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Procedia CIRP 105 (2022) 637–641

www.elsevier.com/locate/procedia

29th CIRP Life Cycle Engineering Conference

Reducing down-cycling of carbon fibre by fibre architecture preservation: Multi-layer fibre surface quality investigation

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Abstract

Carbon fibre has a high mechanical reinforcement capability associated with fibre architectures. However, it is significantly down-cycled in the current recycling practice as a result of a loss of fibre architecture. Without the use of chopping/shredding process, the architecture of carbon fibre can be preserved, but the surface cleanliness of recycled carbon fibre (rCF) is not clear. In this study, an investigation is carried out on the surface quality of architecture-preserved rCF obtained from multiple layers of a carbon fibre reinforced polymer (CFRP). Carbon fibre woven fabrics are manufactured into CFRP, recycled using a pyrolysis technique, and inspected using visual and microscopic techniques. The results indicate a good preservation of fibre architecture in all five layers of CFRP. Nonetheless, the residue from the pyrolysis of resin is increased in the internal layers (4th and 5th) of rCF in comparison to the external layers (1st to 3rd). The results suggest that fibre architecture preservation has a potential to reduce the down-cycling of carbon fibre, but the impact is limited in internal fibre layers due to reduced fibre surface cleanliness. The insights from this study provide a further understanding on the approach to reduce the down-cycling of carbon fibre and move the carbon fibre industry towards circular economy.

Keywords: Carbon fibre; Recycling; Fibre architecture; Material functionality; Circular economy;

1. Introduction

Carbon fibre is an engineering material with superior mechanical properties. With a high specific strength and stiffness, carbon fibre is often used in structurally significant applications in the aerospace, wind power, sporting and automotive industries [1]. It is usually manufactured into carbon fibre reinforced polymers (CFRP), with a thermoset or thermoplastic polymer matrix. The arrangement of carbon fibre in CFRP has an important impact on the mechanical performance of CFRP. The reinforcement potential of carbon fibre is optimised when carbon fibres are packed in regular architectures such as woven and unidirectional architectures (Fig. 1a) [2]. In these architectures, carbon fibres are closely packed, and hence a high fibre content in the range of 50-80% volume fraction can be achieved in the CFRP [2,3]. CFRP with a high fibre content exhibits a high tensile stiffness and strength in the reinforcement directions. The use of carbon fibre as mechanical reinforcement in CFRP parts is considered a key function of this material [4]. Carbon fibre that enables a CFRP part to have a higher maximum specific tensile stiffness is considered to have a higher functionality [5–7].

Carbon fibre experiences a significant reduction in the functionality after the current recycling process, due to a loss of fibre architecture. Commercial carbon fibre recycling starts with chopping or shredding processes to reduce the size of the CFRP waste [8–10]. This is followed by a recycling process to recover carbon fibres from the waste. A further chopping process is usually required to regulate the length of the recycled carbon fibre (rCF) [1,10]. The use of chopping and shredding

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10.1016/j.procir.2022.02.106

processes leads to a loss of fibre architecture by converting the fibres into a short and unorganised form (Fig. 1b). Although rCF is usually further processed into a non-woven mat for better reuse [11,12], only a fibre volume fraction up to about 30% can be practically achieved when remanufacturing CFRP [13–15]. The reduction in fibre content and fibre length leads to a significant reduction in the tensile modulus and strength of the remanufactured CFRP (Table 1). High-performance vCF with intact fibre architectures from structural aerospace applications is down-cycled to sheet moulding compounds or fillers in semi- or non-structural applications [1,10]. This is a significant reduction in the functionality of carbon fibre, which has a high production energy consumption and cost [4]. Improving the functionality of rCF is beneficial for increasing the number of useful life cycles of carbon fibre and moving it towards material circularity.

