

Impact of the carbon fiber type on the properties and performances of C/C composite for ramjet applications

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Abstract

Ceramic Matrix Composites, especially Carbon/Carbon composites, play a crucial role in the development of next-generation supersonic and hypersonic vehicles for structural applications. The current study, involving a collaboration between ArianeGroup GmbH and MBDA France, evaluates the performance of CARBOTEX® material fabricated using two types of ex-PAN carbon fibers (A & B), featuring initial similar properties. The examination considered the composites' behavior from manufacturing to performance in ramjet environments, focusing on permeability and mechanical properties. The investigation revealed that while permeability, assessed through the Darcy coefficient, remained fairly consistent between the two composites (CMC-A and CMC-B) in both standard and ramjet environments, mechanical properties displayed significant differences. The composite CMC-B, made from fiber B, exhibited superior tensile strength, ultimate elongation, and reduced property dispersion. Physico-chemical microscale analyses indicated that the rough surface and deep grooves on fiber B enhanced mechanical adherence with the pyrocarbon matrix, whereas fiber A's smoother surface and sizing residues led to a stronger chemical bonding. Consequently, composites from fiber B had fewer manufacturing defects and greater reliability. The findings underscore the importance of the fiber/matrix interface and surface conditions in determining composite performance. Surface roughness, sizing composition, and residue presence significantly influenced handling, preform integrity, and mechanical properties, reinforcing the need for comprehensive characterizing methods such as XPS, Raman spectrometry, and TEM, beyond manufacturers' elemental data. This study illustrates that even similar carbon fibers can yield significantly different composite properties, necessitating thorough analysis tailored to specific application needs.

Keywords: *Carbon/Carbon Composites, Carbon fibers, Mechanical properties, Physico-chemical properties, Ramjet.*

Nomenclature

Acronym

AFM – Atomic Force Microscopy
CMC-A – CMC made out fiber A
CMC-B – CMC made out fiber B
C/C – Carbon/Carbon Composites
CMC – Ceramic Matrix Composite
EBC – Environmental Barrier Coating
F/M – Fiber/Matrix
PyC – Pyrocarbon
SEM – Scanning Electron Microscopy
TGA – Thermogravimetric Analysis

Latin

CoF – Coefficient of Friction

e – Thickness of the porous wall (m)

K_D – Darcy Coefficient (m^2)

$\dot{m}$ – Mass flow ($kg.s^{-1}$)

ΔP – Pressure difference between the internal cavity of the panel and the outside (Pa)

PyC – Pyrocarbon

S – Panel porous surface (m^2)

Greek

μ – Viscosity (Pa.s)

ρ – Fluid density ($kg.m^{-3}$)

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1. Introduction

Ceramic Matrix Composites (CMCs) are highly studied and used for the range of supersonic and hypersonic applications over the world. With the collaboration of ArianeGroup GmbH (AGG), MBDA France has been developing such materials for hypersonic vehicles for more than two decades. Since the early 2000s, MBDA, and its customer DGA, has selected the CARBOTEX® as the CMC that can be the structural material constituting scramjets, dual-mode ramjets and high speed air-breathing vehicles. Over the years, many different fibers have been tested for the manufacturing of CARBOTEX® but only one have shown the best overall performances.

This paper focuses on two kind of carbon fibers that have been tested and used for the manufacturing of such composites. It details the process unfolded in order to assess the performances of the CARBOTEX® elaborated from the two types of selected fibers, from their manufacturing ability to tests in ramjet environment, in order to select only one type.

In the following, the two fibers are noted "Fiber A" and "Fiber B". Despite similar mechanical properties, the two fibers have shown quite different results when using them for manufacturing CARBOTEX®. As a matter of fact, interactions of fibers A with the metallic tooling during the preform manufacturing were reported, generating fibers damage inside the preform and yarn misalignments.

The elaborated Carbon/Carbon composites (C/C) display a 2.5D architecture, with a strong and a weak direction, and are densified by a CVI-process [1] and protected with a silicon carbide (SiC) environmental barrier coating (EBC). In the following sections, the two composites made out of type A fibers and type B fibers will be respectively noted CMC-A and CMC-B.

First, this paper presents the assessment of permeability efficiency of CARBOTEX® made out of fibers A and B in standard conditions and in a ramjet environment. The tensile properties of the two C/C composites were assessed and will be discussed in a second stage. Finally, elemental investigations on fibers their selves were performed and the fiber/matrix interface was studied to better understand the impact of the change of carbon fibers' type at C/C state, especially regarding the mechanical properties.

