensive. Knight made a process simulation and scale up of SCWS (chapter 6 [17]) where he gave details about the energy and water required to treat 150 kg of CFRP which then produced 75 kg of rCF (Table 4). The dwell time considered is 2 hours which correspond to the worst case to decompose a multilayer aerospace system with highly cross-linked matrix.

5. Environmental assessment of the recycling by SCFS

The environmental assessment was made under OpenLCA with the database EcoInvent 3.0 and the impact method of CML 2001 (baseline). The functional unit is to treat 150 kg of CFRP in order to produce 75 kg of rCF and to remanufacture 150 kg of rCFRP. All of the input data were global data except the electricity and the natural gas which were US data. The recycling has a beneficial effect as illustrated in [25].

5.1. The process inside the EOL of CFRP

During the EOL of CFRP wastes, several other operations are necessary to produce rCFRP such as the cleaning of rCF, the realignment and the remanufacturing.

Okajima, Jiang and Knight indicated that the last residues on rCF are removed by acetone [17, 21-22]. The amount of acetone is evaluated at 1,5 L per kg of CFRP wastes.

The realignment machine uses heating lamps and drums with the power of 2 kW and 1 kW, respectively. The nylon represents 2% of the pack of rCF. The flow rate of the I2M machine is about 5 kg/h.

For the remanufacturing (see Section 2.2), the electricity is estimated at 1000 kWh for heating during the molding and the amount of resin is the same as rCF.

Table 5. Data considered for the cleaning, realignment and remanufacturing

	Realignment	Cleaning	Remanufacturing
Electricity	45 kWh	Ø	1000 kWh

Chemicals	1,5 kg of PA	79,1 kg of acetone	75 kg of epoxy resin

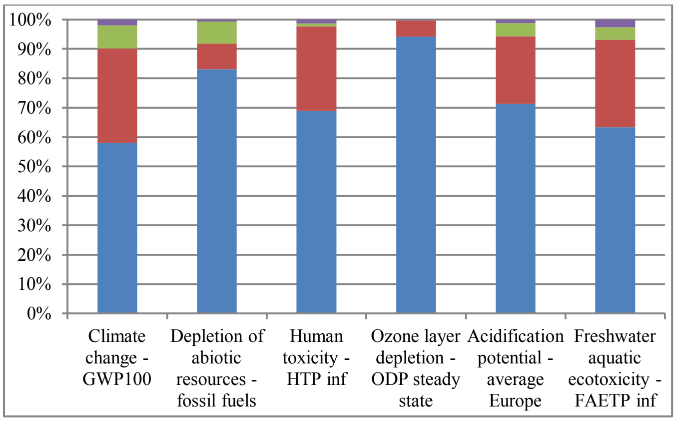


Fig. 5. Environmental assessment of the CFRP recycling by the SCWS in blue, by the cleaning with acetone in green, by the realignment in purple and by the remanufacturing in red

The realignment and the cleaning represent less than 5% in each impact (Fig 5). The remanufacturing corresponds to the quarter of most of the impacts. The SCWS is the most impacting of all of the operations.

5.2. Global impact of the process

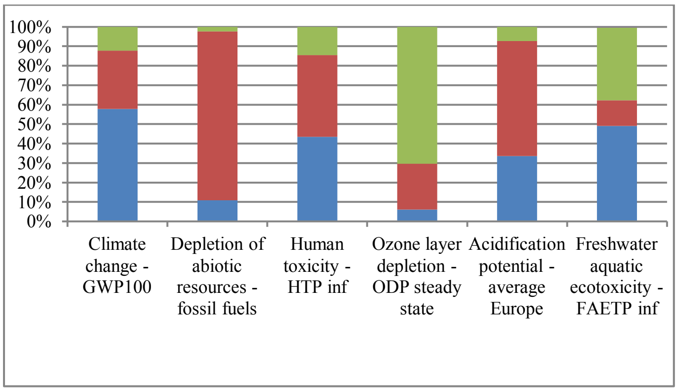


Fig. 6. Environmental impacts of SCWS alone with the electricity in blue, the natural gas in red, the tap water in green and the deionized water in purple

The deionized water is not visible on the Figure 6 because it is insignificant (0,2%) compared to the other components. The electricity and the natural gas represent each more than a third of the impacts. On the other hand, the tap water is never the major element except for the impact on ozone layer depletion. The natural gas is particularly more impacting for the depletion of fossil/fuel resources.

5.3. Impacts of the chemicals

The potassium hydroxide is often employed as a catalyst in SCFS [11, 17, 21-22]. The concentration goes from 0,05 M to 0,5 M [17-18] thus for 700 L of water, the amount of catalyst is 1,96-19,6 kg. Although it increases the environmental indicators of only 1-8%, it emphasizes the depolymerization. The time benefit decreases the energy consumption and makes the process more environmental friendly.

