RESEARCH ARTICLE

Macromolecular Symposia

www.ms-journal.de

Optimization of Pyro-gasification of Carbon Fiber Reinforced Polymers (CFRPs)

Francesco Montorsi, Gianluca Brancolini, Laura Mazzocchetti, Tiziana Benelli, and Loris Giorgini*

This work focuses on the optimization of pyro-gasification process of carbon fiber reinforced polymers (CFRPs) with the aim of recovering carbon fibers (CFs) with properties suitable for the production of new more sustainable composites with high performances. In particular, the pyro-gasification process is carried out on cured CFRPs panels based on both epoxy (EC) and vinyl ester (VC) matrices, which are the two most used resins for CFRPs. The matrix degradation is evaluated via sample's weight loss measurement and the recovered CFs obtained after different time of treatment are analyzed to identify convenient pyro-gasification conditions to avoid damaging of the recovered CFs. The obtained results highlight the importance of the thickness of the composites to be treated for the identification of the more suitable pyro-gasification conditions.

1. Introduction

Carbon fiber reinforced polymers (CFRPs) exhibit an optimal combination of good premium properties, such as low density and lightness, high strength, stiffness, and fatigue resistance. This combination determined an expansion of the CFRPs applications in order to replace metal traditional materials.[1] Their disposal, however, is so far one of the main unsolved issues, especially in the automotive field.[2]

This issue is becoming more and more relevant as demonstrated by "European Union Directive 2000/53" which establishes that at least 95% of end-of-life vehicles mass has to be recovered and 85% recycled. Furthermore, in order to develop recycling activities, EU in "Directive 2008/98/EC" has introduced the concepts of "secondary raw material" as a recycled material that can be used in manufacturing processes instead of or alongside virgin raw material. One of the most promising processes to recycle CFRPs end-of-life and scraps is pyrogasification process,[3–5] which, besides producing a liquid/gaseous phase that can be used as energy and chemical feedstock, allows to obtain a high added-value carbon fibers (CFs) fraction[3–5] that can be reimpregnated, possibly with sustainable biobased resins.[6] Pyrolysis can be widely applied to many difference substrates,[7,8] but in order to recover CFs the overall process requires two steps:

1) Pyrolysis, the matrix degradation under inert atmosphere leads to the formation of a solid residue composed of unmodified CFs covered with a carbonaceous layer.
2) Gasification, an oxidative isotherm treatment which allows to remove the outward char layer obtaining CFs with properties not far from virgin ones.[9]

In this work, the pyro-gasification treatment is applied to cured CFRPs panels based on both epoxy (EC) and vinyl ester (VC) matrices, which are the two most used resins for CFRPs. In particular, while EC CFRPs are widely used in hand lay-up processes for high standard small productions, VCs are increasingly applied within sheet molding compound (SMC) processes which are the key toward mass production, as more and more sought after by the market. While widely a vast literature reports attempt at recycling EC resin CFRPs, a far smaller number of papers have been devoted to recovery of VC composites which, in view of the higher production rate, might represent soon a significant fraction of discarded composites. Hence, the present paper aims at comparing a well-established process proved valid for EC-based composites in the attempt at recovering VC-based materials starting from comparable conditions.

2. Results and Discussion

The study and the optimization of pyro-gasification treatment of cured CFRPs panels, based on both EC and VC matrices, was carried out with the aim of obtaining undamaged recycled carbon fibers (rCFs) suitable to produce new composites with high performances. It is worth noting that the treated EC and VC panels have a thickness of 1 and 3 mm, respectively.

The fibers/matrix ratio of the composite samples was determined by a previously reported procedure[4] which allows to remove the organic polymeric fraction and the char layer,

F. Montorsi, G. Brancolini, L. Mazzocchetti, T. Benelli, L. Giorgini
Department of Industrial Chemistry "Toso Montanari"
University of Bologna
Viale Risorgimento 4, Bologna 40136, Italy
E-mail: francesco.montorsi3@unibo.it