2. Permeability efficiency in a ramjet environment and mechanical properties

Depending on its application, CARBOTEX® can be used as a sandwich structure for active cooling application. Hence, a very high permeability efficiency of the CARBOTEX® is required [2, 3]. Permeability tests were carried out in standard conditions on composites CMC-A and CMC-B, but also during and after exposure in a ramjet environment. This study aims to determine which composite present the lowest permeability coefficient in a ramjet environment and the highest mechanical properties.

2.1. Samples definition for permeability tests

The tested samples made out of CMC-A and CMC-B were 100x100mm² sandwich panels endowed with an internal closed cavity so the pressure of the fluid could build up (**Fig. 1**). In order to better compare the two specimens, the manufacturing process remained unchanged for both. For each composite, two panels were manufactured, called: CMC-A-1, CMC-A-2, CMC-B1 and CMC-B-2.

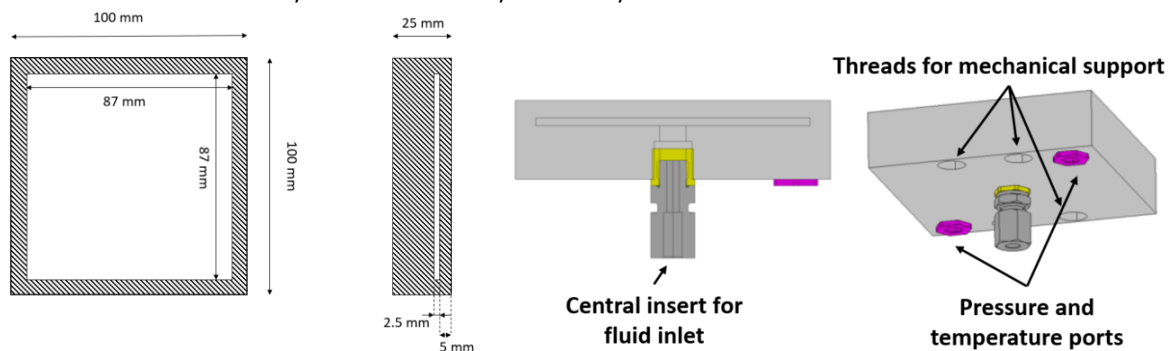


Fig 1. Panels definition

The panels were machined so there could be (**Fig. 2**):

- One central insert to feed the panels with a pressurized fluid;
- Two inserts in the corner to record the internal pressure and temperature;
- Four inserts to maintain the panels on their supports.

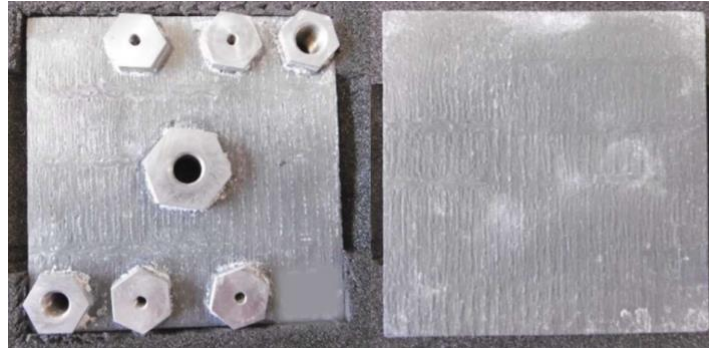


Fig 2. Picture of a CMC-B panel

2.2. Test setup

The experimental configuration involved mounting the test panel at the exhaust of a ramjet engine to subject it to the extreme thermodynamic conditions characterizing the engine's output, including heat flux, stagnation temperature, and convective heat transfer coefficient (**Fig. 3**). To optimize the heat flux incident on the panel, it was inclined at a 15° angle relative to the ramjet exhaust plane.

