PROCESSING AND RECYCLING OF A THERMOPLASTIC COMPOSITE FIBRE/PEEK AEROSPACE PART

M. Roux[a*], C. Dransfeld[a], N. Eguémann[b], L. Giger[b]

[a] *Institute of Polymer Engineering, University of Applied Sciences and Arts Northwestern Switzerland, Windisch, Switzerland,*
[b] *Cross Composite AG, Steckborn, Switzerland*
** Corresponding author (maxime.roux@fhnw.ch)*

Keywords: Thermoplastic, composite, recycling, aerospace.

Abstract
This work presents an alternative way of recycling typical thermoplastic composites (TPC) used in aerospace industry with high contents of carbon fibres. Through a cradle to cradle procedure developed by the authors, TPCs become good candidates for replacing thermoset composites (TSC) and metallic complex parts in aerospace applications, not only due to their low density, excellent mechanical properties and processability, but also regarding the new perspective of recycling that offers a novel grinding process known as the electrodynamical fragmentation.

1. Introduction

1.1. End-of-Life of commercial aircrafts

In the civil aerospace industry, the environmental impacts and the End-Of-Life (EoL) among traditional parameters such as cost, performance and efficiency of the aircrafts are rising up challenges. In the past decades, the ultimate solution for EoL of commercial aircrafts was mainly to collect the most valuable items for the spare parts market such as landing gears, jet engines and avionic system. The rest (i.e. fuselage, wings and interior) was either just stored in large graveyards or grinded out and landfilled [1]. Currently over 2000 aircrafts are in graveyards and over 5000 commercial airliners will be withdrawn from service in the next 20 years [2]. The increase of disposal costs and the EoL regulations [3] push the manufacturers towards more efficient solutions for the EoL of their aircrafts. In addition, the new aircraft generation contains more than 50wt% of high performance composite materials which not only increases their fuel efficiency and comfort but also brings new challenges concerning their recycling compared to traditional metallic structures.

1.2. Recycling of carbon fibre reinforced plastic materials (CFRP)

Concerning CFRP parts, two main industrial recycling ways exist apart from ultimate landfilling. The composite parts can be either pulverized through a mechanical shredding process to be re-used as filler in cement [4] or the fibres can be recovered by removing the polymer matrix. The first solution shows an uneconomic down cycling for the recycling industry. The second alternative is to recover the carbon fibres [5] by removing the thermoset polymer by means of mainly thermal pyrolysis processes. The recovery rate is thus limited to less than 50 percentage in volume (vol%), and the resulting recovered carbon fibres are often short in length with reduced quality and mechanical properties which consequently limit their applications and their economic value [6]. Even if new methods are being developed with the aims of reducing the energy consumption of CFRP recycling, a direct re-use of the recycled material to produce new parts is still not possible. In contrast to CFRPs with a thermoset matrix, thermoplastic composites have better perspective of recyclability with theoretical recovery rates up to 100%. Indeed thermoplastic polymers can be re-manufactured through reversible thermal processes while the curing process of thermoset polymers is considered as non-reversible. The thermoplastic CFRP parts have to be grinded down to small fragments prior reprocessing. While fragmenting aerospace CFRPs, the main problem comes from the high content of carbon fibres which dramatically damaged the shredder blades [7]. Furthermore, important amounts of harmful carbon powder are produced. Given that no solution was proposed in the industry to grind down efficiently high performance thermoplastic CFRPs, the authors choose a novel approach to separate TPC into its constituents without tool wear using high voltage pulses through a technology known as electrodynamic fragmentation (EDF).

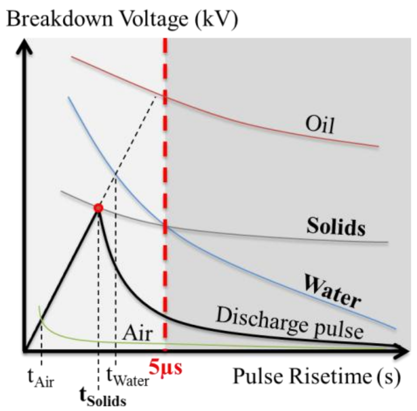


Figure 1. Breakdown voltage as a function of the pulse rising time. Solids have breakdown voltages lower than water below rising time of 5µs. The discharge goes preferentially through the solid.

