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Mechanical recycling of CFRPs: manufacturing and characterization of recycled laminates

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Abstract. Carbon fibre reinforced plastics (CFRPs) are a very attractive family of materials used in various application fields such as automotive, marine or aeronautic, due to their high specific mechanical properties. However, the large use of CFRPs dramatically increases the amount of waste materials that derives from the end-of-life products and the off-cuts generated during the manufacturing. In this contest, especially when thermosetting matrices are considered, the need to further study the recycling process of CFRPs is an open topic, both in academic and industrial research. Therefore, in this experimental campaign, CFRP materials deriving from the aeronautic field were recycled by using a milling process. The obtained chips were sieved and inspected with a confocal microscope aiming to evaluate the presence of residual matrix on the recovered fibre's surface. Then the sieved reinforcement was impregnated with new epoxy resin and three-point bending tests were performed to understand the mechanical properties of the recycled composite materials. To produce recycled composites, two manufacturing techniques, i.e. open moulding and compression moulding were considered.

Introduction

The increasing research for lightweight structural materials with improved mechanical properties makes CFRPs a very attractive alternative to their metal counterpart. The rising demand for this category of materials over the last decades can be attributed to their intrinsic high level of tailorability and design freedom, these aspects allow a large use of CFRPs in various application fields such as aerospace, marine, automotive or energy [1].

Indeed, it was revealed an increasing demand of CFRP in these industrial fields that was around 70 kTons in 2010 and reached a level of almost 170 kTons in 2020 [2]. However, a further increase is expected in the imminent future since it is estimated that the demand for carbon fibre composite materials will increase to around 190 kTons in 2050 [2, 3]. Therefore, the large amount of CFRP materials in all industrial sectors will inexorably increase the amount of waste materials that must be managed when they are decommissioned at the end of life. Then, in this context, it is evident that the need for a second life application of these materials is required, moving toward a circular economy that allows the reuse of the dismissed materials, reducing at the same time the production of additional wastes and toxic chemical agents [4]. Based on these considerations, the disposal and the waste management of the end-of-life CFRPs can be considered a rapid-developing challenge for the industrial sectors; therefore, in this perspective the European Union has implemented some directives such as the 2008/98/EC and the 2000/53/EC that are focused on principles of prevention and smart utilisation of composite materials, amount of recycled fibres in new industrial products and pollution payment [3, 5].

To date, a large part of the dismissed materials is usually disposed in landfill or burned to generate energy from the combustion; however, these methods are not in line with the principles of the circular economy and cannot be considered as an appropriate way to recover carbon fibres [6]. In comparison with landfill disposal and incineration, composite recycling is a more sustainable process that is in accordance with the philosophy of the circular economy. It is possible to distinguish three main recycling methods like thermal, chemical and mechanical that differ from each other by the fibre recovery process [7].

However, it is known from the literature that, although produce clean recovered fibres, chemical and thermal recycling processes require high specific energies and appropriate reactor vessels since aggressive and hazardous chemical substances are used [8–11]. All these aspects make these recycling methods unattractive in comparison with the mechanical process that can be considered suitable without limitations to recover the most used industrial fibre's typologies.

The mechanical recycling process usually consists of a reduction of CFRP materials in small pieces using shredding, milling or grinding techniques that on some occasions can be combined to obtain recycled material with the desired dimension. The shredding process is employed to reduce composite materials in small pieces, usually in form of flakes 50 – 100 mm in dimension. During this process, all fasteners and inserts embedded into the material are removed. Additional machining operations like milling and grinding are usually required to further reduce the dimensions of the recycling material and to obtain recovered fibres in form of bundles [12, 13]. Therefore, at the end of the machining operations, it is possible to obtain recovered composite material that can be classified by dimension in powders smaller than 0.2 mm, fine fibres with a length in a range of 0.2 – 20 mm and coarse fibres with a length of about 50 mm. The classification of the machined composite chips by dimension can be allowed through a cyclone or a shaking sieving machine.

