FIBRE CHARACTERISATION OF STEAM THERMAL PROCESS RECYCLED CARBON FIBRE/EPOXY COMPOSITES

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1 General Introduction

Carbon Fibre Reinforced Plastics (CFRP) are known as high performance materials. Being mostly made from thermoset resin matrix (70%) still known as non-recyclable materials, development of waste composite materials treatments was slowed down for a long time. However, recent European legislation (2000/76 and 2000/53 directives) helpfully contributes to the emergence of waste treatment solutions [1, 2]. Recycling CFRP wastes currently offers interesting economic and environmental perspectives.

Carbon fibre market constantly grows the last few years. World need in carbon fibre grew from 18 000 tons per year in 2001 to 48 000 tons in 2013 [3]. Up to 120 000 tons per year are expected in 2017 with a high contribution of wind energy manufacturing industry on this market [4]. With their increasing applications in the aeronautical, sports and automotive industries, the waste amount of CFRP reaches a significant level, and is currently estimated to 1500 tons per year [5].

Three main recycling processes enable carbon fibre recovery: solvolysis, pyrolysis and steam-thermolysis. Solvolysis is a chemical process based on the organic matrix depolymerisation by the means of solvent. Low temperatures are used. Solvents are often used in supercritical conditions and could be water or different alcohols (propanol, methanol) that have been the most studied [6-8]. Pyrolysis is based on the organic matrix thermal degradation [9]. Steam-thermal process is a thermochemical process using superheated steam at environmental pressure to degrade the organic matrix of the composite and thus to recover carbon fibres [10]. In this study, it is purposed to present an evaluation of the steam-thermal process applied to the CFRP recycling, in terms of recovered carbon fibres quality.

2 Materials and experimental

2.1 Composite manufacturing

Composite samples were made by Liquid Resin Infusion (LRI) process. This process is based on a progressive impregnation of liquid resin through the different plies of a carbon fabric placed in a metallic mould. Infusion is induced by a pressure gradient between the resin input and the output where vacuum is applied. Experimental set-up is shown in Figure 1.

Fig. 1. A picture of the experimental device used for composite manufacturing by infusion (LRI).
A Sicomin SR1710 Infusion epoxy resin was used with a Sicomin SD8822 hardener. That is a low viscosity bi-component system. A 20 hours at environment temperature plus 16 hours at 60°C polymerisation cycle was applied before removing system from the mould. Carbon reinforcement was a carbon fabric 2x2 (Hexcel 46285 U1200) made from AS4C carbon fibres. Sixteen 40 x 40 cm plies were stacked so as to obtain an approximately 800 grams plate, for a 4mm final thickness. The average fibre mass fraction was 66 % in mass. These plates were cut by the mean of a circular saw in order to get 5x12 cm samples. These particular dimensions enable to respect some experimental constrains due to steam-thermolysis reactor geometry.

### 2.2 Recycling carbon fibres

The recycling was conducted in a bench-scale reactor as shown in Figure 2. Previous made composite samples are treated by the steam-thermolysis process so as to reclaim carbon fibres. Steam-thermolysis is a thermochemical process using superheated steam at environmental pressure in order to degrade the organic matrix of the composite. Scrap composites samples are first inserted in the crucible coupled with a thermogravimetric analyser. Once the ordered temperature is reached in the reactor, the crucible is introduced within the reactor (the furnace). A unit made up of a steam generator and a nitrogen input manages atmosphere control.

Three categories of products are then collected: a solid fraction that is constituted of reclaimed carbon fibres, a permanent gaseous fraction principally constituted of methane and carbon monoxides and a last condensable gaseous fraction that is constituted of pyridines, benzene and phenols.

![Fig. 2. A schematic diagram for the recycling process [3].](image)

Experiments were carried out under atmospheric pressure and for two temperatures: 400°C and 500°C. These experimental conditions were selected from a study carried by Sheng Yin Ye during his PhD work focused on the carbon fibres recovery from CFRP by a steam-thermal process [11]. Same materials and geometries were used. For each of these treatments, atmosphere was identical, composed of steam and nitrogen. Although it is easy to say that nitrogen was the main part of the atmosphere, exact composition is however wished to be kept confidential by our industrial partner.

