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Influence of a flame-retardant on the fire-behaviour and the residual mechanical properties of C/PEKK composite laminates exposed to a kerosene flame

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Abstract

This work examines the influence of a phosphorus-based flame-retardant additive (Exolit) on the fire-behaviour and the residual mechanical properties of composite laminates manufactured by a thermo-consolidation process from unidirectional (UD) carbon fibers (C) and a PEKK (Polyether-ketone-ketone) thermoplastic associated with or without Exolit. Depending on the laminates lay-up (orthotropic or quasi-isotropic), the influence of Exolit on the thermal degradation, resulting from a kerosene flame exposure (116 kW/m² and 1100°C), on the composites structural integrity was examined. The changes in the residual tensile properties (axial stiffness and strength) were compared with respect to the virgin materials (experiencing no prior flame exposure) in room temperature (RT) conditions post fire exposure. The discussions on fire- and mechanically-induced damage mechanisms are supported by fractographic analysis of specimens. It is therefore possible to better understand how the fire-induced damages within the laminates micro- and meso-structures modify the mechanical behavior of flame-exposed laminates. Thus, the axial stiffness and strength decrease moderately (-6% and -18%, respectively) in quasi-isotropic laminates with respect to virgin specimens. In orthotropic laminates, the axial stiffness decreases by 15%, whereas the axial strength dramatically decreases (-55%). The obtained results suggests that the flame-retardant additive not only delays the thermal degradation of C/PEKK laminates but also efficiently contributes to maintain the structural integrity of the composites, hence resulting in good mechanical properties. The positive effect of Exolit is particularly noticeable in orthotropic laminates whose mechanical behaviour is driven by 0° carbon fibers.

Keywords: thermoplastic; flame-retardant; fire behaviour; mechanical properties; damages

1. Introduction

The aerospace industry has increased the usage of composites structural components for large aircraft, mainly because of weight reduction and resultant fuel savings [1]. Thermoset (TS) resins have been the mainstays of aerospace composites since their introduction to aircraft. Over the past few years, thermoplastics (TP) based composites represent a promising alternative in aeronautics. There are many types of thermoplastic materials with different thermal, chemical and mechanical properties, but the

most promising for aerospace applications are PEEK (Polyetheretherketone), PEKK (Polyetherketone-ketone), and PPS (Polyphenylene sulfide). The recent development of thermoplastics with improved temperature and solvent resistance fosters the interest for applications in several engineering fields, where they are considered as matrices in high-performance composites [2-3]. They have some attractive properties such as their insolubility in most common organic solvents, repeatable processing and recyclability, excellent impact toughness and low water uptake these qualities make them attractive as matrices for carbon fibers reinforced polymer composites. The important difficulties encountered with high-performance thermoplastics like PEEK concern their processability [4]. Significant efforts have been devoted to develop melt-processable solutions and high compatibility with carbon fibers [5-6]. However, high-temperature resistance and impact toughness are the two most important technical requirements for practical applications of thermoplastic composites especially in aerospace [3][7]. When composites are exposed to high temperatures, the heat propagates through the thickness by conduction triggering physical and chemical transformations [8-9]. Beyond a critical temperature, pyrolysis occurs and gas bubbles are formed. As the viscosity of the condensed phase decreases with temperature, the pressurized pyrolysis gas travels to the surface. This combustible gas will eventually consume the surrounding oxygen and feed the flame enhancing the combustion loop. If any fractions of the polymer remains ungasified, a porous char will form. This thermal degradation of the material rapidly affects the mechanical properties. Therefore, it is very important to understand the structural properties of TP-based composites under fire and to assess their residual mechanical properties. Thus, the changes in both physicochemical and mechanical behaviors due to the interaction of fire on TP-based composites still need investigations.

1.1 Polymer Matrix Composites (PMCs) under fire conditions

The recent air disasters have revealed that the issue of fire is at the heart of the concerns of the aeronautics industry. Over the past few years, here are a few examples of accidents involving planes engines' fire scenarii: a Nauru Airlines plane engine shoots out flames in Brisbane Airport in March 2021, a United Airlines plane engine on fire after takeoff from Denver (February 2021), a plane makes emergency landing after apparent engine fire in Los Angeles (January 2020), an Asiana Airlines A380 engine Caught Fire in Seoul Incheon Airport (November 2019), an Aeroflot plane catches fire during emergency landing in Moscow (May 2019). The use of polymer matrix composite materials in aeronautic applications is today confronted with ever more demanding safety standards to which it is imperative to provide reliable and measurable answers [10-17]. Therefore, it is essential to enable manufacturers to understand/predict the thermomechanical response of composite materials in different configurations of use and, ultimately, of their parts and assemblies. The demand for experimental characterization means representative of critical conditions in service is therefore strong from industrialists who have identified a technological barrier in the fire resistance of polymer matrix composite materials [18]. The combustion process of polymeric-based materials is complex [19],

involving many steps including some that are still unexplored. Depending on the thermal analysis technique, it is sometimes difficult to describe quantitatively the thermal decomposition. For a reliable DSC measurement, the sample mass must be constant. When pyrolysis occurs (which becomes inevitable when thermal decomposition temperatures are reached), such measurement is not reliable anymore as the sample experiences some mass loss. However, when the DSC measurement is coupled with a TGA, the loss of mass is recorded, which makes it possible to readjust the DSC measurement. There are four primary stages: heating, decomposition, ignition and fire propagation. Heat diffuses deeply by conduction and generates physical and chemical transformations through-the-thickness [20]. The mesophase represents the area of the material where phase transitions and chemical reactions occur. In such mesophase, gas bubbles are formed within a condensed phase, the viscosity of which decreases as temperature increases. On the exposed surface, these bubbles burst and release pyrolysis gases that will feed the flame. If any fractions of molten polymer remain ungasified, then they form viscous tar that accumulates on the exposed surface. The melting and bubbling stages usually depend on the nature of the matrix / fiber arrangement.

1.2 Fire-retardant Polymer Matrix Composites (PMCs)

Two strategies for manufacturing fire-retardant polymer-based composites are usually considered [19]. The first is to develop new polymers that are intrinsically fire retardant. The second is the development of new fire retardant formulations using additives flame-retardants. This second route is of major interest for industrial applications, because it only involves a modification of the existing material a posteriori. The flame retarding additives may have a gas phase mode of action (in this case, the inhibitory action will be exerted at the flame level) or a condensed phase mode of action by disrupting the degradation advancement within the thermal properties of the material. A commonly used method to reduce the flammability of composites is the addition of inert fillers (e.g. talc, silica) or thermally active fillers (e.g. hydrated oxides) to the polymer matrix [18]. Fillers are usually inorganic non-reactive compounds that are added to the polymer during the final stages of processing to reduce the flammability of the finished product. The filler particles diameter is often lower than 10 μm , and often in the submicron range. The particles are blended into the liquid resin and must be uniformly dispersed to ensure consistent flame-retardant properties throughout the polymer. Most polymers require a high loading of filler to show an appreciable improvement to their flammability resistance, and the minimum volume content is usually about 20% and the average content is typically 50 to 60%. The selection of a flame retardant for a polymer composite is determined by several factors, including cost, chemical compatibility between the flame-retardant compound and host polymer, decomposition temperature of the compound, and weight. Many flame retardant fillers reduce the mechanical properties of polymers, and this is another consideration when used in structural composites. While flame retardant epoxies and other polymers with low flammability are increasingly used in composite aircraft structures, these materials are often much more expensive and do not have the same

mechanical performance as conventional aerospace-grade epoxies [18]. As reported in the literature, fire retardant additives may or may not have a significant impact on the time-to-ignition. In their recent study, Leventon et al. have tried to quantify (mass loss, char yield, heat release rate) the mechanisms of action of bromine- and phosphorous-based (Exolit OP1230) flame-retardants on the fire-behaviour (flame imposed by a methane burner) of glass-fiber reinforced poly (butylene terephthalate) (PBT) samples manufactured with increasing amounts of weight fraction. They concluded that both flame retardants (at least at the concentrations they tested) can affect wall flame stability and gas phase combustion efficiency but do not affect flame to surface heat transfer in the continuous region of wall flames [21]. More recently, Niu et al have considered phosphates modified by Si₃N₄, AlN, Al₂O₃ and Cu₂O particles incorporated in PEEK matrix composites to improve their heat resistance and mechanical properties [22]. The incorporation of these modified phosphates increases the 30% mass loss temperature by 55 °C, and the compressive strength was increased by about 106%.

1.3 Fire testing of PMCs

In order to test the fire resistance of PMCs, several standard tests specific to aeronautical applications are commonly used [23-24]. In particular, two different types of burner are described in the international standards for civil aircraft fire resistance [21-22], one type of burner using propane as fuel [17] and the other type using kerosene [25]. The standard tests are mandatory for material qualification. However only a few studies have been carried out with these standard burners. In particular, Le Neve et al. have pointed out differences on the qualification results depending on the burner type used to perform the test [26]. Even though flame exposure presents multiple advantages, so far, most of the laboratory scale studies are performed with a cone calorimeter to apply a radiative heat flux on the sample [25]. However, a direct flame impact is a more realistic thermal stress [28-30] and heat flux greater than 100 kW/m² can be easily reached for many fire scenarios [31]. The literature dealing with the fire response of TS-based composites is very rich [18]. But there are fewer references dealing with TP composites. Among the studies available in the literature on TP-based materials, one can find results obtained by means of cone calorimeter [10-16][32], of a propane burner on polyphenylene sulfide composites [13], or of a kerosene burner on PEKK-based composites [29-30]. Thermal degradation analysis based on TGA tests under inert and oxidative conditions have been conducted by Tadini et al. [33], then Grange et al. [34-37]. They concluded that PEKK-based composites have a higher thermal performance than phenolic-based composites due to the PEKK matrix. A NexGen burner designed by the Federal Aviation Administration (FAA) was used to get a standardised flame intended to be a realistic scenario of an in-service or post-impact fire event. Such device allows the investigations of the burn-through resistance and the thermal behaviour of C/PEKK laminates [29-30]. These references only focused on the thermal degradation but no significant attention was paid to the residual mechanical properties.

1.4 Post-fire residual mechanical properties

In literature, most references dealing with the mechanical behavior of composites subjected to fire conditions focus on the residual mechanical properties measured in room temperature conditions after fire exposure. This is not representative of failure criteria in ISO 2685, where the most demanding conditions for burn-through are encountered with simultaneous mechanical and thermal solicitations [24]. While the post-fire mechanical properties of thermoset laminates have been thoroughly investigated [18], the residual properties of thermoplastic composites are not well understood. The reason for the superior post-fire strength of TP composites has not been determined, although it is probably because these materials generally have higher decomposition temperatures, yield high amounts of char, and are less susceptible to delamination cracking than thermoset laminates [10][12]. When the thermal heat flux is high enough to induce the pyrolysis, TP-based composites yield higher amounts of char than TS-based laminates [10]. Char formation is expected to be reflected in the residual properties of laminates, as it is known to retain the structural integrity of a fire-damaged composite by holding the fibers in place after the polymer matrix has been degraded. The thermally insulating properties of char are also expected to protect the material deeper in the sample from thermal decomposition as usually observed in TS-based composites [18]. As a result, the analysis of the post fire tensile properties shows that prior severe fire exposures (medium to high heat flux – long exposure time) are more detrimental to C/Epoxy than to C/PPS laminates. At last, most references dealing with the post-fire mechanical properties of TP-based composites are focused on the influence of cone calorimeter heat fluxes (ranging from 20 to 60 kW/m²). However, very few works have investigated the influence of a kerosene flame exposure on their residual mechanical properties [38].

