How and where we found reclaimed Carbon Fibre for Additive Manufacturing technologies


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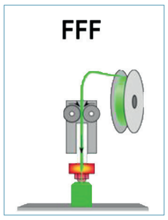
For the need of REPAIR3D European project, a selection of most suitable carbon fibre composites wastes for additive manufacturing technologies is done.
End-of-spool, recycled carbon fibres recovered after supercritical CO_2 extraction and carbon drilling power were selected for reinforcing TP matrix.

The Repair3D (GA n°814588) project aims to address all aspects and stages of thermoplastic and carbon fibre (CF) reinforced thermoplastic 3D printing material development from recycled resources. It tackles selection of suitable waste streams, strategies for material repair, compatibilisation and upgrade to additive manufacturing (AM) processing, compatibility between different thermoplastic matrices and the reinforcing fibres and nanoparticles.
It also covers comparative assessment of various AM thermoplastic processing technologies and closed-loop material optimisation in terms of processability and performance.

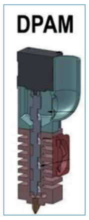
A wide variety of additive manufacturing technologies…

Five industrial demonstrators will be 3D-printed using CF reinforced thermoplastics (TP) in Repair3D. Different extrusion-based AM technologies are used to fulfil this objective, with the advantage of obtaining competitive structural carbon fibre reinforced polymers (CFRP) for high performance, and reliable applications with a good design flexibility.
Some functionalities are added inside the matrix or on the CF surface to obtain self-healing properties and improve end-of-life valorisation. This aspect, however, will not be developed in this paper.

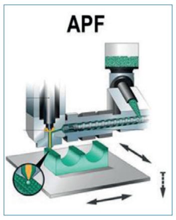
Fused Filament Fabrication (FFF): A filament feedstock is liquefied inside a heated reservoir, extruded through a metallic nozzle, and fused with adjacent material before solidifying.
A wide range of TP materials can be processed with FFF technology.



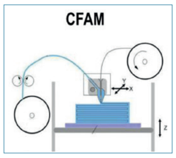
Direct Pellet Extrusion AM (DPAM): Polymer granulates are directly processed, avoiding an additional step to transform them into filament. The advantages are a homogeneity increasing of polymer melting, and the possibility of processing TP and elastomers pellets combined with fillers.



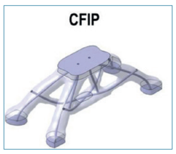
Arburg Plastic Freeforming (APF): As with DPAM, polymer granulates are directly processed. But here, the granulates are melted in the extruder unit and deposited as droplets via a piezo-electrical unit, resulting in better interlayer adhesion and higher mechanical properties. It implies that granulates must be electrically conductive.



Continuous Fibre AM (CFAM): The CFAM process enables continuous fibre to be used to reinforce the polymer during the fabrication process. The technology consists of using a continuous fibre feedstock printhead with an active spreader pin to incorporate matrix material, delivered with a micro extruder, into the composite structure.



Continuous Fibre Injection Process (CFIP): Patented by Spanish technology centre Eurecat, this technology makes it possible to obtain continuous fibre reinforced structures. It involves design and FFF fabrication of a part containing internal tubular cavities, and subsequently injecting continuous fibres and thermosetting resin. This results in post-AM fibre reinforcement of plastic parts which may exhibit up to 10 times increase of tensile strength. The technology is compatible with a wide variety of TP and continuous fibres.



Tab.1: Recycled CF morphologies for AM technologies used in REPAIR3D

AM technology	CFAM	CFIP	FFF & DPAM	APF
CF morphology	Continuous max 6k	Continuous max 24k	Short or chopped ~ 6 mm	Powder +/- 5 µm

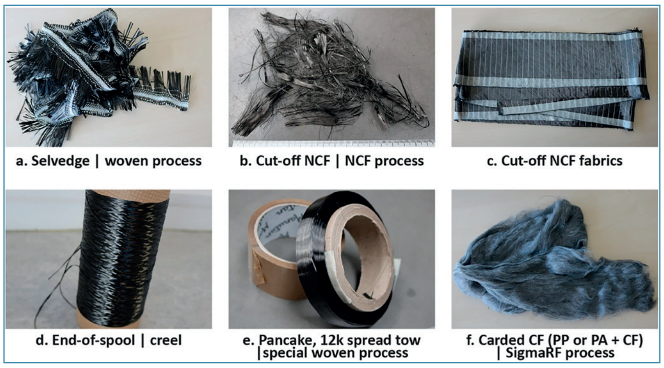


Fig. 1: Sigmatex production wastes

...with different needs in terms of CF reinforcement for TP matrices

These processes can use CF to reinforce matrix mechanical properties. Regarding the nature of AM input materials, CF must be prepared as different morphologies: continuous, short (~6 mm) or in powder form (Table 1).