The alcohols are also tested as supercritical fluids to dissolve thermosetting resin and recover CF. Okajima made a manuscript on CFRP recycling using methanol [20], Jiang et al. chose the propanol [22] and Pinero et al. tried many alcohols to compare their potential [23].

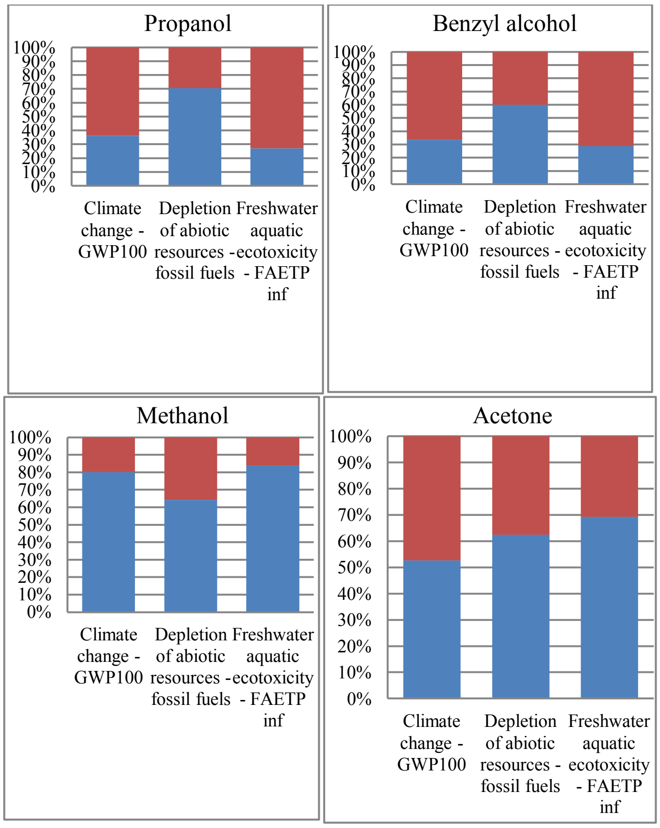


Fig. 7. Environmental impacts of SCFS with the different alcohols as SC fluid in red, and the energy (gas, electricity, tap water) in blue

Figure 7 represents a comparison between SCFS using different solvents. The amount of solvent depends on their SC density and the volume of the tank: 1,91 m^3 [17]. The assessment was made with the same data as SCWS (Table 4), the alcohols replacing the water.

However, the critical conditions are totally different for all these alcohols (Table 6). The temperature is 30-40% lower than for water and the pressure 60-80% lower.

Table 6. Supercritical conditions and density for some solvents [17, 26]

Solvent	SC Density in kg/m^3	SC Pressure in MPa	SC Temperature in °C
Acetone	235	4,7	235
Benzyl Alchohol	447	4,5	323
Methanol	282	8,22	240
Propanol	274	5,17	264

Water	368	24	380

The impacts of the chemicals have a greater significance than in the SCWS process where the deionized water was irrelevant. The process using SC methanol or SC acetone needs to use 20-30% less energy than the SCWS to be more environmental friendly. For the SCFS using benzyl alcohol and propanol, the reduction in energy consumption necessary is higher: 50%. The energy, the pump, the steam boiler and the other components of the SCFS system will be different if the process uses an alcohol as a SC fluid. The reduction is feasible for the SCFS with methanol and acetone but more uncertain for the other solvents.

6. Conclusion

The effect of the sizing removal during the recycling of CFRP on ILSS was quantified. The interlaminar shear strength was 5 MPa lower than that of unsized CFRP. The CF unsized is much more difficult to manipulate in remanufacturing. For the further works on the sizing effect on mechanical behavior, the removal of the sizing shall be done before the realignment operation. The woven fabric unsized transformed into packs of CF will be easier to handle.

The analysis of recycling by SCWS gives a first-hand insight of the environmental impacts of this process and the importance of the chemicals in the case of SCFS with alcohols. A detailed analysis was made with a good estimation of the energy used. The methanol and the acetone seem better SC fluids than benzyl alcohol and propanol. The realignment operation with the I2M machine is not considered to have significant environmental impact. The recycling has the most significant impact on the EOL of CFRP wastes compared to the other operations.

Recycling technologies of CFRP are in the industrialization phase however the reuse of the rCF needs to meet specifications to enhance the rCF market. To design new applications for realigned rCF, improvement should be done on the orientation and the sizing of CF. The form is important to produce homogenous CFRP with high mechanical properties. The rCFRP can fit to applications in automotive or aerospace, even in structural applications [3].

The difficulty in CFRP recycling is the disparity of the wastes. There are many factors contributing to the complexity of recycling CFRP. The priority is to identify the recycling routes for each CFRP wastes. Some scenarios start to emerge such as using SCWS to recycle the fabric wastes and the contaminated EOL pieces by fluid bed treatment.

Finally, before thinking of recycling, the direct reuse should be considered. In McGill, the manufacturing of chopped strands from out-of-life woven fabric is experimented. The retention of the properties is excellent as Meredith proved it [27].

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