



Investigation and Optimization of CFRP Recycling by Pyrogasification Process

Tommaso Amadori,* Emanuele Maccaferri, Jacopo Ortolani, Laura Mazzocchetti, Tiziana Benelli, Stefania Minosi, Stefano Corvaglia, and Loris Giorgini

Carbon fiber reinforced composites (CFRC) are remarkably replacing conventional materials in application requiring high mechanical performance thanks to their light weight and outstanding mechanical properties. Due to the massive increase in their production and application, one of the main drawbacks resides in their disposal, both at the end of their life and as scraps and offcuts. Furthermore, the production of carbon fiber (CFs) requires high energy demand (183–286 MJ kg⁻¹), hence the recovery of composites to reuse CF seems to be a promising option in terms of sustainability and circular economy. With the aim of identifying a methodology to recover and recycle these materials, through this work a case study is shown for optimization of the pyrogasification process.

CFRCs grows from 2018 to 2019 from 128,500 to 141,500 tonnes year⁻¹ and is expected to be around 197,000 tonnes year⁻¹ in 2023.^[4,5] European legislation has imposed more stringent controls on the management of CFRC waste.^[6,7] To date there are several recycling methods for CFRPs, classified into three main types: mechanical, chemical, and thermal recycling. Mechanical recycling involves CFRCs grinding to obtain shreds or powders used as fillers in low-value applications.^[8] Chemical and thermal recycling, on the other hand, are based on more complicated technologies that allow rCF to be obtained with greater added value than mechanical

1. Introduction

Carbon fiber reinforced composites (CFRCs) are increasingly replacing conventional materials in application requiring high mechanical performance, due to their light weight and excellent mechanical properties.^[1–3] As a result, the global demand for

recycling (the length of the starting fibers is maintained).^[9,10] Fibers are completely separated from the matrix from which monomers or petrochemical feedstocks can be recovered. Chemical recycling can be carried out using different operating conditions and solvents. Thermal recycling uses high temperatures to selectively decompose the matrix. One of the most widespread techniques is pyrolysis, which involves the use of an inert atmosphere.^[3] This treatment consumes only 5–10% of the energy required for virgin fiber production and, for these reasons, is the most pursued process on an industrial scale in Europe.^[11] With a view to identifying a methodology to recover and recycle these materials, the aim of this work is to develop a methodology to study and optimize the pyro-gasification process for CFRP scraps, according to the scheme in **Figure 1**.

The materials to be treated can be divided into two types: crude prepreg and cured products, the latter obtained from the processing of the former.

The first part of the work focusses on an in-depth preliminary characterization of the available starting materials used as feeding. In particular, the nature of the polymer matrix of the prepregs has to be investigated by FT-IR spectroscopy (ATR mode) and, secondly, thermogravimetric analyses using TGA needs to be carried out, in order to investigate the degradation kinetics of the polymer matrix and the trend of weight loss as a function of time and temperature. Through TGA analysis, it is possible to determine the optimal degradation temperature ($T > 400$ °C) and the most suitable residence times. The aforementioned data are then used to fine-tune the thermochemical process, implemented in a suitably equipped muffle furnace, still on lab scale. The pyrogasification process involves a double treatment: during the first step (pyrolysis), the samples are treated in an inert atmosphere (N₂) in order to thermodegrade the polymer

T. Amadori, E. Maccaferri, J. Ortolani, L. Mazzocchetti, T. Benelli, L. Giorgini

Department of Industrial Chemistry “Toso Montanari”
University of Bologna

Viale Risorgimento 4, Bologna 40136, Italy
E-mail: tommaso.amadori3@unibo.it

L. Mazzocchetti, T. Benelli, L. Giorgini
Interdepartmental Center for Industrial Research on Advanced Applications in Mechanical Engineering and Materials Technology
CIRI-MAM

University of Bologna
Viale Risorgimento 2, Bologna 40136, Italy

S. Minosi
Leonardo Labs – Materials
Leonardo Spa
Grottaglie, TA 74023, Italy

S. Corvaglia
Aerostructures Division
Leonardo Spa
Grottaglie, TA 74023, Italy

The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/masy.202400020>

© 2024 The Author(s). Macromolecular Symposia published by Wiley-VCH GmbH. This is an open access article under the terms of the [Creative Commons Attribution-NonCommercial](https://creativecommons.org/licenses/by-nc/4.0/) License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.