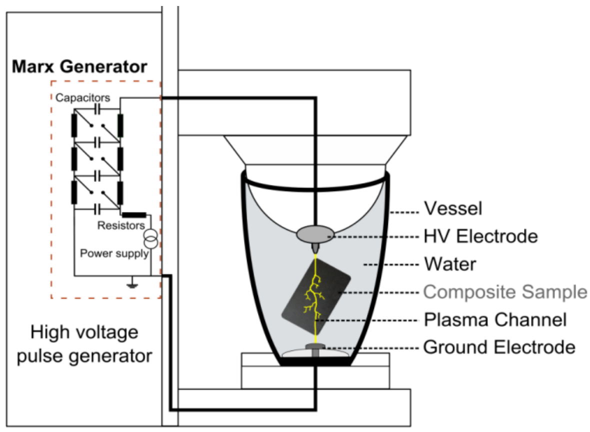


Figure 2. Drawing of a lab scale electrodynamic fragmentation equipment using a Marx generator.

1.3. Electrodynamic fragmentation

Electrodynamical fragmentation was first used in the early 60's by The Tomsk Polytechnic University in Russia [8]. The main application of this method was initially to disintegrate rocks in the mining industry in order to extract crystals and precious stones without aggressive and polluting chemical procedures, by applying electrical discharge through the specimen. The material is placed in water between two electrodes and high voltages between 50 and 200kV are applied. The voltage must be higher than the actual breakdown voltage of the material to be fragmented, but lower than the surrounding medium (Usually water). This is achieved by reducing the pulse rise time below 5 µs for solid material in water using a Marx generator as described in the Figure 1. The electrical discharge brings a high energy (10 to 100 J/cm) creating a plasma channel in the solid. This strong energy induced in the very close area temperatures and pressures up to 10 000°C and 10^4 MPa [9] which create pressure waves exceeding the strength of most materials and leading to the cracking of the weakest materials surrounding the plasma channel. The best fragmentation results are obtained with brittle and heterogeneous materials. The electrical discharges are also attracted toward inclusions with higher permittivity and then follow its boundary, separating it from the rest. Furthermore, stress concentration mainly from material inhomogeneities and internal boundaries also attract the discharges. The separation of polymer materials is more challenging especially with those having high fracture toughness.

2. Materials and methods

2.1. Thermoplastic CFRP Materials

The thermoplastic matrix selected in this study is a polyether-ether-ketone (PEEK) from VICTREX®. The CFRP is supplied in unidirectional directional (UD) 55 vol% AS4 high modulus carbon fibres (Hexcel) pre-impregnated and chopped into 20 mm long “chips” by SUPREM AG, Switzerland. As a material benchmark, parts are also produced with injection granulates having 24 vol% of short AS4 carbon fibres, less than 1mm long.

2.2. Application case: Rotorcraft door-hinge

For aerospace application, complex metallic load introduction in CFRP structures have many drawbacks: steel has a high density while aluminium parts are subjected to severe galvanic corrosion that required expensive protective layers. It is possible to avoid galvanic corrosion by the use of titanium with however a substantial increase of material and production costs [10]. Concerning CFRP, fabric based manufacturing methods are not adapted to the industrial production of complex load introductions. In this work, original CFRP door hinges are compression moulded using a non-isothermal process [11]. Thermoplastic CFRP raw material is dropped into the tool cavity and then pressed using a vertical hydraulic press (Schwabenthan 200T, Germany) with 20 tons clamping force and heated up at 360°C. The part is finally cooled at a rate of 20°C/min and ejected from the cavity. The authors [11] already performed a complete study investigating the influence of the process parameters, the size and type of material used. The weight of the CFRP door-hinge is only 22 g, compared to 134 g of the initial door hinge made of steel which represent a weight reduction of approximately 83%.