1.5 Objectives of the work

Depending on the laminates lay-up (orthotropic or quasi-isotropic), the present work was aimed at investigating the influence of a flame-retardant additive (20 wt. % of PEKK) on the fire behavior and the residual mechanical properties in tension of C/PEKK composite laminates. These investigations are intended to examine the effect of thermal degradation due to kerosene flame exposure on the composites structural integrity by comparing the changes of the tensile properties (axial stiffness and strength) with respect to the virgin materials. The discussions on fire- and mechanically-induced damage mechanisms are supported by fractographic analysis of specimens. It is therefore possible to better understand how the fire-induced damages within the laminates micro- and meso-structures modify the mechanical behavior of flame-exposed laminates.

2. Materials and laminates processing

2.1 Materials

2.1.1 Thermoplastic matrix

In this work, a Polyether Ketone Ketone (PEKK) thermoplastic polymer (Kepstan® 7003PT from ARKEMA) having density equal to $1,29 \text{ g/cm}^3$ and average size $20 \text{ }\mu\text{m}$ powder was chosen as polymer matrix [39]. The main advantage of using PEKK is due to its lower processing temperature than PEEK. In particular, PEKK is well suited for the creation of large structural components. The chemical structure of PEKK consists of two structural units namely terephthalic (70%) and isophthalic (30%) respectively whose ratio controls the thermal properties and crystallization kinetics. PEKK is a semi-crystalline thermoplastic with superior chemical and heat resistance and the ability to withstand high mechanical load. Crystallinity in high-performances polymers is important because it has a strong influence on chemical and mechanical properties: the crystalline phase tends to increase the stiffness and tensile strength while the amorphous phase is more effective in absorbing impact energy. Before processing of the composites, thermal and physico-chemical analyses of PEKK samples were performed (section 3.2). Before processing (section 2.2), PEKK powder was dried at 120°C under vacuum during 16-18 hr.

2.1.2 Carbon fiber (CF)

Polyacrylonitrile-based UD carbon fibres provided by Porcher Industry was used in the work. This carbon reinforcement is made of continuous yarns consisting of 12000 high strength filaments with a diameter of about $3 \text{ }\mu\text{m}$. The density of carbon fiber is 1.5 g/cm^3 . Its tensile mechanical properties are a 270 GPa Young's modulus and a 700 MPa tensile strength. Before processing, the carbon fibers were dried at 80°C for 24 hours in an oven. There is 20% of Exolit in the polymer matrix mass fraction, which represents 43% of the mass fraction of the composite.

2.1.3 Flame-retardant additive

There are many classes of compounds, which are useful as flame-retardants [40]. Inorganic minerals, organo-phosphates, and halogenated compounds are commonly used for their ability to inhibit combustion and smoke generation in plastics and other materials. In this study Exolit® OP 1400 – provided by Clariant was used as a flame-retardant additive [41]. This additive consists of powder compounds under the form of Exolit particles to be exfoliated in a polymer matrix. It is a phosphorus-based flame retardant having density $\rho=1.240 \text{ g/cm}^3$ and phosphorus content varied up to 24.5-25.5%. Phosphorous-containing flame-retardants mainly influence flame-retardancy in the condensed phase [19]. They are particularly effective in materials having high oxygen content, such as cellulose and

some oxygen-containing plastics. We can mention that this is the case for PEKK matrix used in this work. The basic flame retarding mechanism involves the thermal conversion of the phosphorus-containing flame-retardant to phosphoric acid in the condensed phase of the plastic. The phosphoric acid extracts water from the burning plastic, causing it to char. The char insulates the plastic from flame and heat, preventing volatile, combustible gases from exiting the bulk [40].

2.2 Composite laminates processing

To fabricate the composite laminates, the polymer powder is combined with reinforcing fibers via the powder impregnating method. Powder impregnating method consists in associating reinforcing fibers with a polymer matrix powder. Heat is then applied on both sides by means of heating plates to melt the matrix and wet the fibers with the matrix. For this purpose, we used the thermo-compression molding technique to process carbon fibers reinforced PEKK laminates. PEKK powder and carbon fibers were placed layer by layer. Before processing the composite laminates, all the samples were dried at different pre-drying temperatures as mentioned previously. Flame retardant additive (20 wt. % of PEKK) were added in PEKK powder and mixed for 30 min in order to get a homogenous dispersion. The attention has been taken during the composites plates' fabrication process to ensure the uniformity between each plies. The required amount of carbon fibers and matrix polymer weight in each compression molding run has been determined based on the pre-defined volume fraction and mold dimension. The volume fraction of carbon fibers is fixed to 50%. Thus, calculated weight of Carbon fibers and PEKK powder were equally applied between each plies (lay-up) to fully wet out the fibers in each composites plate. Finally, the optical microscopy techniques have been used to examine the uniformity and adhesion between carbon fiber and PEKK on fabricated composites plates as depicted in the following Figure 1. As described by the manufacturer, the median particle size of the material Exolit-OP 1400 is between 20 and 40 μm .

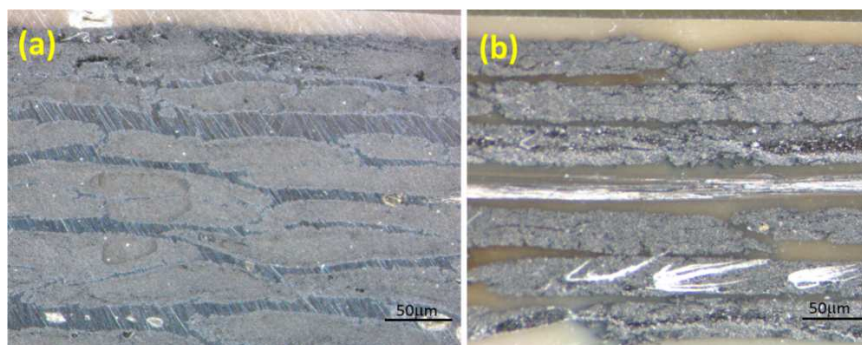


Fig. 1 – Optical microscopy images of transverse cross sections in C/PEKK laminates: (a) orthotropic
- (b) quasi-isotropic

The determination and optimization of the processing parameters is an empirical and time-consuming process, so an efficient and accurate study is needed to obtain the most accurate processing

parameters. To prepare the plates, samples were molded at 350°C during 20-30min without applying any pressure. After 30min, a 68 bars pressure was applied at 350°C during 30min then the sample was cooled down at room temperature. All the compressed molded plates were prepared in the size of 160 × 180mm panels with a nominal thickness of about 3.5 mm. For all the samples fabricated, the same molding temperature, molding time and pressure were used. Laminates plates with two different stacking sequences were processed in the present work: $[0]_8$ orthotropic and $[0,+45,-45,90]_s$ quasi-isotropic plates. Tensile test specimens were cut by water jet from the different plates subjected to prior kerosene flame. The geometry of the specimens complies with the test standard described in [44]. Three samples were tested in each of the following configurations:

- orthotropic without exolit (referred to as PUD),
- orthotropic with exolit (referred to as PUDE),
- quasi-isotropic without exolit (referred to as PQI),
- quasi-isotropic with exolit (referred to as PQIE).

Index “K” refers to specimens exposed to a kerosene flame.

3 Experimental set-up

3.1 Kerosene burner bench

The burner shown in Figure 2 is made with a domestic device (Cuenod manufacturer). The kerosene is injected in a nozzle generating a hollow cone spray with an angle equal to 80° and a maximum flow rate of 0.3 g/s. This flow rate is controlled with a mass flow meter (MINI CORI-FLOW™, Bronkhorst), and it can be adjusted. Airflow is also controlled with a mass flow meter (EL-FLOW® Prestige, Bronkhorst). The fuel-to-air ratio has been selected at 0.85 of the stoichiometric value, in order to obtain heat flux and temperatures values close to the standard values (116 kW/m² and 1100°C) at the sample location. The flame at the exit of the turbulator is a wide and turbulent jet. Therefore, a 50 mm diameter steel tube is installed after the turbulator to channel the hot combustion gases on the exposed area of the sample. Details of the experimental set-up are presented in Figure 2. With this design, an efficient mixing occurs inside the first part of the flame tube, and in its remaining part, the flow turbulence is strongly damped.

At the flame tube exit, no kerosene droplets are observed implying that the unburned kerosene is fully evaporated. Thus, the thermal stress on the sample is due to the hot gas mixture of the combustion products [42]. The flame tube diameter is chosen according to the size of the sample exposed area. Thus, the hot gas stream close the sample wall corresponds to the stagnation zone of an impinging jet and the wall heat flux is nearly constant, as shown in a previous work on a propane burner [43]. The heat flux is measured using a water-cooled Gardon type gauge at the position corresponding to the sample location, 105 mm from the burner output in the centerline of the tube. The temperature is measured with a comb of 6 K-type thermocouples placed vertically 105 mm from the burner output.

The composite samples described in section 2.2 are placed on a dedicated sample holder for the test. The sample holder is presented in Figure 2. The composite sample is placed between two insulation layers and the assembly is clamped by two steel plates. On both sides of the sample holder, an 80 mm side square aperture is made. On the front side, the sample is facing the burner output. On the backside, the temperature measurement is performed. This sample holder has two major aims. The first one is to prevent the surrounding of the sample by the flame. The second one is to maintain the integrity of the sample border. This is of great interest to perform post-fire mechanical tests. The 80 mm square aperture is chosen in order to maintain a uniform heat flux on the exposed sample surface while maintaining at least 50 mm on the sample border.

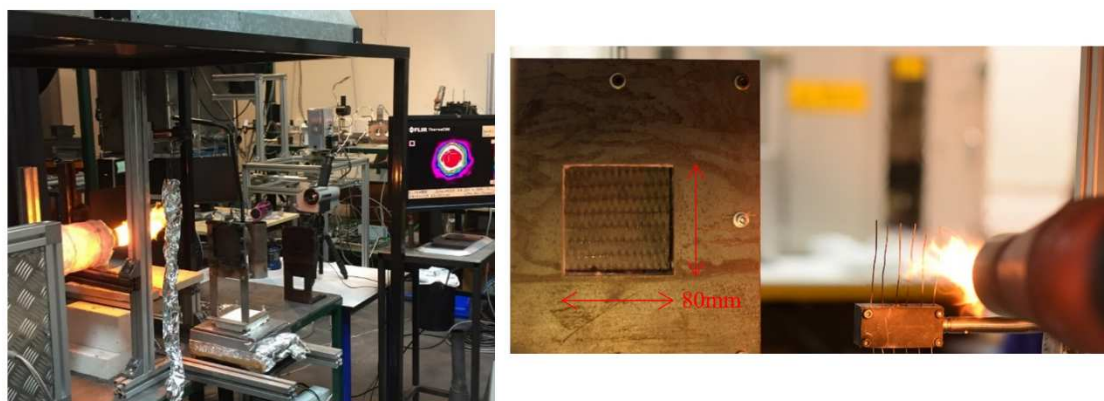


Fig. 2 – Kerosene flame exposure: (a) Experimental set-up - (b) Observations of the sample holder

3.2 Thermal and physico-chemical analysis

Differential scanning calorimetry (DSC) measurement was carried out on DSC Diamond (PerkinElmer) to study the thermal properties of PEKK before processing. DSC tests were applied to study the glass transition and melting point of PEKK powder samples whose weight is about 7 mg. These samples were thermally cycled (heating/cooling/heating) between 50°C and 400°C at a constant heating/cooling rate of 10 °C/min in a nitrogen atmosphere.

Thermogravimetric analyses were conducted using in a first approach a Pyris TGA-1, PerkinElmer device. The measurement was performed with a classical heating rate (10 K/min) on samples of 7 mg (± 0.5 mg) from 50 to 900 °C. Secondly, thermal aggressions at higher rates were assessed on PEKK and PEKK with Exolit in a Thermal Analysis® Discovery apparatus. The experiments were performed on samples of 1.5 ± 0.5 mg under a continuous flow of gaseous nitrogen (25 mL/min) at 10, 20, 50 and 100 K/min. The calibration in mass was done by using calibration standards as references and the weight loss was controlled with calcium oxalate. The calibration in temperature was performed with the Curie point of nickel for each heating rate.

The heating rate during fire tests is estimated around 300 °C/min. TGA and DSC analyses were performed with a lower heating rate but the same order of magnitude was considered.

