

## MANUFACTURING PROCESS AND CHARACTERISATION OF C/C LARGE DIAMETER FILAMENT

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### **Abstract**

*This work aims at manufacturing a large diameter filamentary carbon reinforcement from a non twisted 1K bundle of carbon fibres. The manufacturing process consists in infiltrating the bundle with phenolic resin, and turning it into a carbon/carbon composite after pyrolysis.*

*The first part of the study demonstrates the suitability of the process by preliminary calculations on fibre volume fraction, diameter of the filaments and maximum curvature radius. Then, the next part of the study concerns the definition of the C / phenolic resin filament processing conditions: impregnation method, temperature, and curing cycle. Finally, mechanical characterisation of both precursor and pyrolysed filaments are exposed.*

### **1 Introduction**

Metal matrix composites have found many applications in domains like aeronautics and aerospace, thanks to the combination of high mechanical properties, high temperature resistance and low weight. Among these materials, titanium matrix composites have appeared to be promising materials, aiming at increasing Young's modulus of these light alloys (about 120 GPa). However, processing problems have limited their application, particularly because of the reactivity of titanium at high temperature.

Previous studies [1] have shown the interaction between carbon and titanium may induce only little influence on composite with large diameter filaments like silicon carbide (about 140 $\mu$ m). On the contrary, when the same process was applied to small diameter reinforcement like carbon fibres, the mechanical properties were not as elevated as expected because of this interaction.

This work aims at manufacturing a large diameter filamentary damageable reinforcement for titanium matrix composites, with high stiffness and strength, that could be rolled on a 20 cm diameter coil. The non brittle behaviour can be obtained using a filament shaped carbon-carbon composite, resulting from the pyrolysis of a carbon fibre bundle previously infiltrated by phenolic resin.

The first part of the study concerns preliminary calculations on the filament constituents and properties. Indeed, the influence of several parameters like the diameter, the number of carbon fibres, and the fibre volume fraction have to be studied.

Then, the C / phenolic resin precursor filament processing conditions are defined in a second part. Each step of the process are detailed and optimised to give the best morphology and

mechanical properties to the composite. Finally, the pyrolysis conditions are studied I the last part of the paper in order to obtain the best mechanical properties.

## 2 Preliminary calculations

### 2.2 Preliminary calculations

Before starting the definition of the process, preliminary calculations have to be made in order to evaluate the properties of the filaments.

The material properties used for the next calculations are:

- diameter of an elementary fibre:  $D_f = 7\mu\text{m}$ ,
- Young's modulus of the fibre:  $E_f = 230\text{ GPa}$ ,
- tensile strength of the fibre:  $\sigma_{fR} = 3500\text{ MPa}$ ,
- Young's modulus of the resin:  $E_m = 30\text{ GPa}$ ,
- tensile strength of the resin:  $\sigma_{mR} = 100\text{ MPa}$ .

The first calculation aims at verifying that suitable mechanical properties can be obtained processing a C / Phenolic resin large diameter filament. Indeed, the higher the fibre volume fraction is, the higher the modulus and strength of the filament are, so it must be verified that high fibre volume fraction can be reached. A calculation leads to a maximum compacity of the bundle of 90%. This value indicates the maximum fibre volume fraction that can be theoretically obtained, and allows the calculation of the diameter  $D_f$  of the filament for different fibre volume fractions. Then, the minimum curvature radius  $R_{\min}$  the filament can take is calculated from this diameter following equation 1.

$$R_{\min} = \frac{E_f D_f}{2\bar{\sigma}} \quad (1)$$

where  $E_f$  and  $\bar{\sigma}$  are respectively the Young's modulus and the ultimate strength of the filament.

