Materials Research Proceedings 28 (2023) 1683-1688 https://doi.org/10.21741/9781644902479-181

Unconventional method for recycling CFRPs by using a milling process

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Keywords: CFRPs, Mechanical Recycling, Machining, Impregnation, Bending

Abstract. Composite materials are increasingly employed in many industrial sectors (transportation, infrastructure, electronics). Among the others, carbon fibers are used primarily as reinforcing agents in high-performance composites with synthetic resin matrices such as epoxies, polyimides, vinyl esters, phenolics, and certain thermoplastics. However, when carbon fibers were coupled with a thermosetting matrix, the resulting composites are not easily recyclable. When these products reaching their end-of-life (EoL) there are several difficulties in their recycling and in the reuse of the carbon fiber reinforce. There are several recycling process methods, but one of the most promising and investigated in the last years is the mechanical one that differently from other approaches do not require the use of high temperature or chemical substances to decompose the polymeric matrix. Respect to known mechanical recycling methods like shredding, crushing and hammer milling process, in this work is presented a mechanical recycling that mainly consists in the use of an un-conventional milling process in order to obtain carbon/epoxy chips. Different chips in terms of geometry and size were obtained by fixing the milling process parameters, so the results in terms of chip morphological characteristic were presented. CFRPs chips, after sieving, were then used to manufacture new CFRPs laminates produced starting from recycled materials.

Introduction

Carbon fiber reinforced plastic (CFRP) materials are attracting a significant interest in our day-to-day life because of their interesting mechanical properties combined with the low weight [1].

It is not a surprise that their demand over the last 40 years is grown more and more and during these last years, although the COVID pandemic, the CFRP growing demand reached a current rate of 11% per year due to the increasing need of lightweight materials in different industrial fields. It was estimated that the CFRPs demand was around 120 kTons during the present year [2,3].

It is worth to note that the growing demand of CFPRs is directly connected with an increasing production of virgin carbon fibres (vCF) with expensive and energy intensive processes that generates gases such as ammonia (NH_3), carbon monoxide (CO), carbon dioxide (CO_2) nitrogen oxides (NO_X) and other volatile compounds [4].

It was calculated by a Life Cycle Assessment (LCA) analysis that the amount of energy required for the production of vCF is almost 198 - 595 MJ/kg [5] compared with 13 - 32 MJ/kg required for the production of virgin glass fibre (vGF).

In addition to these considerations, it have to be considered that the growing demand of CFRPs will dramatically increase the amount of waste derives both from scraps produced during the manufacturing of composite products and from the end-of-life products; this latter represents the majority part. A defined waste management and a recycling policy are then required since it is estimated an increasing of CFRP waste of around 20 kTons annually by 2025 also considering that

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around 6000 - 8000 commercial aircrafts (with CFRP components) will reach their end-of-life by the 2030 [6,7].

Based on these considerations, it is clear that there is a strong need to recycle CFRPs by adopting an appropriate recycling process that is in the same time cheap, eco-sustainable, suitable for the industrial scale-up and able to obtain rCF to produce recycled CFRPs with interesting mechanical properties. Among different recycling processes, usually classified in chemical, thermal and mechanical processes, one of the most promising for the future is represented by the mechanical one. Chemical e thermal methods were widely investigated in the last years [8,9] and in spite of interesting mechanical properties are achieved by composites produced using these rCF, both methods are characterized by high costs, specific laboratory apparatus that can obstacle an easy industrial scaling up, long processing time and environmental impact.

The mechanical method is usually used to indicate a broader process's categories such as shredding, crushing and hammer milling that lead to a composite fragmentation into small pieces. An overview on the mechanical recycling process [5,10] leads to the conclusion that these methods produce short recovered fibers that due to their geometrical characteristics, size and the presence of residual matrix, severely affect the overall mechanical properties of the recycled composite material [11]. All these aspects compromise the use of mechanical recycled composite as load bearing structure limiting their use sometimes as fillers in low properties composite materials such as SMC and BMC. In addition, the use of shredding or hummer-milling process implies the use of ad-hoc industrial machine with low flexibility and big size.

