Mechanical and chemical combined recycling process for CFRP scraps

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Abstract. Composite materials are increasingly employed in many industrial sectors. Among others, carbon fibers are primarily used 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 are coupled with thermosetting matrices, the resulting composites are not easily recyclable. When these products reach their end-of-life (EoL), there are several difficulties in their recycling and in the reuse of the carbon fiber reinforcement. Several recycling process methods exist, but one of the most promising and investigated in recent years is the mechanical one, which, unlike other approaches, does not require the use of high temperatures to decompose the polymeric matrix. However, the presence of residual matrix on the surface of the fibers negatively affects their potential reuse for the production of new composites. In comparison to well-known mechanical recycling methods such as shredding, crushing, and hammer milling processes, this work presents a combined recycling process comprising mechanical recycling by milling and a soft chemical treatment at temperatures significantly lower than those reached during conventional thermal recycling processes. Recycled fibers were then used to produce new composite laminates using an epoxy resin as the matrix. The effects of the chemical treatment on the adhesion between recycled fibers and the new resin were evaluated through pull-out and bending tests.

Introduction

The growing exploration of lightweight structural materials with enhanced mechanical properties positions Carbon Fiber Reinforced Polymers (CFRPs) as a highly appealing alternative to their metallic counterparts. The growing demand for this material category in recent decades stems from its inherent tailorability and design flexibility, allowing for extensive use across different sectors such as aerospace, marine, automotive, and energy [1-5].

Indeed, there has been a noticeable surge in the demand for CFRP in these industrial fields, reaching around 70 kTons in 2010 and escalating to almost 170 kTons in 2020 [6]. It is important to highlight that the increasing demand for CFPRs is directly linked to an escalating production of virgin carbon fibers (vCF). This involves costly and energy-intensive processes that result in the emission of various gases, including ammonia (NH_3), carbon monoxide (CO), carbon dioxide (CO_2), nitrogen oxides (NO_X), and other volatile compounds. A Life Cycle Assessment (LCA) analysis revealed that the energy consumption for vCF production ranges from approximately 198 to 595 MJ/kg [7], significantly higher than the 13 to 32 MJ/kg required for the production of virgin glass fiber (vGF). However, a further increase is anticipated in the imminent future, as it is estimated that the demand for carbon fiber composite materials will rise to around 190 kTons by 2050 [6, 8]. Consequently, the substantial amount of CFRP materials in all industrial sectors will inevitably lead to an increase in the volume of waste materials that must be managed when they are decommissioned at the end of their life cycle.

In this context, there is a clear imperative for a secondary application of these materials, aligning with the principles of a circular economy. This approach seeks to reuse discarded materials, concurrently reducing additional waste production and the use of harmful chemicals [9].

Recognizing the imminent challenge posed by the disposal and waste management of end-of-life CFRPs, the European Union has implemented directives like 2008/98/EC and 2000/53/EC. These directives focus on principles of prevention, smart utilization of composite materials, incorporation of recycled fibers into new industrial products, and pollution payment [8, 10].

Presently, a significant portion of discarded materials typically ends up in landfills or is incinerated to generate energy. 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 fibers [11]. In contrast, composite recycling processes comprising thermal, chemical, and mechanical methods, emerges as a more sustainable process aligning with circular economy principles [12]. Chemical and thermal methods have been widely investigated in recent years, and despite achieving interesting mechanical properties in composites produced using these recycled carbon fibers (rCF), both methods are characterized by high costs, specific laboratory apparatus that can impede easy industrial scaling up, long processing times, and environmental impact [13].

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 [14].

A survey of mechanical recycling processes [8] indicates that these techniques result in the generation of short recovered fibers. Due to their geometric features, size, and residual matrix content, these fibers significantly impair the overall mechanical properties of the recycled composite material. Such limitations pose challenges to the utilization of mechanically recycled composites as load-bearing structures, restricting their application to occasions where they can serve as fillers in composite materials with lower properties. Furthermore, the adoption of shredding or hammer-milling processes necessitates the use of specialized industrial machinery, characterized by low flexibility and substantial size.