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Description</th>
<th>Yield of eliminated resin (%)</th>
<th>Average diameter (um)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VF</td>
<td>AS4C virgin fibre used as a reference</td>
<td>-</td>
<td>7,1</td>
</tr>
<tr>
<td>RF400</td>
<td>Recycled carbon fibres from 400°C and 500°C steam-thermolysis</td>
<td>95 %</td>
<td>6,8</td>
</tr>
<tr>
<td>RF500</td>
<td>Recycled carbon fibres from 400°C and 500°C steam-thermolysis</td>
<td>&gt; 99 %</td>
<td>6,8</td>
</tr>
<tr>
<td>RF500_O</td>
<td>RF500 fibre heat treated at 450°C during one hour (air)</td>
<td>-</td>
<td>6,8</td>
</tr>
</tbody>
</table>

Tab. 1. Samples description of the study.
First treatment ST400 is a 400°C steam-thermolysis. The second one, ST500, is a 500°C steam-thermolysis. After epoxy resin was decomposed, and once the system cooled down, recycled carbon fibres were collected from the reactor.

No cleaning of the surface is required before their use. They are respectively named RF400 and RF500. Table 1 gives a description of these two products reclaimed from steam-thermal treatments of this study. The RF500 carbon fibre was also heat treated by an air oxidation treatment at 450°C during one hour in a drying chamber. The heat-treated RF500 fibre is named RF500_O and is listed in Table 1.

2.3 Fibre morphology

Yields of eliminated resin were measured by dissolution of remaining resin with hot sulphuric acid, according to French standard NF EN 2564.

Environmental Scanning Electron Microscopy (ESEM) was used to observe surface texture and morphology of the fibres. Samples were mounted on an adhesive carbon layer stuck onto an aluminium stub. As carbon fibre is conductive, no other specific preparation was needed. The acceleration voltage was 20 kV. Diameters of the fibres were also measured using image analysis. For each sample, an average diameter was determined by measuring a population of 200 fibres.

The specific surface area was also determined by means of BET (Brunauer, Emett and Teller) technique (N2 adsorption). The BET specific surface area (As) was measured using a Micromeritics ASAP 2010 K2 analyser (Micromeritics, Georgia, USA). Fibre samples (0.5 to 1 g) were degassed at 100°C in a flow of carrier gas for 24 hours or longer before taking a measurement. The blank surface area of the instrument was measured and this value was subtracted from the total area of sample and instrument to get corrected surface area values.

2.4 Surface chemistry

Surface chemical characteristics were determined using X-ray photoelectron spectroscopy (XPS). Analyses were realised by IPREM (Institut des Sciences Analytiques et de Physico-chimie pour l’Environnement des Matériaux) of University of Pau. The XPS analysis was conducted using a Kratos AXIS ULTRA 165 with a monochromatic Al-k-alpha X-ray source (1486.6 eV). Survey spectra in the range of 0–1200 eV were recorded for each sample with a pass energy of 80 eV and a step of 0.5 eV, followed by high resolution scanning over C1s range with a pass energy of 30 eV and a step of 0.1 eV. Narrow scans (pass energy = 20 eV) for C1s, O1s, N1s and Si2p were performed three times at three positions on each sample.

The average surface composition was determined from the area beneath the elemental peaks using relevant Kratos sensitivity factors: C1s (0.25), O1s (0.66), N1s (0.42), Si2p (0.23) and Na1s (2.3) (Kratos Analytical Ltd., Manchester, UK). Sensitivity factors are a combination of photoelectric cross section, transmission function and inelastic mean free path factors.