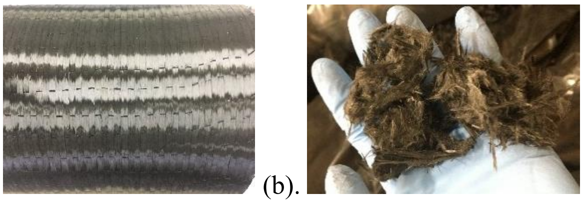


Fig. 1. (a) Unidirectional virgin carbon fibre; (b) chopped, unorganised recycled carbon fibre.

Table 1. Comparison of tensile modulus and tensile strength of virgin CFRP and recycled CFRP with non-woven rCF [13,15,16].

	Tensile modulus (GPa)	Tensile strength (MPa)
Virgin CFRP	69-150	550-1050
Recycled CFRP with ~30v% non-woven rCF	~25	~200

Preservation of fibre architecture in the recycling process has a potential to improve the functionality of rCF. Chopping and shredding processes to reduce the size of wastes are commonly used in the recycling practices for materials such as metals and plastics [17]. However, these processes may not necessarily be suitable for recycling carbon fibre with architectures that, once damaged, cannot be melted and reformed. Without the use of chopping and shredding processes, rCF can retain an architecture similar to that of virgin carbon fibre (vCF) [18–20]. In one study, remanufactured CFRP with architecture-preserved plain woven rCF retained up to 95% of the tensile modulus and 68% of the tensile strength of the original virgin CFRP [18]. The improvement in rCF functionality by fibre architecture preservation also has a potential to reduce the life cycle environmental impact of a recycled CFRP automotive component [5].

Despite the preservation of fibre architecture, recycling CFRP waste without shredding process may create a challenge associated with fibre cleanliness. The most commercialised carbon fibre recycling technique is a pyrolysis-based thermal technique [10]. In this technique, the polymer matrix is thermally decomposed (i.e. pyrolysed) to gases, oil and solid char residue in an inert atmosphere [21]. The char residue covers the carbon fibre and would affect the bonding between rCF and the new polymer matrix [10]. It results in a poor fibre-matrix interface in the remanufactured CFRP and hence needs to be removed by an oxidative process in air. Chopping and shredding processes increase the contact area between waste and the recycling environment, hence can promote the complete removal of polymer matrix and the char residues. Without the chopping/shredding process, the thoroughness of the removal of resin and residues from CFRP is not clear.

This paper aims at understanding the surface quality of architecture-preserved rCF in various layers of a composite. A CFRP laminate is manufactured and then recycled using the pyrolysis technique. rCFs from different layers of the composite are inspected to investigate the fibre architecture and fibre surface quality. The results from this study will deepen the understanding on the impacts of fibre architecture preservation on the functionality of rCF as mechanical reinforcement.

2. Methodology

An experimental investigation was carried out to evaluate the extent of architecture preservation and surface cleanliness of rCF. As these two attributes of rCF significantly affect the mechanical performance of CFRP, the results will indicate the change in the functionality of rCF as a mechanical reinforcement. It should be noted that although this observation does not quantify the mechanical properties of rCF, it provides a qualitative understanding on the potential change in the functionality of rCF. Major steps in this study include composite manufacturing, lab-scale recycling and fibre inspection.

2.1. CFRP manufacturing

A CFRP laminate was manufactured for recycling. The RIM 935 epoxy resin (Hexion) cured with RIMH 937 hardener was used as the polymer matrix. The mixing ratio between resin and hardener was 1:0.38 by weight. Plain-woven carbon fibre fabric, one of the most commonly used fibre architectures, was the fibre reinforcement. Five pieces of 30×20cm fabric were cut and wetted with the resin. The five-layer laminate was then laid up and cured in a vacuum bag at room temperature for 48 hours. Post-curing of the sample at 80°C for 5 hours was carried out to complete the CFRP manufacturing process.