To attempt to overcome these aspects, this study explores the possibility of using a combination of two processes (mechanical and chemical), aiming to harness the advantages of each one while mitigating their respective drawbacks. In detail, the study considered the use of a soft chemical treatment based on acetone applied to coarse fibers obtained from a mechanical recycling process through milling. Consequently, the effect of the chemical treatment on the adhesion strength between fibers and matrix, as well as the flexural properties of recycled samples, was investigated.

Experimental Procedure

For the experimental campaign, carbon fibers tows were manually extracted from a 200 g/m^2 twill wave carbon/epoxy prepreg (150 mm x 150 mm) supplied by Toray. Each tow was placed on a mould plate, paying attention to the optimal alignment of the fibres, and then cured using the compression molding technique at 150 °C for 8 hours with a pressure of approximately 0.8 MPa. At the end of the polymerization phase, all tows were carefully cut into bundles characterized by an overall length of almost 100 mm. Therefore, aiming to understand the effect of the chemical treatment on the adhesion efficiency between the carbon fibers and a new epoxy matrix, the polymerized tows were treated with a peroxide and acetone solution (H_2O_2 20wt.% and C_3H_6O 80wt.%). Subsequently, 10 tows were placed in a cylindrical stainless-steel vessel (110 mm in length and 28 mm in diameter) tightly sealed together with 30g of the chemical solution. The vessel was placed in an oven for 1 hour, and two treatment temperatures were investigated: 100°C and 200°C.

At the end of the chemical treatment, the tows were cooled in air to room temperature and then washed with acetone to remove any trace of the dissolved matrix from the fiber surface.

To produce pull-out samples for both untreated and treated tows, they were immersed in a resin bath (Fig. 1). However, before resin casting, the same prepreg fabric used earlier was employed as tabs applied to the free end of the carbon tow. A total of 3 carbon tows were aligned on the tab, allowing for curing through the compression molding technique at 150 °C for 1 hour with a pressure of approximately 0.3 MPa.

Subsequently, the carbon tows were embedded for a length of 5 mm in an SX10 epoxy resin supplied by Mates and were held upright to ensure the defined embedded bundle length. The epoxy resin was then allowed to cure for a period of 24 hours at room temperature. At the end of the sample preparation, scissors were used to separate the specimens from each other.

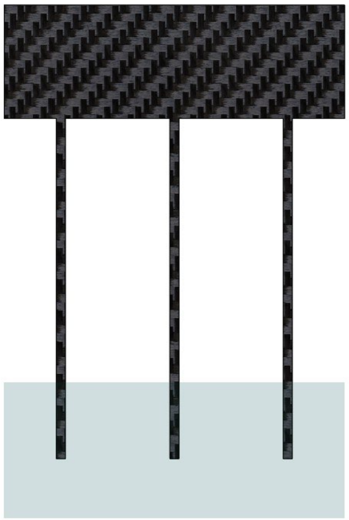


Figure 1. Pull-out samples configuration (image not to scale).

Pull-out tests were conducted using a universal testing machine MTS Alliance RT/50 equipped with a 1kN piezoelectric load cell. A tensile load was applied along the fiber direction of all samples under inspection adopting a testing speed of 1 mm/min.

After evaluating the effect of the chemical treatment on fiber/matrix adhesion, samples for flexural testing were produced using recycled fibers. To achieve this, 20 layers of CFRP pre-preg were used to manufacture a virgin CFRP laminate (200 mm x 200 mm x 4 mm) through the compression molding process. After the laminate polymerization, it underwent a mechanical recycling process through milling. 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 laminate. Machining parameters included a radial depth of cut of 3.00 mm, a feed rate (*f*) of 1000 mm/min, and a spindle speed (*s*) of 1000 rpm.