Finding sources of CF waste...

Sigmatex in the United Kingdom, Adamant Composites in Greece, and the Airbus plant in Nantes, France were identified as potential sources of CF waste (textile waste and uncured/cured composite waste).

Textile waste type from Sigmatex

Sigmatex is one of the world's leading independent converters of CF. With the widest range of textile technologies and proprietary manufacturing equipment, Sigmatex supplies a wide spectrum of advanced composite materials. Their manufacturing processes produce various pre-consumer waste types: woven, non-crimp fabrics (NCF), recycled fabrics (sigmaRF) and spread tow processes, and from creel (Figure 1).

The weaving process produces waste from the fabric edge called 'selvedge'. It is made of short CF strands interwoven with polyester yarn. The length of the carbon fibre can vary from 3 to 8 cm (Figure 1a) but for each batch, the length is homogeneous. For the Repair3D project, Sigmatex focused on developing a process for separating and extracting the carbon fibre tails from the polyester yarn. Once this is done, the carbon can be blended with recycled thermoplastic fibre such as polypropylene (PP) and polyamide (PA), formed into a sliver (Figure 1f) and then spun to create a commingled yarn.
Fabric set-up waste composed of pure carbon fibre woven at the start of production is also available.
CF waste in NCF manufacturing is very similar in length and form (Figure 1b) and the fabric waste usually contains polyester stitching and a small amount of glass fibre (Figure 1c).

Other CF waste, in continuous forms, are possible to obtain from end-of-spools (Figure 1d). In textile processes, yarns are usually fed from spools placed on a creel. To limit wastage, Sigmatex prepares the right quantity of fibre, but it is common to have around 10 to 50 metres which remain at the end.
CF tape, or 'pancake' could be another interesting source of reusable waste. The tape is typically 15 to 20 millimetres wide and made from 12k or 15k carbon fibre (Figure 1e). These tapes are produced to a very tight width specification and under-width spools could be reused in a continuous form.
Finally, Sigmatex already processes its own cut-off fibre to make carded CF used to produce sigmaRF fabrics. In Repair3D, this is an interesting semi-product for making comingled rCF (Figure 1f).

Composite waste types from Adamant Composites and the Airbus Nantes plant

Adamant Composites (Greece) provides the aerospace industry with high-added-value quality products and services for nano-enabling composite materials throughout their product cycle. They use CF pre-impregated with epoxy resin in different typologies (various CF types and resin), and their waste come in two forms. The uncured prepreg is unused expired prepreg, it is still flexible and tacky and has to be stored at -18°C to remain usable. The cured prepreg, composed of scraps from processes, is hard and difficult to cut. The Airbus Nantes plant has a significant amount of cut-off cured composites parts, and uncured prepreg from cut-off and expired rolls.
For the Repair3D project, uncured prepreg (expired type) is very interesting as it is possible to cut them to the length desired (in our case, 6 mm for compound preparation). This is a typical type of waste for the aerospace industry. IRT Jules Verne developed an innovative recycling approach [1] for this project using supercritical CO_2. This process has a lower environmental impact and good cost balance compared to pyrolysis and virgin CF production [2], even if this material must be stored at -18°C until extraction is performed. The Airbus Nantes plant provides IMA/M21E prepreg for the needs of the project. Finally, milled CF wastes produced during finishing operation were also tested for APF. This powder is mainly composed of carbon and cured epoxy.

...and selecting the best rCF for each AM technology

For CFAM and CFIP

After some processing trials, the discovery was made that pancake and carded CF commingled yarn are difficult to process and not compatible with additive manufacturing. Two main issues arose. The first is that they are too large for the current process used in Repair3D. The second involves the pancake. Due to its morpholo-

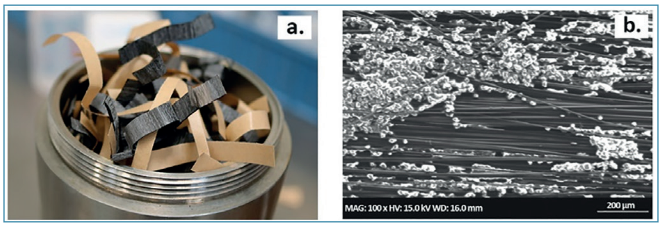


Fig. 2: a: Photograph of 6 mm recycled CF prepreg after supercritical CO_2 extraction; b: corresponding SEM image

gy (very thin and well spread), it is very tricky to unwind without braking or fraying the fibres. End-of-spool was therefore selected for Repair3D (3k for CFAM and 24k for CFIP).