2.2. Lab-scale recycling

The pyrolysis-based thermal recycling technique was used to recycle carbon fibre from the CFRP laminate. It is adopted by commercial recyclers such as Gen 2 Carbon (previously known as ELG Carbon Fibre) [12] and CFK Valley Stade Recycling [8]. However, unlike the commercial processes that begin with chopping/shredding of CFRP waste, the process in this study recycled the complete CFRP laminate while maintaining the fibre architecture.

The optimal recycling process parameters were determined by thermogravimetric analysis (TGA). TGA tracks the change in sample mass at various temperatures and hence demonstrates the thermal behavior of a material. It has been used in previous studies to determine the pyrolysis recycling conditions for CFRP [22,23]. The epoxy resin underwent a two-step analysis.

This is a resupply of March 2023 as the template used in the publication of the original article contained errors. The content of the article has remained unaffected.

Firstly, neat cured resin was heated to 800°C at 5°C/min in N_2. This was to resemble the pyrolysis process and to understand the starting temperature for the pyrolysis of resin. Secondly, the char residue left from the resin pyrolysis was heated to 800°C at 5°C/min in air. This was to resemble the subsequent oxidative process and to understand the starting temperature for the oxidation of char residue. Neat carbon fibre was also heated to 800°C at 5°C/min in air to understand the starting temperature for fibre oxidation. From these analyses, the optimal recycling temperature and time were determined to maximise resin and char removal while minimising the degradation to carbon fibre.

With the pre-determined recycling parameters, carbon fibre recycling process was carried out in a furnace. A LABEC SF-13-SD furnace with N_2 and compressed air supply was used. The CFRP laminate was placed on the flat ceramic plate in the furnace (Fig. 2). The top layer of fibre in the CFRP laminate is labelled the 1st layer, while the bottom layer is the 5th layer, for later reference. A temperature program was established according to the recycling parameters. As introduced, the recycling process consisted of two steps. In the first step, the furnace was supplied with N_2 at a flow rate of 5L/min. The pyrolysis of the epoxy resin matrix occurred in this step. In the second step, the furnace temperature remained unchanged, but the gas supply to the furnace was switched to compressed air to remove the char residue from the resin pyrolysis. Upon completion of the recycling process, the rCF was collected by flipping the sample into a plastic bag. At this point, the carbon fibre had no support from the matrix, hence the collection process was done with care to avoid disruption to the fibre architecture.

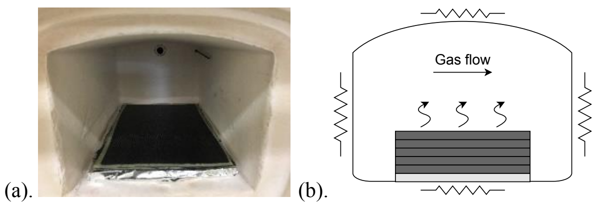


Fig. 2. (a) A CFRP laminate placed in the recycling furnace; (b) Recycling process with the five-layer CFRP laminate (thickness exaggerated).

2.3. Fibre inspection

The rCF from different layers and virgin carbon fibre (vCF) were inspected using visual, optical microscopic and scanning electron microscopic techniques. A single-lens reflex camera was used for visual inspection of the overall layout of the fibre tows within the fibre architecture to understand the orderliness of the architecture. A Nikon Eclipse E200 optical microscope with 5X magnification was used to focus on the fibre tows and the tow intersections to understand the amount of resin residue between fibres. Finally, a Zeiss UltraPlus FESEM scanning electron microscope was used with a working distance of 3.5-3.8 mm and an accelerating voltage of 3 kV to inspect individual fibre surface and evaluate the surface cleanliness. To allow comparability between the SEM images of vCF and rCFs, the vCF was first cleaned with acetone to remove the sizing layer. Sizing layer was applied onto fibre surfaces by carbon fibre producers to improve the ease of fibre handling and improve the fibre-matrix adhesion. The results from fibre inspection under these three different techniques indicate the extent of fibre architecture preservation and resin removal.

