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Experimental investigation of the fire behaviour of a carbon-PEKK composite used for aeronautical applications

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ABSTRACT

Composite materials used for aerospace applications are vulnerable when exposed to high temperatures. Therefore, the development and the using of these materials are strictly framed by aviation regulations where severe fireproof requirements must be accomplished. In the light of this, experimental research is of crucial importance in the understanding of the thermal behaviour of composites materials for aircraft parts, especially when they might be exposed to high-temperature or fire conditions. In this context, thermal degradation of the thermoplastic resin polyether-ketone-ketone (PEKK) with carbon reinforcement is studied. This composite belongs to the polyaryletherketone (PAEK) family, which is known for its high performances. The carbon-PEKK thermal behaviour is evaluated from small scale to medium by scale by means of thermogravimetric analysis, Differential scanning calorimetry, Py-GC-MS and cone calorimeter. The different experiments demonstrate the high thermal performance of the carbon-PEKK composite. Indeed, the latter does not present any decomposition below 500°C, as well as a low amount of volatiles emitted during the resin decomposition. The cone calorimeter experiments confirm the results obtained at small scale and demonstrate that the low yield of volatiles induces a low amount of heat release when exposed to a radiative heat flux. Moreover, the samples present a reduced temperature on the backward face. Finally, these results suggest that the carbon-PEKK might ensure the confinement of a fire as well as a limitation of the fire spread.

KEYWORDS:

Aircraft Composite material, Thermal degradation, cone calorimeter, py-GC-MS
INTRODUCTION

Nowadays, composites materials are widely employed in several engineering fields and especially in aerospace industry. They represent more than half of the constituent elements an aeronautical vehicle. For instance, approximately 50 percent in mass of the Boeing 787 Dreamliner is made by carbon-reinforced composites; in this sense, another example is the Airbus A350-XWB with 52 percent in mass [1], as well as the Bombardier CSeries with a percentage of 47% [2]. Besides the high structural performance requirements, the use of these composite materials is based on the respect of a high-level standard used for the aviation safety especially for fire safety. In 2017, according to the Annual Safety Review, edited by the European Aviation Safety Agency, the second most frequent cause of fatal events, involving airplanes, was the post-impact fire/smoke [4]. This highlights the crucial need to understand the thermal behaviour of composites exposed to high temperature and hazardous fire aggression, to improve the ability to predict their thermo-structural behaviour, when employed as system or engine components.

The present study aims at characterizing the thermal degradation of the carbon-reinforced thermoplastic resin Poly-ether-ketone-ketone (PEKK), originally developed for automotive and aerospace applications in particular for exterior structures and cabin interiors. Carbon-PEKK belongs to the Polyaryl-Ether-Ketone (PAEK) family, known for their high mechanical performance and high temperature stability as demonstrated by Riviere et al. [5]. This composite is receiving a particular attention for its multiple applications. Indeed, PEKK-based composites show due to their low flammability and limited smoke emissions when subjected to fire [6]. Thus in order to evaluate the thermal behaviour of carbon-PEKK composite, different characterizations have been performed from small scale up to medium scale with samples directly cut from large panel. At small scale, Thermogravimetric analysis has been performed under both inert (argon) and oxidative atmosphere (air) up to 1000°C to evaluate the mass loss and thermal stability. The pyrolysis gases are then assessed at small scale using a Py-GC–MS apparatus for different temperatures defined from the previously obtained TG curves. Finally, fire behaviour of the composite is evaluated at medium scale with a cone calorimeter apparatus at a fixed heat flux of 100 kW.m⁻². The latter value corresponds to the heat flux encountered on large-scale samples (116 kW/m²) during the aeronautical standard fire tests [3]. These experiments aims to provide physical quantities such as Heat Release Rate (HRR), surface temperature and Mass Loss Rate (MLR). In particular, MLR which is one of the most important parameter as it is directly linked to the pyrolysis gas flow rate and represents the initial factor of the combustion process [7].