DOI: 10.1002/masy.202400020

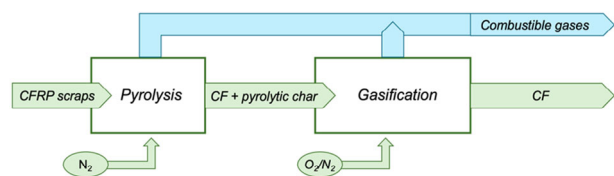


Figure 1. Pyro-gassification process scheme.

matrix; on the other hand, the second phase (gasification) differs from the first in the use of an oxidizing environment (typically air, or oxygen deprived air) in order to decompose the char formed during the pyrolytic step into CO_2 resulting in clean recycled carbon fibers (rCF) where the matrix has been completely removed.

During all tests, the variable investigated and optimized has only been the residence time of both pyrolysis and gasification step, given that during the pyrogasification tests, all samples were placed directly inside the reactor at a temperature above $400\text{ }^\circ\text{C}$, in order to simulate the behavior of an industrial recycling plant (under construction) operating with a continuous feed.

For each treatment the sample weight loss was calculated after each process step. All rCFs obtained were subjected to morphological and statistical characterization: samples considered satisfying were subjected to morphological characterization by scanning electron microscope (SEM) to verify the absence of surface char and possible degradation and measure fiber diameters, mechanical characterization through a single-fiber tensile tests and, finally, atomic mapping (EDX) in order to determine the surface distribution of oxygen and carbon of the rCFs. Mechanical properties and morphological characteristics of rCFs were compared with the respective virgin starting fibers in order to verify both the possible degradation of the fibers (with a consequent decrease in diameters and mechanical properties) and the presence of undegraded residual polymer matrix.

2. Experimental Section

Due to the internal geometry of the muffle furnace, both prepreps and cured materials were cut into small pieces using rotating

blade in order to obtain samples of approximately 10 cm in length and 2 cm in width. For each test performed, the weight loss after both the pyrolysis and gasification step was determined using an analytical balance in order to calculate the percentage of degraded matrix. Samples obtained under the best operating conditions were subjected to morphological and statistical characterization of diameters using SEM through comparison with starting virgin fibers, after metallization with Au/Pd, by sampling a small quantity of the samples, with the following magnifications: $260\times$, $500\times$, $1000\times$, $3000\times$, $5000\times$, $10\ 000\times$. Single-fiber tensile tests were performed with the aim of investigating the effect of pyrogasification treatment on the mechanical properties of recycled fibers compared to virgin fibers. For this purpose, about 15 single fibers per pyrogasification batch and about 30 virgin fibers were tested using a dynamometer equipped with a 10 N load cell, in order to obtain and compare the average values of Young's modulus, tensile strength, and strain %, i.e., those mechanical properties that will later be the most important parameters for new applications of recycled carbon fibers. Due to the small size of the fibers under examination (diameter varying between 5 and $6\ \mu\text{m}$), it was necessary to fix them individually on appropriately sized paper frames (**Figure 2**). The crossbar speed was set to $1\ \text{mm}\ \text{min}^{-1}$ while the length for the useful length was 30 mm.

Thanks to the Energy Dispersive X-ray Spectrometry (EDX) detector combine with the SEM spectroscopy, it was possible to compare the quality of the rCF with the starting virgin fibers. After performing both statistical analyses on the diameters (in order to minimize error) and EDX mappings (to check whether the chosen treatments did not degrade the fibers), it was possible to recalculate the mechanical properties obtained from the single-fiber tensile tests by normalizing the force (N) on the fiber surface (m^2) in order to obtain the mechanical values with Pascal unit.