3. Results

Optimal recycling temperature and time were determined for the carbon fibre. Fig. 3 shows the mass loss rate of resin char residue and carbon fibre in air. The char residue oxidises in air at a lower temperature threshold (around 400°C) in comparison to the oxidation of carbon fibre (around 550°C). This is consistent with results from previous studies that show different temperature windows for the oxidation of char residue and the carbon fibre [22,23]. A temperature range in which the resin residue would be oxidised but the carbon fibre stays undamaged can be seen. The initial fluctuation of the resin residue curve above zero on the mass loss scale was due to the inaccuracy of measurements at small sample sizes. This is insignificant compared to the mass loss in the residue oxidation process. The optimal recycling parameters were determined and shown in Table 2.

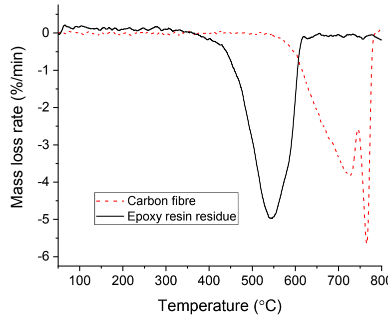


Fig. 3. Mass loss rate of carbon fibre and epoxy resin residue in air.

Table 2. Processing parameters for carbon fibre recycling.

Recycling temperature (°C)	Heating rate (°C/min)	Pyrolysis time in N_2 (min)	Char removal time in air (min)
500	10	30	60

After the recycling process, the fibre architecture in various layers of the CFRP laminate is preserved. Complete pieces of rCF fabric were recovered from the CFRP laminate (Fig. 4). Each layer of rCF fabric was able to be separated from one another. The fibre tows are still restrained in the architecture in all five layers of the composite (Fig. 5). Nonetheless, it was noticed that the fibres at the edge of the rCF fabric are loosely constrained and can easily fall out of the fabric structure. In addition, the gaps between fibre tows in the rCF architecture (Fig. 5b-f) are smaller than those in vCF (Fig. 5a), similar to a previous observation [20]. This is likely a result of the widening of fibre tows, due to the pressure applied during the vacuum bagging process and/or the removal of the sizing layer that used to hold vCF in a tow.

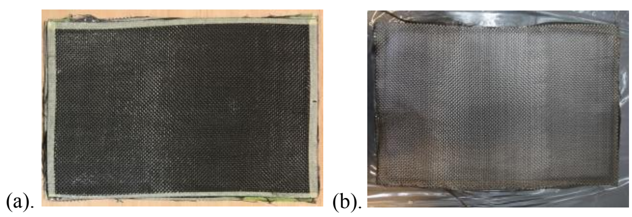
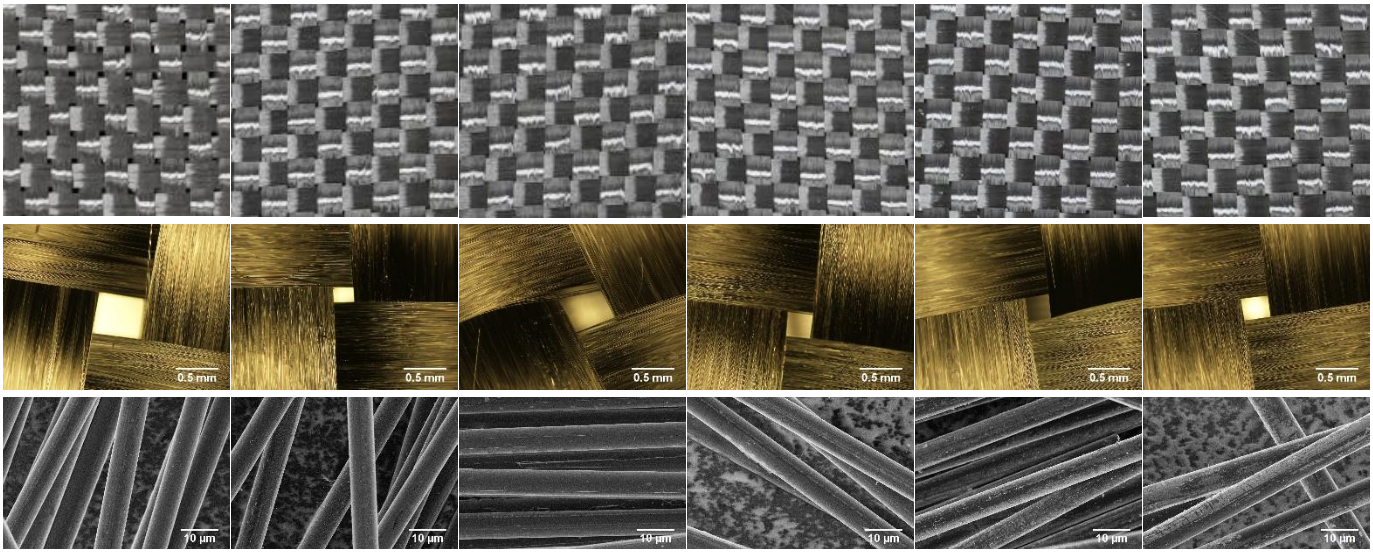