MATERIALS AND METHOD

Materials

The carbon-reinforced (fibres of approximately 7 μm diameter) polymer resins considered is a thermoplastic PEKK (66 wt% fibre ratio) provided by Daher. PEKK is a semi-crystalline thermoplastic material belonging to the family of PAEK, known for their high mechanical performance and high temperature stability [5]. PEKK-based composites find their main use in aerospace applications, especially for exterior structures and cabin interiors, due to their low flammability and smoke emission when subjected to fire [6]. The PEKK monomer is characterized by three aromatic groups bonded together by ether (R–O–R’) and ketone (RC(=O) R’) links (see Figure 1-left). The glass transition temperature is around 156 °C and the melting point 338 °C [8].

![Fig. 1. Overview of the PEKK Monomer (left) and carbon-PEKK sample (right).](image)

Experimental set-up

At small scale, thermogravimetric (TG) measures were performed with a SETARAM SetSys-16/18 TG, under both inert (argon) and oxidative (air) conditions at atmospheric pressure. This device consisted of a vertical-type TG where the Al₂O₃ crucible was hung to the electronically controlled balance. All the inert experiments were carried out with an argon flow rate of 16.6 ml.min⁻¹. Three non-isothermal heating rate of 5, 15 and 25°C.min⁻¹ and a final temperature of 1000°C were fixed. Samples were prepared in form of particulate of masses of 7–9 mg directly cut from virgin plate representative of the industrial material, in order to limit the
temperature gradient inside the samples. DSC measurements are also performed at small scale on same sample type. The experiments have been carried out under nitrogen atmosphere (volume flow rate of 40 ml.min\(^{-1}\)) and atmospheric pressure using a Nietzsch STA 449 F3 DSC from ambient to 1000°C, with a heating rate of 15 °C/min. Two tests have been carried out on the two samples extracted from two different locations of the plate. Pyrolysis gases of the sample were estimated with a Pyroprobe 5000 (CDS) for three pyrolysis temperatures defined along the decomposition of the composite. A solid composite sample of 1–2 mg, directly cut from large panel was placed inside a quartz tube which was then introduced into the pyrolyser and heated up at 5 °C.ms\(^{-1}\) to the desired temperature and maintained 10 s at this temperature. The pyrolysis products are transported to the GC-MS by a helium flow via a heated transfer line. GC separations were performed with a Trace Ultra GC (Thermo) equipped with a SLB-5ms capillary column (30 m long, 0.25 mm i.d., 0.25μm film thickness). The column temperature was programmed from 60°C to 300°C at a rate of 5 °C.min\(^{-1}\) and finally held for 1 min at 300 °C. Mass spectra were recorded with a Thermo DSQ II quadrupole in the electron ionization mode at 70 eV. The identification of the pyrolysis products has been based on the comparison of their mass spectra with the NIST mass spectral library.

Cone calorimeter experiments are finally carried out according to the ISO 5660-1: 2002 standard [9] on medium scale samples representative of structural parts materials. Samples with an exposed surface of 88.4 cm\(^{2}\) are located at 35 mm from a heat source (to assess a similar exposition between the different configurations) producing a constant heat flux of 100 kW/m\(^{2}\). Samples are placed successively in horizontal (standard cone calorimeter sample holder) and vertical configurations (hang into a support and isolated on the side of the samples) as presented in Figure 2. This heat flux level correspond to the requirements of the aircraft fireproof certification standards tests on large-scale samples. Two samples per configuration (Experiment 1 & 2) have been tested to ensure the repeatability of the measurements with a thickness of 1.68±0.05 mm (12 plies) and their average masses are about 26±0.3 g. The vertical configuration allows measuring the backward temperature using a Flir A600 infrared thermography apparatus. The Camera measures the temperature of a zone located at the centre of the backward face of the sample covered by a graphite layer (with a known emissivity of 0.95). The horizontal configuration allows measuring the mass loss (i.e. MLR) during the tests thanks to a load cell situated under the sample holder. The HRR is determined in both configurations using the oxygen depletion principle based on the concentration of O\(_2\), CO and CO\(_2\) [10]. To this end, a smoke absorption is performed at 24 l/s with a gas sampling of 58.3 ml/s.