Composite materials recycling is an open challenge in the research world since many works are focused on this issue; i.e. Palmer et al. [14] investigated the mechanical properties of recycled composite materials reinforced with recovered carbon fibres and the possibility to use these fibres in place of virgin glass fibres. At the end of the experimental campaign, the tests revealed a reduction of the flexural modulus and flexural strength of almost 3% and 9% in comparison with composite materials reinforced with virgin glass fibres. The research group attributed the reduced performances to the poor adhesion between the recovered fibres and the new resin. Thomas et al. [15] studied the influence of using recovered carbon fibres to increase the mechanical properties of epoxy resin. The mechanical tests revealed that the sample produced with 20% by weight of recycled carbon fibres is characterised by an increase in the flexural strength of almost 30% in comparison with the sample in pure resin.

An overview on the state of the art revealed that the researchers in their works find out that the use of mechanical recovered carbon fibres, although increase the mechanical properties of the pure resin, when used in recycled composite materials are characterised by reduced mechanical properties if compared with virgin CFRP materials [14–18]. This drawback that defines recycled composite materials can be attributed to geometrical characteristics and short dimensions of the recovered fibres and to the presence of residues of matrix that affect the adhesion efficiency at fibre-matrix interface. However, limitation in the mechanical properties can be further ascribed to the production technologies of the recycled composite materials, because in some cases several voids can be entrapped significantly, affecting the mechanical properties of this category of materials.

Therefore, based on these observations, in this research work CFRP materials have been machined with a milling recycling strategy and the recovered carbon fibres have been reused for the production of recycled composite materials adopting different production strategies in order to overcome the technological limitations and then increase the mechanical properties of composite materials reinforced with recycled fibres.

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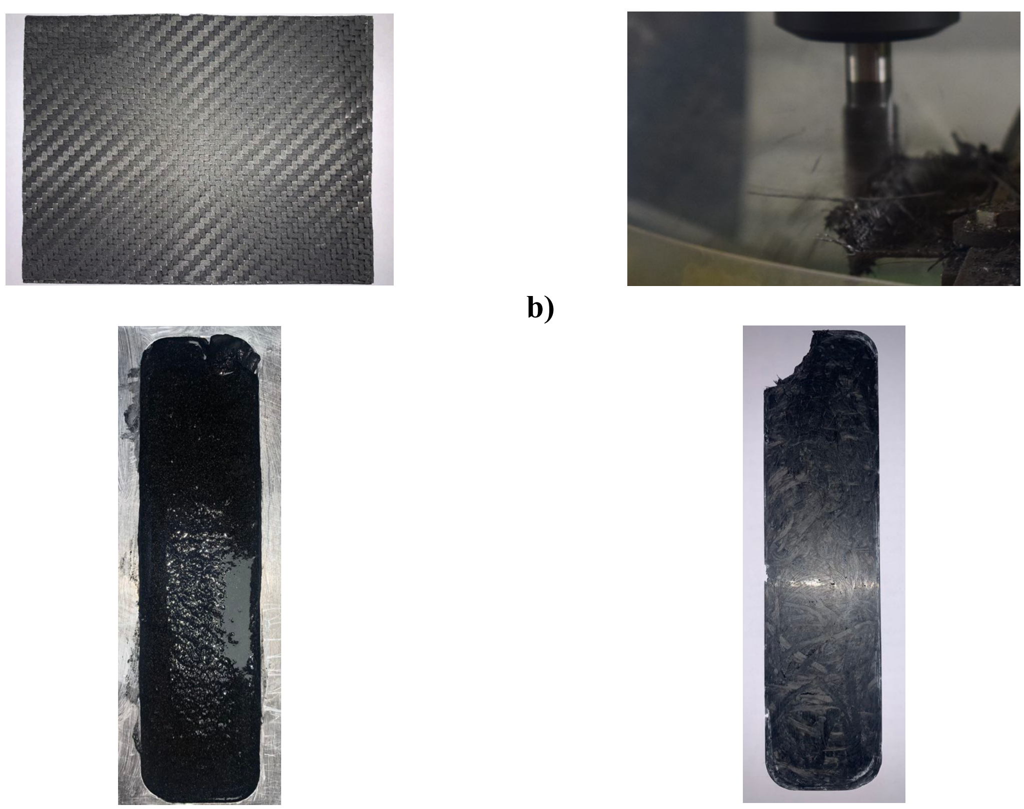
Materials and methods