The evaluation of  $\bar{\sigma}$  needs any assumption concerning the composite's behaviour. Indeed, the fracture mechanism depends on the relative values of the elongation at break of fibres and matrix. In our study, we can consider that the elongation at break of the fibres is the greatest, so during the deformation of the composite, matrix breaks earlier than the fibres. In order to avoid the fracture of the composite, the volume fraction of fibres  $V_f$  has to be superior to the volume fraction  $V_{ftrans}$  calculated following equation 2.

$$V_{ftrans} = \frac{\sigma_{rm}}{\sigma_{rm} + \sigma_{rf} - \sigma_{rm} \frac{E_f}{E_m}} \quad (2)$$

In the case where  $V_f > V_{ftrans}$ ,  $\bar{\sigma}$  is calculated thanks to equation 3, and in the other case, equation 4 is used.

$$\bar{\sigma} = V_f \sigma_{rf} \quad (3)$$

$$\bar{\sigma} = [E_f V_f + E_m (1 - V_f)] \frac{\sigma_{rm}}{E_m} \quad (4)$$

Using the properties previously given for carbon fibre and phenolic resin, the calculation leads to a value  $V_{ftrans} = 0.035$ . As the reinforcing filament must have high mechanical

properties, the fibre volume fraction has to be kept above 50%, so the value of  $\bar{\sigma}$  is given by equation 3. The preliminary evaluations of these properties for the example of a 1K bundle (1000 carbon fibres) are presented in table 1.

<b>Fibre Volume fraction (%)</b>	60	70	80	90
<b>Diameter of the filament (<math>\mu\text{m}</math>)</b>	286	265	247	233
<b>Young's modulus (GPa)</b>	150	170	190	210
<b>Minimum curvature radius (mm)</b>	10,2	9,2	8,4	7,8

**Table 1.** Results of preliminary calculations for different fibre volume fraction

The results give an idea of the possible diameters of filaments with this kind of fibre. These values of minimum curvature radius allow the use of more than 1K bundles, but it would result in much bigger diameters (about 500 $\mu\text{m}$ ). As this bundle is the smallest available, and in order to keep the filament as near as possible of the SiC one, the 1K bundle is selected to manufacture the composite.

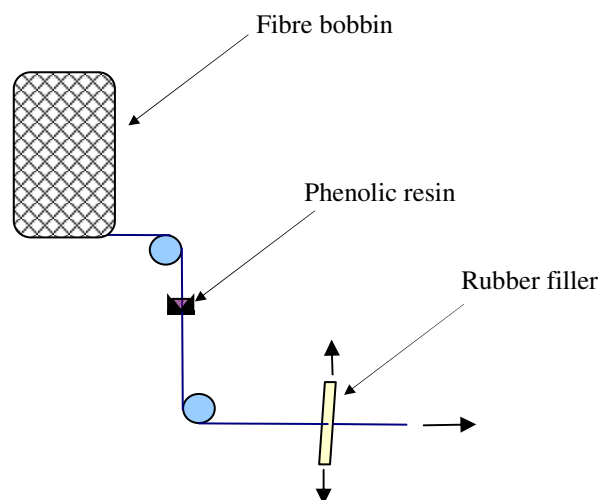
As described before, the manufacturing process is composed of 2 steps: (1) realisation of an impregnated bundle of fibre and (2) carbonisation of the resin of this product. The structure of the filament obtained after the first steps greatly influences the properties of the final product, so it seems important to optimise this operation.

### 3 Optimisation of the processing conditions of carbon fibre / phenolic resin composite

The requirements of the realisation of the 1D-C / phenolic filament by infiltration are:

- a complete infiltration of the bundles or only the surrounding,
- a constant diameter of the filaments,
- undamaged fibres,
- perfectly aligned fibres.

The manufacturing process of the precursor filament consists in a kind of pultrusion: the fibre bundle is infiltrated and calibrated by passing through a rubber filler, in order to obtain a circular section with the suitable volume fraction (figure 1).



**Figure 1.** Manufacturing process of the precursor C / Phenolic resin filament

The phenolic resin (reference: Hexcel PHV78900) is selected because of interesting properties for this first step (low viscosity) and for its high efficiency during the pyrolysis. As the use of a very small filler to calibrate the pultruded filament would be difficult and could damage the bundle, a 200µm diameter filler is used. What's more, the Young's modulus and minimum curvature radius obtained for the precursor are promising for pyrolysed filament.

