DOI: 10.13009/EUCASS2022-4611

Analysis of the fire reaction of fibre reinforced polymer matrix composites exposed to a flame

Wang X., Schuhler E.*, Vieille B.**, Coppalle A.**
**CORIA INSA Rouen*
Site Universitaire du Madrillet - BP 12
76801 Saint Etienne du Rouvray cedex
*** GPM INSA Rouen*
Site Universitaire du Madrillet - BP 12
76801 Saint Etienne du Rouvray cedex

Abstract

An important issue for fibre reinforced polymer matrix composites is that they may be exposed to a flame, during a malfunction of the engines or after a crash. Under such circumstances, the composite is degraded and it loses its performances. In order to test the fire reaction of these materials, a new bench test was built in order to analyse at small scales, typically with sample size of a dozen of centimetres, the behaviour of composites under a kerosene flame. Compared to standard tests, more measurement setup can be installed allowing scrutinizing in details the behaviour of the sample during tests, and analyses can be easily done on a larger number of samples. The temperature of the rear face has been observed using an IR camera, and the sample mass losses monitored during tests with a load cell. As an example, the test results for two carbon fibre reinforced polymer matrix composites, a thermosetting-based (epoxy) and a thermoplastic-based (PEEK), will be shown and analysed. The comparison of the temperature and the mass loss during the tests will highlight the main differences observed on the behaviour of these composites exposed to a kerosene flame.

1. Introduction

In the aircrafts, composite materials are now widely used. An important issue is that they may be exposed to a flame, during a malfunction of the engines or after a crash. Under such circumstances, the composite is degraded and it loses its performances. In order to test the fire reaction of the materials, there are several standard tests specific to aeronautical applications [1], in particular some of them use propane or kerosene impinging flames [2-3]. However, they are expensive, time consuming and requires heavy equipment. They can be used only for certification, and it is hard to use them for development and optimisation of new materials with improved fire reaction.

The performance and strength of a composite is established incrementally through a program of analysis and a series of experimental tests conducted using specimens of varying size and complexity [4]. As shown in fig. 1, the process is based on a so-called 'testing pyramid' approach with tests at each of the following levels: (i) Coupon, (ii) Structural detail, (iii) Component, and (iv) Sub-structure or full structure. The process is long and costly. Therefore, before certification, it is better to analyse and to optimize the new products at the levels 1 or 2. These are typically the aim of laboratory tests at small scales. This is often achieved with a cone calorimeter that apply a radiative flux on the sample [5-6]. However, the maximum thermal stress is limited to 100kw/m2, which is well beyond the values encountered in real scenarios, and a direct flame impact is a more realistic thermal stress.

DOI: 10.13009/EUCASS2022-4611

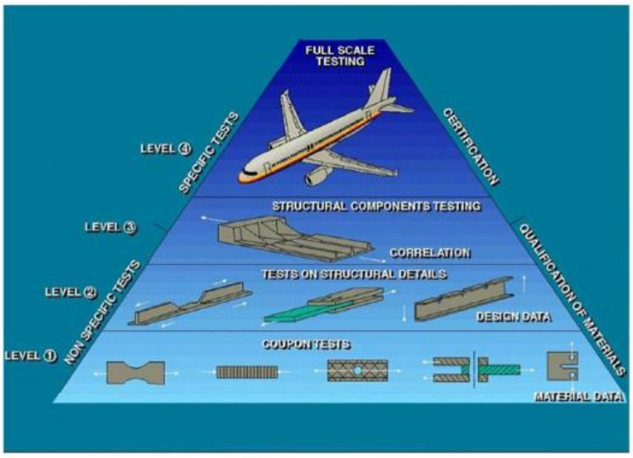

Figure 1: From small to full scales, the testing pyramid

Therefore, a new bench test was built in order to analyse at small scales, typically with sample size of a dozen of centimetres, the behaviour of composites under a kerosene flame. Compared to standard tests, more measurement setup can be installed allowing scrutinizing in details the behavior of the sample during tests, and analyses can be easily done on a larger number of samples.

As an example, the two carbon fiber reinforced polymer matrix composites, a thermosetting-based (epoxy 914) and a thermoplastic-based (PEEK), have been exposed during 15mn to the flame. The comparison of the temperature and the mass loss during the tests will highlight the main differences observed on the behaviour of these composites exposed to a kerosene flame. After tests, the samples are cut in the middle and the slices are observed under a microscope, in order to analyse the levels of degradation through the thickness.

2. The test bench

The bench is composed of different elements: a rail on which heat flux meter, thermocouples weighting cell and sample holder are fixed. On the front of the rail and its equipment is the burner’s flame tube and on the back are the infra-red camera and visible cameras. All the elements are shown on the Figure 1 and described below in further details.

