RECYCLING OF COMPOSITES BY RECOVERING CARBON FIBRES FROM PREPREGS, AND THEIR RE-USE

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Abstract

Due to the rapid growth in the use of composite materials, environmental concerns have become an increasingly influential topic, making recyclability of composite materials a key issue. Furthermore, several related European laws have been passed to minimize the environmental impact of composite structures and to make rational use of landfills. However, the amount of composites currently recycled is less than 5% of the total amount produced. This work studies the mechanical properties of recycled carbon fibres, recovered by pyrolysis from composites with a thermoset polymer matrix.

The objective is to reuse the fibres in new, lower cost composites with similar properties. Starting from a pyrolysis step, followed by oxidation, an evaluation of the different parameters of the recycling process has been performed. The characterization of the fibres includes tensile tests, scanning electron microscopy, and Raman spectroscopy. The recycled fibres presented a 10% reduction in their initial tensile strength. Then, remanufacturing of laminates using the recycled fibres was achieved by resin film infusion, obtaining laminates with properties similar to the brand-new composites. These results have the potential to be exploited by the automotive, aeronautical, wind energy, construction, and other sectors.

1. Introduction

The remarkable characteristics of fibre-reinforced plastics (FRPs) –high durability and specific stiffness, and strength-to-weight ratio- led to rapid increase of their use. In the aeronautical sector, the use of composites reaches up to 50% of the total weight of a modern commercial aircraft. Other industries where weight-efficient performance is a key factor, such as the automotive, naval, and wind energy sectors, are likewise increasing the use of composite materials (annual growth rate of 12–14%) [1]. Therefore, the increment in demand and use of composites results in more and more waste being generated throughout the life cycle of these materials; in fact, it is estimated that 30–40% of pristine carbon fibres are wasted during the manufacturing process, and significant amounts of off-cuts,

rejects, and put-of-date prepregs are generated, causing a significant negative impact on the environment. The excess of carbon fibres that is generated per year equals about 20–25% of the total amount consumed during 2015 [2]. Evidently, the recycling of composite materials is a high priority. In adition, several European Directives were implemented in order to make better use of landfills (EU 1999/31/EC) [3]; to reduce waste management (EU 2000/53/EC on End-of-Life vehicles) [4]; to prevent or limit the emission levels produced by incineration plants (Directive 2000/76/EC) [5]; as well as to prevent and remedy the environmental damage (2004/35/EC on Environmental Liability) [6]. All in all, recycling composites not only makes sense from environmental and economic perspectives; it could also be a key in increasing the penetration of these lightweight but expensive materials in high-volume markets such as automotive and aeronautical industry.

In this study, a two-step carbon-fibre recycling process is proposed: pyrolysis followed by oxidation. An optimization of the method in terms of sustainability of the technique and the characteristics of the fibres was carried by performing surface, microstructure, and mechanical testing of the recovered fibres. With respect to mechanical performance, fibre strength distribution and fracture toughness were the properties analyzed. In addition, the remanufacture of laminates by means of resin film infusion using the recycled fibres is postulated. The mechanical performance of the resulting laminates was similar to the brand-new composites.

2. Recycling process

2.1. Scrap material

The composite material used as the basis for the optimization of the experimental parameters was a scrap (HexPly® F593, supplied by AIRBUS OPERATIONS S.L., Getafe, Spain) composed of a plain woven prepreg made of epoxy resin reinforced with Toray T300/3 k carbon fibres [7] (55–60% carbon fibres [by mass] and 40–45% resin; fibre area weight = 193 g/m^2) [8].

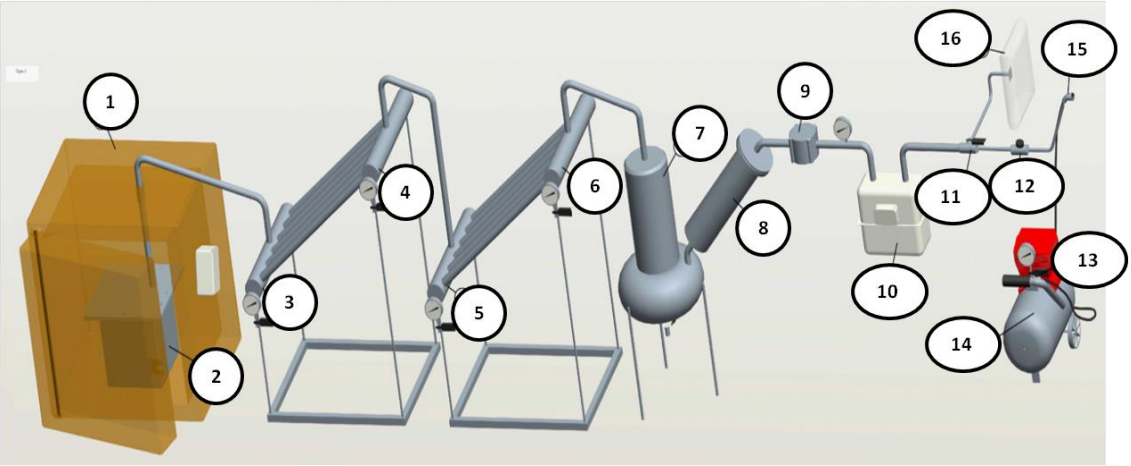

Figure 1. Installation used for the pyrolysis of the carbon fibres [23].