The resulting CFRP chips were then sieved using a shaking table to achieve satisfactory separation between fibers with a mean size > 0.1 mm (referred to as coarse fibers) and powders (mean size < 0.1 mm). The powders were discarded and not used in this study. Subsequently, the coarse fibers underwent the chemical treatment as described earlier.

To produce recycled CFPR samples, the obtained recycled fibers (both treated and untreated) were washed in acetone and then dried at 70°C for 30 minutes. Subsequently, the fibers were manually impregnated with SX10 epoxy resin and placed in a mold at room temperature for 24 hours to produce different samples that differ in the type of reinforcement fibers, i.e. treated and untreated. The fiber weight percentage content was fixed at 25%.

The flexural behavior of each sample type was then investigated according to ASTM D790 standard, with three specimens tested for each sample type. For this purpose, three-point bending tests were carried out using the same testing machine adopted for the pull-out test. Specimens (120 mm x 21 mm x 4 mm) were tested with a span length of 64 mm (span-to-depth ratio equal to 16). Additionally, three unreinforced samples were also tested as reference. The flexural strength was calculated by means of the following equation:

$$\sigma_f = \frac{3FL}{2bt^2}$$

All tested specimens were examined using a 3D Digital Microscope HRX-01.

Results and discussions

In Fig. 2, the results of the pull-out tests are presented. These results clearly demonstrate the positive impact of chemical treatments on the adhesion force between the carbon fibers and the epoxy resin. The pull-out force increased by approximately 152% compared to that of untreated fibers when a chemical treatment at 100 °C was performed and by about 252% for the chemical treatment at 200 °C. These enhancements can be attributed to the synergistic effects of the constituents in the chemical solution.

Specifically, acetone (C_3H_6O) played a crucial role in cleaning the fibers by removing the original epoxy matrix from the fiber surface. Thorough cleaning is essential to ensure optimal adhesion between the fibers and resins.

On the other hand, hydrogen peroxide (H_2O_2) was employed to activate the surface of the fibers through a controlled oxidation process. As a known oxidizing agent, hydrogen peroxide enhanced the chemical reactivity of the fiber surface, thereby increasing their susceptibility to chemical bonding with polymeric resins, such as epoxy resins.

These results were further validated by examining Fig.3, where the samples at the end of the pull-out tests were illustrated. In this figure, the embedded length was denoted as L1, and the capillary rise length was denoted as L2. Notably, the capillary rise length exhibited an increase when the chemical treatment was applied, reaching its peak value of approximately 1760 μm at a treatment temperature of 200 °C. The capillary rise length is directly linked to the wettability of the fibers by the resin; hence, a higher length signifies improved wettability.

v

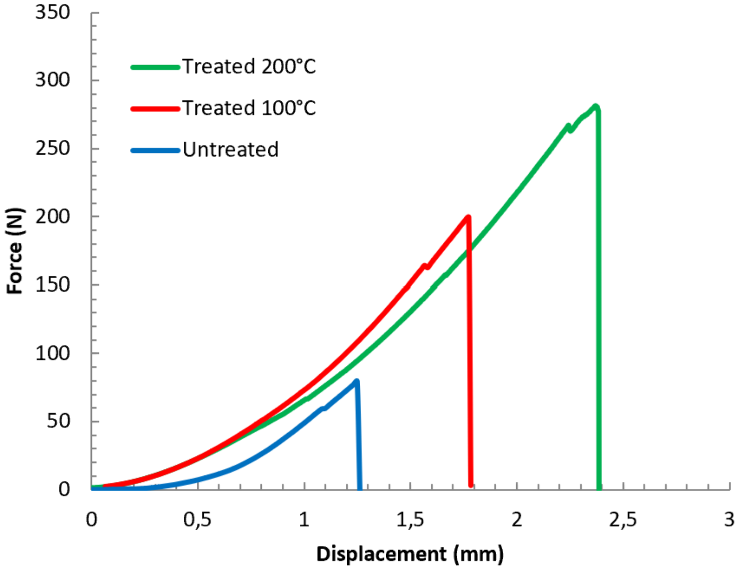


Figure 2. Typical force vs displacement curves carried out from the pull-out test for each sample type.