For the experimental campaign, a CFRP material was manufactured using a 200 g/m^2 twill wave carbon/epoxy prepreg supplied by Toray. A total number of 20 layers 200 x 200 mm^2 in dimensions were layered up producing $(0/90)_{20}$ laminates 4 mm in thickness. The composite materials were produced using the compression moulding technique and was cured at 130 °C for 8 hours with a pressure of about 0.8 MPa. At the end of the polymerization phase, CFRP laminates were mechanically recycled by using the milling process in order to obtain carbon fibre chips. To this purpose a CNC machine (C.B. Ferrari) equipped with a 20 mm in diameter three flute HSS end mill tool was used. A well-defined cutting strategy was applied for the mechanical recycling process of the CFRP laminates; in detail, a spindle speed *s* and a feed rate *f* of 1000 rpm and 1000 mm/min were respectively adopted and a depth of cut of 3 mm was used to produce a material removal rate *MRR* of 0.33 mm/tooth.

At the end of the machining operations, the recovered carbon fibres (rCFs) were sieved with a shaking table allowing to a chips dimension classification: (i) coarse fibre with a length >10 mm, (ii) fine fibres with a length in a range of 0.2 – 10 mm and (iii) powders with a length <0.2 mm. The rCFs were used to produce new composite laminates by using two manufacturing techniques, i.e. open mould and compression moulding techniques. In both cases, the classified chips were manually impregnated with epoxy resin and were placed into the mould at room temperature for 24 hours. Different recycled CFRP samples, that differ in the dimension of the reinforcement (powders, fine and coarse fibres) were produced using both the production strategies but fixing the same amount of recovered fibres, that is around 20% in weight of the overall fibre-matrix mixture. A further sample of pure epoxy resin was produced adopting the open mould technique and was used as reference. In the following figure are reported the main production steps adopted for the production of the recycled samples.



a) b)

c) d)

Figure 1: *Main production steps: laminate's manufacturing (a); mechanical recycling phase (b); recycled sample's production (c); recycled sample (d)*

The experimental campaign provided flexural tests in accordance with the ASTM D790 standard on each sample typology. For this purpose, a universal testing machine (Alliance RT/50) equipped with a 1kN piezoelectric load cell was used to evaluate the bending behaviour of the recycled samples. Then, a reference pure epoxy resin sample and a total number of three specimens for each family were tested by fixing the span-to-thickness ratio equal to 32. The bending behaviour, in terms of flexural strength was evaluated by means of the following equation:

$$\sigma_f = \frac{3Pl}{2bt^2} \quad (1)$$

where σ_f is the maximum stress in MPa, P is the maximum load in N, l is the support span in mm, b and t are respectively the width and the thickness in mm of the testing specimen.

Results and discussion

The mechanical recycling process of the CFRP laminates leads to rCFs in form of bundles that differ in dimensions. In detail, Figure 2 reports the weight distribution of the recovered fibres as function of the overall amount of recycling material.

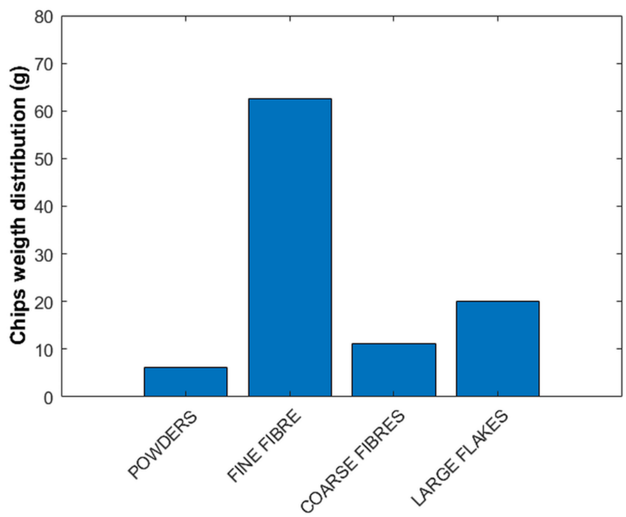


Figure 2: *Weight distribution of recovered carbon fibres as function of the total amount of machined material.*