3. Results and Discussion

The nature of the polymer matrix of the prepreps was investigated by FT-IR spectroscopy (ATR mode) and in the present case study

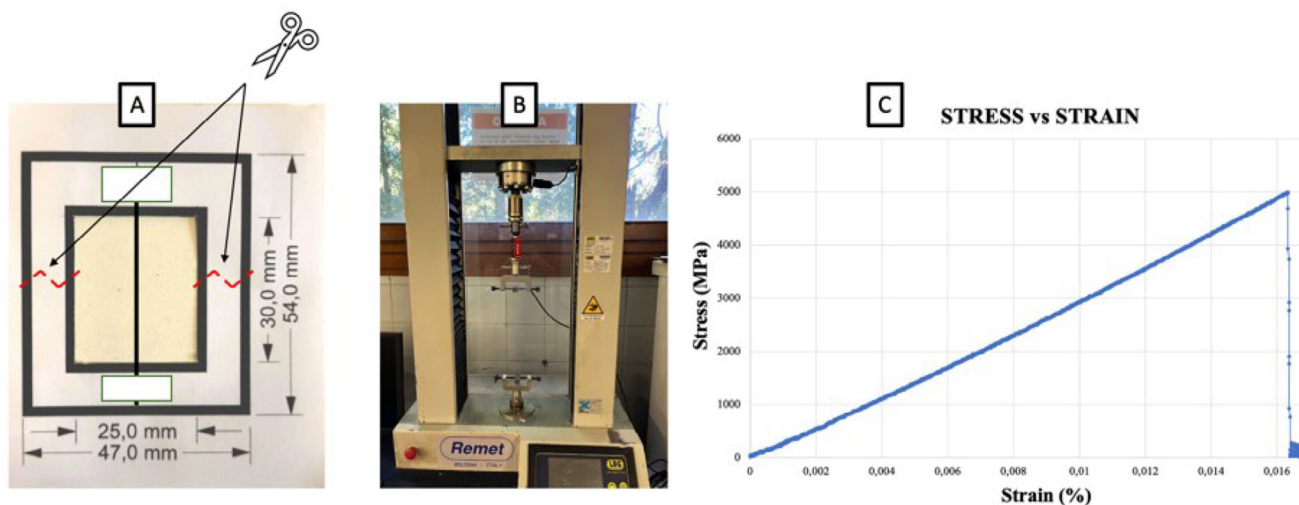


Figure 2. Single-fiber tensile tests: A) sized paper frames, B) dynamometer, C) stress–strain graph.

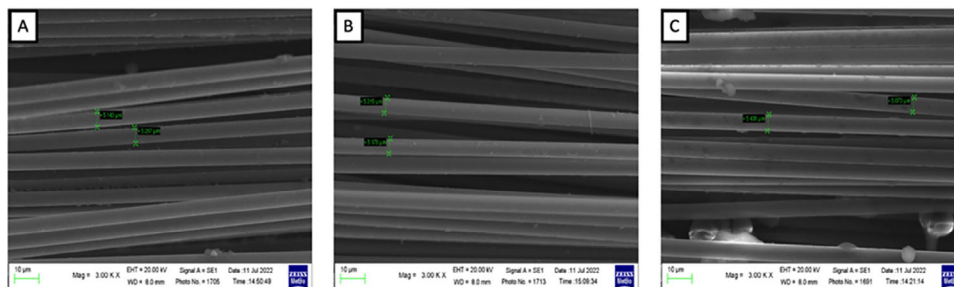


Figure 3. 3000× magnification obtained using SEM: A) prepreg, B) cured material, C) virgin fibers.

