Composites Science and Technology 139 (2017) 99–108

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: http://www.elsevier.com/locate/compscitech

Recovery and reuse of discontinuous carbon fibres by solvolysis: Realignment and properties of remanufactured materials

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ARTICLE INFO

Article history:
Received 26 May 2016
Received in revised form
3 November 2016
Accepted 5 November 2016
Available online 9 November 2016

Keywords:
Carbon fibres
Discontinuous reinforcement
Recycling
Directional orientation

ABSTRACT

Discontinuous carbon fibre tows were recovered after solvolysis of an aeronautic type composite made with RTM6 epoxy resin. A Sohxlet extraction method was used to quantify the organic residue on the fibre tows and showed that less than 3 wt% was remaining on the surface. The recovered tows were therefore reused directly to manufacture a plate with randomly distributed carbon fibres and then three plates with realigned carbon fibres. The latter were then characterised and tested and the results obtained were compared to the material manufactured using the same type of virgin fibres by the same method. The materials made from recycled carbon fibres showed very good properties in comparison to the virgin fibre material, despite the presence of flaws such as quality of the fibre surface after solvolysis, alignment and voids). This is the first time in the open literature that carbon fibres recovered from solvolysis were reused in this way together with characterisation of the resulting materials.

1. Introduction

The usage of carbon fibres is increasing year after year, especially in transport applications. Currently aeronautics is the biggest consumer due to the recently developed planes (Boeing 787, Airbus A380 and A350), whereas the automotive industry seems rather reluctant to use them because of the expense and the slow manufacturing processes. In order to see more widespread usage, the cost of the carbon fibre would need to decrease to about $5 to 6 per pound (10–12 € per kg) [1]. Forecasts have also indicated that the current carbon fibre production volume would not be able to satisfy an increase in demand over the coming years. If every car manufacturer in the automotive industry attains a high-volume use of carbon fibre reinforced polymers (CFRP), the current carbon fibre production would not satisfy the demand according to experts at the JEC Americas 2014 [1]. Furthermore, these materials are still not recycled in a closed loop. Their wider usage in transport, and especially in automotive depends on their recyclability and their reuse in accordance with EU regulations. The recovery of carbon fibres by recycling end-of-life materials or production waste represents therefore a substantial resource that could fulfil these three issues (availability, recyclability and cost). Two technologies have particularly been studied and developed to recycle CFRP: pyrolysis and solvolysis. Both techniques have demonstrated the feasibility of separating efficiently the fibres from the resin and of producing very good quality fibres [2]. The main difference between these both techniques lies in what results from the resin degradation; pyrolysis mainly produces gases and oils, and in solvolysis the organic products from resin degradation are dissolved in the solvent system.

When single carbon fibres recovered from either pyrolysis or solvolysis are tested, the results show that their reinforcement properties are almost fully retained. Globally decreases of less than 10% have been observed for their tensile strength and their tensile modulus is unaffected [2]. Recycled and virgin carbon fibres (rCFs

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http://dx.doi.org/10.1016/j.compscitech.2016.11.001

and vCFs, respectively) are therefore similar, except that rCFs are no longer sized after the recovery treatment and in general are currently available in a discontinuous shape [2].

Different approaches have been studied to reuse the recovered fibres into new composite materials. These mainly are carbon fibres in random short fibre mats, pellets and realigned fibre mats, including reshaping into yarns [2]. However the only way to really benefit from the reinforcement capability and the value of the rCFs, is to at least align them. Indeed the alignment of discontinuous carbon fibres can considerably increase both the tensile stiffness and strength, and furthermore, the longer the fibres, the better the alignment and the higher the stiffness and the strength [3]. A few methods have been tried to align recycled carbon fibres in the United States, the United Kingdom and in France in particular [2]. The American company MIT-LLC (now known as Carbon Conversions) have developed a process called 3-DEP enabling the manufacture of three-dimensional preforms and the control of fibre placement and orientation according to the authors [4]. However the alignment quality has not been measured and was based only on a visual assessment. Furthermore the fibre length ranged between approximately 6 and 25 mm and produced preforms leading to a final fibre volume fraction lower than 30%. Researchers from the University of Nottingham have investigated two techniques based on a modified papermaking process as well as a centrifugal alignment process [2]. The second process was further investigated as it gave more promising results in terms of fibre alignment [2,5]. However the fibre length was again quite limited (up to 5 mm), together with the resulting mat overall density [5]. A process named HiPerDiF has been developed at the University of Bristol and produced materials showing a fibre volume fraction between 55% and 67% of the fibres aligned within the range of ±3° [6]. Again the process design limits, the fibre length and the preform areal density were also quite low (219 g/m^2). Furthermore this technique has not been tested on real recycled carbon fibres as yet. Researchers from the University of Bordeaux have recently patented a process to unweave pieces of recycled carbon fibre fabrics and align the fibre tows. The process can work with any fibre length, which is advantageous if one considers that the longer the fibres, the better the alignment [2]. Carbon fibres from other types of material could also be used as long as they are not fluffy. It was possible to produce a preform with 50 mm length fibre tows giving an areal density of 600 g/m^2 [2].