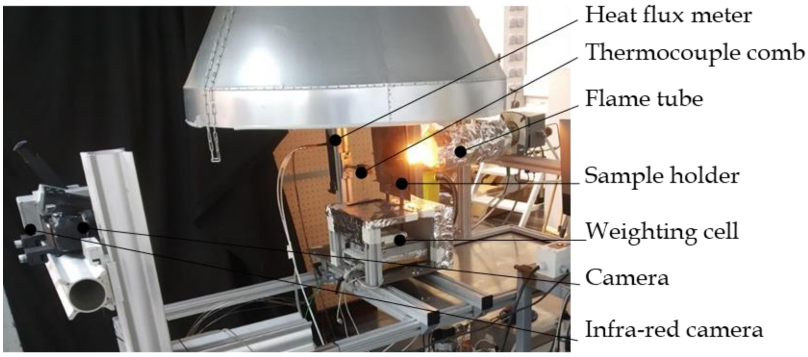

Figure 2: Picture of the kerosene burner bench during a fire test

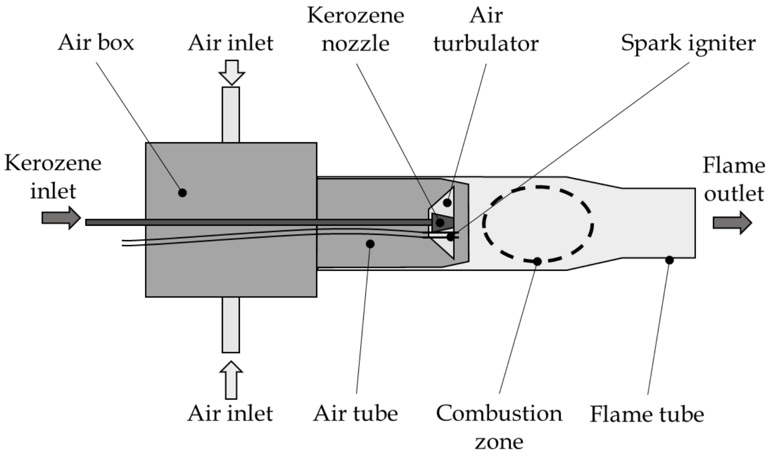

Figure 3: Scheme of the kerosene burner.

2.1 The kerosene burner

The burner shown in Figure 3 is derived from a domestic device. The kerosene is injected through a nozzle at a flow rate of 0,3 g/s. The fuel to air ratio has been selected at 0.8 of the stoichiometric value, this permits to obtain heat flux and temperatures values close to the standard ones at the sample location (120 kW/m2 and 1100°C). The nozzle is chosen to generate a hollow cone spray with an angle equal to 80° in order to optimize the combustion efficiency. The flame at the exit of the nozzle is a wide and turbulent jet. Therefore, a 50 mm diameter steel tube is fixed after the nozzle to channel the hot combustion gases on the small area of the sample. Detail of the setting is presented Figure 3. The design enable an efficient mixing inside the first part of the flame tube, and in the second part, the flow turbulence is strongly damped. At the output of the tube, no kerosene droplet is observed and the combustion is completed. Thus, the thermal stress on the sample is due to the hot gas mixture of the combustion products [7]. The hot gas stream close the sample wall corresponds to the stagnation zone of an impinging jet and the variation of the heat flux on the sample is small, as shown in a previous work with a propane burner [8]. The flexibility of the bench test is that the heat flux can be varied in the range 80kW-180kW/m2, by changing the distance between the flame tube exit and the sample, or the air and kerosene flow rates.

2.2 Control of the thermal stress applied to the samples

Before each test, the temperature and heat flux measurements are carried out in the hot gas jet, at the same distance from the exit of the flame tube as the sample holder. The temperature is measured using a rotating comb of 6 K-type thermocouples, the spacing between each thermocouple being 8 mm. After the burner ignition, a period of fifteen minutes is necessary in order to reach steady conditions in temperature. For all the tests presented in this work, the mean value of the temperature at the centre of the hot jet is close to 1100 °C. After the thermocouple comb is removed, the heat flux is measured using a water-cooled heat flux sensor [9-10] (Captec manufacturer) inserted into a tilting plate. The heat flux value is close to standard , 120 ± 5 kW/m2. Finally, the heat flux sensor is tilted and the sample holder is placed in front of the flame for a 900 s duration.

2.3 Temperature and mass loss measurements during tests

The temperature of the rear face of the samples has been measured using an IR camera (ThermaCam PM595). The camera works on the wavelength range 7.5-13 µm, it is equipped with a filter allowing temperature measurement between 80 and 500 °C. The IR camera is placed at 800 mm from the sample holder to avoid the hot gas flow. The IR camera allows a temperature measurement overall sample back face with an accuracy of +/- 2 °C. However, this method presents a drawback, as it is difficult to know accurately the surface emissivity of the degraded composite during tests. In the present work, the emissivity is assumed to be constant and equal to 0.9. This corresponds to a common value used in the literature for this type of work [11-12].

For the mass loss measurement, the sample holder is put on a load cell (Mettler Toledo), and it is vertical and fixed to an insulating plate. With this layout, the effect of the hot impinging jet on the mass loss measurement is negligible since it acts as a force perpendicular to the sample holder weight. The weighting cell is protected by an insulation fibreboard, and its readability is 0.01 g.

2.4 The sample holder

DOI: 10.13009/EUCASS2022-4611

The composite samples are placed in a dedicated holder for the test. The sample holder is presented in Figure 4. The composite samples are rectangles of 100 x 150 mm2, they are placed behind an insulation layer and two steel plates clamp the assembly. In the front side of the sample holder, a squared window of 50 mm length is made. On this side, the sample is facing the burner. On the backside, the temperature measurement can be done on a rectangle of 90 x 140 mm2 over the surface of the samples. This sample holder with the insulation have two major aims. The first is to prevent the edges of the sample from being damaged by the flame. The second is to maintain the integrity of the sample edge. Maintaining the integrity of the sample border can be of great interest to perform further investigation combining the kerosene burner and a mechanical load. The 50 mm window is chosen in order to obtain a uniform heat flux on the sample exposed surface while maintaining the integrity on the sample border.