2.5 Mechanical properties

Mechanical tests were carried out on fibre bundles using Bundle Tensile Tests (BTT) so as to quantify the tensile strength of the recycled carbon fibres. This test has been developed in INSA Lyon-Villeurbanne [12]. It is based on the random and individual fibre failure within the bundle. Therefore, statistics laws are used for analysis. This statistical data approach enables to take a wide single filament population into consideration.

The Bundle Tensile Test needs a meticulous experimental procedure. One of the difficulties is the measurement of reliable bundle strain. An extensometer is placed on heat shrink tubes previously threaded on each tip of the bundle. That is also a mean to define a gauge length. Each tip will have been impregnated with Araldite 2015 resin and then polymerised at 70°C during one hour. Impregnated tips are inserted in metallic tubes that enable a regular clamping by tensile machine grips. Before loading, the sample is lubricated by petroleum. By this way, friction phenomena between fibres within the bundle can be avoided, and so a too early fracture.

The tensile tests were performed using a pneumatic testing machine with a 500 N cell. They were carried out at room temperature under constant displacement rate on specimens prepared according
to previous procedure [13]. Gauge length was 60 mm. Crosshead speed was set to 0.1 mm/min. Carbon fibres bundles were loaded until failure and the load displacement curve was recorded. At least 3 bundles of 6000 filaments were tested for each sample.

Using the most common technique, Single Fibre Tensile Test (SFT), it is also possible to characterise the stress distribution of the fibres from a wide population of individual fibres. This test was employed to quantify the tensile strength of RF500_O fibre as no data was acquired from BTT. So as to make comparison possible, all samples were finally tested by SFT. Method was based on international standards ISO 11566 [14]. A filament was bonded to a paper window with cyanoacrylate Loctite 409. Then, the specimen was carefully aligned with the tensile testing machine axis and clamped in the grips to be loaded. Each side of the paper window was cut before testing. The gauge length was 25mm. A 5 N load cell was used and the crosshead speed was set to 0.1mm/min. Carbon fibre specimens were loaded until failure and the force displacement curve was recorded. At least 40 filaments were tested for each condition.

3 Results and discussion

3.1 Surface morphology

Figure 3 shows an ESEM image of the virgin fibre VF and recycled carbon fibre RF500. Examination of several images of several fibres from different batches clearly showed no visible alteration to the surface topography due to steam-thermolysis and therefore a similar texture. Surfaces of these fibres are particularly clean. The applied treatment seems to efficiently remove the most part of the resin of the composite material. Concerning the RF500_O fibre, no visible alteration can be noticed after the air oxidation treatment on the ESEM images. Recycled RF400 fibres are shown in Figure 4. A few small particles can be seen on this image and are attributed to resin residues that stuck on the surface. As can be seen from the ESEM images, the particles have a size from 2 to 20 micrometres. These particles avoid the fibres to be properly separated.

These observations are to be related to residual resin quantities measured on the surface of the fibres. RF500 fibre is fully free of resin. However, RF400 fibre keeps 5% by mass of remaining resin. These observations obviously show the importance of temperature on the degradation kinetic. However, a too long exposure of the fibre in a high temperature and oxidative environment could seriously affect its properties, especially mechanical properties.

BET surface area measurements show little difference between the three fibre conditions of this study. Both virgin, RF400 and RF500 fibres have a close surface area, between 10.9 and 14.6 m²/g. These results, in combination with ESEM images, suggest the steam-thermal treatment cause little damage to the fibre surface. Therefore, in a case of reuse of the recycled carbon fibre for composite manufacturing, no alteration of the interfacial adhesion by mechanical interlocking should be expected.
Fibre | Specific surface area (m²/g)  
---|---  
VF | 14.5  
RF400 | 14.6  
RF500 | 10.9  
RF500°O | 19.3

Tab. 2. Specific surface areas.

BET results in Table 2 show that a surface oxidation treatment of RF500 fibres enables to increase surface area from 10.9 to 19.3 m²/g. A higher surface area could bring significant contribution to the interphase adhesion by mechanical interlocking although macro scaled benefits are not obvious and likely not to be easy to measure for such a light increase.