3.3 Mechanical testing

Monotonic tensile tests were performed using a 100 kN capacity load cell of a MTS 810 servo-hydraulic testing machine in displacement-controlled mode. The tensile mechanical properties were determined according to the European standards EN 6035 [44]. The residual mechanical properties were measured in room temperature (RT) conditions post fire exposure.

3.4 Fractographic analysis

Microscopic observations have been carried out by means of a numerical optical microscope Keyence VHX-5000 to build 3D pictures of damaged areas. Fractographic analysis was conducted on samples after kerosene flame exposure as well as after mechanical loading.

4. Results and discussion

4.1 Thermal stability of the constitutive materials

Differential scanning calorimetry (DSC) measurement was carried out to determine the characteristic temperatures of PEKK matrix. From the DSC curve (Figure 3), the glass transition temperature of PEKK is found at 161°C. The melting range is from 320 to 350 °C and the temperature of the melting peak is at 333°C. The melting range should be considered when selecting the molding temperature. Before investigating the influence of kerosene flame exposure on the degradation of laminates micro- and meso-structure, it seems relevant to consider first the properties of the constitutive materials. It is worth noting that Exolit particles (20 wt. % of PEKK) are included into the PEKK matrix. Exolit particles are expected to modify the fire-behaviour of C/PEKK laminates. The thermal stability of Exolit was studied by TGA and presented in Figure 4a. Exolit OP-1400 offers higher thermal stability compared to magnesium hydroxide $Mg(OH)_2$ whose initial thermal decomposition starts at a temperature higher than the processing temperature of PEKK (350°C).

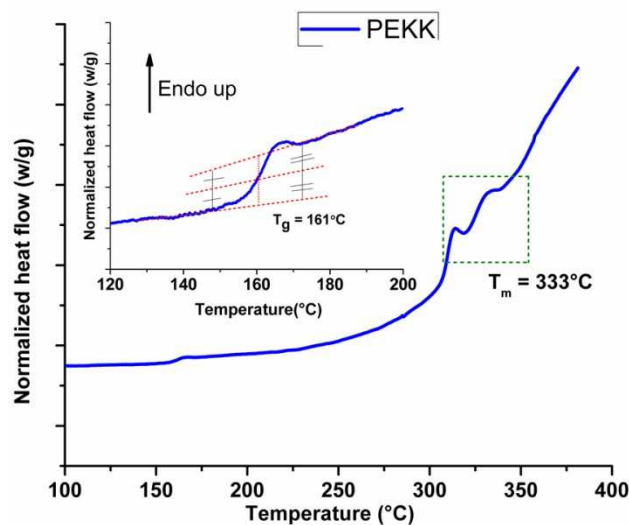


Fig. 3 – DSC curve of PEKK sample used in this study

Thermal decomposition of PEKK was also investigated by TGA tests under a nitrogen atmosphere (Fig. 4b). The TGA curve of PEKK shows a single step of degradation, which is due to the random chain scission [16]. The thermal degradation of PEKK begins around 550°C and the maximum degradation is observed at 600°C. From this result, we can confirm that the PEKK is thermally stable up to 450-500°C and therefore it is a suitable material for high-temperature applications. It seems relevant to consider first the influence of different heating rates on the thermal decomposition of the studied materials under a nitrogen atmosphere. The purpose was here to consider heating rates close to the ones encountered during flame exposure. TGA results show that PEKK and PEKK + Exolit are stable up to 300 °C (Figure 4b), which allows quite broad processing windows. Their thermal decomposition occurs between 450 and 700 °C, and the residual masses range between 50 and 70%. The thermal decomposition occurs in one-step for PEKK and in two steps for PEKK + Exolit, with no impact on the residual mass. The first step of thermal decomposition occurs between 350 and 500 °C and could be attributed to the decomposition of Exolit which maximum rate of degradation has been recorded at 447 °C (Figure 4a). The second step of thermal decomposition may stem from the decomposition of the PEKK. By increasing the heating rate, the TGA curves are shifted towards higher temperatures. This may result from the insulating behaviour of the matrix [45-46].

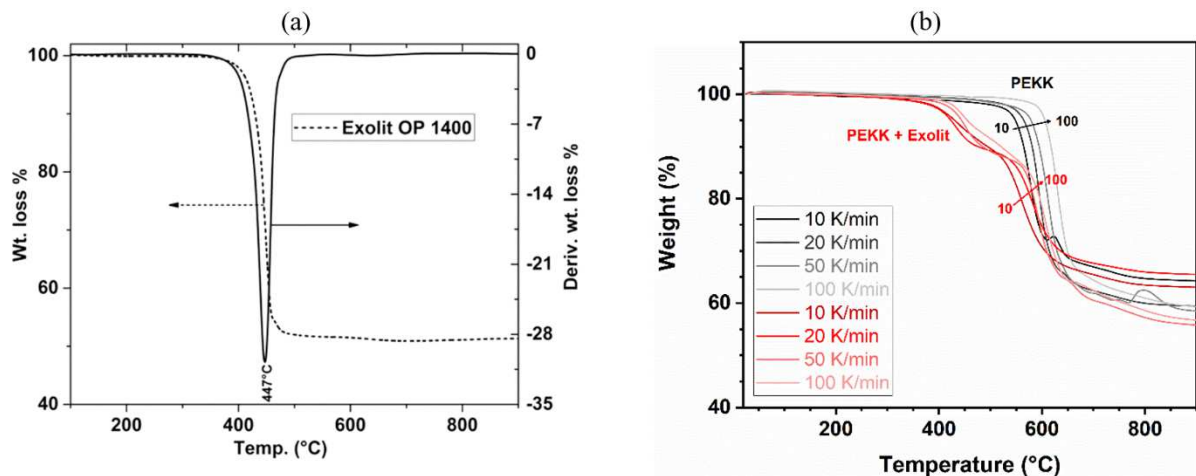


Fig. 4 – TGA tests under N₂ atmosphere: (a) Exolit OP-1400 – (b) PEKK matrix at different heating rates

4.2 Fire behaviour of orthotropic laminates

From the microscopic observations of the outer surface of samples with or without flame-retardant additive (Fig. 5), it clearly appears that the white Exolit particles are homogeneously dispersed into the PEKK matrix whose color is light beige. The microscopic observations of orthotropic laminates edges with or without Exolit show no significant differences, but the main interest of these observations is to highlight the initial virgin state of the samples for comparison purposes after flame-exposure. They also allow distinguishing the orientation of carbon fibers within each ply of the laminates.

After a 5 min exposure to a kerosene flame (corresponding to a thermal aggression of 116 kW/m² and a surface temperature of about 600°C), the macroscopic observations of orthotropic laminates (Fig. 6) show that fire-degraded areas are similar on the exposed surfaces of laminates with or without Exolit (referred to as PUDE and PUD, respectively). Due to the sample holder shape, the degradation of the laminates is limited to an 80 mm side square (Fig. 2). On the contrary, the fire-induced degradation is clearly less significant in laminates with Exolit as indicated by the very moderate colour change on the back surface. For a 5 min exposure time, it suggests that the flame-retardant additive effectively contributes to delay the thermal degradation within the laminates as reflected by the back surface state. It is of the utmost importance noting that tensile specimens were cut in the plate after flame exposure. Of course, the thermal degradation induced by fire exposure depends on the location of these specimens on the plate. The most severely degraded ones are located in the central part of the plate. On the plates edges (positions 1 and 5 in Fig. 6), the tensile specimens look like they are in the virgin state. Therefore, it is expected that the residual tensile properties of the specimens are similar to the virgin state ones, whereas the decrease in the mechanical properties will be the most significant for the specimen in position 3.

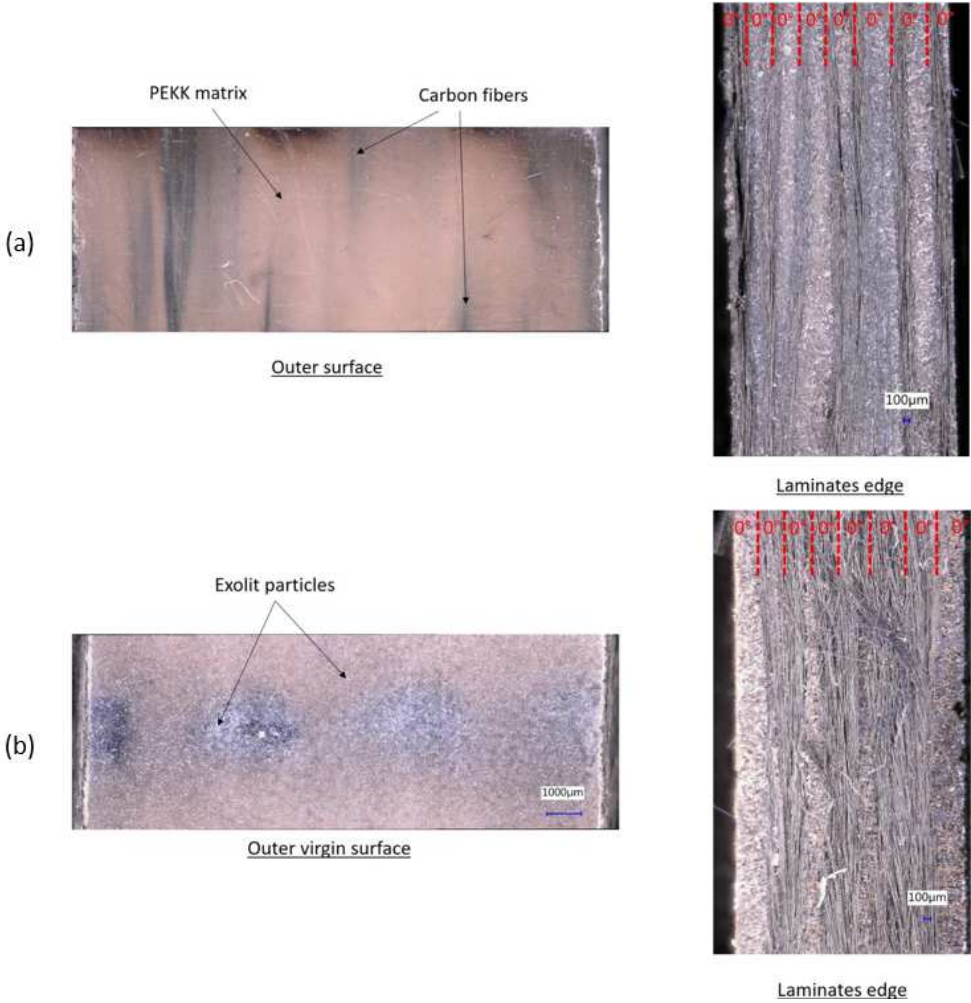


Fig. 5 – Microscopic observations of orthotropic laminates front surfaces and edges:
 (a) without exolit (PUD) – (b) with exolit (PUDE)

To further investigate the influence of flame-retardant additive on the fire behaviour of orthotropic laminates, microscopic observations were conducted on the tensile specimens cut from the plates (with or without Exolit) exposed to a kerosene flame for 5 min. These observations were performed on the specimen located at the centre of the fire-exposed plate (position 3 in Fig. 6) to visualize the most severe thermal and mechanical degradations.