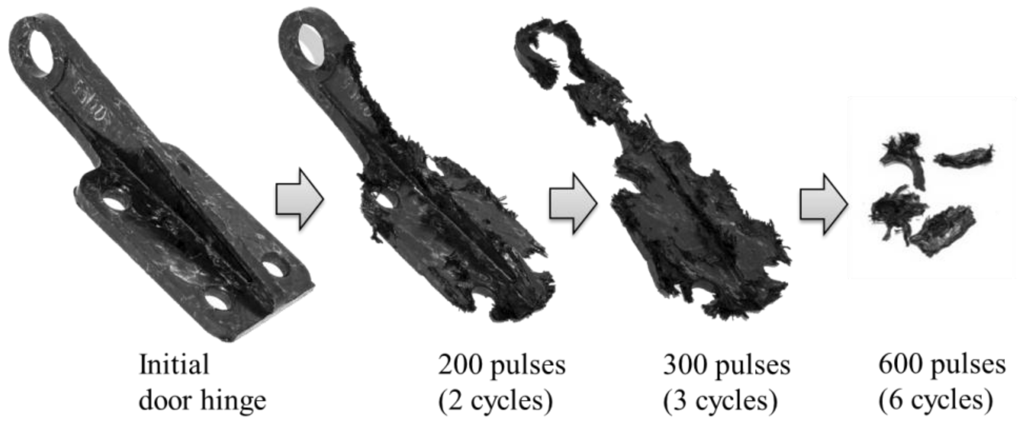


Figure 3. Evolution of the CFRP door hinge during electrodynamic fragmentation process.

2.3.Electrodynamic fragmentation: equipment

The EDF equipment is a lab-scaled unit, *Selfrag Lab* manufactured by Selfrag AG, Switzerland represented in the (Figure 2). The fragmentation is operated in a 3 to 4 litres water closed vessel. For a single door hinge, 6 cycles of 100 pulses each with an applied discharge voltage of 180kV at a frequency of 5Hz are sufficient. Between each cycles the content of the vessel is filtered using at first a metallic sieving grid having a mesh interspace of 4mm, fragments passing through are separated whereas the rest is put back into the vessel. Finally the smallest fragments and the carbon powder generated are separated with respectively a sieving grid having 1mm interspaces and a filter with mesh around 15µm.

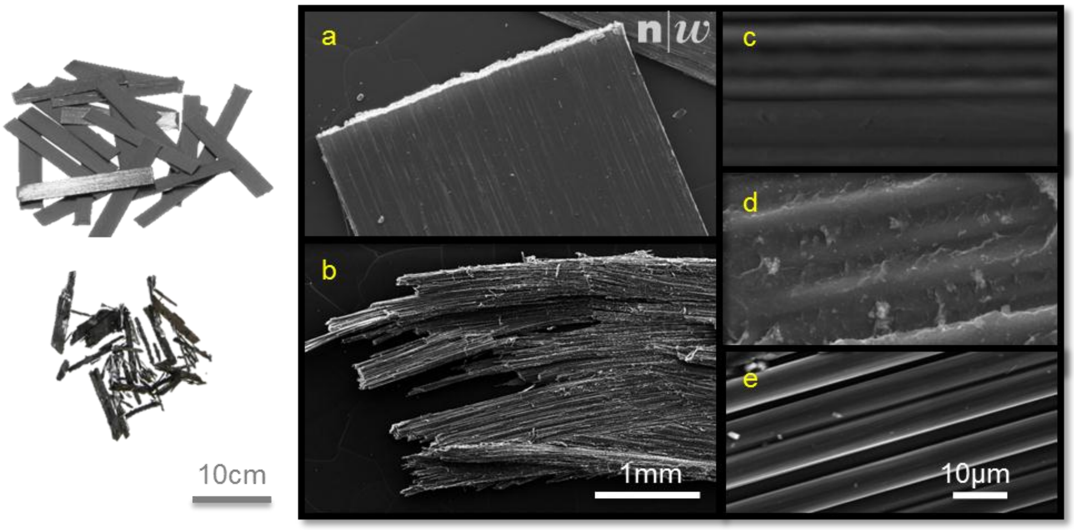


Figure 4. 20mm chopped tapes (a-c) and recycled fragments (b-d-e) under Scanning electron microscope.