![Fig. 2. Overview of the cone calorimeter experiments](image)

RESULTS AND DISCUSSION

Thermogravimetric analysis

In figure 3, the experimental mass loss curve and DTG curves obtained under inert and oxidative atmosphere are presented for the three non-isothermal heating rates. Under inert atmosphere, the PEKK resin is characterized by a mass release of about 20% and does not present any mass variation up to about 515°C; then a faster degradation process occurs, highlighting one global reaction, which comes to end at about 900°C. Similar behaviour is reported in the literature for composites with Poly-ether-ether-ketone (PEEK) resin, which also belongs to the PEAK family [6]. The identified reaction lies between about 510-710 °C and it might be associated with the random scission of ether bonds [7]. In particular, the decomposition process is expected to begin with the rupture of weakest bonds between the aromatic groups, whereas the major volatiles release should
consist of phenol [6]. The onset of this decomposition occurs after the transition phase of PEKK resin, typically observed by DSC measurements around 340 °C [8].

Fig. 3. Experimental mass loss and DTG Curves obtained under inert (a) and oxidative (b) atmosphere.

Under oxidative atmosphere, the samples have been almost completely consumed (no residual mass obtained). As for inert atmosphere, the degradation begins at about 500 °C and concludes between 700-850 °C, depending on the heating rate of the test. Three inflection points are visible in the TG curve corresponding to the three peaks on the DTG curves. This underlines the occurring of a complex reaction pattern. The first inflection peak is associated with resin decomposition, in correspondence of the same temperatures observed in inert conditions, between 550-615 °C. The second appears between 575-689°C while the third follows between 633-862°C. These peaks might refer to the combustion of carbon fibers, whose onset is expected between 600-700 °C which develops simultaneously with resin decomposition and combustion, as well as that of char [6,11]. It can also be seen that, before the first peak, especially for β=15 and 25°C.min⁻¹, a less intense peak is revealed on the DTG curves. This peak might eventually due to the oxidation of the pyrolysis products release by the early scission of the weakest bond [6]. Moreover, by increasing the temperature, also carbon-PEKK shows several further overlapped peaks, revealing a complex kinetic mechanism, driven by the occurring of multi-step reactions.

DSC measurements

In Figure 4, one can see the heat flow (corrected as function of mass loss) measured for carbon-PEKK under inert atmosphere. It reveals a major endothermic peak at about 600°C which corresponds to the single-step decomposition reaction observed previously in TG experiments. Moreover, the DSC analysis highlights the importance of the melting phase observed between 350°C and 550°C. Indeed, a wide endothermic peak is visible on the DSC curves in this interval. It is important to note that this phenomenon could influence the heat transfer in the composite sample while exposed to fire.

Fig. 4. DSC curve of the carbon-PEKK sample

Volatiles Emission

From the TG curves, the pyrolysis temperatures have been chosen to be 450, 590 and 750°C. Looking in details at the pyrolysis products (figure 5), one can see that no compounds are detected at 450°C which is just before the decomposition temperature. At 590 °C, once the thermal degradation started, three hydrocarbons are mainly identified: butane, benzene and toluene. They might be released by the cleavage of the weakest bond in the PEKK monomer (ether bond). At higher temperature (750°C), when the decomposition of the resin is finished an important release of phenol is observed (46 %), probably associated with the cleavage of the ether bond producing phenolic radical which leads to phenol after hydrogen loss, as observed on PEEK resin [6]. Low
amount of aromatic compounds and ketones such as pentanone and p-benzoquinone are also suspected and are also released by the cleavage of ketone bond at this temperature (7%). This low amount of volatiles (only 6 compounds at 75°C) might be a great benefit for the carbon-PEKK compared to other composites. Indeed, this induces a limited combustion on the surface leading to a small heat release when exposed to fire. Such behaviour might be interesting for aircraft safety. In fact, the fire spread would be limited and the smoke would be reduced lowering the potential risk of intoxication and ignition.