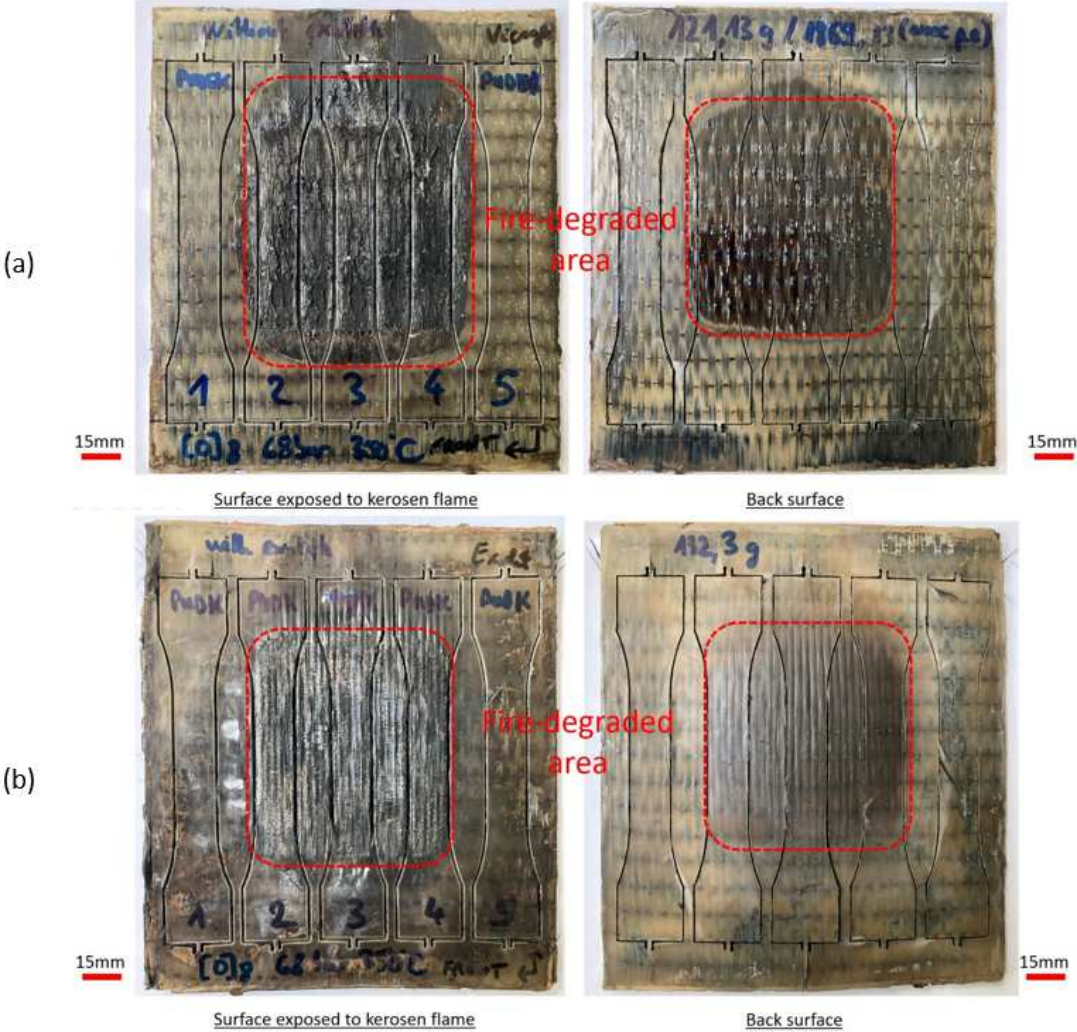


Fig. 6 – Macroscopic observations of orthotropic laminates front and back surfaces:
 (a) without exolit (PUD) – (b) with exolit (PUDE)

In composites without Exolit, Figure 7a shows that the exposed surface is severely degraded. Significant longitudinal splitting is observed as well as tar residue resulting from the thermal decomposition of the PEKK matrix on the exposed surface (at temperatures higher than 600°C in agreement with the TGA results obtained on PEKK – section 4.1). The observation of the back surface reveals that PEKK matrix started melting. Let us recall that the melting range is from 320 to 350°C and the temperature of the melting peak is at 333°C. From the back surface observation, a few bubbles are clearly observed. It suggests that the pyrolysis of the PEKK matrix has started within the laminates

and that pyrolyzed gases tend to migrate from the inner plies to the back surface of the laminates. From the laminates edge observations, one can see that PEKK pyrolysis also leads to a significant delamination of the inner laminates plies whereas the back surface (the one to the left) is nearly undamaged. It is worth noticing that in more realistic ISO 2685 testing conditions (fire + mechanical load + overpressure) burn through would have likely occurred. It could therefore be argued that samples with Exolit where such bubbles are not observed are more likely to pass a real certification test.

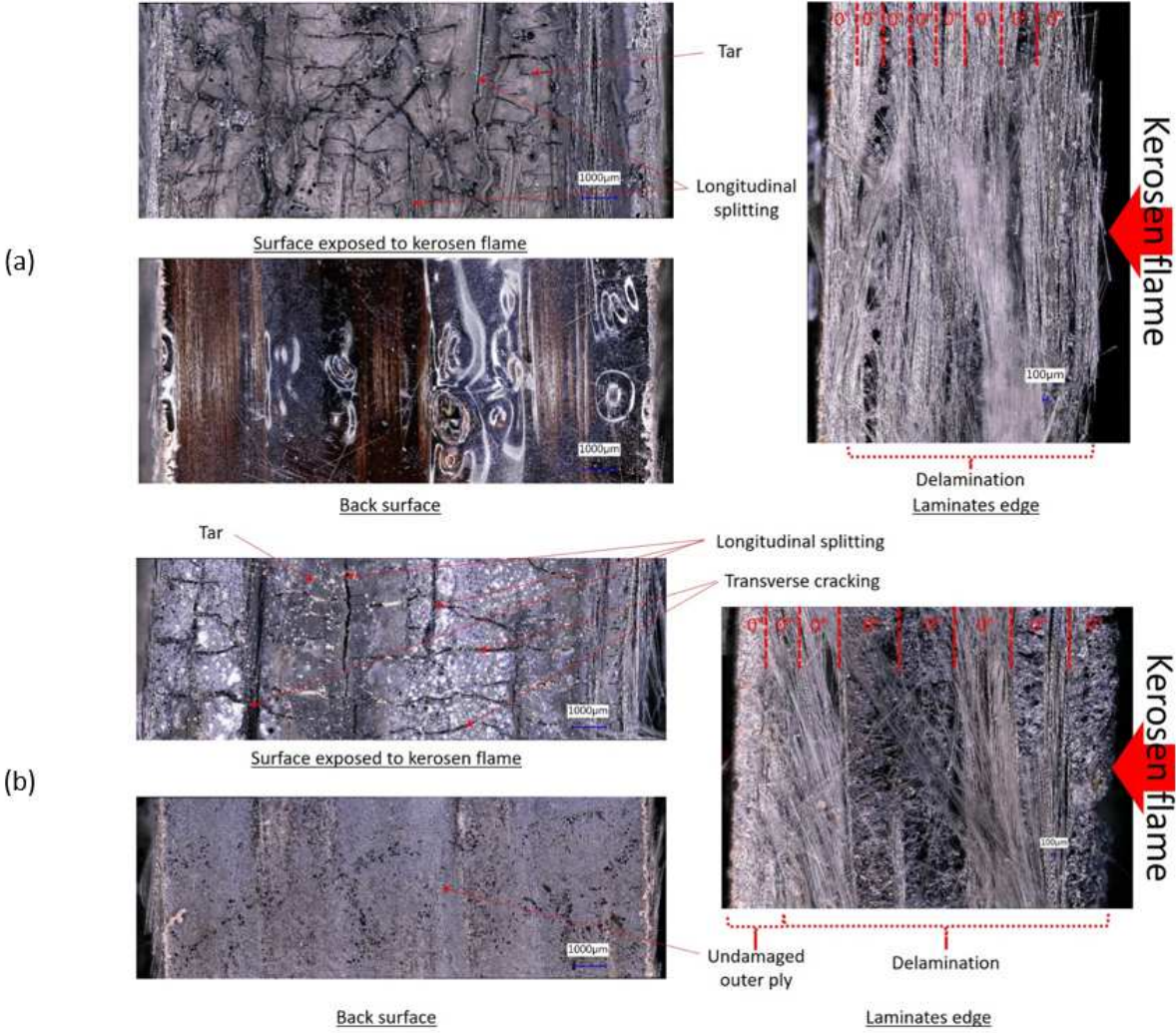


Fig. 7 – Microscopic observations of orthotropic laminates:
 (a) without exolit (PUD) – (b) with exolit (PUDE)

In composites with Exolit, Figure 7b shows that the exposed surface is also severely degraded. In PUDE specimen, the observation of the back surface shows that the PEKK matrix colour changed from beige to transparent. This suggests that the physical state of PEKK in the outer ply has changed. Contrary to what is observed in PUD laminates, the observation of the back-surface reveals that the outer ply is virtually undamaged though its initial colour has changed. This confirms that the flame-

retardant additive efficiently contributes to delay the thermal decomposition of C/PEKK. The observation of the laminates edge also shows that the outer ply is not so highly thermally degraded and delamination is not as extensive as the one observed in composites without Exolit. In order to study the severity of thermal degradation, the residual mechanical properties in tension will be evaluated to quantify the influence of flame-retardant additive. Depending on the location of the tensile specimen on the flame-exposed plate, the previous damages will go from the most severe thermal degradation (central position 3 in Fig. 5) to virtually undamaged state along the plate edges (positions 1 and 5 in Fig. 5). Before considering the influence of flame-retardant additive on the tensile residual behaviour of orthotropic laminates, let us examine now if the fire-behaviour of C/PEKK laminates depends on its stacking sequence, or not.

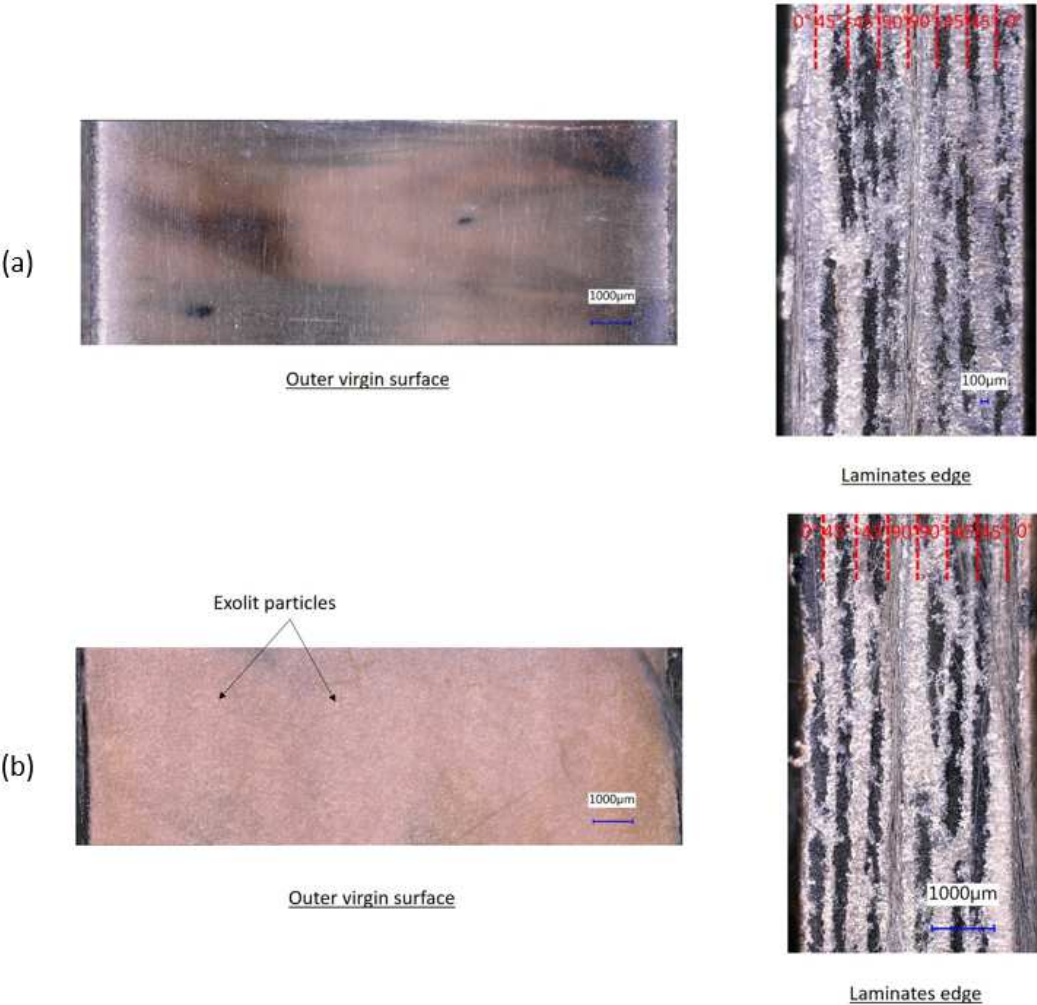


Fig. 8 – Microscopic observations of quasi-isotropic laminates front surfaces:
 (a) without exolit (PQI) – (b) with exolit (PQIE)

4.3 Fire behaviour of quasi-isotropic laminates

As was considered in orthotropic laminates, the outer surfaces of quasi-isotropic laminates with a quasi-isotropic lay-up are used as a reference virgin state to analyse the influence of flame-retardant agent on the thermal degradation of the fire-exposed surface. Once again, the significant mass fraction of Exolit (20 wt. % of PEKK) makes the aspect of the outer surface very different from the composite without Exolit (Fig. 8). However, the laminates edges are very similar and clearly reveal the plies with $\pm 45^\circ$ oriented carbon fibres.