3. Results

3.1. Production of fragments in batch mode

The door-hinges are fragmented following the procedure described previously. The part is first attacked at the edge due to field enhancement (Figure 3). As soon as cracks are created in the part, the discharges will go through the part, separating fragments from it. This process continues until only few grams of composite are left and then stops because the efficiency of the process drops dramatically with very low amounts of material in the process zone. Photos and scanning electron microscopy (SEM) picture analysis (Figure 4) shows that the surface (length and width) of the fragments produced is reduced but the thickness is increased compared to the initial chopped tapes (20x3x0.16mm). The fragments are mainly composed of several tapes one top of each other with shorter length. The amount of PEEK is also slightly reduced in the recycled fragments with 57 vol% carbon fibres measured using TGA. The surface of chips before processing is made of unidirectional carbon fibres well embedded in PEEK polymer (Figure 4c). On the recycled fragments, the surface is irregular and exhibits many broken fibres and analysis at higher magnification display different zones: some are similar to the initial chips with fibres fully covered by polymer (Figure 4d) and others exhibit surface with fibres free of polymer (Figure 4e). In this case, the entire PEEK matrix was removed during the fragmentation process without adding damages to the fibres.

3.2. Manufacturing and testing of the door hinge

The exterior appearance of the recycled door hinge is very similar to the original door-hinges (Figure 5). PEEK polymer content is slightly reduced in the recycled door hinge with a 60 Vol% carbon fibres measured using TGA. During the mechanical tests, the door hinges made from recycled fragments exhibit an elastic behaviour followed by a brittle failure unlike the one made of chopped tapes having an elasto-plastic deformation with a tough failure behaviour. The hinge made of granules is showing less plastic behaviour leading to a brittle failure. The reduction in ultimate load of the recycled door hinge was of 17% compared to the 20mm chopped tapes but was also presenting 18% better mechanical performance than for door hinges produced with injection moulding granules (Figure 6).

Figure 5. Original door hinge (left) versus recycled door hinge (right).

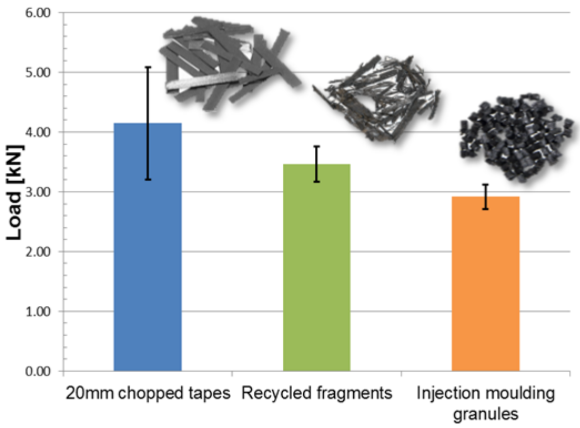


Figure 6. Graphic of the maximal load of door hinges made with granules, recycled chips and chopped tapes [24].