Fig. 4. (a) Carbon fibre reinforced epoxy composite laminate; (b) Recycled woven carbon fibre fabric from the laminate.



(a). (b). (c). (d). (e). (f).

Fig. 5. Overall fibre architecture (top), fibre tows and intersections (middle) and individual fibres (bottom) of (a) virgin plain woven CF; recycled plain woven CF from (b) the 1st (top) layer of CFRP; (c) the 2nd layer of CFRP; (b) the 3rd layer of CFRP; (b) the 4th layer of CFRP; (b) the 5th (bottom) layer of CFRP.

From the optical microscopic images (Fig. 5), there is no significant residue that binds multiple fibre filaments in fibre tows and at the tow intersections, in all five layers. This indicates that the recycling process was able to remove the majority of the polymer matrix binding the fibres. Comparing the architecture-preserved rCF with the current random rCF form (Fig. 1b), the woven rCF architecture is much more organised and compact.

Despite the well-preserved fibre architecture, rCF in the bottom two layers has increased resin residue, in comparison to the upper layers. As illustrated in the SEM images (Fig. 5), the surface cleanliness of rCF from the 1st and 2nd layer of the composite is comparable to the vCF. No significant residue from the epoxy resin is left on the rCF in these two layers. However, starting from the 3rd layer, residue is noticeable on the rCF surface. The surface cleanliness of rCF from the 4th and the 5th layer is considerably poorer than that in the first three layers. As shown in Fig. 2b, the CFRP sample is in contact with a bottom plate, hence the penetration of air through the sample is predominantly downwards. As a result, the bottom layers of the CFRP laminate had less exposure with the air in the recycling process, in comparison to the top layers. The oxidation of residue in the 4th and 5th layers with oxygen could have been limited due to a lack of contact with air. The increased resin residue on the rCF in these layers would reduce the interfacial strength, and more importantly affect the consistency in the quality of the rCFRP.

4. Discussion

The improvement in the functionality of rCF by fibre architecture preservation could be limited by the reduced surface cleanliness of internal fibres. The preservation of fibre architecture would improve the fibre volume fractions in the remanufactured CFRP. Nonetheless, as shown in Fig. 5, the surface cleanliness of rCF reduces in the internal layers, which on the other hand would reduce the functionality of rCF. Hence, it is likely that as the number of layers increases in a CFRP laminate, the functionality of architecture-preserved rCF reduces. Therefore, recycling with fibre architecture preservation is more plausible for CFRP laminates with a small number of layers. In this case, with an improved fibre architecture and a similar surface cleanliness in comparison to the current rCF, the functionality of rCF is likely to be higher.