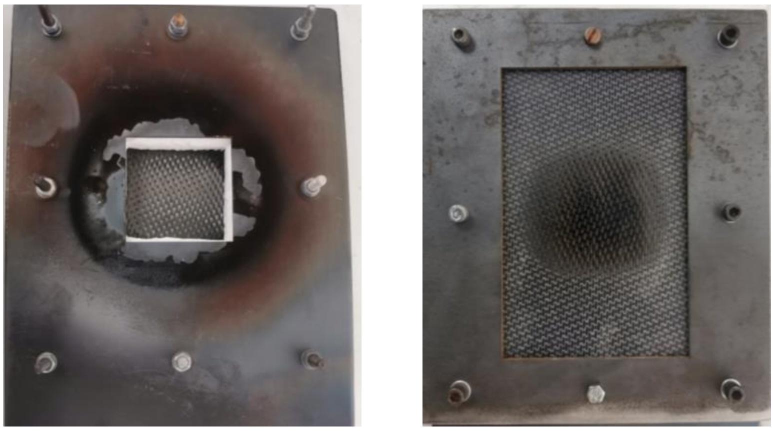

Figure 4: Pictures of a degraded specimen in the sample holder: left, exposed face – right, back face.

3. **The tested materials**

The composite materials studied in this work are carbon/epoxy and carbon/PEEK woven-plies laminates. The prepreg plates are hot pressed according to the layout [(0/90), (±45), (0/90), (±45), (0/90), (±45), (0/90)], and they can be considered quasi-isotropic (Q-I). The prepreg plates are made with 5-harness satin weave carbon fiber fabrics. The volume fraction of fibres is 50% in both composites. The samples are 100 x 150 mm².

The thermoplastic-based laminates (C/PEEK) are seven plies carbon-fiber reinforced PEEK prepreg laminate, with thickness equal to 2.3 mm, supplied by ARKEMA. The thermal degradation of PEEK resin begins around 550 ◦C (onset temperature of pyrolysis) and the maximum degradation rate is recorded above 600 ◦C [13-14]. The residual mass at T = 700 ◦C is about 80%.

The thermosetting-based laminates (C/epoxy) are the same as in a previous work [15], however with 7 plies with a total thickness equal to 2.1 mm.. The glass transition temperature is at 170 °C, the degradation begins around 300 ◦C (onset temperature of pyrolysis) and the peak of thermal degradation is about 390 °C. The residual mass is about 80%.

4. Analysis of the fire reaction of a C-PEEK and C-Epoxy composites

Three different tests have been done for each composite in order to look at the repeatability of the test bench and the results. The test conditions are reported in table 1. The average temperatures at the flame centre are 1113 °C and 1112 °C respectively for the C-PEEK, C-Epoxy laminates and the average heat fluxes on the samples are 120 kw/m2 and 120.9 kw/m2 respectively for the C-PEEK, and C-Epoxy laminates.

Table 1: Test conditions

C-PEEK	**Test 1**	**Test 2**	Test **3**	**Average**
Initial mass (g)	51,30	51,01	51,60	-
Flame temperature at the centre (°C)	1131	1168	1040	1113
Heat flux (kw/m2)	120,6	118.7	120.8	120

C-Epoxy	**Test 1**	**Test 2**	Test **3**	**Average**
Initial mass (g)	47.31	47.45	47.58	-
Flame temperature at the centre (°C)	1142	1086	1109	1112
Heat flux (kw/m2)	124.0	118.4	120.2	120.9

Mass losses (%) and mass loss rates (g/s) are given in Figs. 5 and 6, The mass losses are presented in percentage of the initial mass, i.e. the ratio of the mass at time t to the initial mass. The three experimental datasets with the same composite (C/PEEK or C/epoxy) show that the tests are well repeatable. The greater differences are found after 100 s. This can be explained by the internal damage mechanisms such as the building of cracks, delamination and major pores, that may be different from one test to another, even with similar thermal stress, due to the initial pores and residual mechanical stresses in the virgin laminate after fabrication. The main mass losses, and consequently the main emissions of volatiles, occurs during the first hundred seconds. After 100 s, the mass loss rates are not negligible but low. The total mass loss is much greater for the C-Epoxy compared to the C-PEEK, which is expected if one looks at the onset and maximum temperature degradation of these two materials.