It is also interesting to note that on the portions of the untreated carbon tow that was immersed in the resin (Fig.3a), the surface appears quite smooth and free of matrix residues, suggesting a relatively low adhesion with the epoxy resin SX10. In contrast, for the treated carbon tow, the presence of residual epoxy resin was observed (Fig.3b). It is important to highlight that no fiber failure have ever been observed and that all samples at the end of the test appeared as depicted in Fig.3c, where, by way of example, a specimen treated at 200°C is shown. To obtain the tows depicted in Figs.3a and 3b, these were manually removed from the resin mortar.

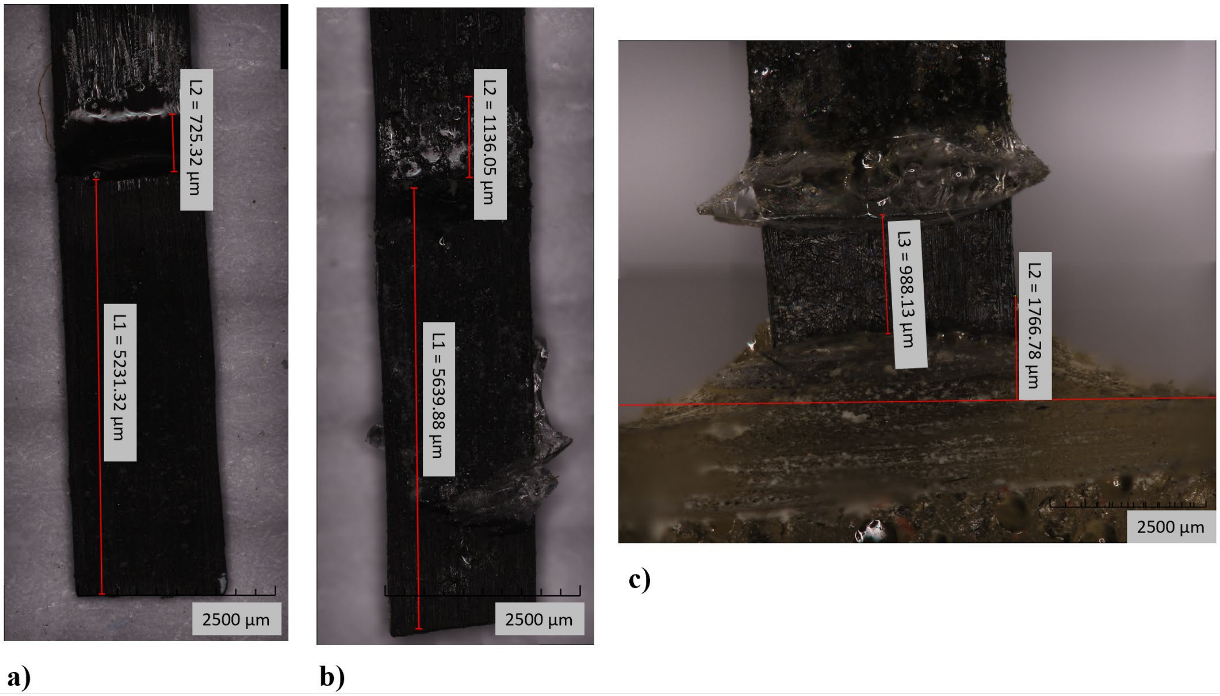


Figure 3. Typical samples at the end of the pull-out tests: a) untreated fibres, b) treated fibres at 100 °C and c) treated fibres at 200 °C.