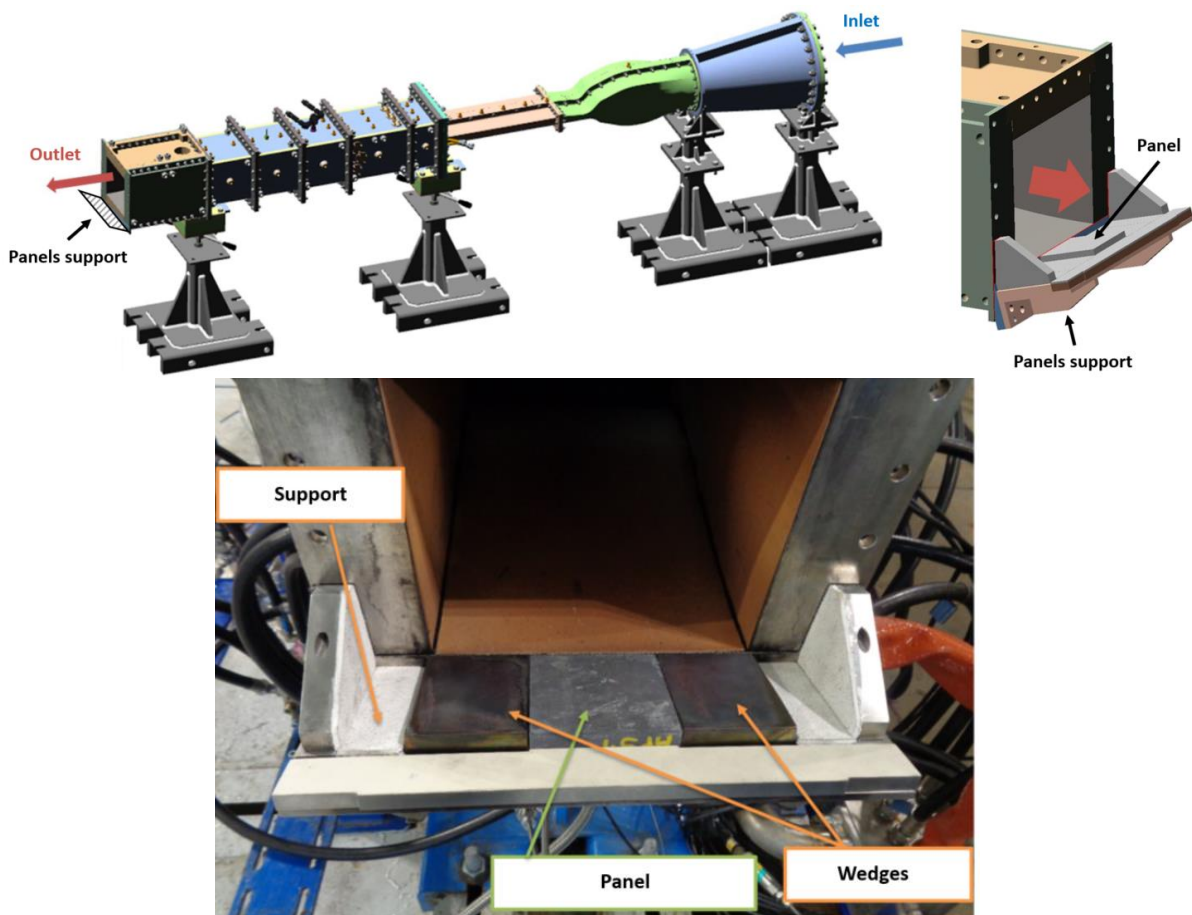


Fig 3. Test setup

The ramjet conditions are the following:

- Total burner pressure: $P_{10} = 12.75$ bar

- Total burner temperature: $T_{i0} = 634K$
- Outlet total temperature $\sim 2100K$

For safety reasons, the fluid used for the experiment was nitrogen so it could be an inert gas pressurized up to 18 bar.

2.3. Methodology

The permeability efficiency of both composites was determined via the Darcy coefficient (K_D). The following method was used:

- The nitrogen is regulated by pressure;
- The inlet massflow to reach the targeted pressure is measured. Therefore, once the targeted pressure is reached, the inlet massflow necessary to maintain that pressure is equal to the "leakages mass flow";
- The Darcy law (1) is applied:

$$\dot{m} = K_D * \rho(P, T) * \frac{\Delta P}{\mu} * \frac{S}{e} \quad (1)$$

The test sequence is the same for both composites. The test consists of pressurizing the panel with nitrogen and measure the inlet mass flow necessary to maintain the targeted pressure.

1st Test at ambient $T^\circ \rightarrow$ 1st Ramjet test $\rightarrow$ 2nd Test at ambient $T^\circ \rightarrow$ 2nd Ramjet test $\rightarrow$ 3rd Test at ambient T°

For each of these tests, the mass flow, pressure and temperature of the nitrogen was monitored live.

2.4. Test results

All test sequences began with a measurement at ambient temperature of the K_D coefficient for each composite panels. They all gave K_D values within the same range of order of magnitude. Yet, the CMC-B-2 panel showed a slightly better permeability. Its value is considered as a reference "normalized" value for the following results.

Table 1 Normalized K_D values of each panel before the ramjet tests

Composite panel	Normalized K_D value
CMC-A-1	1.29
CMC-A-2	1.83
CMC-B-1	1.33
CMC-B-2	1



Fig 4. Photos of the test before, during and after the ramjet test

During the first ramjet test of the CMC-B-1 panel, the measurements were lost therefore no K_D value could be computed. Also, for the CMC-B-2 panel, a technical issue occurred on the ramjet setup leading to a suspension of the test campaign.