3.3. Fractography of the door hinges

Fractures profiles of the door hinges after mechanical testing were visualised using a SEM (Figure 7), in order to understand the mechanisms of rupture and the origin of mechanical performances reduction after recycling process. In the case of the original door-hinge made with chopped tapes (Figure 7a/c), the fracture is mainly going around the chips and is matrix driven. The fracture mechanisms are similar to the ones in a laminate with delamination modes 1 and 2. The geometry of the initial chopped tapes with a very regular surface of well aligned fibres like in (Figure 4) is still visible. At some positions, the fracture is also passing inside the chips especially along the fibres showing shear failures. The overall fracture of the original door hinge demonstrates a very good fibre/matrix adhesion and a good load transfer between both material constituents. At higher magnification (Figure 7c), the chopped tapes along the fracture reveal fibres still fully embedded in PEEK pointing out cohesive failures in the polymer during mechanical testing. The profile of fracture in the door hinge composed of recycled fragments is visualized in Figure 7b/d/e. At higher magnifications two characteristic states are detected in the fracture of the recycled door hinge. These states (Figure 7d/e) are composed of fragments with bundles of aligned and long fibres, similar to initial chopped tapes. In those states, fibres on the surface are either free of polymer (Figure 7d) or partially covered of polymer (Figure 7e). The polymeric matrix clusters well the fibres inside the fragments but also poorly covers the surfaces which highlights adhesive failure between polymer and fibres.

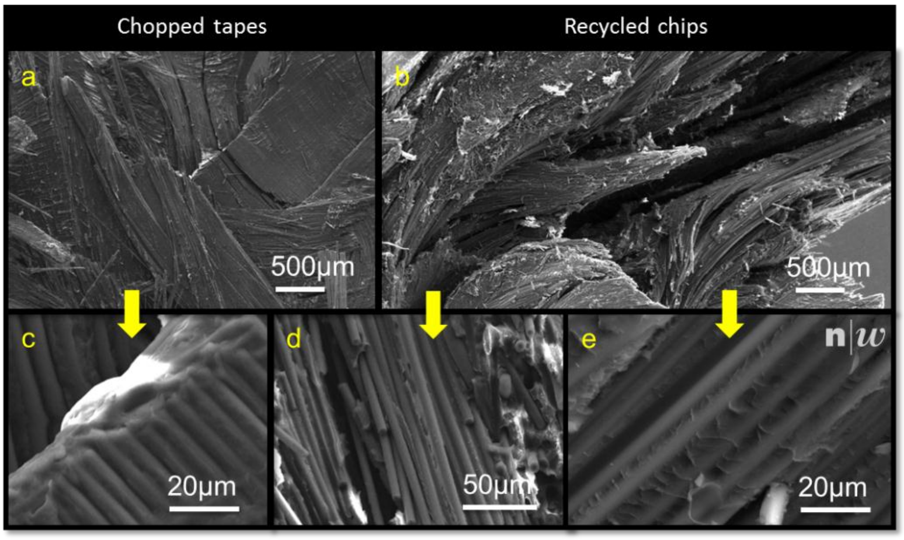
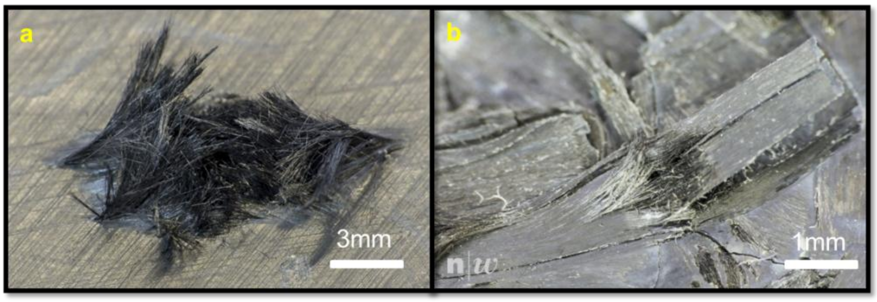


Figure 7. SEM picture of the fracture of door-hinge made of chopped tapes (a) (c) and of the door hinge made with recycled fragments (b) (d) (e).