In this article, the Bordeaux process was used to align discontinuous recycled carbon fibre tows after unweaving of pieces of fabrics recovered by a solvolysis process [7–9]. According to the open literature, it is the first time that recycled carbon fibres recovered after solvolysis were reprocessed to make a new material. The other known work (not published as an article) in which solvolysed carbon fibres were reprocessed was realised in the AERDECO project [2]. However the amount of available recycled carbon fibres was too low to make a substantial mechanical characterisation. In this study, a material with randomly distributed carbon fibre tows and a material with aligned carbon fibre tows were manufactured and the mechanical properties (tensile and shear) were then measured. The results of mechanical testing are presented and discussed in relationship with the material structure and composition. The objective of this work was to assess the effect on the mechanical properties of flaws such as the presence of an organic residue coating the discontinuous recycled fibres recovered from solvolysis, fluffy fibres and not perfectly aligned fibre tows.

2. Material and methods

2.1. Materials

Plates of composite material made of RTM6 epoxy resin and 20 plies of T700 6 K carbon fibre woven fabric were cut into pieces of (50 × 50) mm^2 to (50 × 80) mm^2. Solvolysis was used to recover the carbon fibres as described in our earlier work [7]. The plates had a thickness of (6 ± 0.1) mm and a fibre volume content of (53 ± 1)%. Pieces of Prime Tex 48194 C1270S fabric from Hexcel, made with T700SC 12 K 50C carbon fibres, were cut in sizes similar to the pieces of RTM6 composite materials and manually unwoven to retrieve the virgin fibre tows. In this case, the fibres are sized but the sizing is not known.

A new plate was manufactured in the Laboratoire de Thermocinétique de Nantes (LTN) using the carbon fibres recovered after solvolysis and a commercial epoxy resin, SR 1500 cured with SD 2503 hardener from Sicomin. Four plates were also manufactured at the Institut de Mécanique et d'Ingénierie (I2M) in Bordeaux using carbon fibres recovered after solvolysis and another commercial epoxy resin, Araldite® LY 5052 cured with Aradur® 5052 hardener from Huntsman. Plates using virgin fibre tows of the 48194 C1270S fabric were also manufactured for comparison.

Grilon® polyamide powder (a mixture of polyamides PA6 and PA66, grain size 100 μm) from EMS-Grivory was used to bind the fibre tows together after alignment.

Acetone (analytical grade) was purchased from Sigma Aldrich. Water used in solvolysis experiments was unfiltered mains water.

2.2. Fibre recovery by solvolysis

The experiments were realised in a 5 L hastelloy batch reactor from Parr Instruments. The samples were placed into a stainless steel basket to avoid any contact with the reactor walls and therefore pyrolysis. Seven experiments were conducted with a 2.2 L mixture of water and acetone at 20:80 vol ratio. The composite loading rate was determined to give a resin concentration of (30 ± 1) g/L. The heating phase required about 75 min to reach 320 °C, inducing a pressure of (180 ± 10) bar. The system was maintained at this temperature for 2 h. Due to the weight of the reactor, it was not possible to lift it from the oven to cool, therefore the cooling phase required about 2 h for the temperature to decrease below 200 °C and approximately 18 h to reach 35 °C. After this time the reactor was opened and the pieces of fabrics and the liquid fraction containing the dissolved organic products from the degraded resin were recovered.

2.3. Fibre characterisation

The fibres were analysed by Environmental Scanning Electron Microscopy (ESEM) using a Philips XL30 FEG ESEM. Samples were cut and then mounted to adhesive stub mounts. Although carbon fibres are conductive, the samples were coated in platinum to improve image quality using and EMSCOPE SC500 low-vacuum sputter coater. Once mounted and coated on the stubs the samples were loaded individually into the ESEM and the sample chamber was evacuated. The images were taken at varying magnification levels at an acceleration voltage of 20 kV.

The organic residue on the recovered fibre bundles was measured on samples using a Soxhlet extraction method. The fibre bundles were put into a single thickness cellulose extraction thimble (25 mm diameter x 100 mm length from Whatman) and then placed in a Soxhlet extractor with 110 mL of an acetone carrier solvent. Each extraction cycle took 15 min, and the washing totalled 6 cycles giving an overall rinsing time of approximately 100 min. The mass of the fibre bundles was measured before and after washing, and the proportion of organic residue was determined using equation (1).