it was found to be epoxy resin. The samples were then subjected to thermogravimetric analysis (TGA). These tests determined the optimum working temperature ($T > 400$ °C) and fiber-to-matrix ratio of all tested samples (66–67% by weight). Preliminary information on residence times obtained from TGA analyses was used to fine-tune the thermochemical process on a pilot plant involving first a pyrolysis phase in an inert environment (N_2) and then a gasification phase in an oxidizing environment (O_2/N_2) in a muffle furnace. The samples obtained from the best treatments from the pyrogasification tests at different times were sampled and analyzed using SEM (Figure 3) in order to characterize them morphologically to verify the absence of surface char, possible degradation, and to measure their diameters (comparing them with the relevant virgin fibers).

Considering both CF diameters and the absence of residual matrix of the prepreg and cured material in comparison with starting virgin fibers, it was possible to state that the chosen pyrogasification treatments enabled the quality rCFs to be achieved. Finally, single-fiber tensile tests were performed in order to determine the effect of the pyrogasification treatment, resulting in rCFs that retain about 90% of the mechanical properties compared to the starting virgin fibers.

4. Conclusion

The pyrogasification process can be easily optimized through the fine-tuning of both residence time and temperature, making it possible to obtain recycled carbon fibers with mechanical properties comparable to the virgin starting fibers, which in turn can be used for the production of new products.

Acknowledgements

The authors wish to acknowledge funding from the National Recovery and Resilience Plan (NRRP), Mission 04 Component 2 Investment 1.5 – NextGenerationEU, Ecosyster – Call for tender n. 3277 dated 30/12/2021 Award Number: 0001052 dated 23/06/2022 and European Union – NextGenerationEU for funding via National Sustainable Mobility Center CN00000023, Italian Ministry of University and Research Decree n. 1033 – 17/06/2022, Spoke 11 – Innovative Materials & Lightweighting. T.A. wishes to thank EU – NextGenerationEU with funds made available by

the National Recovery and Resilience Plan (NRRP) Mission 4, Component 2, Investment 3.3 (MD 352/2022) and by Hera SpA for funding his PhD scholarship (CUP: J33C22001390009).

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

carbon fiber, composite, mechanical properties, pyrogasification, recycling, thermal degradation

Received: January 8, 2024

- [1] D. D. L. Chung, D. Chung, *Carbon fiber composites*, Elsevier, Amsterdam **2012**.
- [2] S. Karuppannan Gopalraj, T. Kärki, *SN Appl. Sci.* **2020**, 2, 433.
- [3] L. Giorgini, T. Benelli, G. Brancolini, Mazzocchetti, *Curr. Opin. Green Sustain. Chem.* **2020**, 26, 100368.
- [4] T. K. Das, P. Ghosh, N. Das, *Ch. Adv. Compos. Hybrid Mater.* **2019**, 2, 214.
- [5] M. Sauer, *Composites Market Report 2019*, Carbon Compos. Frankfurt AVK **2019**.
- [6] A. D. La Rosa, D. R. Banatao, S. J. Pastine, A. Latteri, G. Cicala, *Compos. Part B Eng.* **2016**, 104, 17.
- [7] A. D. La Rosa, S. Greco, C. Tosto, G. Cicala, *J. Clean. Prod.* **2021**, 304, 127158.
- [8] Y. Yang, R. Boom, B. Irion, D.-J. van Heerden, P. Kuiper, H. de Wit, *Chem. Eng. Process. Process Intensif.* **2012**, 51, 53.
- [9] B. Wang, X. Wang, N. Xu, Y. Shen, F. Lu, Y. Liu, Y. Huang, Z. Hu, *Compos. Sci. Technol.* **2021**, 203, 108589.
- [10] M. B. M. Zaini, K. H. Badri, *AIP Conf. Proc.* **2014**, 1614, 446.
- [11] G. Scarpone, *Circularità dei Materiali Compositi*, Assocompositi, Milan, Italy **2022**.