### 3.2 Surface chemistry

The detection area of the XPS is about 400 x 400 micrometres. Thus, the XPS analysis listed in Table 3 primarily reveals the surface composition of the fibre.

<table>
<thead>
<tr>
<th>Element</th>
<th>VF</th>
<th>RF400</th>
<th>RF500</th>
<th>RF500°O</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>84.5</td>
<td>77.5</td>
<td>85.7</td>
<td>84.3</td>
</tr>
<tr>
<td>O</td>
<td>14.8</td>
<td>11.8</td>
<td>8.5</td>
<td>10.0</td>
</tr>
<tr>
<td>N</td>
<td>0.2</td>
<td>10.0</td>
<td>4.1</td>
<td>4.7</td>
</tr>
<tr>
<td>Si</td>
<td>0.2</td>
<td>0.4</td>
<td>1.4</td>
<td>0.5</td>
</tr>
<tr>
<td>Ca</td>
<td>-</td>
<td>0.1</td>
<td>0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>O/C</td>
<td>0.17</td>
<td>0.15</td>
<td>0.10</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Tab. 3. Surface elemental compositions and O/C ratios determined by XPS surveys scans.

The main elements present in the XPS analysis are carbon (285.0 eV), oxygen (533.0 eV) and nitrogen (400.4 eV). The RF500 fibre contains about 1.6% of Silicium. The Si concentration decreases for other fibres. It is firstly likely to think about a reactor contamination that could have affected fibres during steam-thermolysis. It can be refuted by presence of Si in VF (virgin fibre) scans that reveals that silicium is likely to be an element that come from carbon fibre manufacturing process, as trace amounts of Na or Ca.

For virgin fibre (VF) chemical environments, the global XPS spectrum shown in Figure 5 indicates that epoxy bonding is detected (533.0 eV) in relation with C1s peak (286.8eV) corresponding to C-O-R environment. Were also detected Si-OH functions. Added to surface compositions analyses, this indicates that sizing is likely to be an epoxy resin. As no nitrogen was detected, an acid anhydride hardener was probably used. In RF400 and RF500 spectra, adsorbed water traces were found. Silicium was found in another form (SiC or SiO2) indicating that the sizing was removed. RF400 fibre shows a high nitrogen amount revealing that residual resin was analysed and not only fibre, as hardening of Sicomin SR1710 epoxy resin is realised with amine. RF500 fibre shows higher silicium quantities. Moreover, nitrogen contents are lower and detected in other forms, indicating that the fibre surface is free from resin. Therefore, no organic components are remaining on the surface of the fibre. However, some oxygenated groups were detected showing the steam-thermal process had probably altered its surface chemistry and thus, played a significant role in the surface
chemistry modification. Nonetheless, we should notice that steam-thermal process is controlled by diffusion: the chemical composition of the resin, the cure process employed, degree of polymerization and all other cure reaction parameters are contributors influencing the degradation of the matrix and thus, surface composition of the fibres.

Table 3 also lists the oxygen/carbon ratio (O/C) for all samples. These results show RF400 and RF500 fibres have different surface composition to the virgin fibre. RF500 had the lowest O/C ratio and then is expected to show the lowest interfacial adhesion by chemical bonding. Virgin fibre had the higher O/C ratio, as a consequence of sizing presence. Finally, as the air oxidation treatment enabled to slightly increase the oxygen amount at the expense of carbon rate, the O/C ratio increased from 0.10 to 0.12 thanks to introduction of oxygenated groups. No further modification was noticed.

3.3 Mechanical properties

Mechanical tensile strengths, their standard deviations and corresponding confidence intervals extracted from statistical analysis are listed in Table 4. One of the experimental curves is shown in Figure 6. It is easy to see that experimental curve and normal distribution based curve were well fitted although a perfectly controlled failure of the bundle has not occurred. For each sample, mechanical properties of carbon fibres are deducted from parameters analysis of the analytical curve.