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/masy.202100384

DOI: 10.1002/masy.202100384

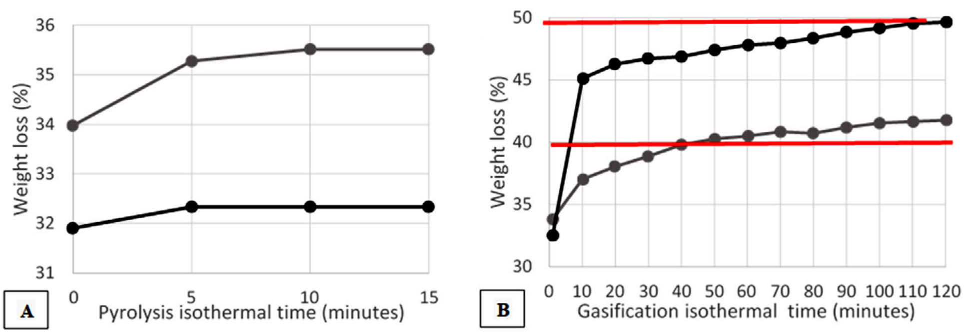

Figure 1. a). EC (gray color) and VC (black color) pyrolysis weight loss in isothermal condition at 500°C after heating from RT to 500°C (heating rate 8°C min^{-1}). b) EC (gray color) and VC (black color) gasification weight loss in isothermal condition at 500°C. The red line represents the ideal solid residue based on fiber/matrix fraction evaluation. EC, epoxy; VC, vinyl ester.

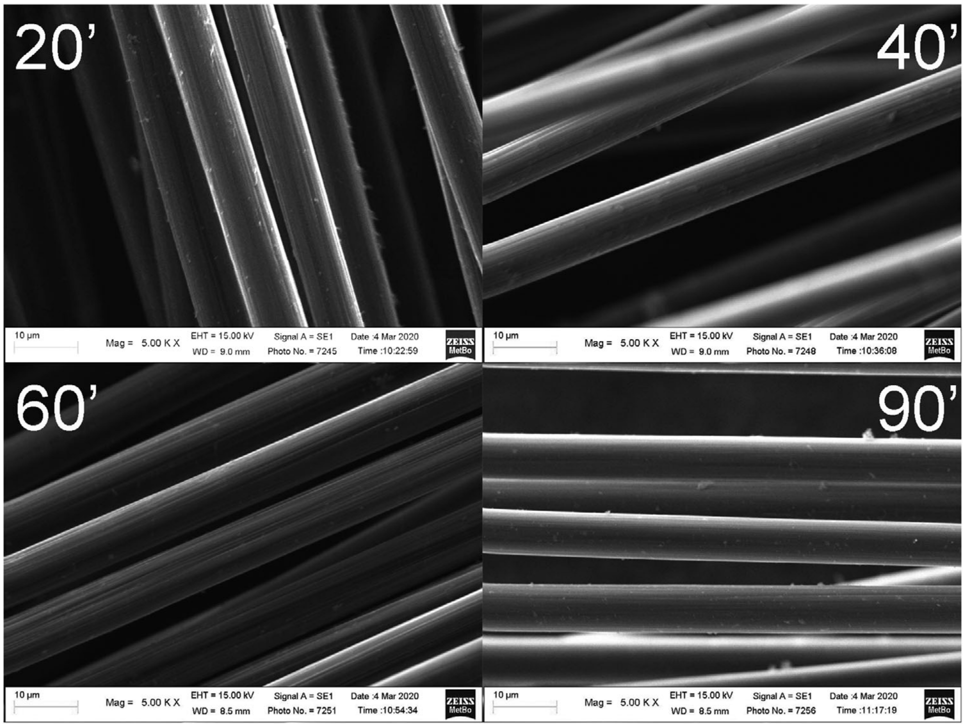

Figure 2. SEM micrographs of EC residues after different gasification time. EC, epoxy; SEM, scanning electron microscopy.

avoiding CFs degradation. The analysis shows a CFs content of about 60% and 50% in EC and VC, respectively; these values will be considered as reference point for the expected weight loss during the thermal treatments.

In order to optimize the pyro-gasification process of VC, each treatment was simulated in an oven starting from the conditions previously studied for EC matrix composites.[4,9] The pyrolysis step was performed by heating the sample in nitrogen atmosphere up to 500°C (heating rate 8°C min^{-1}) and leaving it for 90 min in isotherm. The weight loss was measured at the end of the heating ramp and every 5 min during isotherm until constant weight. As reported in **Figure 1**a, both samples show a weight loss increase during the first 10 min of isotherm, after this time weight loss tends toward a constant value. Such a behavior suggests that the matrix decomposition mainly occurs during the heating ramp and in the first minutes of the isotherm regardless of matrix composition. Furthermore, it is worth noting that in both cases the obtained solid residue fraction is higher than the expected fiber content, thus suggesting the formation of a carbonaceous layer on the fiber surface which consists of residual decomposed polymeric matrix, as previously reported that is kept at the end of the pyrolysis stage.[10]

Taking into account the obtained data, the subsequent pyrolysis simulations were carried out with an isotherm of 10 min with the aim to avoid the damage of the fibers and to optimize the treatment in term of required time and energy. The pyrolyzed samples were then gasified in air at 500°C: in these conditions both composite materials show a further weight loss (Figure 1b) ascribable to the char layer degradation.[4]

Table 1. Fibers diameters and O/C weight % after different gasification time.

EC			VC		
Gasification time [min]	Fibers diameters [μm]	O/C [%]	Gasification time [min]	Fibers diameters [μm]	O/C [%]
20	7.9 ± 0.8	0.009	40	6.9 ± 0.7	0.050
40	7.8 ± 0.6	0.031	60	6.9 ± 0.4	0.054
60	7.5 ± 0.7	0.022	90	6.9 ± 0.5	0061
90	7.5 ± 0.9	0.040	120	6.8 ± 0.6	0.065

EC, epoxy; VC, vinyl ester.

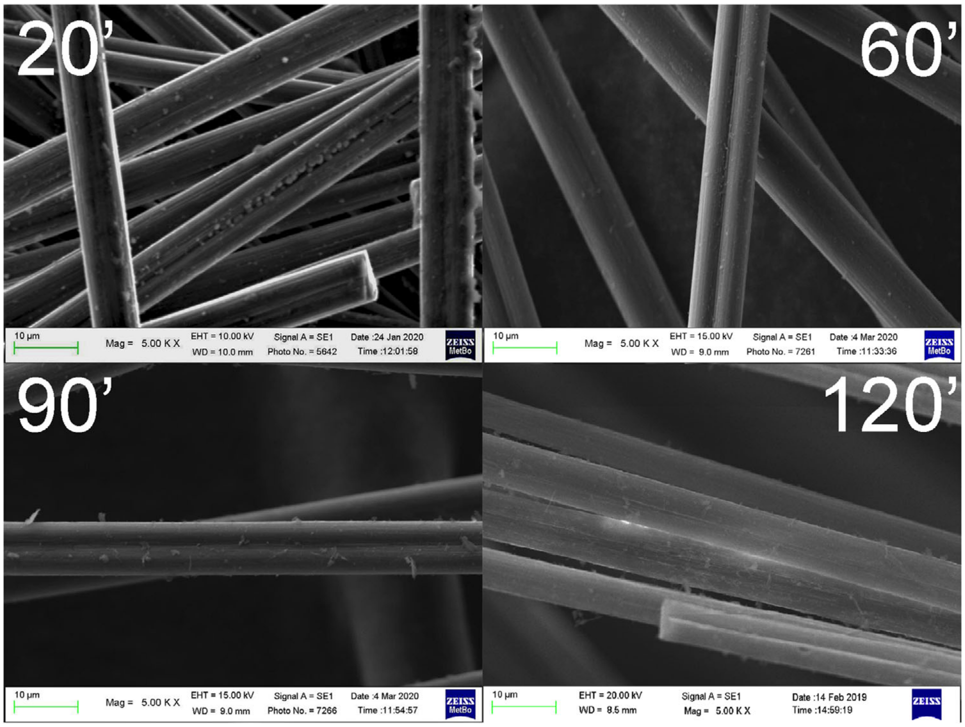

Figure 3. SEM micrographs of VC residues after different gasification time. SEM, scanning electron microscopy; VC, vinyl ester.

VC samples show that, when treated at 500°C in oxidizing atmosphere, they first degrade faster, then the weight loss decreases, and it tends to the expected weight loss value of about 50% only after 120 min. EC samples, instead, show a slower char degradation that continually increases during gasification, reaching the expected weight loss value of about 40% after 40 min of gasification. It is worth to point out that previous work, carried out on pilot plants treating a few kg of raw materials per batch, showed that EC CFRPs need gasification treatment at 500°C for 60 min to completely remove the char from fibers' surface. Such a different behavior could be ascribable to both the different thickness of the treated composites (1 mm versus 5 mm[4]) and the different mass of the overall treated CFRP (10 g versus 5–7 kg[4]) and emphasizes the importance of this in the scale up parameter when trying to optimize processing conditions.[11,12] These results are similar to those reported for VC matrix composites but with glass fibers treated in semi-industrial pilot plant.[8] Investigation of the EC panels residues by SEM shows, indeed, that, after 40 min of gasification, fibers' surface is clean and no spotted resin residue is detected (**Figure 2**); after 90 min, instead, fibers are visibly damaged, showing pitting on the surface. Furthermore, a decrease of gasified fibers diameters was detected by increasing the oxidative treatment duration, thus confirming the char removal but suggesting also a slight erosion of the carbonaceous layer.