### 3.1 Impregnation method

Impregnating a fibre bundle or preform is a classical problem in manufacturing composites. Indeed, methods can be different following the shapes, resin and fibres. Manually impregnated bundles are compared with others passing through a 500µm metallic filler. Both filaments are then pultruded in the 200µm rubber filler, to limit the quantity of resin and ensure a small final diameter.

Each C fibre / phenolic resin filament is observed with numerical microscope to measure the diameter, and tensile tests are performed to evaluate Young's modulus and tensile strength for both impregnation methods. The results are summarised in table 2.

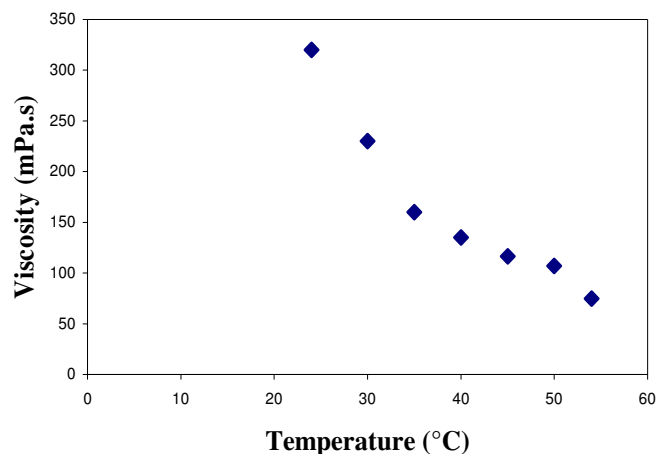
	500 µm filler	Manual impregnation
Diameter (µm)	269	347
Young's modulus (GPa)	116	133
Tensile strength (MPa)	1978	1446

**Table 2.** Comparison of manual and filler impregnation

As it can be seen, the manual impregnation results in a higher Young's modulus (about 15% increase), but the filament diameter is about 70µm bigger and the tensile strength loses about 25%. For all these reasons, added to the fact that manual impregnation is a supplementary operation in the process, the impregnation by metallic filler is chosen for manufacturing the carbon fibre / phenolic resin filament.

### 3.2 Resin temperature and viscosity

Phenolic resin like other thermoset polymer has a variable viscosity as a function of the temperature. Viscosity has been measured by rotational tests at different temperatures (figure 2), enhancing an important decrease between 25 and 50°C.



**Figure 2.** Diminution of viscosity of the resin as a function of the temperature

Then, in order to see if the viscosity has an influence on the quality of the impregnation of the fibre bundle, several filaments are manufactured using resin from 10°C to 50°C.

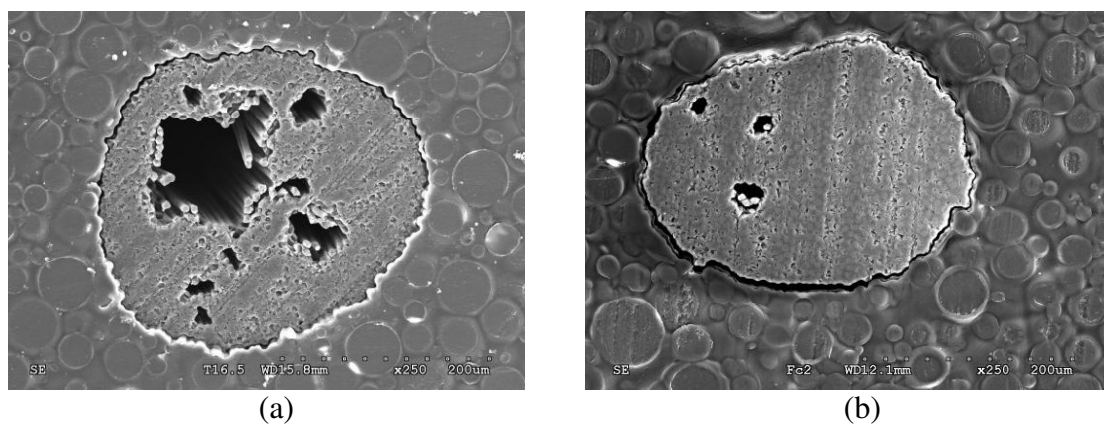
	10°C	20°C	30°C	40°C	50°C
Diameter (µm)	299	298	301	315	328
Young's modulus (GPa)	141	133	114	118	110
Tensile strength (MPa)	1607	1602	1637	1370	1433