![Volatiles emission during carbon-PEKK sample pyrolysis](image)

**Fig. 5.** Volatiles emission during carbon-PEKK sample pyrolysis

**Cone calorimeter experiments**

The figure 6 presents the different results obtained for the cone calorimeter experiments. The two experimental mass loss curves (fig 6.a) highlight a good repeatability of the two tests. Both curves are characterized by two different phases. First, a quasi-constant mass up to 30 s corresponding approximately to the ignition time. Then, the latter is followed by a monotonous behaviour of the mass loss until 160 s where the mass start to stabilize. The mass loss at the end of the experiment represents 15 % of the initial mass of the sample. The thermoplastics PEKK resin has a good thermal stability and high melting point [8]. Moreover, the resin decomposition is characterized by a high yield of stable carbonaceous char (approximately 60 % of the original mass) leading to a superior flammability resistance [6].

![Experimental mass loss (a), HRR (b) and backward face temperature (c) obtained with cone calorimeter experiments](image)

**Fig. 6.** Experimental mass loss (a), HRR (b) and backward face temperature (c) obtained with cone calorimeter experiments.

Experimentally and for both configurations, the HRR (Fig 6.b) presents a rapid increase before reaching a maximum value of approximately 100 kW/m², which is limited compared to other composite materials [12-13]. The HRR values are oscillating within a range of 20 kW/m², which might correspond to the flame oscillation on the surface of the sample. Then, the HRR decreases down to 35 kW/m² at 160 s and seems to remain constant. After 160 s, experimentally, no more flame is visible on the surface of the carbon-PEKK composite, which indicates that internal heat generation process occurs, probably associated with the resin decomposition in the internal plies or the carbon fibre combustion on the surface of the sample. Moreover, Horizontal and vertical configurations present also similar ignition times due to the high value of the cone calorimeter heat flux reducing the convection role in the vertical configuration. However, in the vertical configuration, the buoyancy will generate a boundary layer on the surface of the sample and the bulk of the flow will be pulled up, conducting to a difference of temperature between the top and the bottom of the sample leading to a change in the HRR behaviour. The general trend of the backward face temperature (Fig 6.c) can be divided into two phases, a transient one with a quick increase of the temperature followed by a slow and constant increase of the temperature. The transient phase can be separated into two phases. The first phase presents a fast increase of the temperature between 0 and 30 s followed by a short stabilization at about 300 °C before a second temperature increase of approximately 100 °C between 30 s and 90 s. A last increase of 100°C between 90 s and 180 s is observable at the end and can be associated with the stable phase. The first stabilization at 300°C might be
explained by the high melting temperature of the PEKK resin ($T_m = 338 ^\circ C$ [8]) leading in an absorption of energy when reaching this temperature reducing the increase of temperature on the backward face.

**CONCLUSION**

In this work, the thermal degradation of the thermoplastic carbon-PEKK composite is evaluated in order to contribute to the understanding of its fire behaviour. The different results demonstrate the important thermal stability of the carbon-PEKK, characterized by high temperature resistance, starting its decomposition at about 500 °C. This high performance can be attributed to the chemical structure of the monomer make it as a promising material for aircraft components, especially where severe fire safety requirements must be accomplished. Moreover, the low amount of volatiles emitted during the pyrolysis of the resin limits the heat release and the fire spread risks. The latter is confirmed with the cone calorimeter experiments on medium scale samples. Cone calorimeter experiments also highlight the low mass loss and the moderate temperature on the backward face when sample are exposed to a large heat flux. The achieved results highlight the correlation between the data obtained at small scale and the one obtained at medium scale. Moreover, the different results demonstrate the interesting behaviour of the carbon-PEKK when exposed to fire or large heat flux. Thus, such composite might be interesting as firewalls of fire protection for aircraft parts. In the light of this, the next stage of this study will be focused on the implementation of large-scale fire tests with sample of approximately 500 x 500 mm, sample representative of a full scale aircraft part. The latter will be exposed to a kerosene flame as required in the aeronautical fire standards to confirm the carbon-PEKK fire behaviour.

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