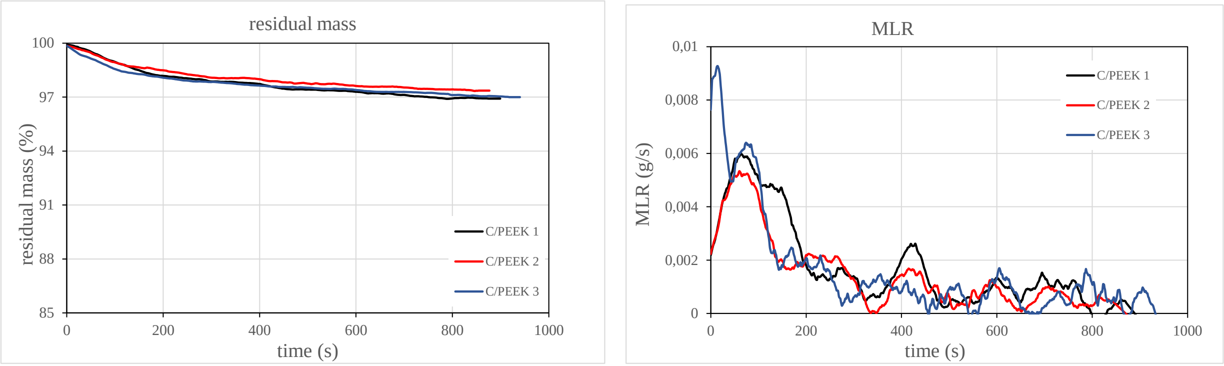

Figure 5: C-PEEK, left, masse loss (%) and right, mass loss rate (g/s) during three tests

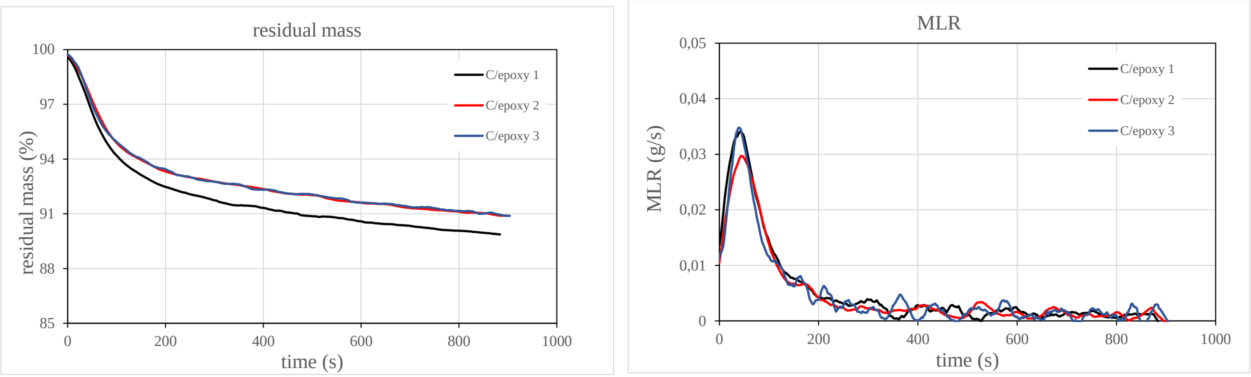

Figure 6: C-Epoxy, left, masse loss (%) and right, mass loss rate (g/s) during three tests

DOI: 10.13009/EUCASS2022-4611

Figures 7 present the temperature distributions, observed with the I.R.camera on the rear face at different times. At the left hand side, arrows represent the fibre orientations inside the laminates. The figures show that the quasi-isotropic stacking sequence results in a regular temperature distribution in the back face, and with curve shapes of isotherm rather rectangular as the contour of the exposed area. There is an heat transfers along the fibre plies, however it is limited compared to the one occurring through the composite thickness, and the temperature are rather homogeneous inside the area corresponding to the exposed zone at the front face. The white dots (points 1 and 2) stand for the location of points where the temperatures are plotted as a function of time on the Fig. 8.

On this figure, the differences between tests with the same composite are small. The repeatability of the results obtained with the test bench is good. Some differences occur after 50s, mainly caused by delamination and cracks that appear at high temperature inside the materials. These may be different from one test to another even with similar thermal stress, as explained previously for the mass loss results. The influence of these cracks induced by the thermal degradation inside the sample is highlight for the C-PEEK test 2. At point 1, between 100 and 200s, the temperature first increases and then decreases during a short period of about 50s. It appears inside the material a thermal barrier, which is able to reduce by a few dozen degrees the temperature at the back face. This process is explained by the apparition of delamination and cracks inside the laminate when it reaches high temperatures.

The temperatures at point 2, that is outside the zone directly exposed to the flame, are much lesser than the ones observed at the centre. The increase of temperature is mainly due to the heat conduction along the plies. The curves as a function of time are regular, suggesting that there exists no or less cracks through the depth at this location, compared to the centre zone. So most of the thermal degradation should be observed inside the zone under the exposed area.