For FFF and DPAM

For these technologies, a compound must be prepared in order to be used directly, or for filament preparation. This required adding carbon fibre in a controlled way to the compounder. Several fibres were tested:

- use of a chopper (Chopcot® T6) for textile wastes:
- for end-of-spool: size control (OK)
- for pancake: no compatible due to unwind issue (NOK)
- after cryogenic milling of textile to reduce the size: too fluffy (NOK)
- after supercritical water solvolysis from cured composite: too fluffy and with no size control (NOK)
- after supercritical CO_2 extraction from uncured prepreg with a preliminary cutting step (OK). The chopped prepregs treated with supercritical CO_2 is used as "green solvent" to extract a fraction of the prepreg matrix. This process stopped the polymerisation reaction due to a partial extraction of bisphenol-A/Fand aminophenol from epoxy resin. As a consequence, the fibres are neither fluffy nor tacky, they become quite simple to process. By previously cutting uncured prepreg with Zünd equipment for instance, it is easy to control the size and get ready to use rCF at the end of the recycling process (Figure 2). In Repair3D, 6 mm was chosen as a standard for compound preparation. Such rCF after extraction was processed with polyamide 12, copolyester and thermoplastic polyurethane matrix.

Sustainability dimension: the environmental and economic features of this novel process indicate that it is a attractive and promising technology in terms of reduced GHG emissions and cost impacts. Techno-economic estimation values for a plant that could process ~145 tons/year would result in producing 6 mm rCF with the same order of magnitude in CO_2-equivalent emissions and cost-per-kg as commercial recycling alternatives. Utilisation of the organic by-product, and potential use as monomers in polymers, would increase the environmental and economic sustainability of the technology. Valorisation of uncured prepreg, a current waste stream in composite manufacture that is difficult to recycle, would have a twofold advantage. On one hand, it would minimise the composite waste going to landfill, and on the other hand, create added-value products through secondary raw materials with similar intrinsic properties than virgin [2].

Focus

Warrant Group (coordinator), NTUA (technical coordinator), Ghent University, Eurecat, ITENE, Leitat, IRT Jules Verne, Sigmatex, Adamant Composites, Cambridge Nanomaterials Technology, Techedge, Dalbello, Centexbel, Maier, Biog3D, IRES, Jotis, Lavrion Technological and Cultural Park.

Focus

IRT Jules Verne is an industrial research centre located near Nantes in western France dedicated to manufacturing. Its vocation is to improve the competitiveness of strategic industrial sectors in France by creating disruptive technologies for manufacturing processes, with the goal of speeding up innovation and technology transfer to factories. One of our missions in Repair3D is to determine what type of recycled carbon fibres can be processed by AM technologies.

For APF

Considering CF powder, two options are evaluated: cryogenic milling for textile wastes and direct use of milled powder from the Airbus Nantes plant.

Cryogenic milling was tested for textile wastes, cured prepregs. This technique is indeed useful for getting milled CF, but for textiles, as already mentioned, carbon fibres are too fluffy to be processable. Several types of wastes can be processed using this technique and are useful for obtaining milled CF. The best results are obtained with cured prepregs. The second option is to directly use the milled CF produced during finishing operations in the Airbus Nantes plant. Compare with the option involving cured prepreg/cryogenic milling and milled waste, these two powders contain epoxy. The choice was therefore made to use Airbus Nantes plant waste for APF technology.

A smart choice to make the most of carbon waste

From the panel of different wastes available in the Repair3D project, we were able to select the best options, and process the fibres to obtain products usable in AM processes. These rCF incorporated in semi-products are now used to produce various demonstrators, in order to be applied to a large panel of manufacturing sectors such as automotive, sport, health, and so on. The proof is in the pudding as to CF recyclability potential: end-of-spool wastes have been used in CFAM technology to produce personalised orthopaedic assistive devices, UD-prepreg CF were integrated in filaments used in FFF technology, and make 3D-printed ski-boots, and milled CF from Airbus used to print wearable electronics devices using APF. □

More information:
www.irt-jules-verne.fr

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[2] Gkika A, Petrakli F, Vlysidis A, Karagiannis P, Moisan S, Koumoulos E, Life Cycle Assessment and Life Cycle Costing on recycled post-industrial composite waste, ECCM 2022