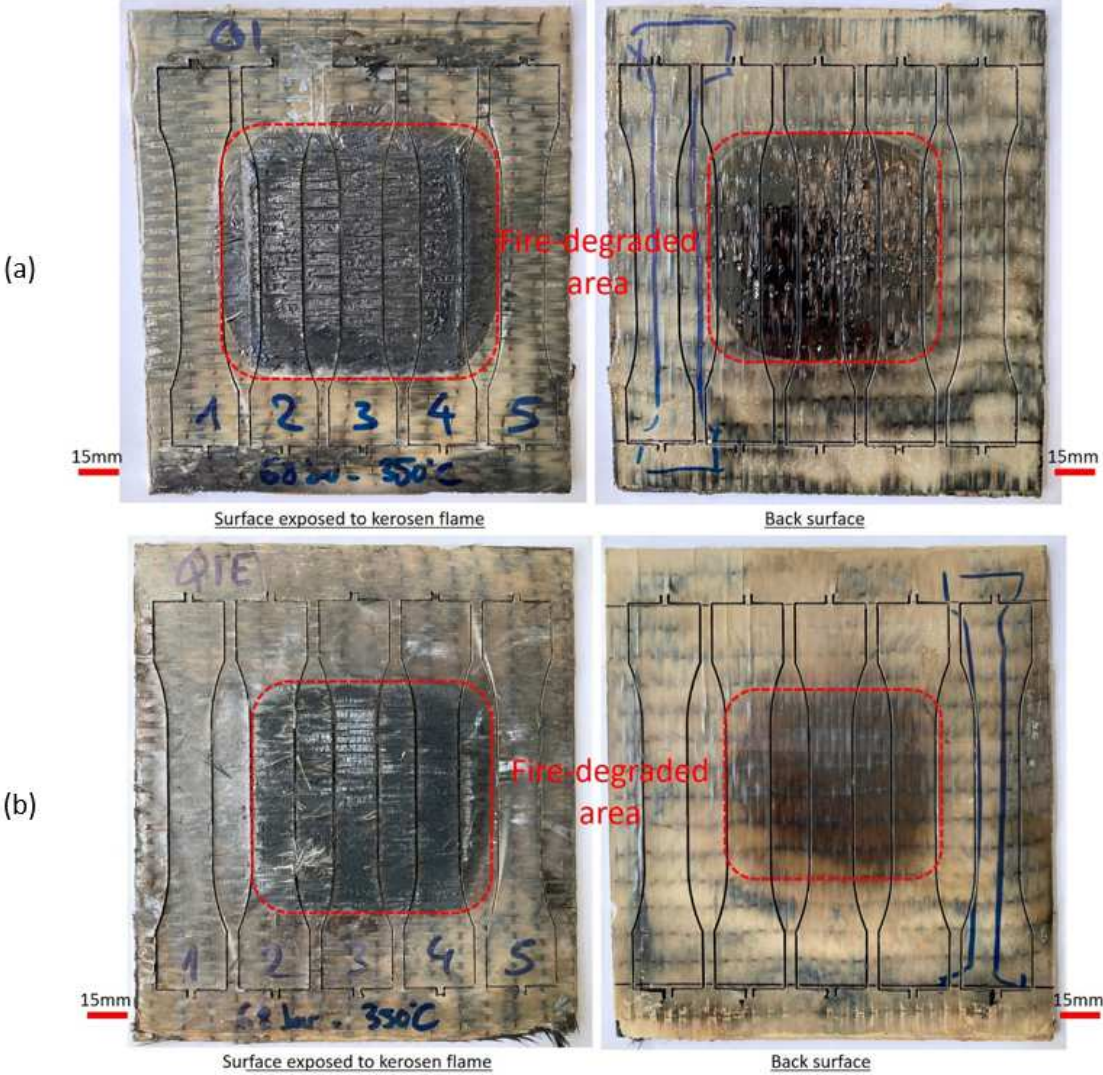


Fig. 9 – Macroscopic observations of quasi-isotropic laminates front and back surfaces:
 (a) without exolit (PQI) – (b) with exolit (PQIE)

After a 5 min exposure to a kerosene flame, the macroscopic observations of quasi-isotropic laminates (Fig. 9) show that the fire-degraded areas of Exolit-based composites (referred to as PQIE) are slightly smaller than the one observed in composites without Exolit (referred to as PQI). In addition, as was already observed in orthotropic laminates, the fire-induced degradation is clearly less significant in laminates with Exolit as indicated by the moderate colour change on the back surface. For a 5 min

exposure time, it also suggests that the flame-retardant additive effectively contributes to delay the thermal degradation within the laminates as reflected by the back surface state. Finally, the stacking sequence does not seem to change significantly the fire behaviour of C/PEKK laminates. This needs to be confirmed by the microscopic observations of PQI and PQIE tensile specimens.

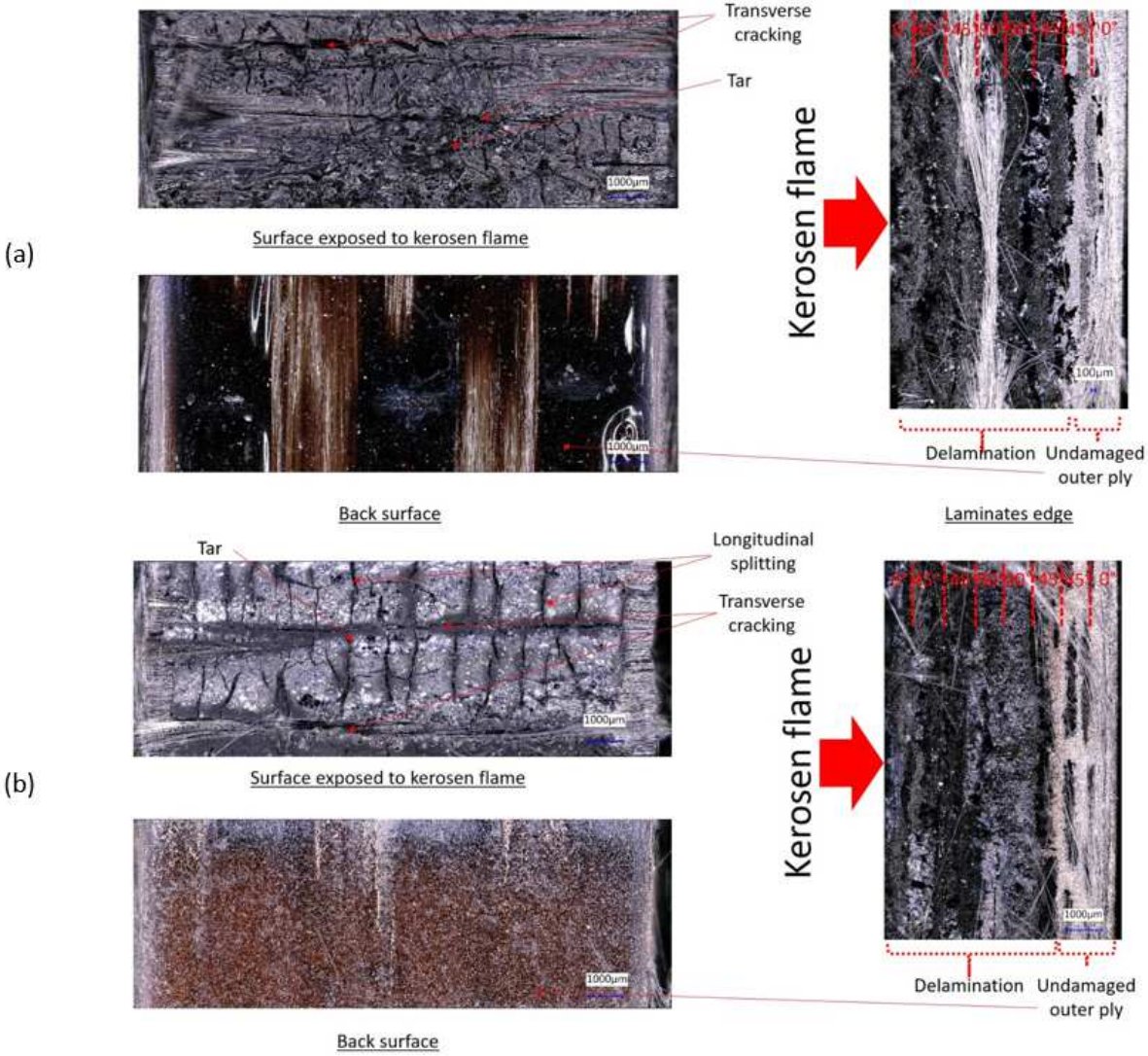


Fig. 10 – Microscopic observations of quasi-isotropic laminates:
 (a) without exolit (PQI) – (b) with exolit (PQIE)

PQI specimens are characterized by significant damages that can be observed on the exposed surface (Fig. 10a). A network of transverse micro-cracks is formed along with tar (residue of PEKK thermal decomposition at temperatures higher than 600°C) during fire-exposure. On the back surface, the PEKK colour turned transparent as already observed in PUD specimens. Contrary to PUD composites, the observations of laminates edge shows two well-defined areas through the thickness. The first one corresponding to the exposed surface side is significantly damaged because of the pyrolysis of the PEKK matrix leading to an extensive delamination. The second one corresponding to the back-surface

side is characterized by two plies that are very little damaged. In addition, there is no transition zone between these two areas suggesting that the second area has been protected during the thermal degradation of the six other plies. The extensively delaminated $\pm 45^\circ$ plies may contribute to the protection of the plies underneath. This could explain why the outer plies of the QI laminates are virtually undamaged.

In PQIE specimens, the observation of the exposed surface shows significant tar formation, a network of longitudinal cracks also known as splitting and macroscopic transverse cracks (Fig. 10b). The edge of the specimen looks very similar to PQI samples in terms of thermal degradation mechanisms. Two well defined areas (a severely degraded one and a virtually undamaged one) are also clearly observable, with no transition zone. However, the undamaged area is represented by three plies seemingly protected by the ones on the other side. It is expected that the residual tensile response (and corresponding properties) of these specimens will significantly depend on these undamaged plies as they should have a good cohesion of both matrix and fibers. In other words, the preservation of the mechanical properties in tension (with respect to virgin specimens) should be better in PQI laminates than the one in PUD composites.