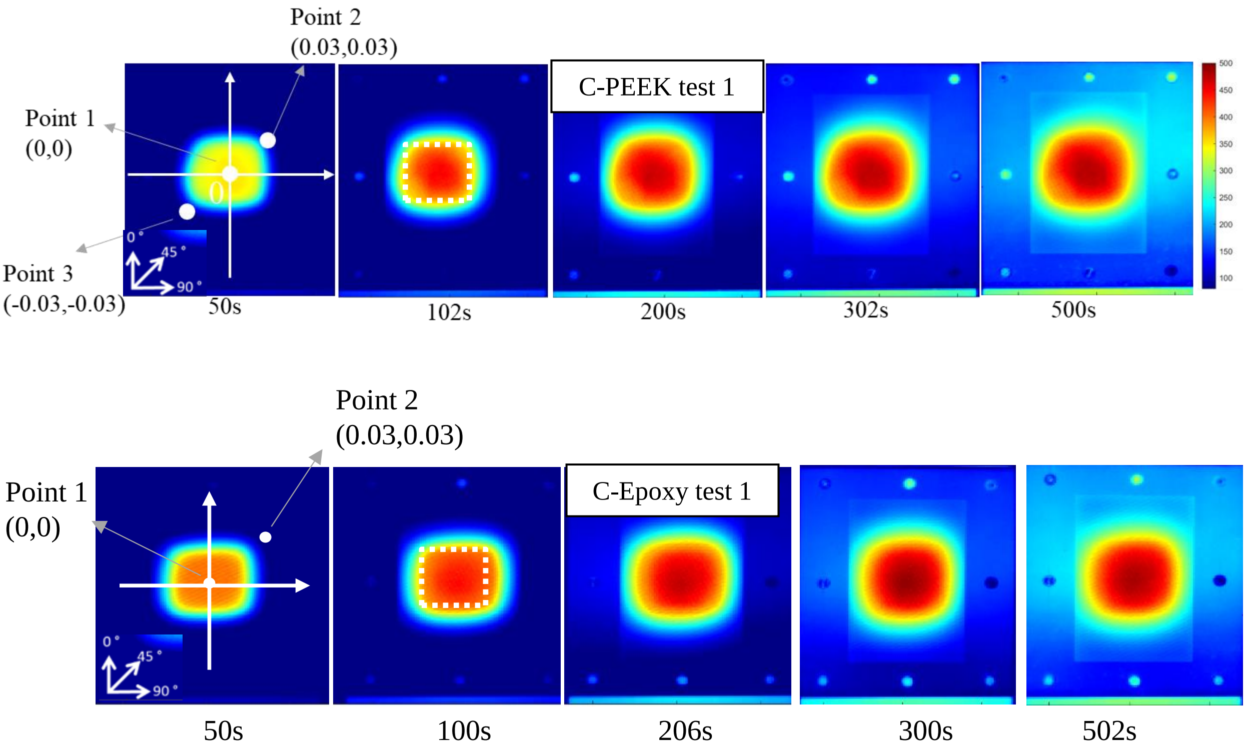

Figure 7: Temperatures observed on the rear face of the samples during the flame exposure.
The dotted lines represent dimensions of the exposed area on the front face.

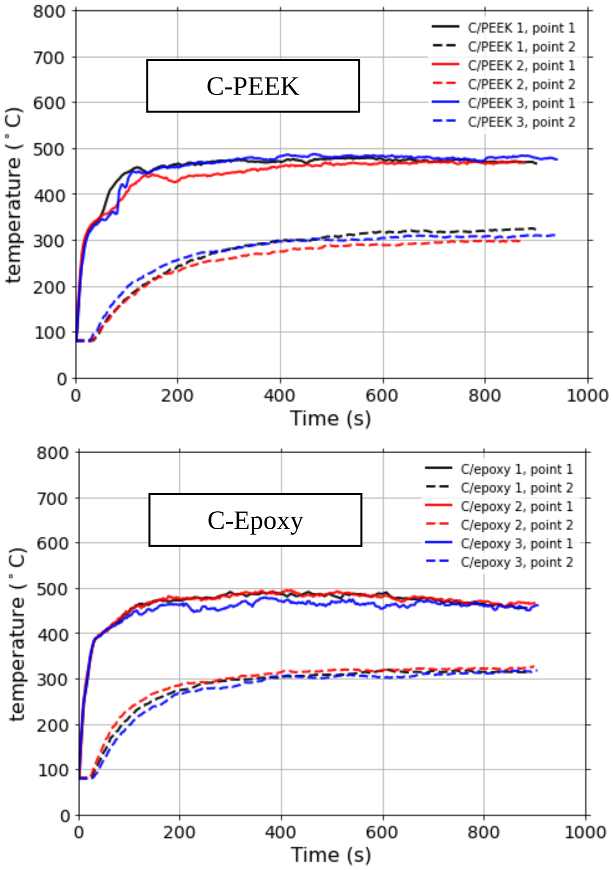

Figure 8: Temperatures at points 1 and 2 during three tests, C-PEEK at top and C-Epoxy at bottom

The results of the three tests were averaged for both C-PEEK and C-Epoxy. The values are reported on Fig. 9 for the relative mass loss and the temperatures at the points 1 and 2. For the two composites, the shape of the temperature curves is more or less similar; the maximum temperature values reached during the tests are close. During the first seconds (<15s), no degradation occurs inside the sample and there is only heat transfer from the flame-side to the back-side. The heating rate is very strong and about 1200°C/s. After that, there is delamination inside the composites, mainly due to the high dilation of the matrix compared to the fibre plies. This causes cracks to appear which act as thermal barriers and reduce the temperature rises close to the back face, as explained before. During the last period of the tests, a stabilized temperature is reached. The value corresponds to an equilibrium between the incoming flux at the front face and the thermal losses at both the front and back faces.