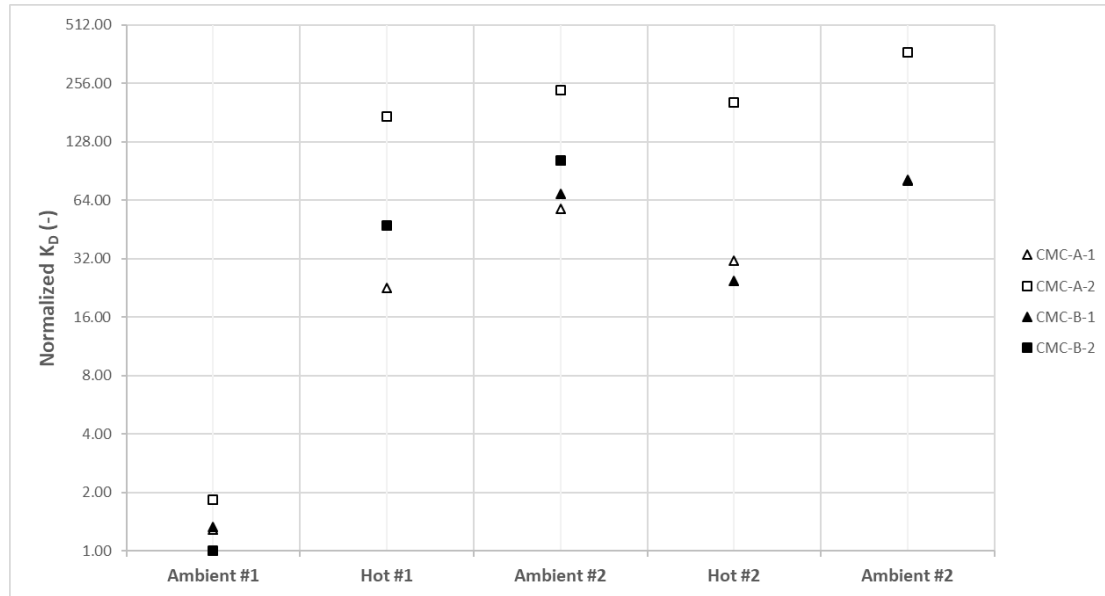


Fig 5. Normalized K_D values for each panel and each test

Fig. 5 illustrates the impact of the ramjet's extreme heat flux on the permeability of the panels. Initially, the normalized K_D values of the four panels were similar and below 2 before the high-temperature tests. However, after the first heating cycle, a significant increase in permeability was observed, with normalized values ranging from 22 to 172. Upon cooling back to ambient temperature, the permeability continued to rise, reaching values between 58 and 237. This behavior, though not fully understood, is likely attributable to the formation of micro-cracks within the ceramic matrix composite (CMC) during the cooling phase. During the second ramjet tests, the permeability of each panel improved, with values ranging from 24 to 204. Subsequently, after cooling back to ambient temperature, the permeability worsened, with normalized values between 80 and 370.

Both composite materials (CMC-A and CMC-B) exhibited similar trends, showing significant sensitivity to the ramjet conditions. This effect can be attributed to the substantial thermal stresses and resulting micro-crack formation within the matrix. Once thermally cycled, the material permeability appeared to follow a consistent pattern: lower permeability during heating and higher permeability during cooling.

Despite similar baseline permeabilities at ambient temperature, the CMC-A composite demonstrated greater sensitivity to the ramjet conditions compared to the CMC-B panels. While CMC-A-1 followed a permeability evolution similar to CMC-B-1 during the tests, CMC-A-2 exhibited a much higher permeability than the other panels. The CMC-B-2 panel also showed increased permeability but to a lesser extent than CMC-A-2, suggesting that CMC-A composites may exhibit higher manufacturing variability. This variability could be due to higher density gradients in the CMC-A panels, leading to a more heterogeneous environmental barrier coating (EBC) layer on the surface.

In conclusion, while the CMC-A and CMC-B composites share similar initial K_D values and permeability trends under thermal cycling, the CMC-A composite exhibited greater deviation. This deviation may be due to a more heterogeneous C/C matrix, resulting in a weaker EBC, or a weaker fiber/matrix interface, leading to larger cracks under high heat fluxes and consequently, higher permeability in a ramjet environment.

2.5. Evaluation of mechanical properties via tensile tests

Mechanical properties, especially the damage caused by tensile stress, are also highly considered for the targeted application. Elastic moduli, ultimate tensile strengths and ultimate elongations of CMC-A and CMC-B composites in their strong direction were assessed via tensile tests (**Fig. 2**).

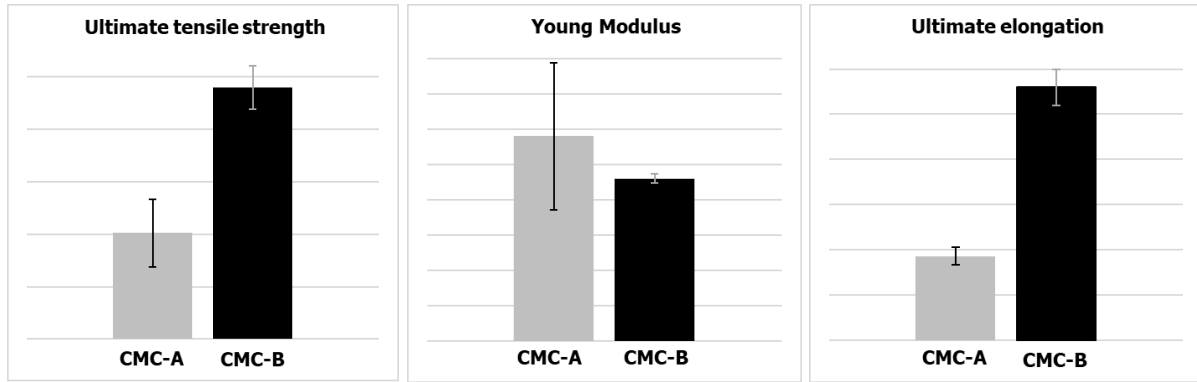


Fig 2. Mechanical properties and dispersion: ultimate strength (left), Young's modulus (middle), ultimate elongation (right)

A massive improvement of the tensile strength from CMC-A to CMC-B up to 137% can be noticed, whereas the tensile moduli remain close (**Table 2**).

Table 1. Mechanical properties of composites CMC-A and CMC-B evaluated by tensile tests in the strong direction

	Ultimate tensile strength (MPa)	Young Modulus (GPa)	Ultimate elongation (%)
Δ	+137%	-21%	+201%

Fracture patterns are examined using Scanning Electron Microscopy (SEM). In CMC-A composites, the cracks appear to propagate directly through the yarns, exhibiting sharp breaks without any deflection at the fiber/matrix (F/M) interface. Furthermore, there are very few, if any, instances of fiber pull-outs observed. These observations indicate a brittle fracture alongside a robust F/M interface. The fracture pattern of the CMC-B composite differs as illustrated **Fig. 3** on the right. The surface of the fractured exhibits irregularities, with several fibers being pulled out over a moderate length. In this instance, the F/M interface appears to possess an intermediate intensity.

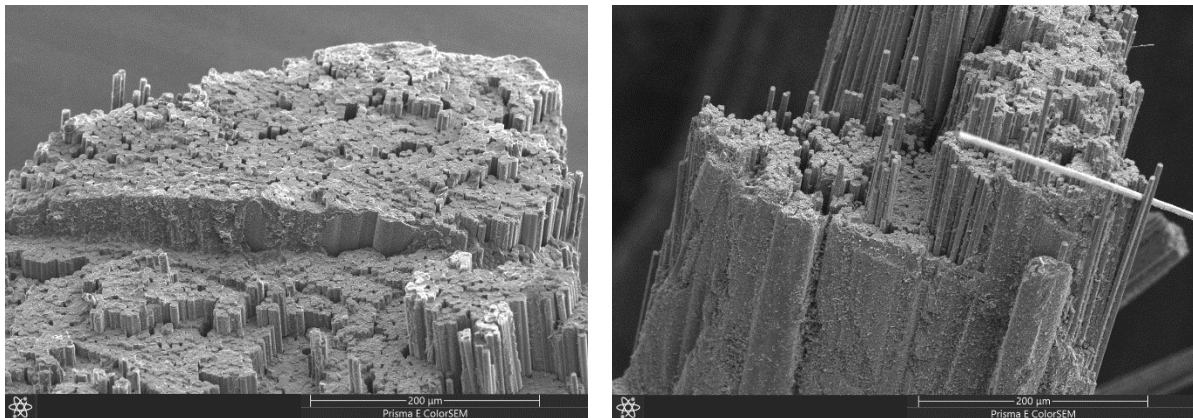


Fig 3. Fracture patterns of CMC-A (left) and CMC-B (right) after tensile tests at 90°.

The enhancement of the mechanical properties appears to be directly associated with the adjustment of the fiber type from A to B, as this is the sole variable parameter. However, the causes leading to this improvement are unclear and will be investigated in the following section.

3. Elemental investigations on fibers and F/M interface

Microscale elemental characterizations are carried out on fibers A and B to investigate the factors responsible for the increase in mechanical properties from composite CMC-A to CMC-B at macroscale. The investigation is focused on two hypotheses: the role of the sizing on fibers property damage during

the manufacturing of the fibrous preform; the modification of the F/M interface intensity due to fibers intrinsic properties.

3.1. Fibers' roughness

SEM micrographies (**Fig. 4**) indicate that the surface topography of the two fibers is drastically different. The surface of fiber B appears very rough with deep grooves, which might favor mechanical adherence with the PyC matrix in the CMC-B composite [4]. Conversely, fiber A is naturally smooth, but it is frequently scattered with sizing residues along its length.

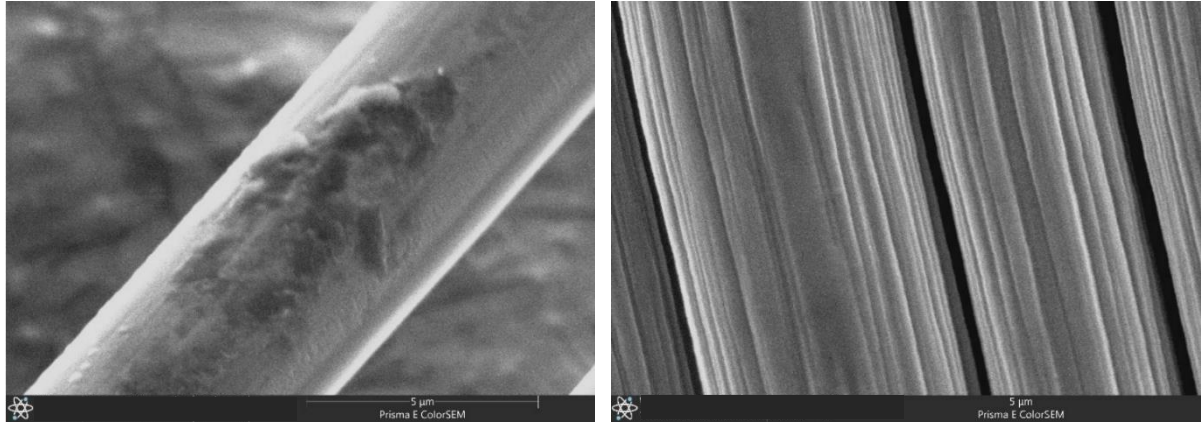


Fig 4. Surface observation by SEM of fibers A (left) and B (right).

These observations are confirmed by Atomic Force Microscopy (AFM) by the assessment of profilometry curves and the average roughness at microscopic scale ($R_{a,micro}$) (**Fig. 5**). Fiber B displays a $R_{a,micro}$ equal to 16 nm, conversely to only 1.9 nm for fiber A providing evidence of its smoothing. However, the profilometry curve of the fiber A surface is irregular, supporting the presence of inhomogeneous sizing residues.

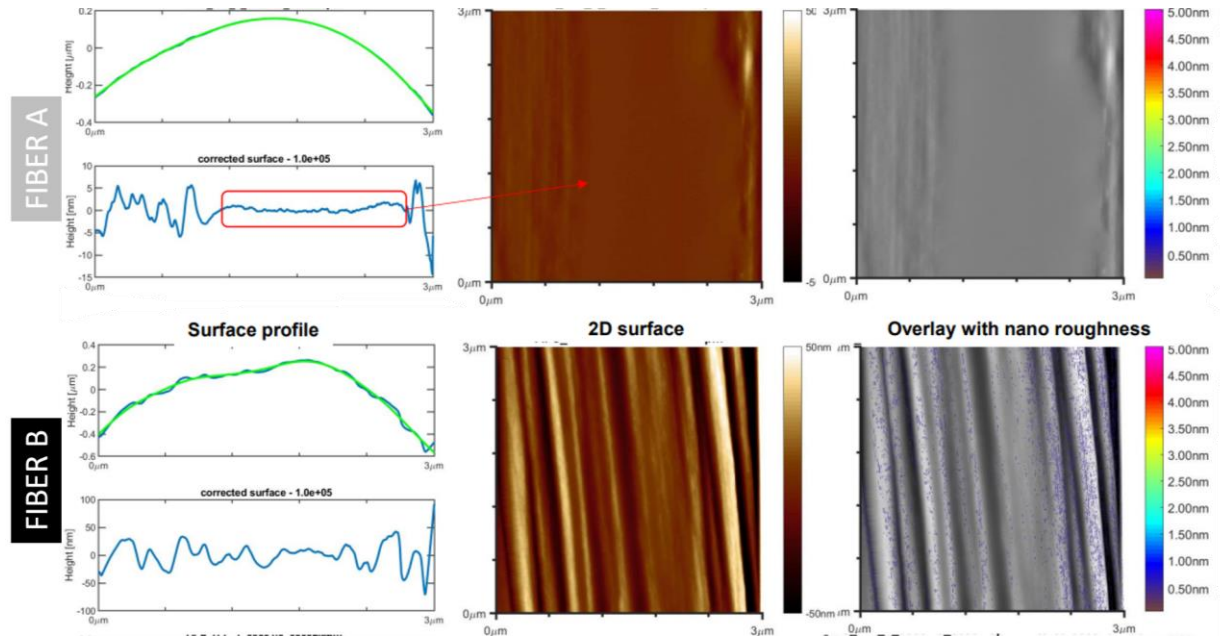


Fig 5. Profilometry and rugosity characterizations of fibers A and B by AFM.