**Table 3.** Filament properties for different impregnation temperatures

The results show that the mechanical properties are unchanged, but the diameter of the filament increases if the impregnation is made above 30°C, so, in order to keep the size near classical reinforcement filaments, the temperature of 20°C is chosen for the impregnation of the fibre bundle.

### 3.3 Curing temperature cycle

The phenolic resin reticulation occurs during a cycle of one hour at 150°C. However, two kinds of curing are tested: (1) simple one with the only step at 150°C, and (2) more complex one with a preliminary step at 80°C during 30 minutes before the step at 150°C. The obtained filaments are then observed by SEM to see the influence on porosity and mechanically tested. The microscopic observations show that the degassing step at 180°C enables a drastic drop in pore size, as illustrated in figure 3.



**Figure 3.** Comparison of pore size for (a) simple and (b) complex curing cycle

Tensile tests are performed on filaments for each curing cycle to compare again the values of the diameters, Young's modulus and tensile strength (table 4).

	1 <sup>st</sup> cycle	2 <sup>nd</sup> cycle
Diameter (µm)	269	270
Young's modulus (GPa)	116	141
Tensile strength (MPa)	1978	2274

**Table 4.** Filament properties for different curing temperature cycles

The results indicate the properties are superior for the filaments manufactured following the second cycle, so it will be applied later for every manufactured filament.

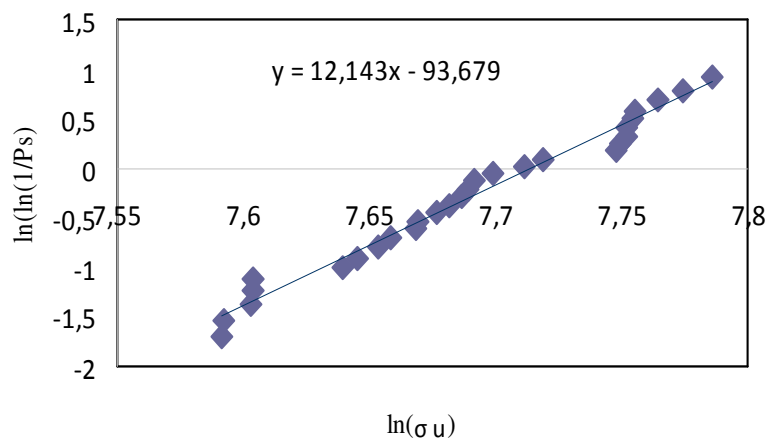
### 3.4 Mechanical characterisation of carbon fibre / phenolic resin filament

Tensile tests are conducted on precursor filaments on an ADAMEL DY 32 testing machine, equipped with a videoextensometer for the measurement of the deformation. The chosen gage length of the specimen is 50mm, and the strain rate is 0.02min<sup>-1</sup>. The results of thsess tests are summarised in table 5.

Mean diameter	Young's modulus	Tensile strength	Elongation at break
283 μm	142 GPa	2153 MPa	1.48 %

**Table 5.** Tensile tests results on carbon fibre / phenolic resin filament

A statistic analysis on the results following Weibull approach can be made in order to characterise the brittle behaviour of this filament and its sensibility to defects [2]. A survey probability  $P_s$  is defined and calculated for each tensile strength  $\sigma_U$ , and results on the following graph (figure 4) showing  $\ln\left(\ln\left(\frac{1}{P_s}\right)\right)$  as a function of  $\ln(\sigma_U)$ .