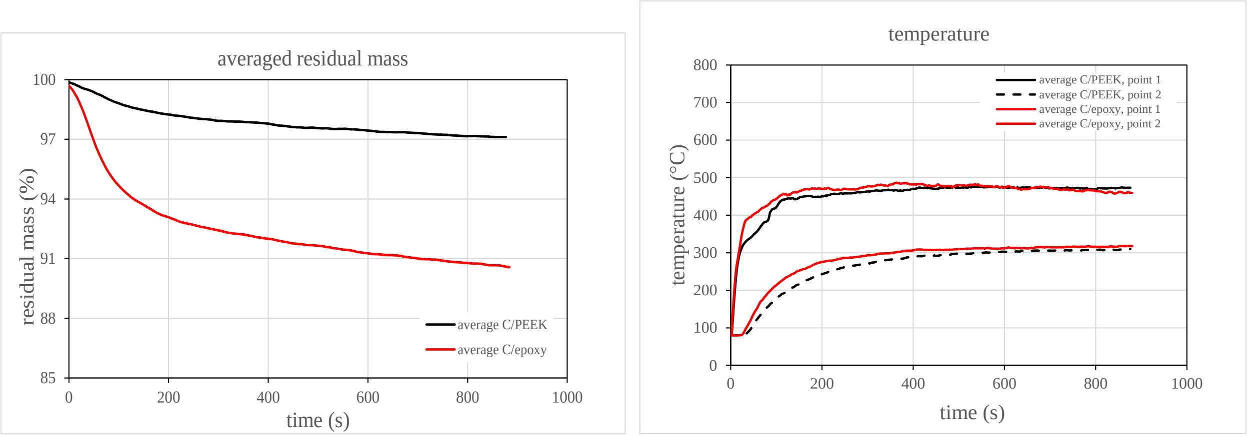

Figure 9: Comparison between mean values of relative mass losses and temperatures of the C-PEEK and C-Epoxy.

On Fig. 9, the variations of relative mass losses are very different between C-Epoxy and C-PEEK samples. At the beginning of the tests, the speed of the mass loss is much higher for the C-Epoxy, and the final value of the mass loss too. This has a strong influence on the residual mechanical properties. With the test bench used, no fibre ablation was observed on the exposed surface, so the mass loss is essentially due to the matrix decomposition. Since one action of the matrix in composites is to equilibrium mechanical stress between the plies, one can expect that the residual mechanical properties for the C-PEEK is better to the C-Epoxy ones.

5. Post-fire observations of the samples

Figure 10 shows the front and back of a C-PEEK sample after a 15-minute test. On the surface exposed to the flame, there is no resin left and the carbon fibres are bare, with no ablation. On the back surface, there remains some matter between the fibre strands, the brown colour suggest that this is degraded resin. However, the edge of the sample are not degraded and remained virgin.

By looking to the microscopic views of a central slice of the sample, it appears white small zones corresponding to the virgin resin between the woven fibre stands, they can be seen easily at the border of the degraded zones (views 1 and 2). It must be noticed that it remains some virgin resin at the centre of the rear zone of the degraded sample (view 2). Long grey lines can also be seen (identified by the red arrows), which are the 4 carbon fibres in the [0] direction. Finally, the dark areas correspond to small pores or long cracks.

There are 2 main cracks and they are close to front surface. There are also many small cracks near back surface. The two big cracks correspond to delamination and separations of the four plies close to the flame (i.e. plies [0/90; +45/-45; 0/90; +45/-45]), since one can see the two [0/90] remaining plies close the back face. The total length of the main cracks is about 59.1mm. At the middle point, the composite thickness is 3.58 mm. Since the initial value was 2.3 mm, the swelling is about 1.28mm. All C-PEEK samples have similar structure along length. From border to centre, small pores appear first and then big cracks appear in the middle.