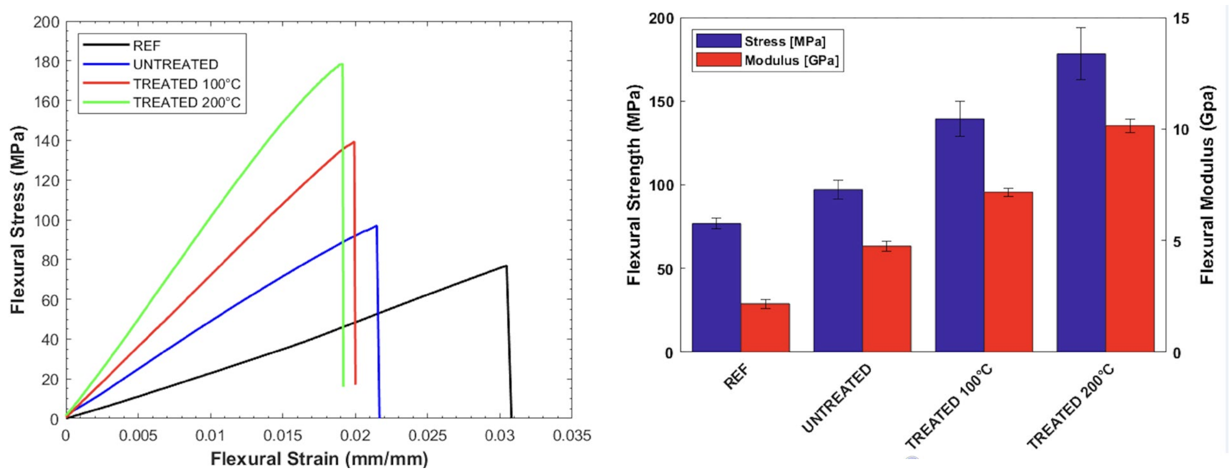
Interesting results were also obtained from the three-point bending tests. In Fig.4, the results of the bending tests are presented, including a reference representing an unreinforced sample type.

The flexural stress-strain curves offer valuable insights into the mechanical properties of the recycled samples in terms of the interfacial adhesion efficiency between the surface of the recovered fibers and the new epoxy matrix.

Specifically, it was observed that all reinforced samples exhibit a linear elastic response with a reduction in the strain at breaking compared to the reference sample type (pure epoxy sample). However, they exhibited higher flexural strength and modulus. The results emphasize how the chemical treatment significantly influences the flexural properties, both in terms of strength and modulus. The flexural strength of specimens reinforced with fibers subjected to chemical treatment, at 100°C and 200°C respectively, experienced an increase of approximately 55% and 100% compared to samples reinforced with untreated fibers. Similarly, the flexural modulus showed an increase of about 75% and 155%, depending on the treatment temperature.

These results were further confirmed by examining Fig.5, where typical samples at the end of the bending tests were reported. It is possible to highlight that the sample reinforced with untreated recycled fibers (Fig.5a) is significantly affected by pull-out and fiber bundle debonding phenomena near the failure region. As observed in the pull-out tests, the surface of the untreated reinforcement is devoid of any trace of the epoxy matrix. This condition can be attributed to the poor adhesion between the untreated recovered fibers and the new matrix.

On the other hand, when observing the sample produced with the treated recovered reinforcement (Fig.5b), a well-defined failure region with limited fiber pull-out phenomena can be detected. In addition, compared to the untreated sample, the individual fibers that characterize the tow are discernible due to the chemical treatment that dissolved the old matrix within the fiber bundle. Moreover, as highlighted in Fig. 3, traces of epoxy resin residues are observed on the fiber's surface, indicating increased adhesion at the fiber-matrix interface. These factors contribute to the enhanced flexural properties exhibited by the treated sample.



a) **b)**

Figure 4. Typical stress-strain curves (a) and mean flexural strength and modulus (b) for each sample category.