4. Discussion

4.1. Explanation of the fragmentation process

In this work, interest is pushed to the comprehension of the mechanisms that lead to the fragmentation of thermoplastic composites. The physic of the electrodynamical fragmentation process in a solid was previously explained in details by Bluhm et Al [9] and was mainly driven by shock waves resulting from electrical discharges going through the parts. In the composite door hinge, the discharge will be attracted by the carbon fibres and the numerous interfaces. In a thermoplastic composite, the effects of high voltage discharges are slightly different from what could be found in the literature for other solid materials. By analysing the composite after just one single pulse inducing a discharge going through the part (Figures 8a), no fragments are created and only the exterior surfaces of the part are affected. The impact on the surface at 180kV is very similar to the damage areas of a CFRP affected by lightning strikes on aircrafts in recent publications [12] [13]. The fibres are free of polymer and broken at the position of the impact (entrance point), which is the direct consequence of the induced temperature that is far higher than the degradation temperature of the composite. This is defined as the fragmentation failure mode I represented in (Figure 9). In the Figures 8b, some composite layers are lifted up and partially delaminated from the main part. In this region three other fragmentation failure modes are defined. Some of the lifted fibres are free of polymer because of the temperature that is lower than the carbon fibre thermal degradation temperature and higher than the polymer thermal degradation temperature (580°C). PEEK pyrolysis is defined as the fragmentation failure mode II. It was noticed in the literature that the production of pyrolysis gases in the composite during lightning strikes lead to a fast increase of the gas pressure in the cavities along the plasma channel and a fast expansion of the interlayers gap causing delamination of the plies (fragmentation failure mode III). The fragmentation failure mode IV comes from the pressure waves transmitted perpendicular to the plasma channel in the material that by excessing the material strengths leads to its destruction with an intensity decreasing as a function of the distance travelled in the material. In the literature it is considered as the main cause of material fragmentation for rather fragile material with low tensile properties. In the case of our material, the composite can be mechanically broken and from a certain distance, only the PEEK polymer is affected.



Figures 8. Impact of high voltage discharges on PEEK/CF composite surface a: First discharge leading to a large damaged area, b: Impact during the fragmentation leading to the delamination of a composite tape.

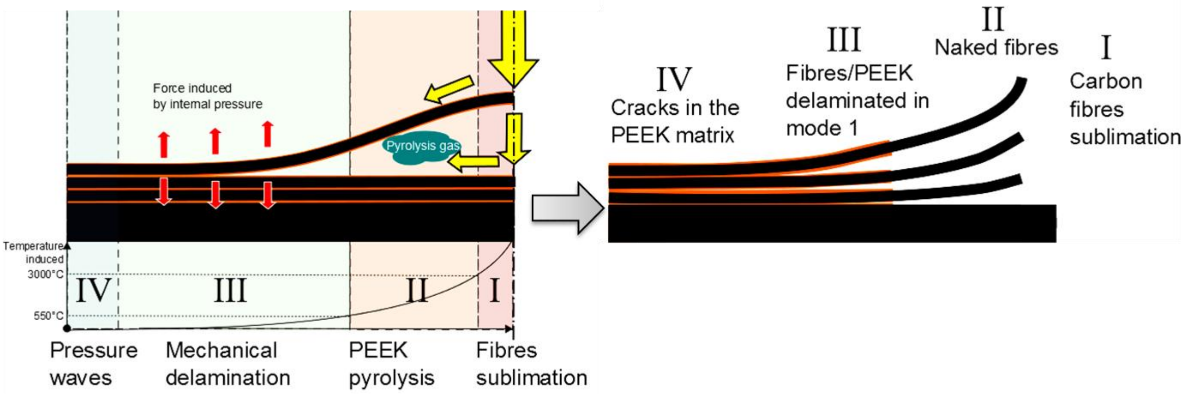


Figure 9. Schematic drawings illustrating the mechanism of fragmentation induced by HV pulses (From [16] modified).

4.2. Decrease of mechanical properties after HVF

As shown in Figure 6, the recycled door-hinges exhibit a slightly decrease of the mechanical properties and brittle failures that have various origins. This change in mechanical properties may not only come from shorter carbon fibres but also from a possible lack of fibre matrix adhesion where the surfaces of recycled fragments were produced by the fragmentation failure mode II. The surfaces of the recycled fragments are not as homogenous as the chopped tapes and will perhaps require adapted compression moulding parameters like a longer processing time in order to allow to the PEEK contained within the fragments to flow and fill gaps between the fragments.

5. Conclusion

In this report, the recycling feasibility of high contents carbon fibre reinforced thermoplastic parts is demonstrated without the typical tool wear in shredder. Door hinges were successfully produced with 100% of recycled materials using the same compression moulding unit as for the original hinges and without any post processing applied on the fragments between the recycling and the re-processing and with a reduction of only 17% of the mechanical performance compared to novel chopped tapes door hinges and 18% better mechanical performance than for door hinges produced with injection moulding granules, it is placing recycled fragments at an attractive economic value between chopped tapes and injection moulding granules. After fracture analysis, it has been clearly demonstrated that this reduction of mechanical performance came from shorter and thicker fragments that are less optimal and from the reduction of polymer on the fragment surface due to thermal pyrolysis reducing the fibre/matrix adhesion and load transfers. A continuous electrodynamical fragmentation process avoiding the time intensive sieving with a continuous flow working machine dedicated to CFRP recycling is under-development in the Clean Sky Eco-Design ITD and SELFRAG AG through a call for proposal.

6. Acknowledgments

This work was supported and conducted within the European project Clean Sky JTI in the Eco-design activity. The authors would like also to acknowledge those companies: Selfrag and Airbus Helicopters.

7. References

[1] WINGNet, The Aircraft at End of Life Sector: a Preliminary Study. UK Engineering and physical Research Council (EPRSRC), 2007.

[2] Airbus, *PAMELA (Process for advanced management of end-of-life aircraft) training kit.* 2008: p. 20.

[3] Council_of_the_European_Union, *Directive 1999/31/CE on the landfill of waste,* 2011, Official Journal of the European Communities: Brussel. p. 19.

[4] Chung, D.D.L., *Cement reinforced with short carbon fibers: a multifunctional material.* Composites Part B-Engineering, 2000. **31**(6-7): p. 511-526.

[5] Witik, R.A., et al., *Carbon fibre reinforced composite waste: An environmental assessment of recycling, energy recovery and landfilling.* Composites Part a-Applied Science and Manufacturing, 2013. **49**: p. 89-99.

[6] Rush, S., *Carbon fiber: Life beyond the landfill.* High Performance Composites, 2007. **15**(3): p. 52.

[7] Schinner, G., J. Brandt, and H. Richter, *Recycling carbon-fiber-reinforced thermoplastic composites.* Journal of Thermoplastic Composite Materials, 1996. **9**(3): p. 239-245.

[8] Bluhm, H., et al., *Application of pulsed HV discharges to material fragmentation and recycling.* Ieee Transactions on Dielectrics and Electrical Insulation, 2000. **7**(5): p. 625-636.

[9] Bluhm, H., et al. *Industrial applications of high voltage pulsed power techniques: developments at Forschungszentrum Karlsruhe (FZK).* in *Pulsed Power Conference, 1997. Digest of Technical Papers. 1997 11th IEEE International*. 1997.

[10] P. Parleviet, C.P., C. Weimer *Ecodesigned thermoplastic composite helicopter airframes structures* SETEC 12 LUCERNE – 7th. INTERNATIONAL TECHNICAL CONFERENCE, 2012: p. 6.

[11] N. Eguémann, L.G., M. Roux, Prof. C.Dransfeld, Prof. Dr. F.Thiébaud, Prof. Dr. D. Perreux, *Manufacturing and recycling of complex composite thermoplastic parts for aerospace application* SETEC 12 LUCERNE – 7th. INTERNATIONAL TECHNICAL CONFERENCE, 2012: p. 6.

[12] Ogasawara, T., Y. Hirano, and A. Yoshimura, *Coupled thermal–electrical analysis for carbon fiber/epoxy composites exposed to simulated lightning current.* Composites Part A: Applied Science and Manufacturing, 2010. **41**(8): p. 973-981.

[13] Feraboli, P. and M. Miller, *Damage resistance and tolerance of carbon/epoxy composite coupons subjected to simulated lightning strike.* Composites Part A: Applied Science and Manufacturing, 2009. **40**(6–7): p. 954-967.