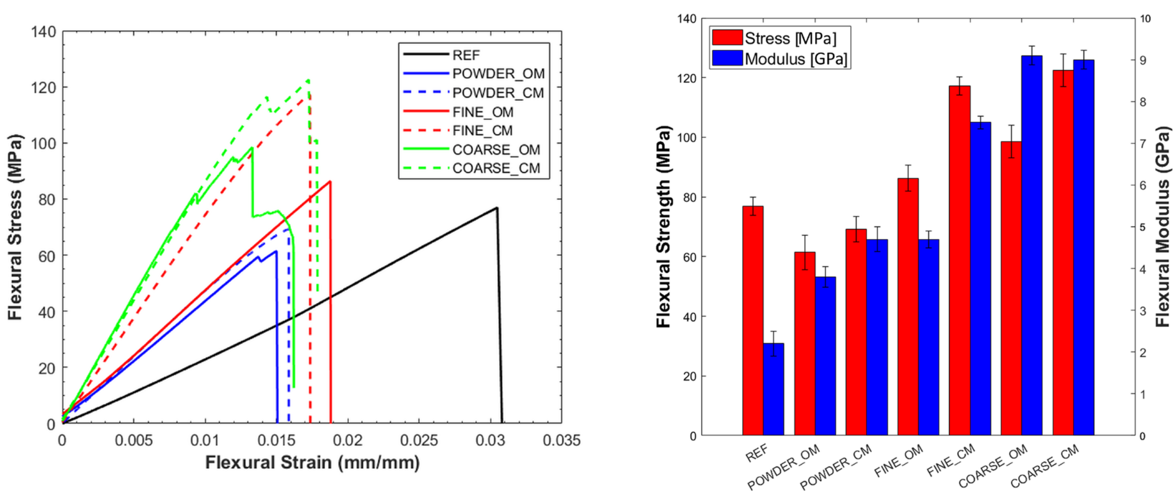
Looking at Figure 2, it is possible to highlight that the process parameters adopted during the machining of the CFRP material lead to a large formation of fine fibres (more than 60% of the recovered material). This chip's composition can be attributed to delaminations and plies fragmentation phenomena that occur when the tooth of the cutting tool impacts on the recycling laminate. However, powders, fine fibres and coarse fibres were used to produce recycled composite samples, whose characteristics are listed in Table 1.

Table 1: *Main properties of the recycled samples*

Label	Production technology	Fibre type	Fibre volume percentage [%]
REF	Open mould	-	-
POWDER_OM	Open mould	Powder	12.00
POWDER_CM	Compression moulding	Powder	20.00
FINE_OM	Open mould	Fine fibres	12.00
FINE_CM	Compression moulding	Fine fibres	20.00
COARSE_OM	Open mould	Coarse	12.00
COARSE_CM	Compression moulding	Coarse	20.00

Looking at the Table 1, it is possible to highlight that when the open mould technique is adopted, the fibre volume fraction of the recycled samples does not exceed the 12%. On the other hand, when the compression moulding is used, although the fibre-matrix composition is the same, the volume fraction raised up to around 20%. The difference in the reinforcement amount is attributed to the strategy adopted during the sample's production, because the compression moulding technique is responsible of a thickness reduction and of the resin flow that pushes away the exceed of resin and the trapped porosities generated during the production phase of the recycled samples. All these aspects can be considered responsible of the increasing of the fibre's percentage that characterises all sample families produced with the compression moulding strategy.