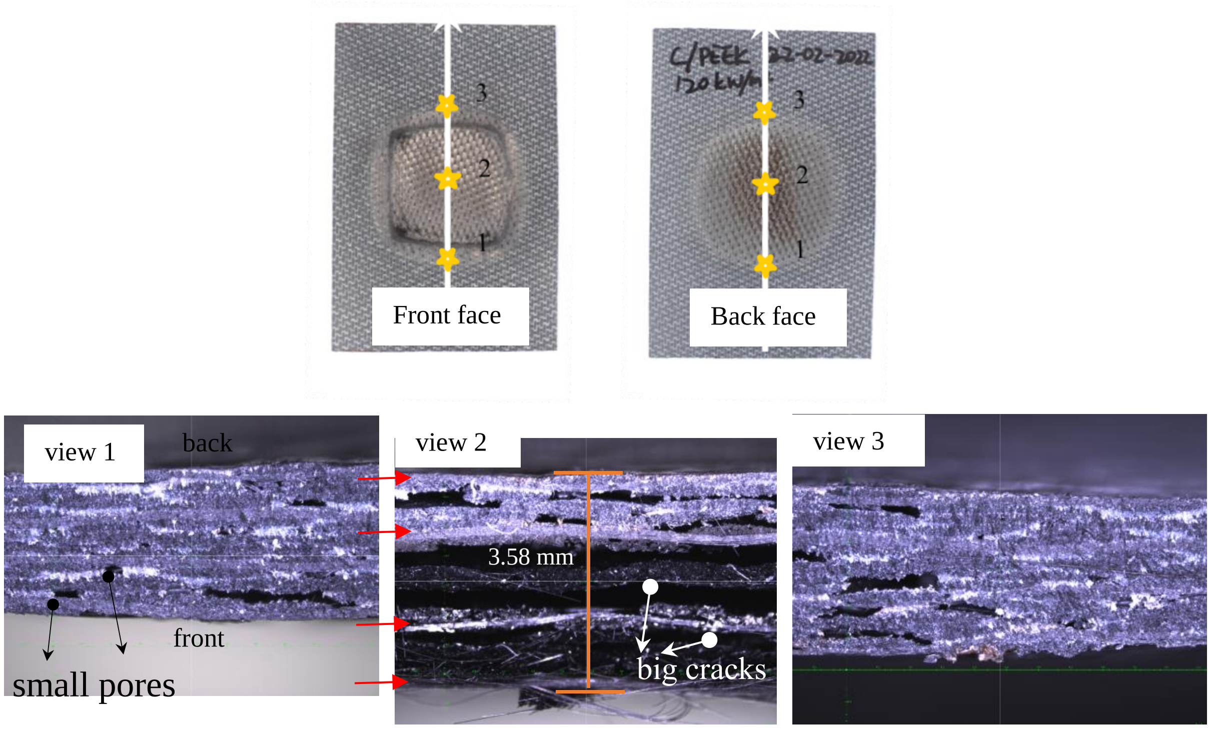

Figure 10: Top figures, aspect of the faces of a C-PEEK (test 1) sample after 15 minutes of exposure to the flame. Bottom figures, microscopic images of a central slice of the sample, view 2 is located in the centre of the slice; views 1 and 3 are at the edges of the degraded area.

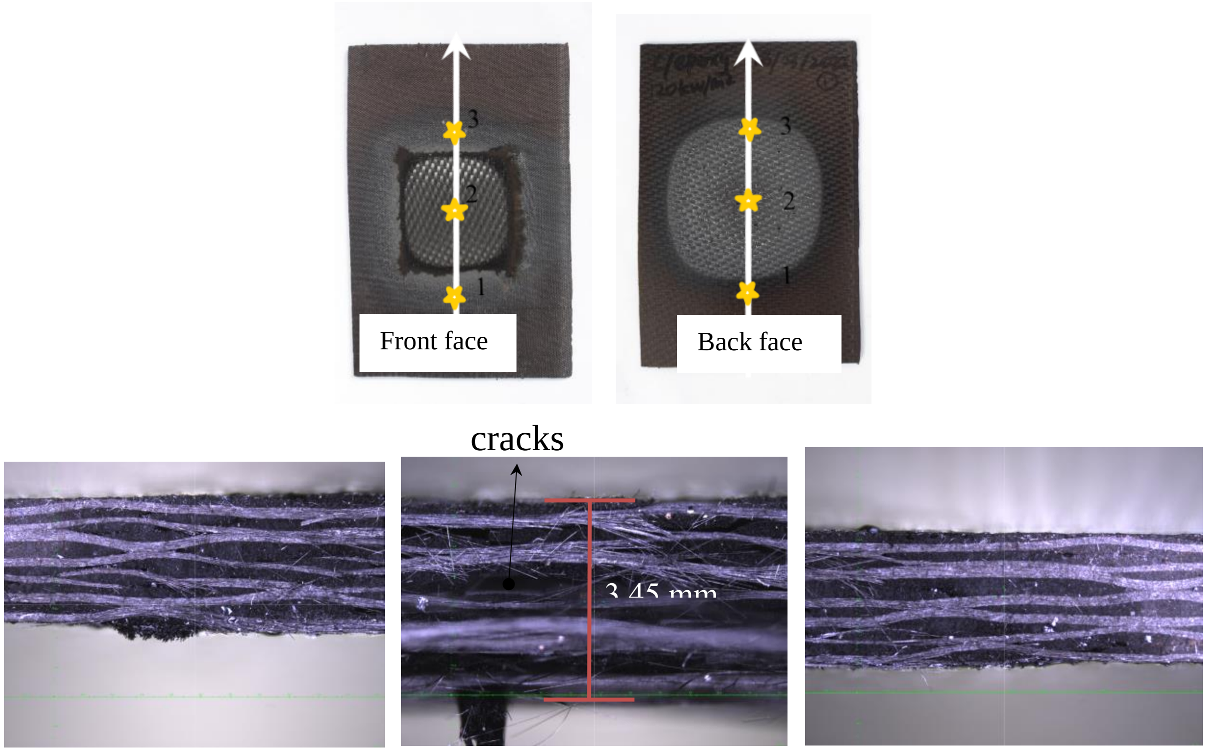

Figure 11: Top figures, aspect of the faces of a C-Epoxy (test 2) sample after 15 minutes of exposure to the flame. Bottom figures, microscopic images of a central slice of the sample, view 2 is located in the centre of the slice; views 1 and 3 are at the edges of the degraded area.

For the C-Epoxy sample, the degradation is stronger than for the C-PEEK. This is explained by the onset temperature of pyrolysis, which values are 300 and 550 °C for the C-Epoxy and C-PEEK composites respectively. On the surface exposed to the flame, there is no resin left and the carbon fibres are bare, without ablation as with C-PEEK. On the other hand, on the back surface, no resin or char are left between the fibre strands. By looking to the microscopic views, no virgin or degraded resin are left in the central zone of the sample (view 2), and at the borders of this zone (views 1 and 3), the virgin resin is much more degraded than for the C-PEEK.
Cracks exist between all the plies. The total length of the main cracks is about 70 mm. At middle point, the composite thickness is 3.45 mm. Since the initial value was 2.1 mm, the swelling is about 1.35mm. As explained before, one can expect that the depletion of the residual mechanical properties are greater for the C-Epoxy than for the C-PEEK.