**Figure 4.** Weibull analysis for carbon fibre / phenolic resin filaments

This kind of analysis shows the process reproductibility is good, because the weibull modulus is 12. Indeed, carbon fibre brittle behaviour often results in weibull modulus values around 5, so the tensile strength dispersion of the studied filament seems quite small.

## 4 Definition of pyrolysis conditions

In order to be an efficient reinforcement for light metallic alloys, the carbon / carbon filament must have high mechanical properties, particularly Young's modulus and tensile strength. In addition, the processing conditions, particularly the carbonisation conditions (temperature, duration...) have to be studied in order to obtain a damageable behaviour.

### 4.1 Pyrolysis conditions

Pyrolysis is a very important step in the manufacturing process because the mechanical properties of the filament can be very different following the conditions. Indeed, a limitation in using C/C composites could be a very brittle behaviour. This phenomenon can be observed

when fibre / matrix bonding is very stiff, because the crack deviation at the interface can't occur [3].

Another problem with pyrolysis is the apparition of pores of different sizes and orientations [4]. Indeed, the gas emission at high temperature, particularly at high heating rates, causes important matrix cracking and results in lower mechanical properties.

In this study, the temperature of 800°C is considered for different durations. In order to avoid the oxidation of the carbon fibre, the pyrolysis is conducted under nitrogen atmosphere. The filament length is limited at 20cm by the size of the isotherm zone of the furnace, which is enough because the gage length of the specimen for mechanical characterisation is 60mm.

#### 4.2 Mechanical characterisation of carbon / carbon filament

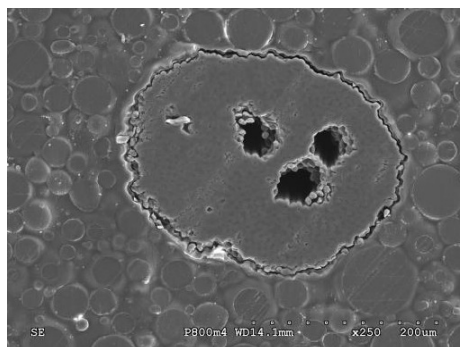
The influence of the duration of the carbonisation is studied with tensile tests after 1 hour or 4 hours pyrolysis operations (table 6).

	Diameter ( $\mu\text{m}$ )	Young's modulus (GPa)	Tensile strength (MPa)
<b>1h</b>	270	127	319
<b>4h</b>	260	147	364

**Table 6.** Properties of pyrolysed filaments

The results indicate that 4h duration seems more suitable for the filaments because final diameters seem smaller, and both modulus and strength are higher. What's more, it must be noted that another pyrolysis temperature (1200°C) should be experimented because the carbon / carbon filament manufactured at 800°C is so brittle that tensile strength drops when compared with carbon fibre / phenolic resin filaments.

These results can be explained by observations of pyrolysed filaments at numerical microscope. As illustrated in figure 5, the observation of the filament cross section shows important pores that may induce a failure under low stress in a brittle material like carbon.



**Figure 5.** Pyrolysed filament cross section

Previous studies showed that pyrolysis temperature has a great influence on brittle behaviour of these composites [5], and higher temperature may allow a weaker bonding between fibre and amorphous carbon. What's more, previous tests indicated, such porosity couldn't be found before carbonisation, so it seems the manufacturing process last step should be optimised to minimise the size of these pores.

## 5 Conclusion

Large diameter carbon filaments have been manufactured and tested in this study, resulting in circular cross section filaments with suitable stiffness. The manufacturing process of the precursor filament has been optimised in order to obtain few porosity and variations of diameter and properties.

However, the final step of the process still has to be studied because the pyrolysis generates too much porosities, resulting in a low tensile strength for the filament. In a further study, other conditions (temperature, duration...) should be tried, aiming at making the filament less brittle and more resistant.

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