In Figure 3 the main results of the three-point bending tests carried out on each sample typology in accordance with the ASTM standard are represented. In detail, the typical stress-strain curves (Figure 3a) and the flexural strength and modulus (figure 3b) are reported. This test can be very attractive since it can be used to have a better insight into the mechanical properties of the recycled composite materials in terms of interaction between the recovered fibres and the new resin. A global overview on the flexural curves (Figure 3a), lets to conclude that all samples under inspection reveal a linear trend of the flexural stress because of the imposed deformation. A further inspection of the flexural curves revealed that all samples produced with recovered material are characterised by an improved elastic modulus and a reduced strain at failure in comparison with the sample in pure epoxy resin used as reference. This behaviour can be related to the presence of the reinforcement that makes the sample stiffer than the reference.



a) b)

Figure 3: *Typical stress-strain flexural curves (a); mean value of the flexural stress and modulus (b) of each sample typology*

Focusing the attention on the recycled sample reinforced with the shortest fibres (POWDER_OM), it is possible to highlight that even if it revealed a modulus increase of almost +72.7% (3.8 GPa) in comparison with the pure resin sample (2.2 GPa), it is characterised by a reduction of the flexural strength of around -20.1% if compared with the reference (76.9 MPa). The premature failure of this sample typology can be attributed to the geometry of the recovered material which is in form of particles that, in conjunction with physical porosities that generate into the fibre-matrix system during the production phase, acts as preferential surface where internal cracks propagate leading to the failure of the sample. Analogous conclusions can be drawn when the same fibre typology is used with the compression moulding technique (POWDER_CM sample). As highlighted in Table 1, this production technology leads to an increase in fibre volume fraction and then to an overall improvement of the elastic modulus and flexural strength respectively of almost +23.7% and +12.7% (respectively 4.7 GPa and 69.2 MPa) in comparison with the POWDER_OM sample. However, although the increase of the fibre's content, it is possible to assert that the flexural behaviour is still strongly influenced by the geometry of the recovered fibres, because the POWDER_CM sample revealed a reduction of the flexural strength of almost -10% in comparison with the pure resin sample. As well as for the POWDER_OM sample, the premature failure can be attributed to the dimension of the reinforcement that generates preferential cracks propagation surfaces.

On the other hand, when fine fibres are used for the production of recycled material (FINE_OM sample), it is possible to appreciate the effect of the reinforcement geometry over the mechanical properties since this sample typology revealed an increase of both the elastic modulus and flexural strength of almost +23.7% and +40.5% (4.7 GPa and 86.3 MPa) respectively if compared with the POWDER_OM type and around +113.6% and +12.2% respectively in comparison with the reference sample. However, the slight properties increase of FINE_OM sample respect to the reference can be attributed to the well-known poor adhesion efficiency between recovered fibres and new matrix that generates pull-out and debonding phenomena. A magnification of the mechanical recycled materials (Figure 4) shows the presence of residues of old matrix on the fibre's surface that is responsible for the poor adhesion efficiency then, for the reduced mechanical properties. However, the mechanical properties can be further affected by residual porosities that generate in proximity of fibre agglomerations (Figure 5), that as well as for the sample typologies reinforced with the shortest recycled fibres, act as cracks propagation ways. Interesting results can be observed when recovered fibres with the same dimensions reinforce a recycled composite material produced with the compression moulding technique. In this case, the increase in the fibre volumetric percentage leads to an improvement in the elastic modulus and flexural strength of respectively +59.6% and +35.8% (7.5 GPa and 117.2 MPa) in comparison with the FINE_OM sample. However, the FINE_CM sample revealed very interesting mechanical properties since if compared with the pure resin, it is characterised by an elastic modulus that is more than doubled (+240%) and a flexural strength that is almost 52.4% higher; therefore, it is possible to appreciate the contribution over the flexural properties of the recovered fibres.

Among the samples produced with the open mould process, the best results were achieved with the COARSE_OM sample since it revealed an improvement in the flexural properties of almost +313.6% (9.1 GPa) in modulus and +28.1% (98.5 MPa) in flexural strength if compared with the reference sample. However, an insight on the flexural curves revealed a clear drop of the flexural stress in correspondence of the failure of the FINE_OM sample; therefore, as well as that sample typology, it is possible to ascribe the failure of the COARSE_OM sample to the same mechanism that characterise the FINE_OM one.