6. Conclusions

A kerosene-flame test bench has been developed at laboratory scale in order to analyse and compare the behaviour of composites exposed to a flame, mainly for aeronautic applications. The kerosene and airflow rates can be been chosen in order to produce similar thermal-stress conditions as in the standards. During the test duration, the mass loss of the sample and the temperature on the back face are continuously measured.
With this test bench, it has been possible to analyse and compare the fire behaviour of two carbon fibre reinforced polymers, a thermosetting-based (C/epoxy) and a thermoplastic-based (C/PEEK), with the same thickness and the stacking sequence.
The thermosetting-based laminate is decomposed fast. After 15 minutes, the thermoplastic-based composite is not fully decomposed. Post-fire observations of the samples show that all the plies are damaged for the C-PEEK laminate and it remains some plies which are not strongly degraded at the back zone of the C-PEEK.
Due to the reliability of the device and the repeatability of the tests, this test rig can be used to better understand and to optimize the fire behaviour of thermosetting and thermoplastic-based composites used in aeronautics.

References

[1] A. P. Mouritz, A.G. Gibson. Fire Tests for Composites. In: Fire Properties of Polymer Composite Materials. Solid Mechanics and Its Applications, vol 143 (2006). Springer, Dordrecht. https://doi.org/10.1007/978-1-4020-5356-6_11

[2] ISO2685:1998(E). Aircraft-environment test procedures for airborne equipment – resistance to fire in designated fire zones.

[3] FAR25.856(b):.Title 14 code of Federal – test methods to determine the burnthrough resistance of thermal/acoustic insulation materials (Appendix F, Part VII), 2003.

[4] Serra J., Pierré, J.E. and Passieux, J.C, Périé, J.N., Bouvet C. Christophe, Castanié B., Validation and Modeling of Aeronautical Composite Structures Subjected to Combined Loadings:the VERTEX Project. Part 1: Experimental Setup, FE-DIC Instrumentation and Procedures. (2017) Composite Structures, vol. 179. pp. 224-244.

[5] S. I.Stoliarova, S. Crowley. R. E.Lyon, G. T.Linteris. Prediction of the burning rates of non-charring polymers. Combustion and Flame, 156 (2009), 1068-1083. https://doi.org/10.1016/j.combustflame.2008.11.010

[6] N. Grange, K. Chetehouna, N. Gascoin, A. Coppalle, I. Reynaud, S. Senave. One-dimensional pyrolysis of carbon based composite materials using FireFOAM, Fire Safety Journal 97 (2018) 66–75. https://doi.org/10.1016/j.firesaf.2018.03.002

[7] E. Schuhler, A. Chaudhary, B. Vieille, and A. Coppalle, “Fire behaviour of composite materials using kerosene burner tests at small-scales,” Fire Safety Journal, vol. 121, p. 103290, May 2021, doi: 10.1016/j.firesaf.2021.103290.

[8] E. Schuhler, B. Lecordier, J. Yon, G. Godard, and A. Coppalle, “Experimental investigation of a low Reynolds number flame jet impinging flat plates,” International Journal of Heat and Mass Transfer, vol. 156, p. 119856, Aug. 2020, doi: 10.1016/j.ijheatmasstransfer.2020.119856.

[9] Robert Gardon, “An instrument for the direct measurement of intense thermal radiation,” Review of Scientific Instruments, vol. 24, no. 5, pp. 366–369, 1953, doi: https://doi.org/10.1063/1.1770712.

[10] G. M. Carlomagno and A. Ianiro, “Thermo-fluid-dynamics of submerged jets impinging at short nozzle-to-plate distance: A review,” Experimental Thermal and Fluid Science, vol. 58, pp. 15–35, Oct. 2014, doi: 10.1016/j.expthermflusci.2014.06.010.

[11] M. McKinnon, Y. Ding, S. I. Stoliarov, S. Crowley, and R. E. Lyon, “Pyrolysis model for a carbon fiber/epoxy structural aerospace composite,” Journal of Fire Sciences, vol. 35, pp. 1–26, 2017, doi: 10.1177/0734904116679422.

[12] J. B. Henderson and T. E. Wiecek, “A mathematical model to predict the thermal response of decomposing, expanding polymer composites,” Journal of composite material, vol. 21, no. 4, pp. 373–393, 1987, doi: 10.1177/002199838702100406.

[13] B. Vieille, A. Coppalle, E. Schuhler, A. Chaudhary, A. Alia, N. Delpouve, A. Bourdet, “Influence of kerosene flame on fire-behaviour and mechanical properties of hybrid Carbon Glass fibers reinforced PEEK composite laminates”, Composite Structures 279 (2022) 114786

[14] P. Patel, T. Hull, E. Lyon, S. Stoliarov, N. Walters, S. Crowley, N. Safronava, “Investigation of the thermal decomposition and flammability of PEEK and its carbon and glass-fibre composites”, Polymer Degradation and Stability 96 (2011) 12-22.

[15] B. Vieille, C Lefebvre, A. Coppalle, “Post fire behavior of carbon fibers Polyphenylene Sulfide- and epoxy-based laminates for aeronautical applications: A comparative study”, Materials and Design 63 (2014) 56–68.