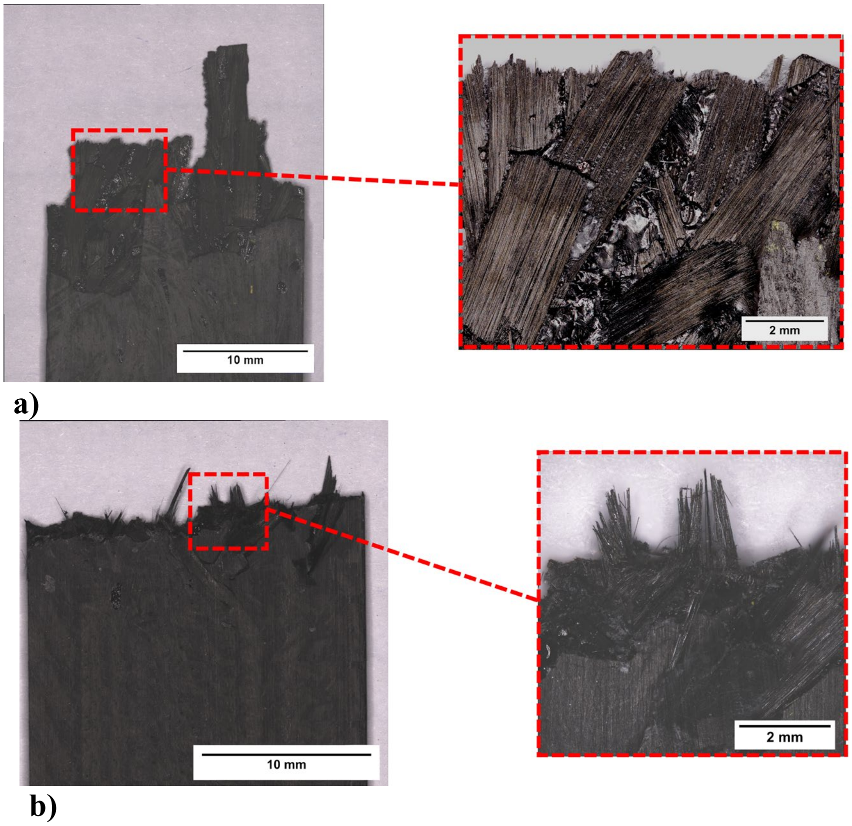


Figure 5. Typical detail area of the fracture zone of specimens at the end of the flexural test: (a) specimen reinforced with untreated fibres, (b) specimen reinforced with fibres treated at 200°C.

Conclusions

In this study, a preliminary investigation into the potential utilization of a mechanical recycling process involving milling, combined with a soft chemical process using a solution based on acetone and peroxide, has been presented. The results demonstrate that mechanical milling can be a valuable approach for mechanical recycling, utilizing common CNC machines. This is in contrast to the common use of shredding or hammer-milling processes, which implies the use of dedicated industrial machines with low flexibility and large size.

The use of soft chemical treatment has indeed proven effective in removing the residual matrix from the fibers. In contrast to common chemical recycling processes, no particularly hazardous solvents or excessively high temperatures were employed.

Pull-out test results have shown that the adhesion strength between chemically treated carbon tows and the new epoxy resin can increase by 250% compared to untreated tows. This result is further emphasized by bending tests conducted on specimens consisting of recycled short fibers and epoxy resin as the matrix. In this case, increases of 100% and 155% were observed, respectively, for flexural strength and flexural modulus.