3.2. Friction coefficients

As the surface condition of the fibers has a direct impact on their handling and the ability to manufacture the preform, the coefficient of friction (CoF) of the fibers was assessed. Friction tests on a metallic drum were performed and the CoF was derived from the ratio of the normal and tangential forces applied by the fibers yarns on the drum (**Fig. 6** left). The CoF of fiber A has been assessed as 1.3 times

higher than that of the fiber B (**Fig. 6** right), probably due to the presence of the inhomogeneous repartition of the sizing along the fiber of type A. Then, yarns made of type B fibers should less interact with metallic tooling than type A fibers, being easier to process and leading to less fibers damage, yarns misalignments and preform defects [5]. The preservation of composite mechanical properties is largely dependent on these factors, which could account of the performance improvement with the type B fiber.

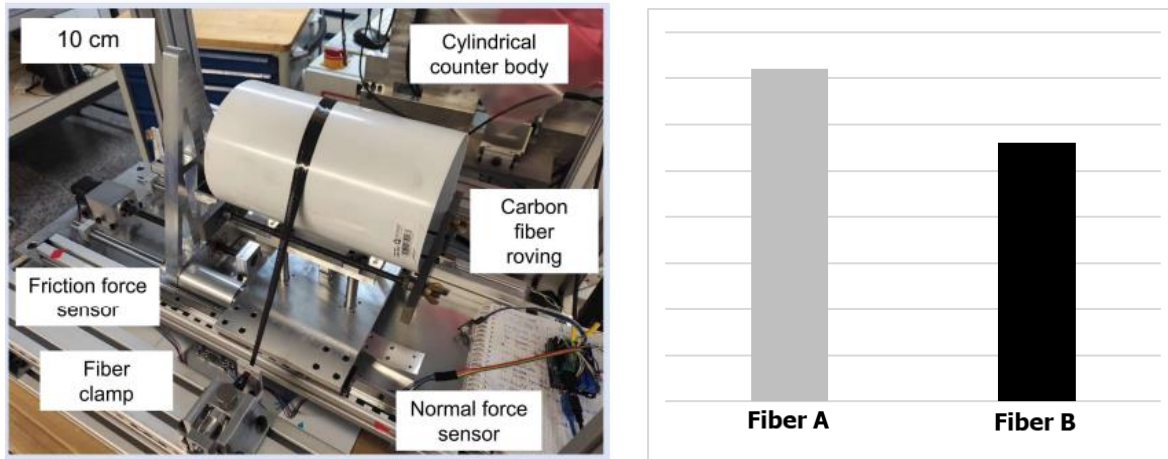


Fig 6. Friction coefficient measurement experimental set-up (left), friction coefficient results of fibers A and B (right).

3.3. Sizing composition and thermal decomposition

The volatile products emitted during the thermal decomposition of the sizings were analyzed to identify their initial compositions. Fibers were heated in a ThermoGravimetric Analysis (TGA) apparatus under N_2 up to $750^\circ C$ with a heating rate of $10^\circ C/min$. The only mass loss occurs between $350^\circ C$ and $450^\circ C$ and reaches approximately 1% regardless of the fiber type. It is associated to the decomposition of the sizing (**Fig. 7** left). The gaseous products released at the highest mass loss between 350 and $450^\circ C$ were analyzed by Fourier Transformed InfraRed spectroscopy (**Fig. 7** right). Based on literature, the sizing is similar for the two fibers types, belonging to the epoxy family [6]. However, the amount of desorbed CO_2 suggests that the decomposition of the sizing of fiber A is less advanced than of fiber B.