2.2. Recycling methodology

The process used to recover the fibres consisted of two steps: a thermolysis or pyrolysis (P) and a gasification or oxidation (O). In the first one, the separation fibre/resin takes place; in the second stage,

the char deposited on the surface of the fibres is removed. However, this second step is critical because it can result in the reduction of the mechanical properties of the fibres.

The selection of the pyrolysis temperature for the degradation of the resin was performed by conducting tests runs at 500, 600, and 700°C for 6 h. Values below 500°C did not effectively remove all the resin; and values higher than 700°C caused a high degradation of the recovered fibres. The optimum oxidation step was determined by varying the oxidation times between 30 and 90 min.

3. Recycled fibres

To determine the optimum oxidation time, analyses of fibre surface quality, fibre composition and mechanical properties of the recovered fibres were performed.

3.1. Composition

Independently of the oxidation time, the surface of the recycled fibres presented a low amount of residual char and was otherwise clean, showing no evidence of fibre damage.

The crystallite structure of the recycled carbon fibres was analysed by Raman spectroscopy. The results showed that, independently of the zone evaluated, all first-order Raman spectra for the recycled carbon fibres exhibited two broad peaks at about 1350 and 1580 cm^{-1} corresponding to the D and G bands, respectively.

The surface chemistry of virgin and recycled carbon fibres was examined by X-ray photoelectron spectroscopy by López et al. [8]. It revealed that the C content remains practically constant, the O content increases with gasification time and the N content decreases. The increase in the O/C ratio with gasification time is indicative of the degree of fibre oxidation, which can lead to undesirable alterations. The smaller ratio obtained was for a gasification time of 30 min.

3.2. Mechanical properties

The tensile strength and the fracture toughness of the recovered fibres were determined in order to achieve an objective determination of the optimum oxidation time based on mechanical properties.

Firstly, the tensile properties of the carbon fibres were determined through tensile testing using a gage length of 20 mm. The cross-section area of the fibres was estimated from the linear density [10], determined using the frequency method according to the ASTM D1577 standard [9].

The average fibre diameter (D), elastic moduli (E), and tensile strength (σ_u) of fibres recycled with different gasification times are given in Table 1. Athough the modulus is practically constant, the tensile strength decreases as oxidation time increases. This is caused by the presence of a large number of defects on the surface of the thermally oxidized fibres. Consequently, gasification times of 60 min already led to severe reductions in tensile strength.

Table 1. Average diameter and mechanical properties as a function of the oxidation time.

Fibre sample	Diameter, D (μm)	Tensile strength, σ_u (GPa)	Elastic modulus, E (GPa)
Virgin	7.5±0.1	3.3±0.5	195±18
Recycled: P-500°C/O-30 min	7.2±0.1 (-4%)	2.9±0.4 (-10%)	198±6 (+2%)
Recycled: P-500°C/O-60 min	7.2±0.3 (-5%)	2.7±0.5 (-18%)	195±9 (-0.2%)
Recycled: P-500°C/O-90 min	7.0±0.5 (-7%)	2.5±0.6 (-23%)	198±23 (+1%)

Secondly, the fracture toughness of the recoveres fibres was determined from tensile tests of pre-notched fibres. A focused ion beam (FIB) was used to introduce the artificial notched in the fibres [10, 11]. This methodology allows precise monitoring of the notch geometry in terms of length, depth, and tip radius. Upon tensile loading, the fracture process started from the crack tip induced by FIB milling, and the response was linear and elastic up to failure.