4.4 Residual tensile behaviour of orthotropic laminates

In the previous section, large plates ($180 \times 160 \text{ mm}^2$) of C/PEKK laminates were exposed to a kerosene flame whose diameter is about 50mm. The prior exposure of laminates to a kerosene flame is expected to have a significant influence on the residual tensile properties as fire conditions lead to a heterogeneous temperature distribution on the exposed surface as well as through the thickness. The residual mechanical properties were measured in room temperature (RT) conditions post fire exposure. It is therefore not representative of failure criteria in ISO 2685, where the most demanding conditions for burn-through are encountered with simultaneous mechanical and thermal solicitations. It is also expected that effect of Exolit on mechanical properties would be observed under more realistic testing conditions (fire + mechanical load + overpressure), when the matrix temperature is well above its glass transition temperature.

As shown in Figure 6, tensile specimens are directly cut from by waterjet from the flame-exposed plates. These tensile specimens are more or less thermally-degraded depending on their location on the plates. As a result, a gradual decrease in the residual tensile properties should be observed from the specimens located along the edges (positions 1 and 5) to the specimens located in the more severely degraded area of the plate (positions 2-3-4). The tensile mechanical responses of orthotropic laminates is elastic quasi-brittle. It is consistent as the mechanical behaviour of $[0]_8$ laminates is driven by the tensile behaviour of 0° fibres. For comparison purposes, the representative responses of virgin specimens are represented to illustrate the severity of flame-exposure depending on the presence of flame-retardant additive (Fig. 11). When comparing the mechanical properties of orthotropic laminates in the virgin state (PUD and PUDE - Fig. 12), both axial strength and stiffness are 10% lower in

C/PEKK laminates with Exolit (Table 1). In orthotropic laminates without Exolit exposed to a kerosene flame, it appears that the structural capabilities of C/PEKK has significantly decreased in the most detrimental conditions (specimen taken from position 3). With respect to the virgin state, the axial stiffness decreases by 15%, whereas there is a dramatic decrease (-55%) in axial strength (Fig. 12).

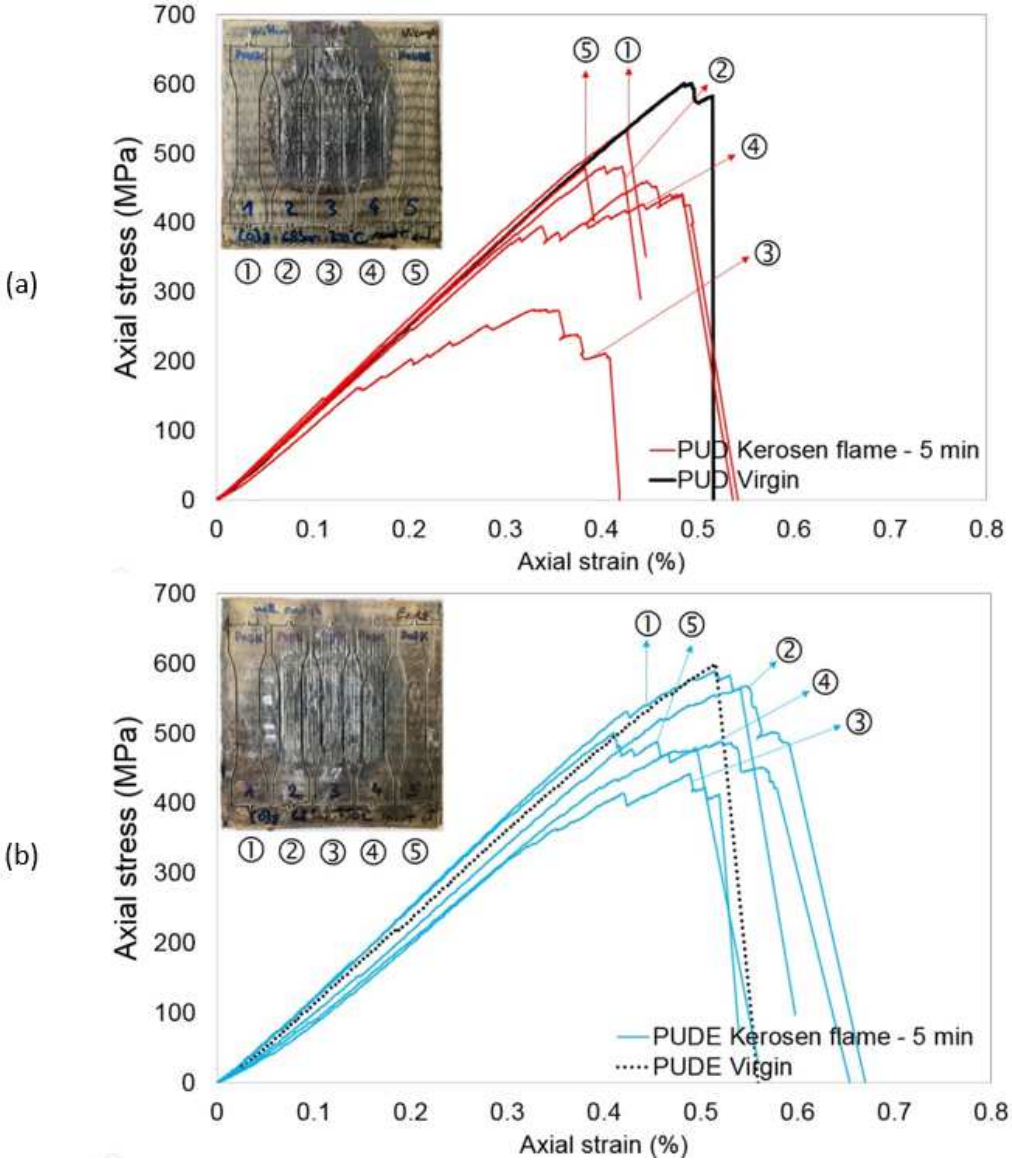


Fig. 11 – Macroscopic tensile response of orthotropic laminates:
 (a) without exolit (PUD) – (b) with exolit (PUDE)

In orthotropic laminates with Exolit exposed to a kerosene flame, the preservation of tensile properties (stiffness and strength) is very good with a moderate decrease (-14%) in axial strength and an axial stiffness that is virtually unchanged in the most detrimental conditions (specimen taken from position 3). It therefore suggests that the flame-retardant additive not only delays the thermal degradation of

C/PEKK laminates but also efficiently contributes to maintain the structural integrity of the composites, hence resulting in good mechanical properties (Fig. 12).

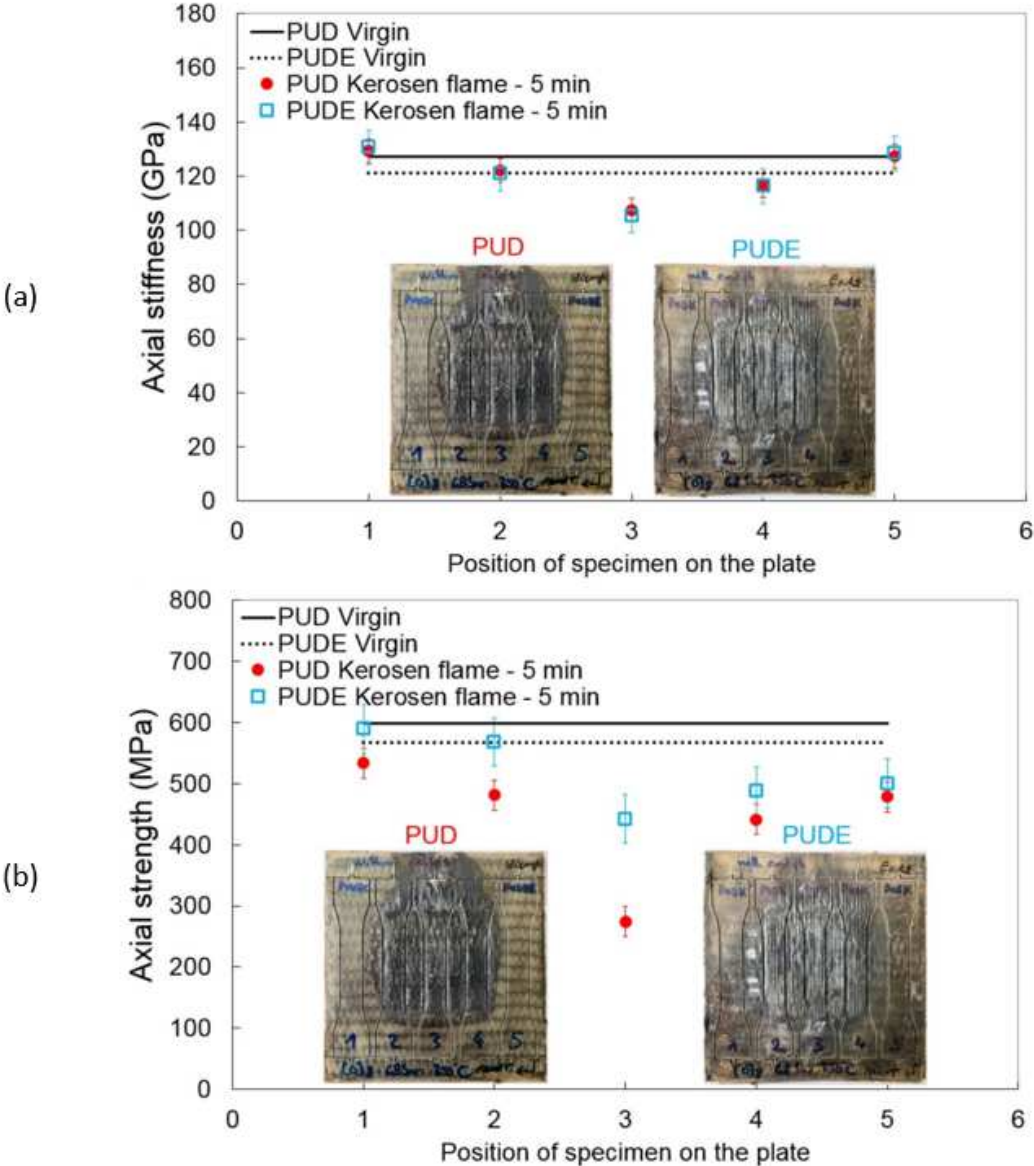


Fig. 12 – Influence of flame-retardant additive on the tensile properties of orthotropic laminates:
 (a) Axial stiffness – (b) Axial strength

In addition, the comparison of PUD and PUDE composites shows that Exolit improves the axial strength under flame exposure (+20%), but has virtually no influence on the axial stiffness after a 5 min exposure to a kerosene flame. One can also notice that the stiffness of specimens located along the flame-exposed plate (positions 1 and 5) are unchanged with respect to C/PEKK samples in the virgin state. These conclusions are supported by the macroscopic observations of front/back surfaces as well as the laminates edges (Fig. 13). It was chosen here to consider only the fractographic analysis of the most severely degraded specimens (position 3 on the flame-exposed plate) to observe the consequences of the most critical service conditions.

