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One-dimensional pyrolysis of carbon based composite materials using FireFOAM

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A B S T R A C T

Composite materials used for aerospace applications are vulnerable when exposed to high temperatures and may generate toxic fumes and particles when submitted to fire stress. This hazard is strictly framed by aviation regulations. Thus, research on composite behavior under fire now aims to develop reliable physical models to be implemented into Computational Fluid Dynamics (CFD) codes in order to meet this challenge and better understand the physics of fire growth and materials flammability. The initial chemical reactions (pyrolysis and ignition) should be evaluated first and then validated against experimental data at the mesoscale. A cone calorimeter provides realistic degradation conditions and a large heat flux range (from 30 to 120 kW/m^2), making it a good tool for validation. In this study, the FireFOAM CFD solver was used to predict the one dimensional pyrolysis of the condensed phase of two carbon-reinforced composite materials, a thermosetting phenolic resin and the thermoplastic Poly (Ether-Ketone-Ketone) (PEKK). The numerical results were compared to cone calorimeter experiments at the mesoscale, and provided a good prediction of the mass loss and heat release rate for the materials considered. A maximum relative error of 5% was found between experiments and numerical simulation of the mass loss for the carbon-PEKK and the carbon-phenolic composites. Moreover, the numerical heat release rate presented a good reproduction of both peak intensity and time. A sensitivity analysis was performed to evaluate the reaction of the model to the variation in different parameters, and highlighted the strong influence of the material density when considering the thermophysical properties and activation energy for the kinetic parameter.

1. Introduction

Nowadays composite materials are extensively used in transportation systems such as trains [1], planes [2], automobiles [3] and even bicycles [4]. They have received increasing attention in past decades due to their advantages in weight reduction [5] and strong mechanical properties [6]. However, these kinds of materials have some drawbacks. They are vulnerable when exposed to high temperatures and produce toxic fumes and particles under fire stress [7]. To handle these issues, researchers and engineers usually perform extensive fire experiments on composite materials to understand, predict and certify their behavior when exposed to fire. In particular, standard fire tests such as ISO 2685 [8] or FAA AC0-135 [9] are used in the aerospace industry involving large flat panels or even complex airplane parts. Research in this area focuses on the modeling of fire using numerical simulations such as Computational Fluid Dynamics (CFD), which provide a cost-effective alternative to experiments [10] in order to understand the physics of fire growth as well as materials flammability. CFD codes are widely used by fire protection engineers for performance-based design as well as disaster analysis, and are of increasing interest in the fire community [11]. However, the numerical investigation of large scale fires implies the modeling of multi-scale and multi-physics phenomena, requiring the coupling of fluid mechanics, gas phase combustion, oxidation, radiation, condensed phase heat transfer and pyrolysis in order to predict the solid behavior when exposed to a flame.

In a previous study, CFD numerical simulations were conducted in order to understand the thermal behavior of carbon-phenolic composite materials during a standardized fire test [12]. These simulations highlighted the importance of modeling the early stage combustion process as well as the pyrolysis phenomenon. In the present work, pyrolysis was

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further investigated and validated against experimental data such as mass loss rate, heat release rate and backward face temperature at the mesoscale (samples about 10 cm). The latter was carried out using a cone calorimeter device, which has already been used to understand the fire behavior of composite materials and to estimate the heat release rate [13], the flammability [14] or the fire performances [15]. Moreover, this standard test [16] provides realistic degradation conditions under a large heat flux range (from 30 to 120 kW/m^2). It also appears to be an interesting tool for numerical code validation, especially for pyrolysis of various materials [17] at high heat flux (100 kW/m^2) as the latter value is close to the heat flux encountered on large scale samples (116 kW/m^2) during the above-mentioned standard fire tests [8,9]. Thus, it provides physical quantities such as Heat Release Rate (HRR), surface temperature and Mass Loss Rate (MLR) that are required for validation of the numerical model. In particular, MLR is one of the most important parameters as it is directly linked to the pyrolysis gas flow rate and is the initial factor in the combustion process [11].

There are several numerical models in the literature to predict solid pyrolysis, such as Gpyro [18], a solid phase solver coupled to the CFD code Fire Dynamic simulator [19], Thermakin [20] or the FireFOAM pyrolysis model. They are usually used on materials such as wood [21], organic material [22] or a non-charring polymer such as PMMA [23]. Considering the complexity of future large scale fire simulations, the FireFOAM CFD solver [24], which is part of the OpenFoam toolbox [25, 26] was used to predict the one dimensional thermal degradation of two carbon-reinforced composite materials cured from pre-impregnated fibers, using a kinetic mechanism with three reaction steps, as suggested by Mouritz and Gibson [7]. The first reaction is associated with decomposition of the resin, the second one represents the oxidation of the char (resin decomposition residual), whereas the third reaction describes the combustion of the carbon fibers.