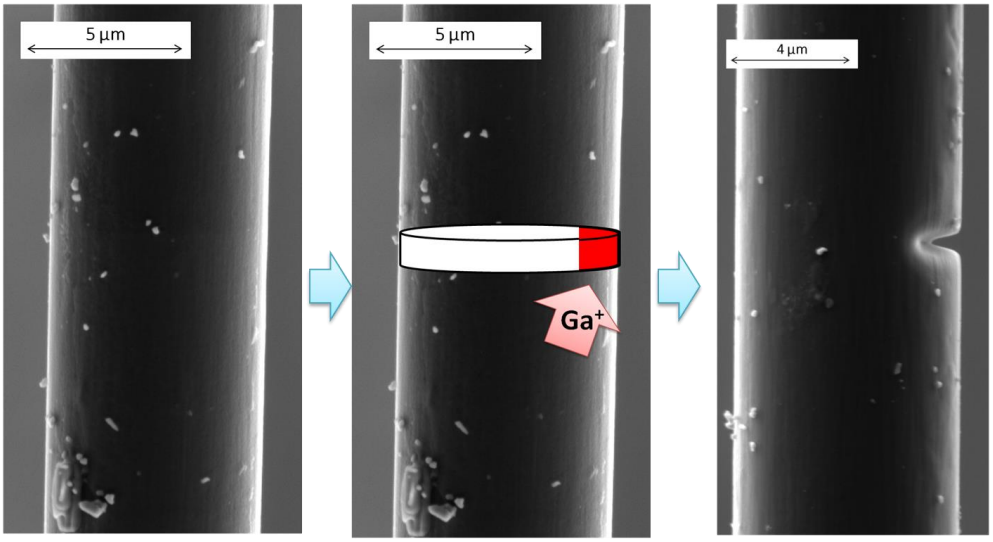

Figure 2. SEM micrographs of the fibre before and after the Ga+ ions hitting; (a) original fibre; (b) Gallium ions focusing; (c) notched fibre.

The residual strength of the notched fibre was determined from the failure load and the corresponding area of the cross section of the fibre. The mode-I apparent fracture toughness, K_{IC}, and the critical energy release rate, or fracture energy, G_{Ic}, were evaluated Linear Elastic Fracture Mechanics (LEFM).

Table 2. Mechanical properties of the pristine and the recovered fibres at 30 min of gasification time.

Fibre sample	Apparent fracture toughness, K_{IC} (MPa·m$^{1/2}$)	Apparent fracture energy, G_{IC} (J·m^2)
Virgin	1.2±0.2	10±3
Recycled: P-500°C/O-30 min	1.2±0.3	10±4

Given the results achieved, it can be concluded that the optimum recycling process conditions consist on a thermolysis step at 500°C for 6 h followed by gasification step for another 30 min. These conditions result in retentions of 100% of fibre elastic modulus and fracture toughness and 90% of fibre tensile strength.

4. Remanufacturing of composites

The resin film infusion technique (RFI) was used for manufacturing new laminates using the recovered fibres. In this way, the recycled fibre tows were laid down next to each other to complete a thin fibre bed layer. The fibre layers were interleaved with layers of semi-solid epoxy resin film Letoxit® LFX 060 [12][1] for subsequent consolidation. The final kit was introduced in a close-mold and cured in a hot-plate press, applying pressure (0.7 MPa) and heat (125°C for 25 min) simultaneously [13].

4.1. Properties of remanufactured composites

After confirming that the laminates were free of major pores, voids, or delaminations, thermogravimetric analyses (TGA) were carried to evaluate the composition of the laminates. The nominal fibre volume fraction, V_f, was determined to be 61%.

In order to compare the mechanical properties of the recycled laminates with the laminates made using pristine fibres, the interlaminar shear strength (ILSS) was evaluated by means of Short Beam Shear tests. The results showed a decrease of approximately 50% in strength for laminates with recycled fibres with respect to those with virgin fibres (see Table 3). More studies are needed to understand the decrease in ILSS of the recycled laminates. A possible cause for the decrease in ILSS is the deterioration of fibre-matrix interface properties due to the aggressive recycling process. The problem with the adhesion suggests that a sizing for protection of the fibres and for compability with the polymer matrix should be applied, and this will be subject of further studies.

Table 3. Short-beam strength of the pristine and the recovered fibres at 30 min of gasification time.

Fibre sample	Short-beam strength, F^{sbs} (MPa)
Virgin	75.8±0.4
Recycled: P-500°C/O-30 min	34±2

5. Conclusions

A highly reliable and repeatable recycling process of carbon fibres starting from epoxy based composite scrap was achieved, consisting of a pyrolysis step at 500°C for 6h, and a oxidation step at 500°C for 30min. The recovered fibres presented a clean surface, a complete retention of the elastic modulus, and fracture toughness and a small degradation of 10% in their tensile strength.

The recycled fibres were used to manufacture composite laminates using the resin film infusion technique. The manufacturing parameters were optimized in terms of thickness control, fibre bed deposition, fibre/resin ratio and porosity. However, a decrease of 50% in ILSS was observed in the laminates manufactured with recycled fibres, with respect to those with virgin fibres, presumably due to deterioration of matrix-fibre interface strength. The problem with the adhesion suggests that a sizing for protection of the fibres and for compability with the polymer matrix should be applied, and this will be the subject of further studies.

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