With the aim of roughly estimating the fibers' oxidation degree, EDX maps of C and O atomic distribution were also recorded: as shown in **Table 1** the O/C atomic ratio increases significantly with treatment duration.

In **Figure 3**, micrographs of CF recycled from VC panels treatment are reported too. It is worth noting that the char removal appears almost complete only after 120 min: for lower time fibers present a rough surface and spotted resin residues.

Moreover, the fibers diameter is almost constant (Table 1) but some damages are highlighted by SEM analysis and the O/C atomic ratio increases; this suggests that a too long gasification time provokes a considerable oxidation of fibers, which are consequently damaged and weakened.

3. Conclusion

In the present work, the application of a pyro-gasification treatment was assessed both on EC and VC matrices CFRPs, with the aim to obtain recycled CFs suitable to produce new composites with high performances. Pyrolysis simulations up to 500°C (8°C min^{-1}) highlighted that the matrix decomposition mainly occurs during the heating ramp and in the first isotherm minutes, regardless of matrix composition; the carbonaceous layers deriving from the matrix degradation can be then removed after gasification step. The analysis of solid residues proved that the thickness of the composite to be treated is an important parameter.

Acknowledgements

The authors wish to acknowledge Progetto Alte Competenze granted by Regione Emilia-Romagna for funding F.M. Post-Doc fellowship (CUP J44I20000570002).

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data will be provided upon request.

Keywords

CFRP, pyro-gassification, pyrolysis, recycled carbon fibers

Received: September 22, 2021
Revised: October 25, 2021

[1] F. Rondina, S. Taddia, L. Mazzocchetti, L. Donati, G. Minak, P. Rosenberg, A. Bedeschi, E. Dolcini, *Compos. Struct.* **2018**, *192*, 368.
[2] N. de Werken, M. S. Reese, M. R. Taha, M. Tehrani, *Compos. Part A* **2019**, *119*, 38.
[3] L. Giorgini, T. Benelli, L. Mazzocchetti, C. Leonardi, G. Zattini, G. Minak, E. Dolcini, I. Montanari, C. Tosi, *Polym. Compos.* **2015**, *36*, 1084.
[4] L. Mazzocchetti, T. Benelli, E. D'Angelo, C. Leonardi, G. Zattini, L. Giorgini, *Compos. Part A* **2018**, *112*, 504.
[5] L. Giorgini, T. Benelli, G. Brancolini, L. Mazzocchetti, *Curr. Opin. Green Sustain. Chem.* **2020**, *26*, 100.
[6] S. Merighi, L. Mazzocchetti, T. Benelli, L. Giorgini, *Polymers* **2020**, *12*, 3054.
[7] L. Giorgini, T. Benelli, C. Leonardi, L. Mazzocchetti, G. Zattini, M. Cavazzoni, I. Montanari, C. Tosi, *Environ. Eng. Manag. J.* **2015**, *14*, 1611.
[8] L. Giorgini, C. Leonardi, L. Mazzocchetti, G. Zattini, M. Cavazzoni, I. Montanari, C. Tosi, T. Benelli, *FME Transact.* **2016**, *44*, 405.
[9] L. Mazzocchetti, T. Benelli, G. Zattini, E. Maccaferri, G. Brancolini, L. Giorgini, *AIP Conf. Proc.* **2019**, *2196*, 020036.
[10] L. Giorgini, T. Benelli, L. Mazzocchetti, C. Leonardi, G. Zattini, G. Minak, E. Dolcini, C. Tosi, I. Montanari, *AIP Conf. Proc.* **2014**, *1599*, 354.
[11] L. Giorgini, L. Mazzocchetti, T. Benelli, G. Minak, E. Poodts, E. Dolcini, *Polym. Compos.* **2013**, *34*, 1506.
[12] G. Zattini, L. Mazzocchetti, T. Benelli, E. Maccaferri, G. Brancolini, L. Giorgini, *Key Eng. Mater.* **2020**, *827*, 110.