Further research is necessary to quantify the impact of fibre architecture preservation on the functionality of rCF as a mechanical reinforcement. This study presents an observation of surface quality of architecture-preserved rCF, with a qualitative understanding on the potential change in the rCF functionality. Nonetheless, the impact of increased resin residue in internal layers on the mechanical properties of remanufactured CFRP needs to be quantitatively investigated. Furthermore, it is not certain if the reduced gap size between fibre tows in the woven rCF in comparison to vCF changes the permeability of the fabric for resin flow and potentially affects the resin content of the remanufactured CFRP. Remanufacturing of CFRP with the architecture-preserved rCF and mechanical testing are required to quantify the functionality of the rCF.

Insights for the carbon fibre industry can be drawn. A more flexible and diversified approach is beneficial for integrating fibre architecture preservation into the current carbon fibre recycling system. As discussed above, the number of fibre layers, or the thickness of the CFRP, has an impact on the surface cleanliness of architecture-preserved rCF. Hence, recycling with fibre architecture preservation would not suit every kind of CFRP waste. In the current recycling practice, although the chopping and shredding processes damage the fibre architecture, the cleanliness of all fibres can be relatively consistent, due to a more thorough exposure of CFRP waste with air. Hence, the current approach with extensive size-reduction is still suited for wastes with a large thickness as it can minimize resin residue. In addition, the current recycling approach also suits CFRP wastes with an irregular and small size, such as manufacturing offcuts, that do not yield high-value rCF even with the fibre architecture preserved. Recycling with fibre architecture preservation is more suitable for large and thin pieces of end-of-life CFRP waste such as retired parts from aircrafts or wind turbine blades. Hence, there is value in separating CFRP wastes with and without a potential for fibre architecture preservation. The separation process can be based on the thickness of the CFRP waste and the recycling process design (ie. whether CFRP waste is exposed to air on one side or both sides). This would optimise the functionality of rCF from different types of CFRP waste, by tailoring the recycling process.

5. Conclusion

In this study, complete woven carbon fibre fabrics are recycled with fibre architecture preserved from a five-layer CFRP laminate. Optimal pyrolysis recycling conditions are determined by thermogravimetric analysis of the carbon fibre, epoxy resin and pyrolytic residue of the resin. The fibre architecture and surface quality of the recycled carbon fibre (rCF) are inspected by visual, optical microscopic and scanning electron microscopic techniques. Results indicate that the woven fibre architecture is preserved in all five layers of recycled carbon fibre fabric. Nonetheless, the 4^{th}-5^{th} layers of carbon fibre have increased char residue from the pyrolysis of the epoxy resin, in comparison to the 1^{st}-3^{rd} layers, due to a lack of exposure to air in these layers.

Carbon fibre recycling with fibre architecture preservation has a potential to reduce the down-cycling of carbon fibre seen in the current recycling practice. However, this effect is limited for carbon fibre in the internal layers of a CFRP, due to a reduction in the fibre surface cleanliness. Further research into the mechanical performances of architecture-preserved rCF and the remanufactured CFRP will be needed to quantify the effect on functionality of rCF as a mechanical reinforcement material. In spite of this, the insight from this study indicates a need for a flexible and diversified approach to optimize the functionality of rCF, by identifying CFRP wastes with a value for fibre architecture preservation. Improving the functionality of recycled carbon fibre can increase the useful life cycles of this material and move it towards material circularity.

Acknowledgements

This study was supported by the Australian Research Council (ARC Training Centre in Lightweight Automotive Structures, grant no. IC160100032). The authors would like to thank Umesh Kaini, Graeme Poleweski for their technical support. The authors also acknowledge the facilities and the scientific and technical assistance of Microscopy Australia at the Advanced Imaging Precinct, Australian National University, a facility that is funded by the University, and State and Federal Governments.

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