To overcome this limitation, in this work it is studied the possibility to use the milling process as mechanical recycling method in order to obtain carbon/epoxy chips used to produce recycled CFRP laminates.

Materials and Methods

The CFRP materials used in this experimental campaign were manufactured using 20 unidirectional carbon/epoxy prepregs (0.2 mm in thickness) supplied by Toray. Composite laminates $(0/90)_{20}$ were produced using the compression molding process under a pressure of 8 bar and a temperature of 130°C for 8 hours. At the end of the polymerization phase, the cured composite laminates (4 mm in thickness) were cut in plate 200 mm x 200 mm to allow the machining of the CFRP material. For this purpose, a CNC machine (C.B. Ferrari) and a three flute HSS end mill tool (20 mm in diameter) were used for the peripheral down-mill machining of the produced samples. A radial depth of cut of 3.00 mm with a feed rate, *f*, of 1000 mm/min and a spindle speed, *s*, of 1000 rpm were adopted as machining parameters.

The obtained CFRP chips were then sieved using a shaking table aiming to achieve a satisfying separation between fine and coarse fibers (mean size > 0.1 mm) from powders (mean size < 0.1 mm).

Therefore, in order to produced recycled CFPR samples, the obtained chips were manually impregnated with an epoxy resin and placed in a mold at room temperature for 24 hours. Different typologies of samples were produced, they mainly differ in the size of the recycled reinforcement (greater or smaller than 0.1 mm) and in its percentage weight content equal to 14, 17, 20 and 25%. Then, the flexural behavior of each sample typology was investigated according to ASTM D790 standard testing three specimens for each sample typologies. For this purpose, three-point bending tests were carried out using a universal testing machine (MTS Alliance RT/50) equipped with a 1 kN piezoelectric load cell. Specimens (120 mm x 21 mm x 4 mm) were tested using a span length of 64 mm (span to depth ratio equal to 16). Three un-reinforced samples are also tested as reference. The flexural strength was calculated by means of the following equation:

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

where σ_f is the maximum stress in the outer fibers at midpoint, F is the maximum load of the load-deflection curve, b is the width of the specimen, t is the thickness of the specimen and L is the support span. The flexural elastic modulus was evaluated as the ratio, within the elastic limit, of stress to corresponding strain.

Results and Discussions

The machining operation of virgin CFRP samples produced chips of different sizes. In detail, the results after sieving are reported in Table 1 and in Fig. 1 are showed typical chip images for each sieving size.

Table 1. Size dimension distribution of CFRP chips obtained after the machining operation.

	Chip size <0.1 mm	**Chip size >0.1 mm**	**Chip size >0.3 mm**	**Chip size >1.5 mm**
Weight content [%]	3.49	20.96	40.98	34.57

In Fig. 2 is instead reported the results of the bending tests. The flexural stress-strain curves can give precious indication about the mechanical properties of the recycled samples in terms of interfacial adhesion efficiency between the surface of the recovered fibers and the new epoxy matrix. In detail, it was observed that for samples produced by using recycled materials with a mean size smaller than 0.1 mm the results were not affected by the reinforcement weight content.

Then, for a better readability of the results, in Fig. 2 it is plotted only one stress-strain curve for representing this sample category.

The results showed that all reinforced samples are characterized by a linear elastic response with a reduction of the strain at breaking in comparison with the reference sample type (pure epoxy sample); this difference decreases as the reinforcement content increases.

Looking at both Fig. 2a and 2b it is clear that the sample reinforced with rCF smaller than 0.1 mm showed the worst performances and despite a flexural modulus improvement respect to reference sample (around 40%) an evident reduction of both the strain at breaking and the flexural strength was detected. The reduction of the flexural strength is due to the small size of the reinforcement phase that acted more as defect than as reinforce, in addition it barely can stop the propagation of internal cracks nucleated in proximity of possible porosity within the sample.

Differently, when the reinforcement phase was represented by rCF chips with a mean size greater than 0.1 mm both the flexural strength and modulus were higher than those of the reference sample and they increase as the rCF chips weight content increases. In detail an increasing of about +46% of the flexural strength was detected when 25 wt.% of rCF chips was adopted.

In spite of this interesting results, it has to be considered that the mechanical properties achieved following this method do not allow the use of this recycled composite for structural applications where high performance are required. This is due to two main reasons: (i) the obtained rCF are short fiber, then the properties cannot reach those of long fibers and (ii) the mechanical recycled fibers are characterized by the presence of matrix residues on their surface and this involves a reduced adhesion efficiency between the recovered fibers and the new resin. By way of example, in Fig. 3 it is showed a magnification of a rCF chip where it is evident the presence of residual matrix on its external surface.

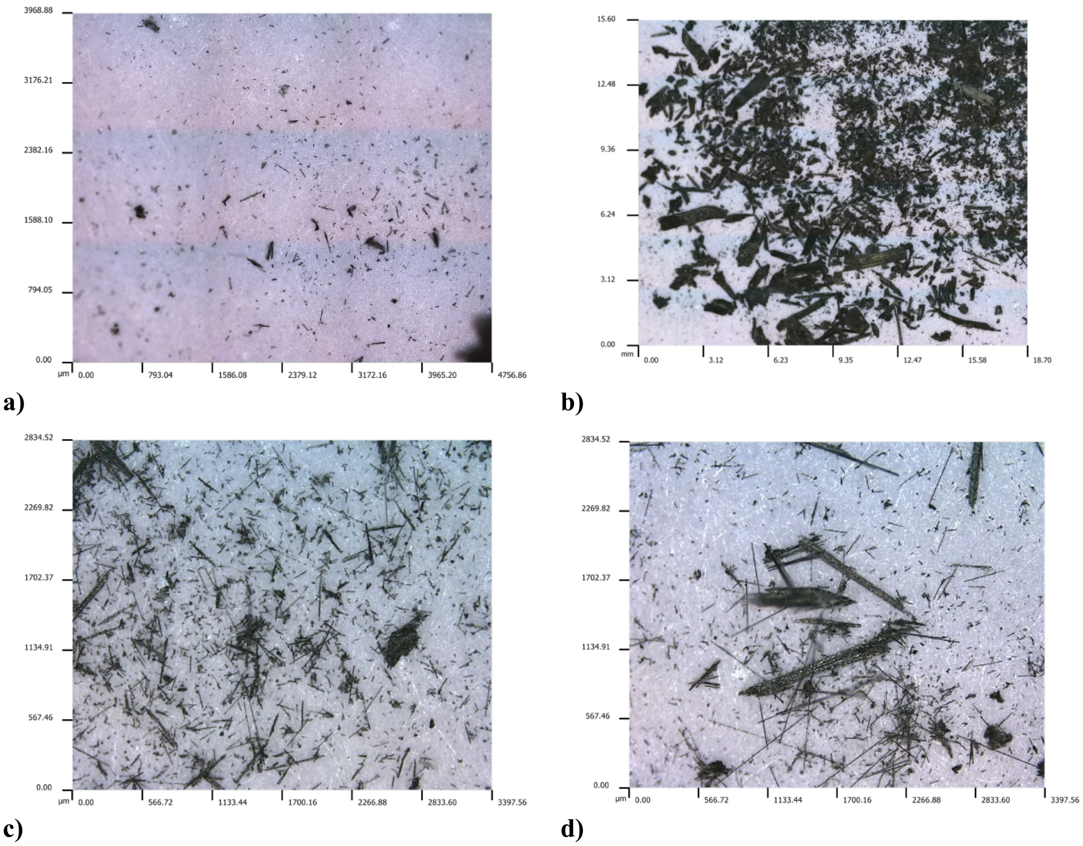

Fig. 1. Typical chips obtained after the milling process: size dimension <0.1 mm (a), size dimension >0.1 mm (b), size dimension >0.3 mm (c), size dimension >1.5 mm (d).

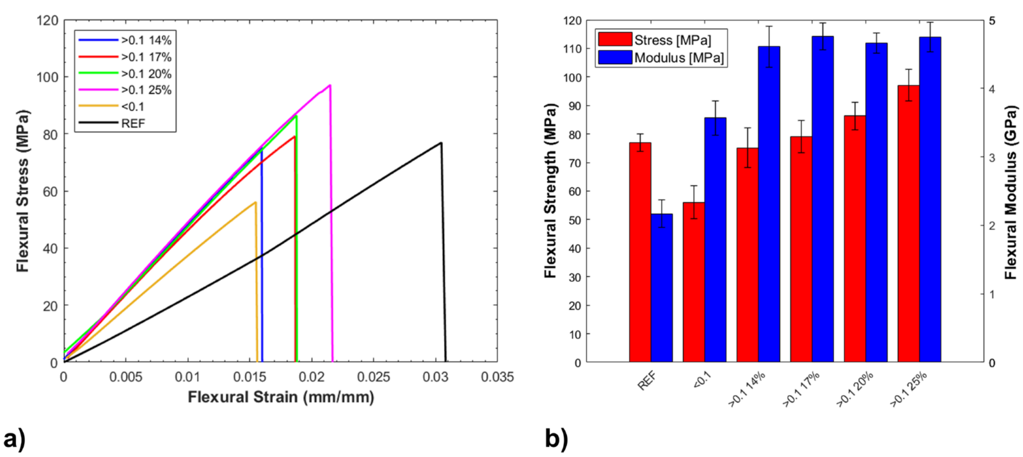

Fig. 2. Typical stress-strain curves (a) and mean flexural strength and modulus (b) for each sample category.

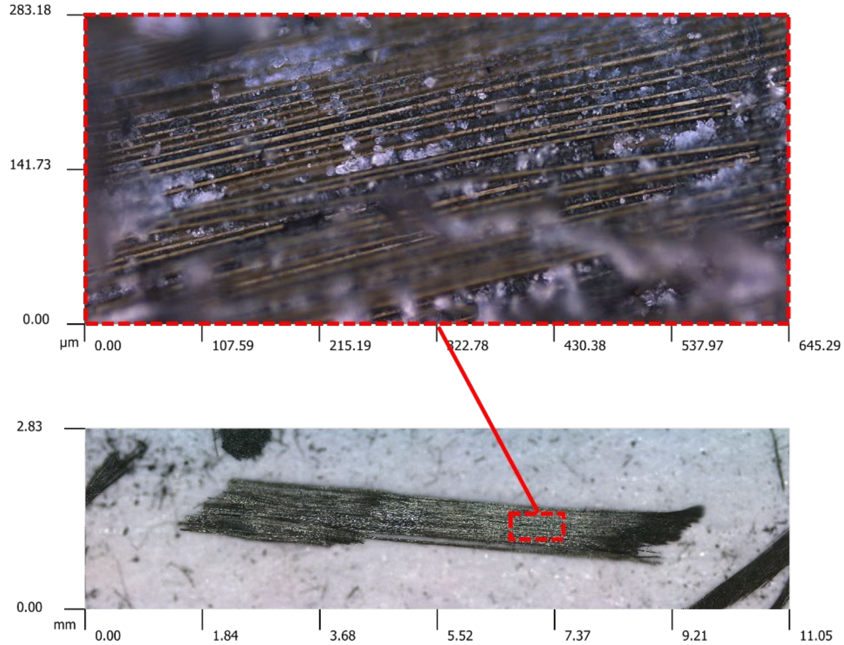

Fig. 3. Details of a rCF chip with the presence of residual matrix on its surface.

Summary

In this work it was presented a preliminary study on the use of a milling process to obtain rCF chip usable as reinforcement for the production of recycled CFRPs. The results showed that the flexural properties were affected by the rCF chip size, in particular the use of the smallest one (mean size < 0.1 mm) did not involve any advantages, contrary to what obtained when greater rCF chips were adopted. Indeed, the use of rCF chips with a mean size greater than 0.1 mm allowed the production of recycled CFRPs characterized by a flexural strength 46 % higher respect to pure epoxy sample. The results showed that according to the proposed procedure, it is possible to use the recycled carbon fibres as reinforcement of the epoxy resin reaching a flexural strength of around 100 MPa and a flexural modulus of around 115 GPa.

It is also important to note that after sieving, it was highlighted that only 3.9 wt.% of the rCF chips was comprised of those with a mean size smaller than 0.1 mm. This means that the proposed recycling procedure is characterized by a high efficiency since the 87.1 % of the obtained waste can be successfully reutilized to produce recycled CFRPs.

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