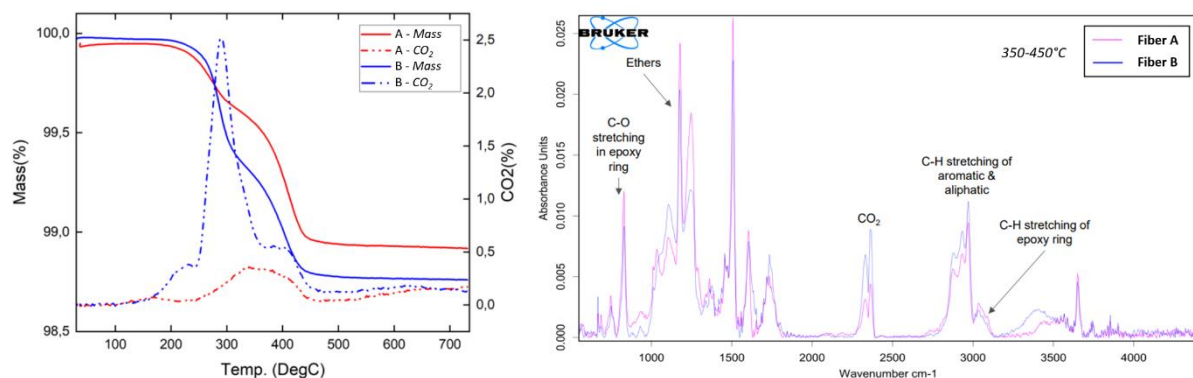


Fig 7. TGA characterization up to $750^\circ C$ under N_2 (left) and FTIR spectroscopy analyses between 350 and $450^\circ C$ (right) of fibers A and B.

The SEM observations acquired after TGA analyses revealed that the sizing decomposition of the type B fibers is complete, but not complete for the type A, which still display residues (**Fig. 8**). Then, type A fibers are likely to develop chemical adherence with the matrix through the presence of functional groups on sizing residues.

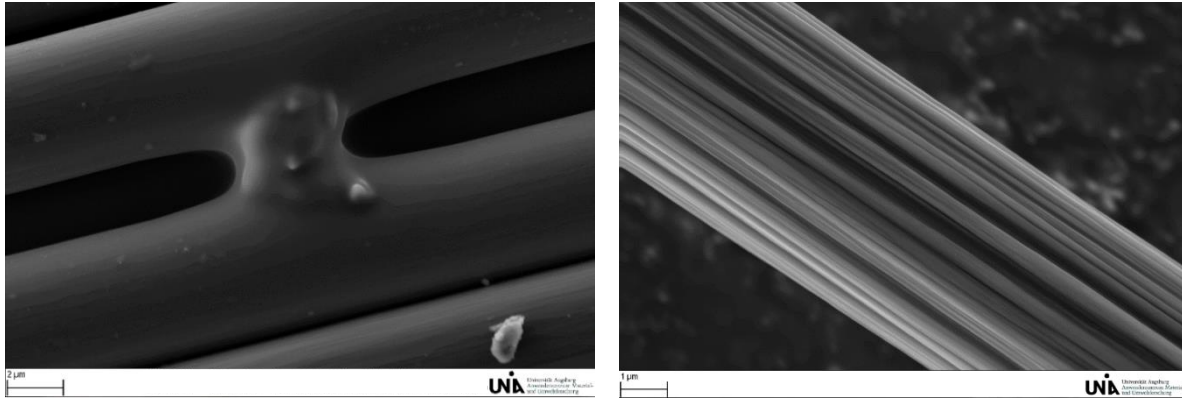


Fig 8. Surface observation of fibers A (left) and B (right) after TGA experiments up to 750°C by SEM.

4. Conclusion

This study investigated the impact of carbon fiber type on the permeability efficiency and mechanical properties of CARBOTEX®. The mechanical and physico-chemical properties of the selected fibers were alleged to be identical by the manufacturers. However, it was proven that the permeability efficiency, under standard conditions and in a ramjet environment, was not significantly affected by the switch from Fiber A to Fiber B. Yet, the macroscale mechanical behavior of the composites was significantly influenced by this change, with a substantial improvement in tensile properties and increased reliability of the results.

The surface conditions of Fiber A and Fiber B were analyzed to identify the factors leading to the improvement of mechanical properties, focusing primarily on roughness and the presence of sizing. Firstly, a scattered distribution of sizing along Fiber A appears to be responsible for handling and manufacturing issues, due to a higher friction coefficient, which causes fiber integrity losses in the textile preform. Variations in the mode and intensity of F/M adherence also seem to have a positive impact on the composite's mechanical properties. Based on the fracture patterns and the physicochemical characterizations carried out so far, the intensity of the F/M interface of Fiber A might be of chemical nature and more intense than the mechanical adherence of Fiber B. However, other physico-chemical parameters might directly influence F/M adherence, such as the carbonization state of the carbon fibers, the presence of functional groups on the fiber surface, the graphitization state of the carbon fibers, the presence of bulk micro-porosities, and their evolution with densification. These factors should be thoroughly characterized to determine the type and intensity of F/M adherence for each fiber type through complementary characterizations such as XPS, Raman spectrometry, and Transmission Electron Microscopy (TEM).

In conclusion, it is essential not to rely solely on the manufacturers' stated elemental qualities of the fibers. These specifications do not ensure the same ability to handle and manufacture the preform, nor the same behavior once the composite is densified, due to specific interactions with the deposited matrix. These observations are notably relevant concerning mechanical properties. Indeed, the latter are deeply influenced by the F/M interface, which is affected by the surface conditions of the fibers.

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