All the issues about the presence of residual porosity into the composite material, poor adhesion at the fibre-matrix interface and the instauration of debonding and pull-out mechanisms are in part overcome with the compression moulding process. Indeed, even if the COARSE_CM sample

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revealed a flexural modulus that is comparable with that of the COARSE_OM one, it is characterised by an increased flexural strength of almost 24.4%. However, these results are not fully encouraging since this sample, although it is produced with the same production technology, revealed a flexural strength that is just +4.5% higher than the FINE_CM sample. A further focus on the bending curve of the COARSE_CM sample revealed the presence of a clear stress drop on the loading portion of the curve and a not sharp failure behaviour. However, despite the COARSE_OM sample, these singularities are typical of a progressive bending failure of the fibre bundles that reinforce the recycled composite material.

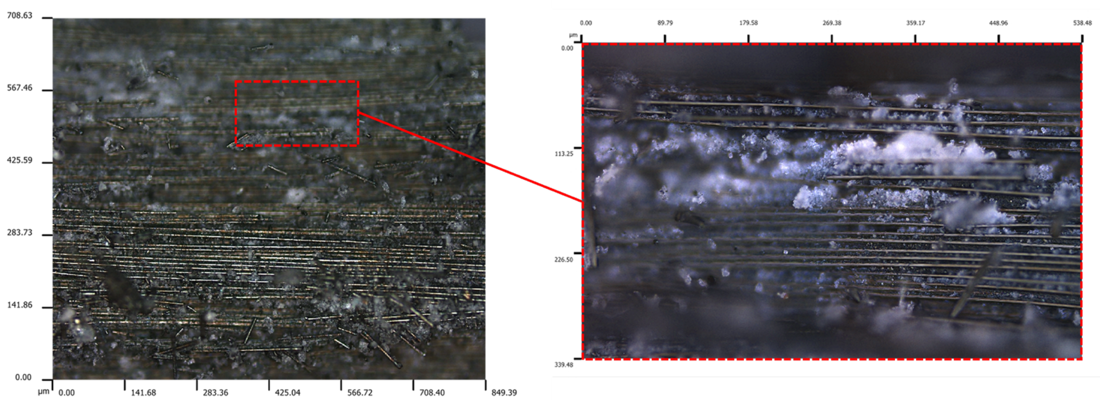

Figure 4: *Magnification of the milled fibres with residues of old matrix on their surface*

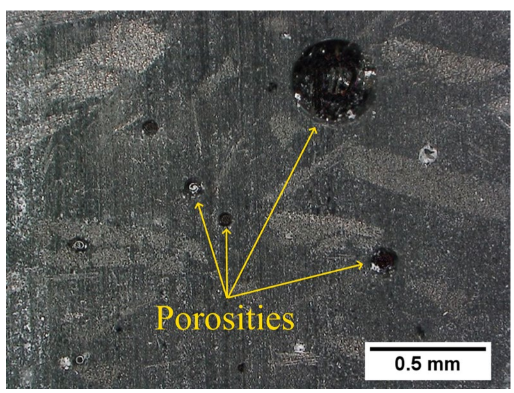

Figure 5: *Residual porosity localised in proximity of fibre agglomerations*

Conclusions

In the present research work it is done a preliminary study on the mechanical recycling process of CFRP material by using the milling method and on the application of different production strategies to obtain recycled CFRP materials. At the end of the experimental campaign, it was pointed out that by using the same production technique, the flexural properties are affected by the chip's geometry since an increase in dimension leads to an improvement of the mechanical properties of the recycled material. For both the production techniques analysed in the present study, the use of the reinforcement in form of powders leads to a recycled material with mechanical properties that are globally lower than the reference. In case of open mould production process, fine and coarse fibres reveal a flexural strength that is respectively +12.2% and +28.1% higher than the pure resin. However, it was showed that the open mould technique limits the mechanical properties of the recycled composite materials since it is responsible for the formation of residual porosity and the occurrence of debonding and pull-out mechanisms. These limitations can be overcome with the compression moulding strategy since it is able to emphasise the properties of the recovered fibres with an increase of the flexural strength of almost +52.4% and +59.3% respectively of FINE_CM and COARSE_CM samples in comparison with the reference in pure resin.

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