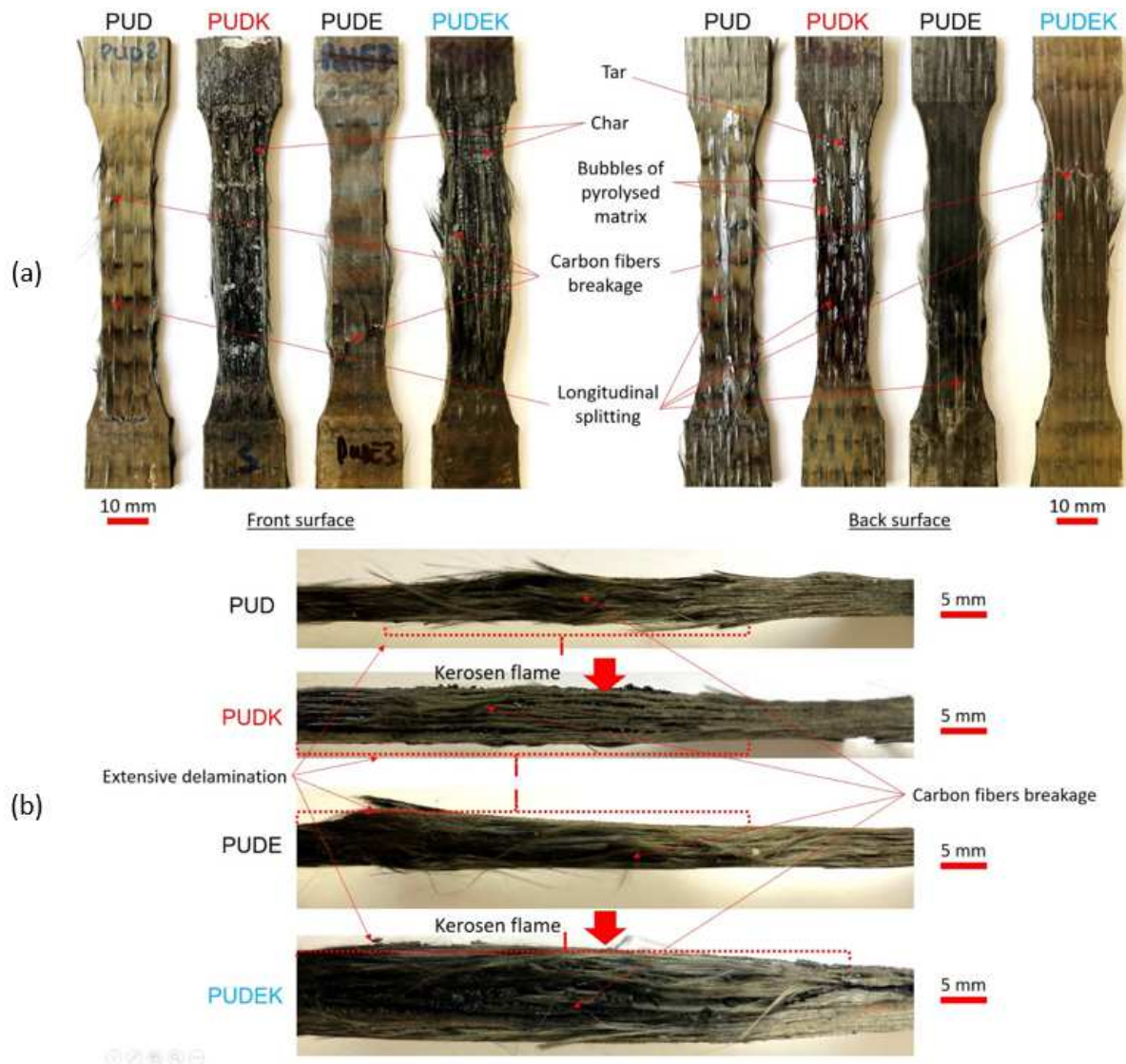


Fig. 13 – Influence of flame-retardant additive on the damage mechanisms in orthotropic laminates:
 (a) Front and back surfaces – (b) Laminates edge

On the one hand, the comparison with specimens that are not exposed to flame (PUD and PUDE) is relevant as it emphasizes the specific damage mechanisms resulting from fire conditions. On the outer plies of the laminates, there is no major difference between virgin specimens as they are simply characterized by longitudinal splitting as well as carbon fibres breakage. The macroscopic observations of laminates edges show an extensive delamination in both specimen types.

On the other hand, let us recall that damages caused by flame-exposure slightly differ between PUD and PUDE specimens (Fig. 7). These thermally-induced damages primarily consisted in delamination coming along with PEKK matrix pyrolysis, they are expected to significantly influence the mechanical behaviour and fracture mechanisms.

The exposed surface of the laminates is severely degraded. Char facilitates longitudinal splitting and ultimately the breakage of carbon fibres. On the back surface, very little damage is observed in

specimens with Exolit except the transverse breakage of carbon fibres. This is consistent with the thermally-induced damage observed in section 4.1: the observation of the laminates edge shows that the outer ply is not significantly thermally-degraded and delamination is not as extensive as the one observed in composites without Exolit (Fig. 13). This may explain why specimens with Exolit (PUDEK) have a higher preservation of their tensile strength after flame-exposure in relation to specimens without Exolit (Fig. 12b). The axial stiffness of specimens in tension is primarily associated with the stiffness of carbon fibres. The oxidation of carbon fibres is limited to the exposed surface as the plies underneath are protected by the formation of a char layer on the outer ply [16]. Thus, the axial stiffness is not significantly affected by kerosene flame aggression. However, the extensive delamination of C/PEKK laminates (coming along with the PEKK matrix pyrolysis) alters significantly the load transfer between the laminates plies. This is detrimental from the strength standpoint as each ply bears a portion of the tensile loading and once a ply fails, the mechanical load is not taken up by the neighbouring plies. The outer plies of PUDEK specimens being less degraded (“undamaged outer ply” on Fig. 13), the capability of these plies to bear the tensile loading is virtually unchanged with respect to virgin specimens. Ultimately, Exolit seems to significantly improve the axial strength under flame exposure (+20%), but has virtually no influence on the axial stiffness after a 5 min exposure to a kerosene flame.

4.5 Residual tensile behaviour of quasi-isotropic laminates

The tensile mechanical responses of all specimens is elastic-brittle though there are only two plies oriented at 0° (the outer ones). For comparison purposes, the representative responses of virgin specimens are represented to illustrate the severity of flame-exposure depending on the presence of flame-retardant additive (Fig. 14). When comparing the mechanical properties of quasi-isotropic laminates in the virgin state (PQI and PQIE), both axial strength and stiffness are virtually unchanged (about -5% in strength and -10% in stiffness) in C/PEKK laminates with Exolit (Table 2). This evolution is similar to the one observed in orthotropic laminates.

In QI laminates without Exolit exposed to a kerosene flame, it appears that the structural capabilities of C/PEKK are rather well maintained in the most detrimental conditions (specimen taken from position 3). Indeed, the axial stiffness only decreases by 6%, whereas there is a moderate decrease (-18%) in axial strength with respect to the virgin state (Fig. 15).

In QI laminates with Exolit exposed to a kerosene flame, the preservation of tensile properties (stiffness and strength) as they are virtually unchanged. It therefore suggests that the flame-retardant additive not only delays the thermal degradation of C/PEKK laminates but also efficiently contributes to maintain the structural integrity of the composites, hence resulting in good mechanical properties (Fig. 15). In addition, the comparison of PQI and PQIEPU composites shows that Exolit improves the axial strength under flame exposure (+10%), but has virtually no influence on the axial stiffness after a 5 min exposure to a kerosene flame, as was already observed in orthotropic laminates. It also appears

that there is less dispersion in the experimental data. These results also suggest that the influence of Exolit on the tensile properties is less significant in QI laminates with respect to orthotropic laminates. This difference may stem from their mechanical behaviour that is not only driven by 0° fibres but also by $\pm 45^\circ$ oriented plies. As indicated in section 4.2, fire-induced damages primarily consist in PEKK matrix pyrolysis coming along with extensive delamination. $\pm 45^\circ$ angle-ply having a matrix dominated tensile behaviour, it is therefore expected that their individual contribution to the macroscopic tensile response of QI laminates is not significant.

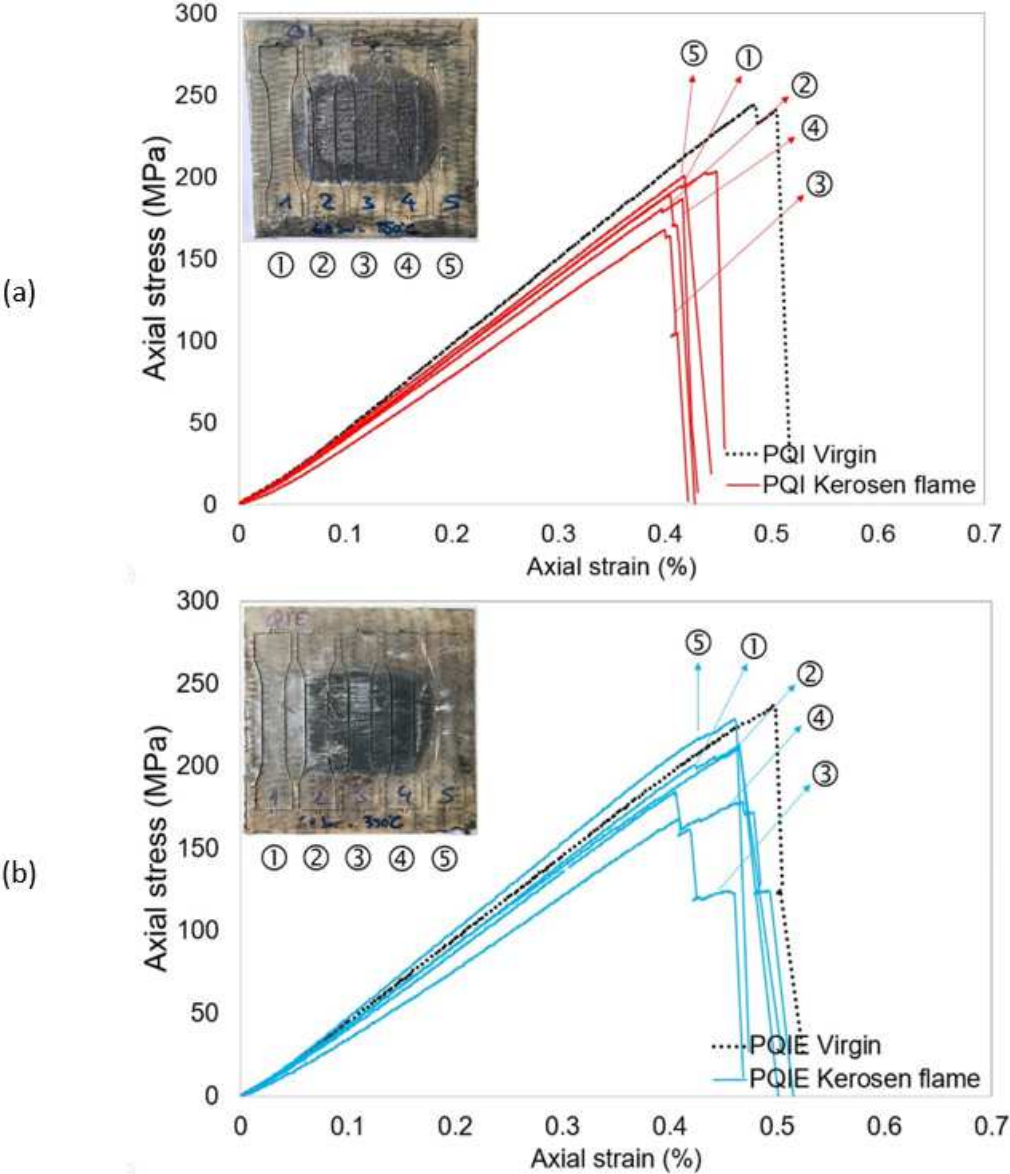


Fig. 14 – Macroscopic tensile response of quasi-isotropic laminates:
 (a) without exolit (PQI) – (b) with exolit (PQIE)

As was shown in section 4.2, damages caused by flame-exposure are very similar in PQI and PQIE specimens (Fig. 9). After being exposed to a kerosene flame, these specimens are characterized by

two-well defined areas (a severely degraded one and a seemingly undamaged one) with no transition zone. However, the undamaged area is represented by two or three plies that seem to be protected from thermal degradation by the ones on the other side. It was expected that the residual tensile response (and corresponding properties) of these specimens would be better as these undamaged plies still have a good fibres/matrix cohesion. Let us recall that the axial stiffness and strength decrease moderately (-7% and -18%, respectively) in QI specimens with respect to virgin specimens. In orthotropic laminates, the axial stiffness decreases by 15% (Fig. 15), whereas the axial strength dramatically decreases (-55%). These results therefore confirm that the preservation of the tensile properties is better in PQI laminates than the one in PUD composites.