References

[1] F. Pinto, L. Boccarusso, D. De Fazio, S. Cuomo, M. Durante, M. Meo, Carbon/hemp bio-hybrid composites: Effects of the stacking sequence on flexural, damping and impact properties, Compos. Struct. 242 (2020) 112148. https://doi.org/10.1016/j.compstruct.2020.112148

[2] P. Boisse, R. Akkerman, P. Carlone, L. Kärger, S.V. Lomov, J.A. Sherwood, Advances in composite forming through 25 years of ESAFORM, Int. J Mater. Form. (2022) 15-39. https://doi.org/10.1007/s12289-022-01682-8

[3] A. Viscusi, M. Durante, A. Astarita, L. Boccarusso, L. Carrino, A.S. Perna, Experimental Evaluation of Metallic Coating on Polymer by Cold Spray, Proc Manufact. 47 (2020) 761-765. https://doi.org/10.1016/j.promfg.2020.04.232

[4] I. Papa, P. Russo, A. Astarita, A. Viscusi, A.S. Perna, L. Carrino, V. Lopresto, Impact behaviour of a novel composite structure made of a polymer reinforced composite with a 3D printed metallic coating, Comp. Struct. 245 (2020) 112346. https://doi.org/10.1016/j.compstruct.2020.112346

[5] A. Formisano, L. Carrino, D. De Fazio, M. Durante, A. Viscusi, Enhanced Aluminium Foam Based Cylindrical Sandwiches: Bending Behaviour and Numerical Modeling, Int. Rev. Model. Simul. 11 (2018). https://doi.org/10.15866/iremos.v11i4.15631

[6] Y. Yang, R. Boom, B. Irion, D.J. Van Heerden, P. Kuiper, H. de Wit, Recycling of composite materials, Chem. Eng. Process. Process Intensif. 51 (2012) 53-68. https://doi.org/10.1016/j.cep.2011.09.007

[7] F. Meng F, E.A. Olivetti, Y. Zhao, J.C. Chang, SJ. Pickering, J. McKechnie, Comparing Life Cycle Energy and Global Warming Potential of Carbon Fiber Composite Recycling Technologies and Waste Management Options. ACS Sustain. Chem. Eng. 6 (2018) 9854–65. https://doi.org/10.1021/acssuschemeng.8b01026

[8] D. De Fazio, L. Boccarusso, A. Formisano, A. Viscusi, M. Durante, A Review on the Recycling Technologies of Fibre-Reinforced Plastic (FRP) Materials Used in Industrial Fields, J. Mar. Sci. Eng. 11 (2023) 851. https://doi.org/10.3390/jmse11040851

[9] E. MacArthur, Towards the circular economy, economic and business rationale for an accelerated transition, Ellen MacArthur Foundation, Cowes, UK, 2013.

[10] S. Gharde, B. Kandasubramanian, Mechanothermal and chemical recycling methodologies for the Fibre Reinforced Plastic (FRP), Environmental Technology & Innovation, 14 (2019) 100311. https://doi.org/10.1016/j.eti.2019.01.005

[11] D. De Fazio, L. Boccarusso, A. Formisano, A. Langella, F. Memola Capece Minutolo and M. Durante, Mechanical recycling of CFRPs: manufacturing and characterization of recycled laminates, Italian Manufacturing Association Conference: XVI AITeM, Materials Research Forum LLC, 35 (2023). https://doi.org/10.21741/9781644902714-48

[12] S.J. Pickering, Recycling technologies for thermoset composite materials-current status, Composites Part A: Applied Science and Manufacturing, 37 (2006) 1206-1215. https://doi.org/10.1016/j.compositesa.2005.05.030

[13] L. Mazzocchetti, T. Benelli, E. D'Angelo, C. Leonardi, G. Zattini, L. Giorgini, Validation of carbon fibers recycling by pyrogasification: The influence of oxidation conditions to obtain clean fibers and promote fiber/matrix adhesion in epoxy composites, Compos. Sci. Technol. 112 (2018) 504-514. https://doi.org/10.1016/j.compscitech.2018.07.007

[14] M. Durante, L. Boccarusso, D. De Fazio, A. Formisano, A. Langella, Investigation on the Mechanical Recycling of Carbon Fiber-Reinforced Polymers by Peripheral Down-Milling, Polymers 15 (2023) 854. https://doi.org/10.3390/polym15040854