Two different materials were compared in this study. The first material is a thermosetting phenolic resin, which has multiple applications in industry for thermal protection, especially in the aerospace industry [7], but is also used for automotive components or fire barriers in offshore oil platforms [27]. Under fire conditions, carbon-phenolic composites are characterized by a high yield of char (up to 50% of the initial mass) and a low thermal conductivity involving a slow ignition time and an easy extinguishment [28]. The second composite material is the thermoplastic Polyether-ketone-ketone (PEKK) belonging to the PolyArylEtherKetone (PAEK) family, known for their high mechanical performance and high temperature stability, as demonstrated by Riviere et al. [29]. Due to its low flammability and limited smoke emissions when subjected to fire [30], this polymer was originally developed for automotive and aerospace applications [31] in particular for exterior structures and cabin interiors.

In the present study, the thermophysical properties of the materials and the kinetic parameters obtained from previous experimental studies are first introduced, and the cone calorimeter experiments are then presented. Then, the numerical modeling approach is described and the numerical results such as the backward face temperatures, mass loss ratio and heat release rates are compared to the experimental measurements. A detailed local sensitivity analysis on the different parameters of the model is also presented.

2. Material and methods

2.1. Determination of thermophysical properties and kinetic parameters

The thermophysical properties of the materials considered, such as density (ρ), specific heat capacity (C_p) and thermal conductivity (λ), are essential inputs for pyrolysis modeling in CFD codes. As mentioned above, the pyrolysis kinetic mechanism of the studied composite materials involves the degradation of resin, char and carbon fibers. It is therefore necessary to determine their thermophysical properties. To this end, thermal analysis was performed on cured virgin samples (with diameters between 4 and 20 mm) taken directly from a large panel (cf. Fig. 1) to obtain the desired properties from ambient temperature to 1000 °C, taking into account the different phase transformations of the polymeric matrix [32].

The density evolution was obtained by measuring the variation in thickness of the sample with the increase in temperature using a dilatometer [33] combined with the mass loss measured on the same sample using a thermogravimetric apparatus (TGA). The unidirectional thermal expansion of the sample thickness during the test was ensured using a stainless steel guide around the sample. Assuming a constant fiber density on the considered interval from the literature [34,35] and knowing the fiber volume fraction, it is possible to estimate the resin density as:

$$\rho_m = \frac{\rho - \rho_f V_f}{1 - V_f} \tag{1}$$

where ρ denotes the measured density of the composite material and V_f is the fiber volume fraction. Subscripts f and m denote respectively the fiber and the matrix (i.e. resin). By using the density value calculated from Eq. (1), the carbon fiber specific heat given by Pradere et al. [36] and the density of the composite material measured by Differential Scanning Calorimetry [37], the specific heat of the resin can be written as:

$$C_{p,m} = \frac{\rho_c C_p - V_f \rho_f C_{p,f}}{\rho_m (1 - V_f)} \tag{2}$$

The thermal diffusivity of the composite material was measured by the laser flash technique [38,39] and combined with the density and the specific heat, yielding the thermal conductivity. The thermal diffusivity was measured for a virgin composite under the defined decomposition temperature (deduced from TG) whereas the thermal diffusivity above the decomposition temperature was measured on a previously decomposed sample heated to the desired temperature. Using the thermal

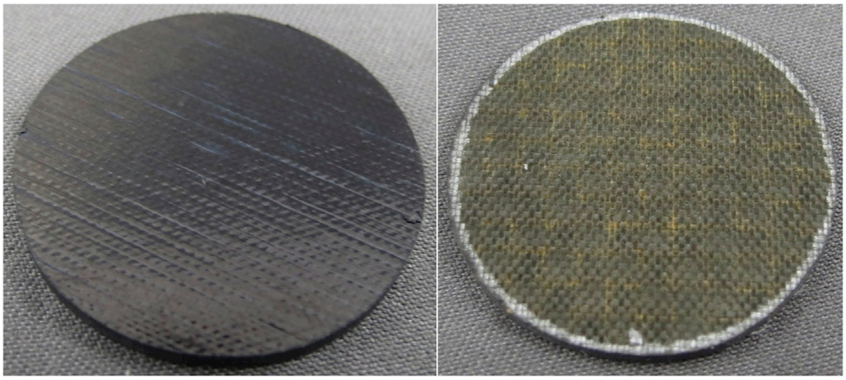

Fig. 1. Cured Virgin sample of carbon-PEKK (left) and carbon-phenolic (right).