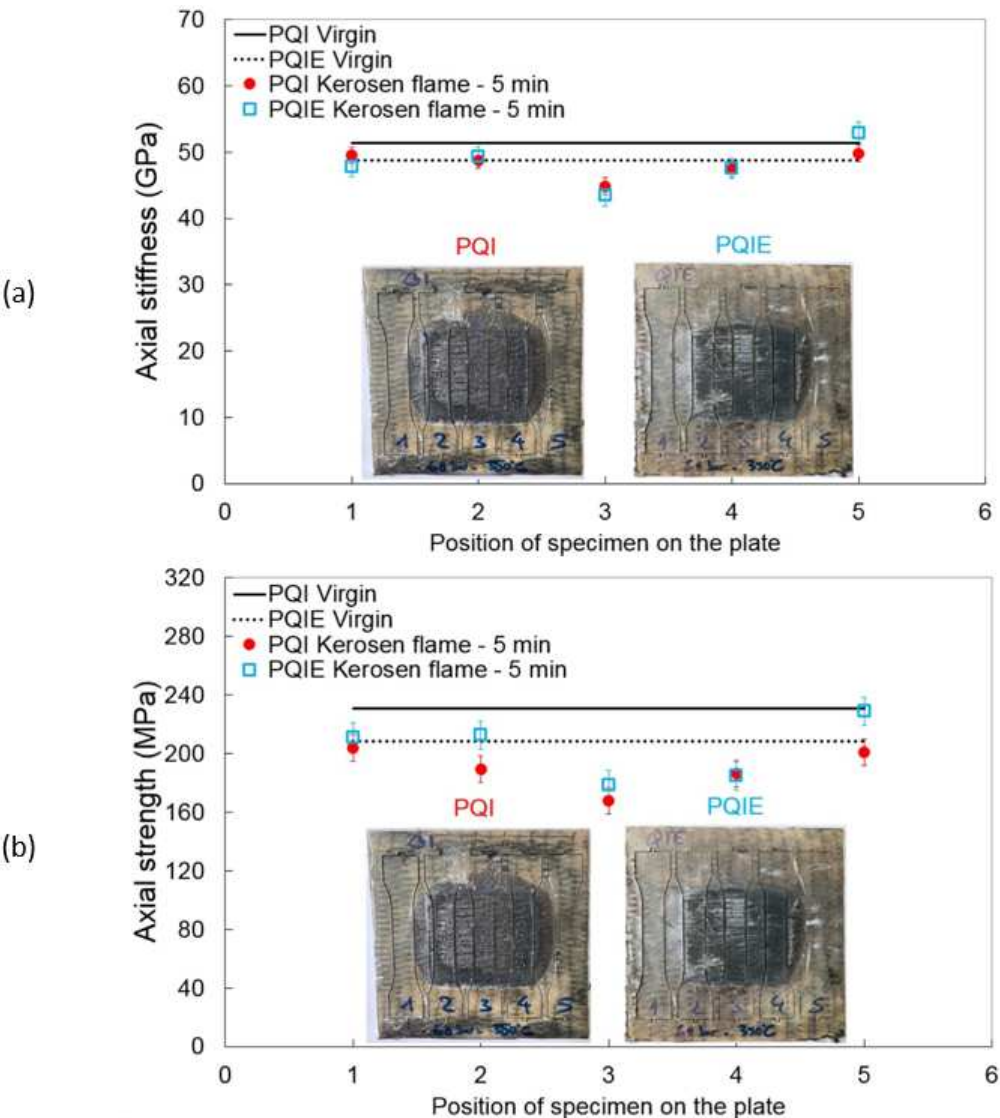


Fig. 15 – Influence of flame-retardant additive on the tensile properties of quasi-isotropic laminates:
 (a) Axial stiffness – (b) Axial strength

These conclusions are supported by the macroscopic observations of front/back surfaces as well as the laminates edges (Fig. 16a). As already done in orthotropic laminates, it was chosen here to consider only the fractographic analysis of the most severely degraded specimens (position 3 on the flame-exposed plate – Fig. 9) to observe the consequences of the most critical service conditions. Virgin specimens (PQI and PQIE) are characterized by the breakage of 0° oriented carbon fibres on the outer plies and extensive delamination. As was observed in orthotropic specimens, specimens are severely degraded on the exposed surface. Char facilitates transverse cracking and ultimately the breakage of 0° carbon fibres. On the back surface, very little damage is visible on specimens with Exolit except the transverse breakage of carbon fibres. Bubbles of pyrolyzed matrix coming along tar formation are observed. The observations of edges reveal that flame-exposed specimens experience mostly delamination. However, delamination is less extensive in QI laminates compared to orthotropic laminates (Fig. 16b). This may stem from the better contribution of “undamaged” plies (after thermal aggression) to the tensile response.

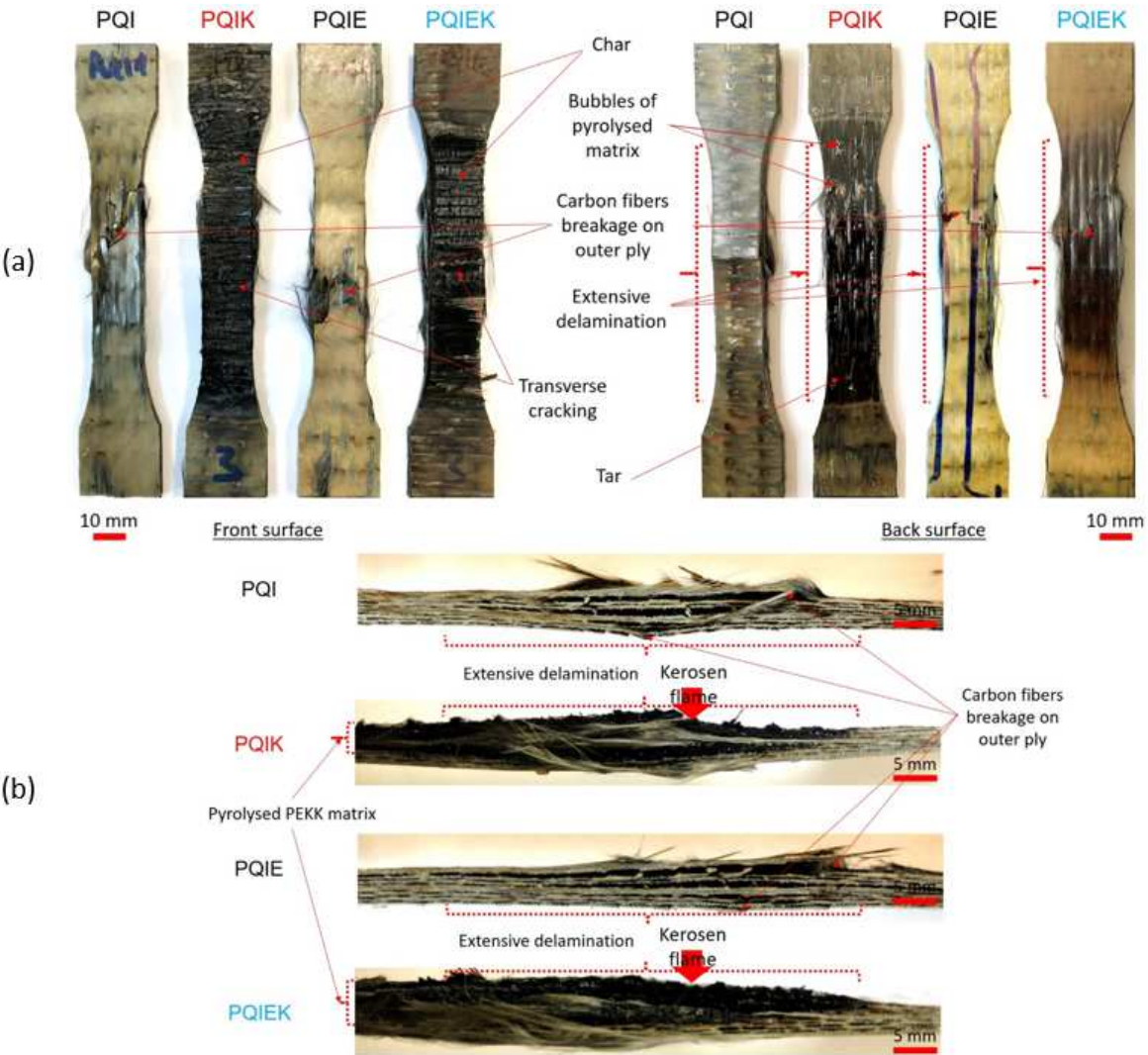


Fig. 16 – Influence of flame-retardant additive on the damage mechanisms in quasi-isotropic laminates: (a) Front and back surfaces – (b) Laminates edge

5. Conclusions

The question of coupling between thermal degradation and mechanical behaviour in polymer-based laminated composites is poorly addressed in the literature. In most references, the influence of flame-retardants is only analyzed in terms of fire-behaviour but not in terms of residual mechanical properties. This was the double objective of the present work. Composite laminates were manufactured using a thermo-consolidation process from UD carbon fibers and a PEKK thermoplastic associated with or without a phosphorus-based flame-retardant additive (Exolit).

Depending on the laminates lay-up (orthotropic or quasi-isotropic), the influence of Exolit on the thermal degradation, resulting from a kerosene flame exposure (116 kW/m^2 and 1100°C), on the composites structural integrity was examined. The changes in the tensile properties (axial stiffness and strength) were compared with respect to the virgin materials (experiencing no prior flame exposure).

After a 5 min exposure to a kerosene flame, the microscopic observations of orthotropic laminates (with or without Exolit) show that the flame-retardant additive efficiently contributes to delay the thermal decomposition of C/PEKK, as the fire-degraded areas significantly differ when considering the edges of laminates. In the most detrimental conditions (specimen taken from position 3), the axial stiffness decreases by 15%, whereas there is a dramatic decrease (-55%) in the axial strength of specimens without Exolit, with respect to the virgin state. The back surface of orthotropic laminates with Exolit seems to be relatively undamaged. As a result, the preservation of tensile properties is very good with a moderate decrease (about -14%) in both axial stiffness and strength. It therefore suggests that the flame-retardant additive not only delays the thermal degradation of C/PEKK laminates but also efficiently contributes to maintain the structural integrity of the composites, hence resulting in good mechanical properties.

After being exposed to a kerosene flame, quasi-isotropic laminates are characterized by two-well defined areas (a severely degraded one and a seemingly undamaged one) with no transition zone. However, the undamaged area is represented by two or three plies that seem to be protected from thermal degradation by the ones on the other side. It was expected that the residual tensile response (and corresponding properties) of these specimens would be better as these undamaged plies still have a good fibres/matrix cohesion. The obtained results prove that the preservation of the tensile properties is better in PQI laminates than in PUD composites.

Ultimately, the use of a phosphorus-based flame-retardant additive efficiently contributes to attenuate the thermal degradation of kerosene-flame exposed C/PEKK laminates, but also maintains the material tensile mechanical properties. The positive effect of Exolit is particularly noticeable in orthotropic laminates whose mechanical behaviour is driven by 0° carbon fibres.

Acknowledgements

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Tables

	C/PEKK		C/PEKK + exolit		Influence of flame	
	Virgin	Flame exposure	Virgin	Flame exposure	Without exolit	With exolit
E_X (Gpa)	127.2±4.0	120.5±8.8	121.2±3.9	120.4±10.1	-5%	≈
σ_X^u (Mpa)	598±49	442±99	567±62	517±60	-26%	-9%

Tab. 1 – Influence of flame-retardant additive on the residual tensile properties of orthotropic laminates subjected to a kerosene flame for 5 min – Average values

	C/PEKK		C/PEKK + exolit		Influence of flame	
	Virgin	Flame exposure	Virgin	Flame exposure	Without exolit	With exolit
E_X (Gpa)	51.3±0.5	48.1±2.0	48.7±3.7	48.2±3.1	-6%	≈
σ_X^u (Mpa)	230±34	190±14	208±29	203±19	-18%	-3%

Tab. 2 – Influence of flame-retardant additive on the residual tensile properties of quasi-isotropic laminates subjected to a kerosene flame for 5 min – Average values