Manufacturer data gives a tensile strength of 4320 MPa. As a consequence, bundle tensile test measurements are up to 25% lower. As shown in Figure 7, RF500 mechanical properties are nearly not affected by steam-thermolysis. Indeed, looking at the frame given by the 95% confidence interval, no significant difference can be noticed between RF500 fibres and VF fibres, indicating that steam-thermolysis enables to retain tensile strength of the reclaimed carbon fibre RF500. On the other hand, a significant decrease of almost 600 MPa affected RF400 fibres. These samples actually contained about 5% of residual resin on the surface. Resin nodules are a direct contribution to the friction increase between filaments during the bundle tensile test. Friction in BTT leads to a premature failure of the neighbouring fibres in the bundle and, thus, contributes to a decrease of the tensile strength, in spite of lubrication. Resin nodules are also known to be stress concentrators that can lead to the same consequences.
significant consequence on the tensile strength. A slight decrease is observed, indicating that there was no important alteration of the fibre during the treatment. Regarding BET, XPS and BTT results, air oxidation does not seem to bring significant benefits for improving interfacial adhesion. In this aim, air oxidation treatment seems not to be the most appropriate treatment and further investigation has to be done in this way, other oxidation treatments existing like chemical, electro-chemical or plasma oxidation treatments.

<table>
<thead>
<tr>
<th></th>
<th>VF</th>
<th>RF400</th>
<th>RF500</th>
<th>RF500_O</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>BTT tensile strength (MPa)</strong></td>
<td>4094</td>
<td>3243</td>
<td>4083</td>
<td>-</td>
</tr>
<tr>
<td><strong>Standard deviation (MPa)</strong></td>
<td>+/- 1070</td>
<td>+/- 598</td>
<td>+/- 805</td>
<td>-</td>
</tr>
<tr>
<td><strong>95% confidence interval (MPa)</strong></td>
<td>20,2</td>
<td>20,2</td>
<td>21,8</td>
<td>-</td>
</tr>
<tr>
<td><strong>SFT tensile strength (MPa)</strong></td>
<td>3776</td>
<td>3272</td>
<td>3610</td>
<td>3527</td>
</tr>
<tr>
<td><strong>Standard deviation (MPa)</strong></td>
<td>547</td>
<td>672</td>
<td>540</td>
<td>590</td>
</tr>
<tr>
<td><strong>95% confidence interval (MPa)</strong></td>
<td>145</td>
<td>179</td>
<td>144</td>
<td>157</td>
</tr>
</tbody>
</table>

Tab. 4. Mechanical data properties from BTT and SFT tensile tests.

4 Conclusions
Steam-thermal process was used in a bench-scale reactor to recycle carbon fibre from epoxy resin/carbon fibre composites. Properties of the recycled carbon fibres were characterised using ESEM, BET, XPS, single fibre tensile test and bundle tensile test. Carbon fibres are properly separated from polymer matrix during the treatment showing that a steam-thermal treatment is efficient and enables to reach high resin elimination levels. In terms of reactional kinetic, temperature is an important factor. Otherwise, it plays an important role on morphological, surface, chemical and mechanical properties of reclaimed carbon fibres.

A 400°C treatment does not allow to reclaim good quality carbon fibres as their surface is not totally clean and mechanical properties are not maintained. However, for a 500°C treatment, reclaimed carbon fibres have a similar surface texture to virgin fibres. No degradation of the tensile strength was observed and the fibre conserved its intrinsic properties. Valorisation of these fibres could be possible. A composite formulation work from recycled carbon fibres is in progress. Properties of composites made from recycled carbon fibres should be measured so as to reveal the viability of such a process to produce recycled carbon fibres from epoxy based composite materials. The recycling of CFRP will acquire a considerable importance in the next few years due to legislative context, and the need to find sustainable solutions for waste processing. Steam thermal process has demonstrated its abilities in this field.

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References
[3] Toray’s Strategy for Carbon fiber Composite Materials:


